Abstract

HARTMAN, JEFFREY DAVID. Characterization of the Growth of Aluminum Nitride and Gallium Nitride Thin Films on Hydrogen Etched and/or cleaned 6H-SiC(0001) Surfaces. (Under the direction of Dr. Robert F. Davis).

The surface morphology and atomic structure of nitrogen doped, n-type 6H-SiC(0001) wafers before and after various surface preparation techniques were investigated. As-received wafers were exposed to in-situ cleaning with or without excess silicon to obtain either a (\(\sqrt{3} \times \sqrt{3})R30^\circ\) or a (3 x 3) reconstructed surface. The resulting surfaces were characterized using reflection high-energy electron diffraction, photo-electron emission microscopy, and atomic force microscopy. An atomically clean, reconstructed surface was obtained via thermal annealing at 950°C. Cleaning with excess silicon resulted in the formation of silicon islands on the surface.

The surface morphology of hydrogen etched wafers depended upon their doping concentrations. Wafers with doping concentrations of \(\geq 2.5 \times 10^{18}\) and \(\leq 6.5 \times 10^{17}\) \((N_D-N_A)/cm^3\) were investigated with the former exhibiting more surface features. The microstructure of all the samples showed regions with full and half unit cell high steps. An atomically clean, ordered, stepped surface was achieved via annealing at 1030°C. Chemical vapor cleaning resulted in the formation of silicon islands.

The initial growth of AlN and GaN thin films on the cleaned, hydrogen etched 6H-SiC(0001) substrates were investigated using PEEM and AFM. The AlN films nucleated immediately and coalesced, except in the areas of the substrate surface which contained half unit cell height steps where pits were observed. The GaN films grown at 800°C for 2.5 minutes exhibited nucleation and three-dimensional growth along the steps.
The GaN films deposited at 700ºC for 2 minutes grew three-dimensionally with coalescence of the film dependent upon the step structure. Almost complete coalescence occurred in regions with unit cell high steps and incomplete coalesce occurred in regions with half unit cell height steps.

Films of AlN grown for 30 minutes via GSMBE on hydrogen etched surfaces exhibited two-dimensional growth and had an RMS roughness value of 4 Å. Films grown at 1000ºC exhibited an SK growth mode and had rocking curve FWHM of 150-200 arcsecs. MOCVD grown films on hydrogen etched wafers had an RMS roughness value of 4 Å and a XRD rocking curve FWHM of ≈260 arcsecs.
CHARACTERIZATION OF THE GROWTH OF ALUMINUM NITRIDE AND GALLIUM NITRIDE THIN FILMS ON HYDROGEN ETCHED AND/OR CLEANED 6H-SIC(0001) SURFACES.

by

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To Cathy
**Biography**

Jeffrey David Hartman was born on October 29th, 1970 in Danville, Pennsylvania to Carey and Nancy Hartman. He is the oldest of two brothers, the younger of which is Michael. He spent his informative years, from preschool to high school in Harrisburg, Pennsylvania, graduating from Central Dauphin high school in 1989. Jeff then attended Rensselaer Polytechnic Institute in Troy, NY, where he received a Bachelor of Science degree in Materials Engineering in May of 1993. Two days after graduating, he and his wife, Catherine Menk, were married. Over the next three years, Jeff held positions of process engineer and an associated engineer. In January, 1997, his graduate school career began at North Carolina State University in the Materials Science and Engineering Department under advisement from Dr. Robert F. Davis.
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1 Introduction to the Properties and Thin Film Growth of III-Nitrides and Silicon Carbide.

1.1 Properties of III-Nitride Semiconductors

1.1.1 Introduction

The growth of III-Nitride epitaxial films and device structures by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) matured sufficiently to allow commercialization of light emitting diodes (LED's), lasers (LDs), and high mobility transistors (FET's). These devices have utilized the short-wavelength, high-power, and high-temperature characteristics of these semiconductors. However, to improve the microstructural characteristics and lifetime of the present devices and to develop the next generation of devices, an in-depth understanding of the factors that effect growth must be realized. The main limiting factor in the growth of III-nitrides continues to be the lack of sufficiently large and inexpensive substrates for homoepitaxial growth. For example, in the gallium arsenide industry, large area substrates produced by Czochralski, Bridgemen, or liquid phase electroepitaxy methods and having low defect densities are available [1,2]. The wafers derived from these bulk substrates provide a footprint on which highly efficient devices may be fabricated for many applications. The growth of the nitrides is achieved heteroepitaxially on substrates such as silicon carbide and sapphire. This introduces a new set of growth issues and problems that must be understood and solved.

The growth of III-nitrides on these aforementioned substrates has been analyzed extensively over the past several years using various characterization tools. Important
information has been collected regarding the surface preparation of the substrate, the
colorization of the initial growth processes under various conditions, and the factors
such as interfacial reactions that affect the quality of the bulk material. In the following
sections, a review of the crystallography, the theory of nucleation and growth, and the
growth of III-nitrides will be reviewed.

1.1.2 Crystallography

The III-Nitride semiconductors may occur as two different crystal structures,
namely either wurtzite or zincblende. The zincblende structure is a cubic \( \bar{1} \) unit cell with
F43m symmetry that generally grows on cubic substrates such as silicon and GaAs. The
stacking sequence along the c-axis is denoted as …ABCABC… The structure may be
seen as two interpenetrating face center cubic unit cells offset \( \frac{1}{4} \frac{1}{4} \frac{1}{4} \) along the \(<111>\)
direction. Figure 1.1 shows the wurtzite structure for GaN, which consists of a hexagonal
unit cell with 6 atoms of group III and 6 atoms of group V elements. This structure may
be described as two interpenetrating hexagonal close packed sublattices off set from one
another by \( 5/8 \) of the cell height. The unit cell is described by two lattice constants, \( a \) and
\( c \), where the former is the distance along one side of the hexagon and the latter is the unit
 cell height. The structure is described as 2H consisting of an ..ABAB.. stacking sequence.
The hexagonal structure is generally used in opto-electronic applications due to its direct
bandgap. Table 1.1 lists some common properties of the 2H-AlN and 2H-GaN
semiconductors.
1.2 Growth Processes and the Growth of III-Nitride Films

1.2.1 Basic Theory of Growth

As mentioned in the introduction, the majority of the III-nitride growth is conducted heteroepitaxial due to the lack of sufficiently large and plentiful bulk III-Nitride substrates. The two most popular methods of growth include molecular beam epitaxy and chemical vapor deposition. Descriptions of these methods of growth will be discussed in the next section along with some growth results. The different growth procedures start with various reactants such a volatile compounds in CVD to evaporation beams in MBE. Epitaxial growth occurs with the interaction of one or more species on the surface of a single crystal substrate. In these growth methods, reactants must be transported to the surface, adsorb, react, and the byproducts removed. In the following sub-sections, a brief background into the theory of growth starting with adsorption and finishing with the different types of growth modes is presented.

1.2.2 Sticking and Accommodation Coefficients

Two parameters that must be considered when growing epitaxial films include the accommodation coefficient and the sticking coefficient, especially in molecular beam epitaxy (MBE). In the case of MBE, incoming species from an effusion cell arrive at the substrate with a temperature of the source due to the large mean free path associated with high vacuum systems. At the moment the species impinges on the surface, the surface must accommodate the excess energy of the species through phonons. The accommodation coefficient is a measure of the extent to which the arriving atoms reach
thermal equilibrium with the substrate. The accommodation coefficient, $b$, is given by:

$$\beta = \frac{T_i - T_e}{T_i - T_s}$$

(1)

where $T_i$ is the temperature of the incident atoms, $T_e$ is the temperature of the atoms re-evaporating from the substrate, and $T_s$ is the temperature of substrate. Even if the accommodation coefficient is one, there may not be complete adsorption or sticking of the impinging species due to desorption. The accommodation coefficient is only a measure of the ability to accommodate the excess energy.

The sticking coefficient is defined as the ratio of the number of atoms adhering to the substrate to the number of atoms arriving at the surface. The sticking coefficient is determined by measuring the deposited film and dividing by the amount of material that arrived at the substrate during deposition. In heteroepitaxial growth, the sticking coefficient is generally less than one and depends on the adsorption energy and the substrate temperature.

1.2.3 Adsorption

The next step for the growth of an epitaxial film is the adsorption of molecules on the surface. The impinging species may adsorb in either a physisorption and/or chemisorption state. The physisorption state occurs when the species impinging are bonded to the surface via Van der Waals forces. In the chemisorption state, the impinging species is chemically bonded to the surface. All impinging atoms will pass through the physisorption state, but not all are chemisorbed. This leads to some of the atoms being desorbed during processing.
Once the atoms are adsorbed, there are four possible states for the atoms. In general the atom will remain on the surface for a time, $t_s$, and diffuse a mean square distance of $x^2$. If the atom does not find a suitable site to bond to in the distance $l_s$, which is the square root of the mean free distance, then the atom will desorb from the surface. The other three possible states are concerned with the possible surface sites on which the atom may bond. A diffusing atom is more likely to bond to a kink, than to a terrace or a step, due to the larger reduction in the internal energy of the system. If a kink is not available in the distance, $l_s$, then the next highest reduction in energy occurs when the atom bonds at a step. Finally, if the atom cannot make it to a step or kink, it may initiate or continue nucleation on a terrace and possibly create a new phase.

1.2.4 Heterogeneous Nucleation

Once the atoms begin to bond on and to the surface, nucleation of islands is initiated. The nucleation rate is the number of nuclei that form per unit volume per unit time. The equations presented below assume that the impinging species will cause the initial clusters to either grow in size or disintegrate through dissociation. Adatoms on the surface will diffuse on the surface, as discussed above, and bond to the clusters and nuclei. From the microscopic notions in the capillary theory, the nucleation rate, $N'$, is obtained thermodynamically as the product of three terms; the equilibrium concentration of stable nuclei, $N^*$, the critical area, $A^*$, and the rate of species impingement, $w$ [3]. In equation form,
The equilibrium concentration of stable nuclei is given as a function of all the possible nucleation sites, \( n_s \).

\[
N^* = N^* A^* \omega
\]  

(2)

where \( T \) is the temperature of the substrate, \( k \) is Boltzman’s constant, and \( \Delta G^* \) is the critical energy barrier to the creation of a stable nuclei. For heterogeneous nucleation, \( \Delta G^* \) is identical to that for homogeneous nucleation except it contains a correction factor term that includes the contact angle of the film:

\[
\Delta G^* = \left( \frac{16 \pi \gamma_{vf}^3}{27 \sigma^2 \Delta G^2} \right) \left( 2 - 3 \cos \theta + \cos^3 \theta \right)
\]

(4)

where \( \gamma_{vf} \) is the interfacial tension between the film and vapor, \( \Delta G_v \) is the chemical free-energy change per unit volume, and \( \Theta \) is the contact angle. The first term is the \( \Delta G^* \) for homogeneous nucleation and the second term is a correction factor based on the wetting of the film.

The second term describes the rate at which the species impinge on the nuclei, which is a function of the adatom jump frequency and the vapor impingement rate. This term is related to the adatom diffusive jumps of the species through

\[
\omega = \frac{\tau \rho N \nu \exp \left( \frac{E_s}{kT} \right)}{\sqrt{2 \pi MRT}}
\]

(5)
where $P$ is the pressure, $N_a$ is Avogadro's number, $\nu$ is the vibrational frequency of the adatom on the surface, $E_s$ is the activation energy for surface diffusion, $M$ is the molecular weight, $T$ is the temperature and $t_s$ has been described previously. The last term is the critical area of the nuclei, $A^*$. Two of the main variables effecting the nucleation process are the substrate temperature and the deposition rate. If there is a large critical radius and a large barrier to nucleation, deposition of a monocrystalline film should occur at a high substrate temperature with a low deposition rate. If deposition occurs on a substrate at a low temperature and a high deposition rate, the film will be polycrystalline.

### 1.2.5 Growth Modes for Epitaxial Films

Epitaxial nuclei and films grow via three basic thermodynamic modes: Frank-van der Merwe, Volmer-Weber, and Stranski-Krastanov, as shown in Figure 1.2 [3]. The type of growth depends on the magnitude of the substrate/ambient, film/ambient and the film/substrate interfacial energies.

The Frank-van der Merwe or layer by layer mode is shown in Figure 1.2a, is the layer by layer, or Frank-van der Merwe growth. This process occurs when the smallest stable nucleus grows in two dimensions, resulting in complete monolayer coverage of the surface. The second layer may begin to grow before the first is complete. In terms of the theory of wetting, this type of growth occurs when the film/ambient interfacial energy, $S_o$, and the film/substrate interfacial energy, $S_i$, is less than the substrate/ambient interfacial energy, $S_s$; i.e., $(S_s > S_o + S_i)$. An analogous way of stating this is that two-dimensional growth occurs when the adhesive energy between the atoms of the substrate
and the deposited atoms is greater than that of the cohesive energy of atoms within the deposited layer. The deposition of the film is energetically favorable if a reduction in the internal energy is achieved. In this case, the strain energy within the film is small.

Volmer-Weber or island growth, shown in the Figure 1.2b, occurs when the smallest stable nucleus grows in three dimensions. The islands formed on the surface by the impinging atoms grow vertically rather than across the surface. In this case, the substrate/ambient interfacial energy is less than the sum of the substrate/film interfacial energy and the film/ambient interfacial energy \((s_s < s_o + s_i)\). In other words, island growth occurs when the energy of cohesion between the atoms being deposited is greater than the energy of adhesion between the deposited atoms and the substrate. Minimization of the internal energy of the system occurs at some percentage of coverate of the substrate by the film (including zero coverage). The individual islands may or may not have the same crystal structure as the substrate; however, the concept of epitaxy demands they be related at the film/substrate interface. Upon extended growth times, the islands may coalesce and form a continuous film.

The last type of growth mode shown in Figure 1.2c is the Stranski-Krastonov (SK growth), which is a combination of the previous two modes. Initially the film nucleates and grows two dimensionally for the first few monolayers, but the mode changes to three dimensional growth as a result of the accumulation of strain energy, \(s_d\), from the mismatch in the atom-atom distances between the film and the substrate. As the film grows, the strain energy term increases. In this case, the substrate/ambient interfacial energy is greater than the sum of the film/ambient interfacial energy, the film/substrate
interfacial energy, and the strain energy ($s_s < s_o + s_i + s_m$). SK growth is the most common growth mode because most films are grown heteroepitaxially on foreign substrates.

1.2.6 Epitaxial Growth of III-Nitrides

1.2.6.1 Substrates

Two of the most popular substrates for the epitaxial growth of III-Nitrides are sapphire and silicon carbide. Sapphire continues to be the principal substrate due to its low cost and the fact that films of sufficient quality for light emitting diodes can be grown on it. The surfaces of both substrates can be readily cleaned via annealing and can withstand the elevated temperatures used during chemical vapor deposition of III-Nitride films.

Sapphire substrates are limited by two main drawbacks: mismatches in lattice parameters and coefficients of thermal expansion with all III-Nitride compounds and alloys and the fact that it is an electrical insulator. The most commonly used orientation of sapphire is the [0001] (c-plane). The mismatch in lattice parameters between GaN and sapphire is approximately 15%. As such, the crystal orientation of the c-plane of the GaN or AlN buffer layer and subsequently grown film is rotated 30° with respect to that of the sapphire to reduce the in-plane strain. The high electrical resistivity of sapphire prohibit the use of backside contacts for use in vertical devices.

Silicon carbide is electrically and thermally much more conductive than sapphire, but it is presently cost prohibitive for most cases. It has only a 3.5% and an 0.8% mismatch in lattice parameters with GaN and AlN, respectively. The substrate may be
heavily doped either n or p type, to enhance its electrical conductivity for backside contacts. However, when designing vertical devices, AlN nitride and high Al content AlGaN should be avoided, as they are electrically resistive even when doped. A more detailed discussion of the structure and properties of silicon carbide will be presented in section 1.2.

Other substrates investigated for the growth of III-nitrides include Si, GaAs, MgAl₂O₄, ZnO, LiGaO₂, and small crystals of GaN grown at high pressures. Each of these substrates possess some properties that could make them a better candidate than SiC or sapphire. However, most contain limiting characteristics including decomposition at high growth temperatures in the presence of H₂ (ZnO and LiGaO₂) and interfacial alloying (Si) and considerable mismatches in lattice parameters and coefficients of thermal expansion (Si, GaAs, and MgAl₂O₃).

1.2.6.2 Growth by Chemical Vapor Deposition

Maruska and Tietjen grew the first gallium nitride single crystal, epitaxial film and developed the procedures for hydride vapor phase growth of this material [4]. In their vapor transport process, the Ga metal is converted to GaCl via reaction with flowing HCl. This GaCl subsequently reacts with ammonia at the substrate to form gallium nitride via the reaction:

\[ \text{GaCl} + \text{NH}_3 = \text{GaN} + \text{HCl} + \text{H}_2 \]

The films grew very rapidly, at a rate of 0.5µm/min; however they contained a very high n-type carrier concentration of $10^{19}$ cm⁻³. This technique is currently the method of choice for high rate deposition of GaN. In the interim, metalloganic vapor phase epitaxy
has been developed for the growth of GaAs based films, and this technique has been widely adopted by the III-Nitride community. The group V source is usually triethylgallium, trimethylaluminum, or trimethylindium and ammonia is the group III source. Many studies have been conducted to understand and improve the growth of GaN and AlN via this latter method on both SiC and sapphire substrates. Some of the results from these studies will be presented in subsequent sections. Recently, advances in lateral epitaxial overgrowth and pendo-epitaxy, have reduced the density of dislocations in GaN and Al\textsubscript{x}Ga\textsubscript{y}N films [5-7]. Today, due to the improvement in the growth and quality GaN and AlN epitaxial films, large scale devices, such as blue LED’s, are fabricated on a consistent basis.

1.2.6.3 Molecular beam epitaxy

In 1970 the term molecular beam epitaxy (MBE) was coined for the growth of GaAs using two thermal beams and causing a reaction on a crystalline surface. Since that time, MBE has become a valuable tool in both the manufacturing of devices and in the understanding of the growth mechanisms of semiconductors. This technique allows control of monolayer growth which permits both the growth of device structures with abrupt interfaces and detailed studies regarding the growth modes of the deposited films. The development of MBE of the III-nitrides has been inhibited by point defect generation in the growing films by high energy nitrogen molecules/atoms generated by various plasma sources or by the slow rate of pyrolysis of ammonia, since film growth is generally conducted at lower temperatures than in CVD due to the rapid dissociation of the nitrides at elevated temperatures under UHV conditions. Additional discussions
regarding these sources and the associated problems are given below. However, these
problems are presently being addressed, and device quality material has been produced
via this technique [8,9].

Figure 1.3 shows a general schematic layout for a molecular beam epitaxy chamber for
use in the growth of III-nitride films. The system contains one source for the nitrogen
(Group V) and one or more sources for the group III metals. Additional n- or p-type
doping sources are also common. In general, the group III source is evaporated from a
Knudsen or effusion cell at a set temperature, which controls the flux of material. The flux
of atoms or molecules that strike a unit area of the substrate per second from the Knudsen
cell is given by:

\[
J = (1.118 \times 10^{22}) \frac{pA}{l^2 (MT)^{1/2}} \frac{\text{molecules}}{\text{cm}^2 \text{sec}}
\]  

(7)

where A is cell orifice, p is the pressure in the cell, l is the distance from the substrate, M is
the molecular weight, and T is temperature. The distribution of atoms leaving the k-cell
follows a \( \cos^n f \) angular distribution, where \( f \) is the angle between the normal to the
source and the sample surface and n is a number used to determine the geometry of
evaporated beam. For optimum growth rate, the effusion needs to be pointed directly at
the substrate. For the growth AlN and GaN, the sticking coefficients of Ga and Al have
been determined to be near unity at temperatures below 710°C [10].

As indicated above, several different sources have been used to supply nitrogen
for MBE growth of nitrides, including an electron cyclotron resonance (ECR) microwave
plasma, a radio frequency (RF)-radical plasmas, and ammonia. The first two sources
produce reactive nitrogen in the form of atomic nitrogen and $N_2^+$ ions. The ECR microwave plasma source produces reactive nitrogen via coupling microwave energy of 2.45 GHz with the resonance frequency of electrons in a static magnetic field. The lower the microwave power, the less energetic the ions, the better the film quality and the slower the growth rate. The RF plasma source is operated at 13.56 MHz. The reactive nitrogen is generated through inductive coupling of the RF energy into a water-cooled discharge chamber filled with nitrogen. These sources not only produce atomic nitrogen, but also produce high energy $N_2^+$ ions that bombard the surface and damage the epitaxial layers, as noted above.

Ammonia was originally employed as the source of nitrogen for MBE growth of the III-nitrides. Yoshida et al. [11] grew AlN films on sapphire and silicon substrates using ammonia and Al evaporated using an electron beam. As noted above, the use of ammonia in MBE has been limited due to the lower temperatures used for growth to prevent the dissociation of III-nitrides under UHV conditions. Ammonia decomposition and incorporation is low below 700°C, e.g., 0.5% at 500°C, but films have been grown at temperatures as low as 450°C [12]. The process of dissociation of ammonia on the surface is shown schematically in Figure 1.4. Ammonia is adsorbed on the surface and dissociated through a five-step process:

$$\begin{align*} 
NH_3 &\rightarrow NH_3_{\text{ad}} \\
NH_3_{\text{ad}} &\rightarrow NH_2_{\text{ad}} + H_{\text{ad}} \\
NH_2_{\text{ad}} + H_{\text{ad}} &\rightarrow NH_{\text{ad}} + 2H_{\text{ad}} \\
NH_{\text{ad}} + 2H_{\text{ad}} &\rightarrow N_{\text{ad}} + 3H_{\text{ad}} \\
Ga_{\text{ad}} + N_{\text{ad}} &\rightarrow GaN_s 
\end{align*}$$

$$(8)$$
which leads to the formation of either GaN, as in this case, or AlN.

The growth of Ga nitride using ammonia may occur in three distinct regimes[13]: (1) the incident gallium completely reacts with ammonia to form gallium nitride, (2) the incident gallium forms gallium nitride and also desorbs, and (3) the gallium reacts to form gallium nitride and gallium droplets on the surface. The formation of only GaN without desorption occurs at approximately 725ºC occurred at ammonia fluxes above 2.1 x 10^{-6} beam equivalent pressure. In the other regimes, GaN desorption or Ga accumulation occurs. In the research described in the following sections, ammonia is utilized as the source of nitrogen for the growth of both AlN and GaN.

1.2.6.4 Growth Modes and Morphology of the III-Nitrides

As discussed in the previous section, there are several different substrates and methods for the growth of III-nitride semiconductors. Many combinations of substrate and growth methods have been reported. Two important areas of research have focused on the surface morphology of the grown epitaxial films and the growth modes of the nitrides with emphasis on the effect of surface preparation and processing conditions. A summary of some of the research results from the past 20 years is presented in the following paragraphs.

The growth mode of GaN and AlN and their alloys is dependent upon many factors, as discussed above. A summary of some reported research results regarding the growth modes of GaN and AlN using various growth techniques is presented in Tables 2, 3, and 4. As stated in the tables, the growth mode of the epitaxial nitride films may be affected by: surface preparation of the substrate, the power of the nitrogen source, the
temperature of the substrate, and the growth method. In general, the results consistently show that when GaN is grown directly upon SiC without a buffer layer the growth mode is 3-D [14-16]. On sapphire, 3-D or SK growth has been reported to occur [15,17]. However, nitriding of the latter surface produces an amorphous AlN layer that changes the growth mode of the subsequently deposited GaN to the 2-D mode [18-20]. A deposited AlN buffer, on SiC has been shown to promote 2-D growth of GaN [14,21].

The growth of AlN films has been observed to be layer-by-layer growth [15,16] except when it was grown on off axis SiC substrates (more island than layer-by-layer [22]). When AlN was grown on GaN at 800ºC, the growth mode was reported as layer-by-layer [21].

Several research groups have studied the effect of growth parameters on the surface morphology of the epitaxial GaN films grown via MBE. The effect of the III/V ratio on the surface morphology for GaN films has been reported for both homoepitaxial and heteroepitaxial growth[23-25]. In general, two regions were reported to exist, each of which produced a different surface morphology. In a Ga-stable (or nitrogen limited) environment, where growth had been conducted at a high III/V ratio, the surface displayed a smooth structure. In the nitrogen stable (or gallium limited) region, which is grown at a low III/V ratio, the surface morphology showed a faceted structure with high density of stacking faults [25]. Held et al. [24] confirmed these results from the growth of GaN via GSMBE on the (000-1)_N face of GaN. The nitrogen stabilized regime produces a granular film with pyramidal hillocks that have been attributed to inversion domains which originated from defects at the substrate/nucleation layer interface[23].
For example, inversion domains that are (0001) oriented grew at a faster rate than the (000-1) oriented matrix under the nitrogen excess regime. The samples grown under excess gallium did not show the hillocks, even though the defects existed on the nucleation layer. This was attributed to the suppression of the different growth rates on the different crystallographic planes.

The surface morphology of AlN grown by MBE is also strongly influenced by the III/V ratio [26]. Atomically flat films were obtained when the film was grown under stoichometric conditions. The surface roughness increased further away from stoichometric conditions the films were grown.
1.3 Properties of Silicon Carbide

1.3.1 Introduction

The interest in silicon carbide has been cyclic over the past two centuries since its discovery in 1824 by Jons Jacob Berzelius [27,28]. Since natural occurring silicon carbide is rare and has been only discovered in meteorites, interest in the material did not occur until the manufacturing of silicon carbide was improved by Achesen around 1892 using an electric smelting furnace [28]. The resulting material was used in polishing applications due to its extreme hardness. In 1907, the Marconi company of Italy measured the first electrical property, electroluminescence. However, the data was essentially unnoticed for approximately 50 years [29]. Interest in silicon carbide was renewed in 1955 following the development of a sublimation process to produce free standing silicon carbide platelets from the deposition of the sublimed vapor at the cooler regions in a thermal gradient [29]. Tairov and Tsvetkov improved upon this process in 1978 when they introduced a SiC seed crystal on which the vapor deposited resulting in a boule of the material [29]. Today, the interest is silicon carbide is high and several corporations have formed to produce large boules having a particular crystal structure (see below) and controlled concentrations of impurities that determine the electrical and optical properties. Single crystal wafers to 4 inches in diameter and cut from the boules are available. Currently silicon carbide wafers and films grown on these wafers are used in applications ranging from substrates for heteroepitaxial growth of III-Nitride films to high power/temperature devices. The following sections are concerned with the
crystallography, the defect microstructure, and the preparation of surfaces of the SiC wafers.

1.3.2 Crystallography and Polytypism

The crystallography and polytypism in silicon carbide play important roles in controlling the properties and the nature of the surfaces available for the epitaxial growth of III-nitride semiconductors. The Si-C equilibrium phase diagram presented in Figure 1.5 shows that SiC is the only stable compound [30]. The fundamental unit in the SiC structure is a covalently bonded tetrahedron with 4-fold symmetry, consisting of either SiC$_4$ or CSi$_4$, as shown in Figure 1.6. In the case of CSi$_4$, the carbon atom sits at the center of mass of the tetrahedron, which gives a distance of 1.89 Å for the C-Si bond. The distance between Si-Si atoms is approximately 3.08 Å. Taking one of Si-C bonds to coincide with the c-axis direction, the distance between the silicon layers, shown in Figure 1.6b, is approximately 2.5 Å. The unit cell is bonded through the corner atoms of the tetrahedron, which satisfies the four - fold coordination at any structural point in the crystal [31]. There are two possible orientations, rotated by 60°, of adjacent tetrahedra, as shown in Figure 1.6b [32]. The various rotations and translations lead to the many different polytypes, or stacking arrangements of the Si-C bilayers along the c-axis.

Figure 1.7 shows the possible atomic arrangements of the atoms in the hexagonal wurtzite unit cell. If the atoms in the basal plane are labeled A, then the atoms in the next layer may sit at either position B or position C. Thus the structure is composed of bilayers in an …ABAB… sequence. The cubic (zincblende) structure, is composed of bilayers in the sequence …ABC… with the same orientation. Thus, the zincblende polytype is
related to the wurtzite polytype by rotations and translations within the unit cell. The more polytype structures in silicon carbide may be a combination of these two. In this ABC notation, a rotation of 180° in the hexagonal description is indicated by a prime next to the layer descriptor. For example in Figure 1.8, A and A' are in the exact spatial registration, but are rotated by 180°. There are two more common ways to describe the crystal structures in the silicon carbide system.

The first method was proposed by Jagodzinski [31,33,34] in which each layer is described as having either a local cubic (k) or hexagonal (h) structure, based on the position of the center atom, or centroid, of the immediate layer neighbors. If the positions of the centroid in the layers above and below are different, then the structure is described as cubic. Therefore, an ABCABC stacking sequence describes a cubic bilayer structure, since the layers above and below any one layer do not align. If the centroid of the two layers above and below is in the same spatial position, then the layer is described as hexagonal. In the case of the ABABA stacking sequence, the layer above and below any one layer is the same, therefore each bilayer may be described as hexagonal in nature. Based on the notation by Jogodzinski, two stacking sequences exist; sequences with layer transitions only, which is denoted by "kkkk", and sequences with layer transitions and rotations denoted by "hhhh". For example, (hkk)₂ and hkkhk describes a unit cell with six bilayers and 4 bilayers respectively. As will be discussed in the next paragraph, these stacking sequences represent the 6H and 4H unit cells, respectively.

The second method of describing the structures of silicon carbide was proposed by Ramsdell[35] and is based on hexagonal symmetry. In this notation, a letter is used to
describe the crystal symmetry (hexagonal (H), cubic (C), rhombohedral (R)) and a number is used to describe the number of layers along the c-axis (2, 4, 6…) that are necessary to produce a unit cell. In the silicon carbide system there are 5 small period polytypes which occur most often within the crystal structures and may be considered the 'basic' structures: 2H, 3C, 4H, 15R, and 6H.. Each of the longer period polytypes may be considered as a combination of these 5 short period polytypes. This latter notation will be utilized in the remainder of the dissertation.

Figure 1.8 shows the stacking sequence of the 6H, 4H, and 3C unit cell structures. The 6H unit cell is constructed by taking a basal plane, denoted as “C’’ and constructing a 6 bilayer structure along the c-axis. In Figure 1.8, the first three bilayers after the base layer all have the carbon atoms positioned forward of the silicon atom, i.e. out of the page, in these images. At the C bilayer, the bilayers are rotated 180º and are denoted by the prime next to identification letter. The carbon atoms on the (11-20) face are now into the page and behind the silicon atom. Again, these layers follow the zig-zag pattern until the A face is reached and the pattern is repeated. The 4H follows the same type of construction except that it consists of only 4 bilayers. This may be seen in Figure 1.8b. The 3C structure, as seen if Figure 1.8c, consists of 3 bilayers repeating indefinitely by translation without the rotation contained in the hexagonal structures. Each polytype has different mechanical and electrical properties as shown in Table 1.1.

1.3.3 Defects in Silicon Carbide

Defects in the silicon carbide wafers play an important role in the surface preparation of the wafers and the properties of subsequently grown nitride films.
Macroscopic defects, which in general can not be eliminated, include pin-holes, pits, second polytype inclusions, and micro-pipes. These defects directly affect the microstructure and physical properties of epitaxial film grown on the wafers, if they continue into the overgrown layers. In general, the frequency of these defects is low, except around the edge of each wafer. One exception is the polishing scratches on the surface that occur over the entire wafer. However, these may be removed with various types of etching. This procedure will be discussed in Section 1.1.5. There are also several microscopic defects that can affect the surface preparation of the silicon carbide.

The microscopic and macroscopic defects that occur throughout the wafer and that directly affect the surface morphology of the etched substrates are stacking faults, screw dislocations, and polytype inclusions in the wafer. Stacking faults occur on the basal plane of the silicon carbide unit cell. They may be introduced into the silicon carbide by either introducing or removing a close packed layer. To relieve the strain of the faulted region, atoms rearrange themselves, which is accommodated by the creation of Shockley partial dislocations. These partial dislocations readily occur in silicon carbide due to its low stacking fault energy, which has been reported as either 2.5 mJ/m² [36,37] or 1.9 ergs/cm² [36,37]. The differences in stacking fault energies have been attributed to differences in the tested materials. The Shockley partials are created from a total dislocation with a Burgers’ vector of 1/3<11-20>, that splits into the partials having Burgers’ vectors of:

\[1/3<11-20> \rightarrow 1/3<10-10> + 1/3<01-10>\] (9)
The formation of stacking faults may be one of the defects necessary to nucleate a different polytype within a single crystal of silicon carbide.

The second type of dislocations in silicon carbide are screw dislocations. Screw dislocations run along the [0001] direction and may be found at the center of growth spirals. Filled (a.k.a. closed) and unfilled screw dislocations occur in SiC crystals; the former are predominate. The unfilled dislocations have a hollow center down the c axis of the defect [38]. When this hollow center becomes large or joins with another unfilled dislocation, micropipes form in the structure. Screw dislocations have been identified as one cause of localized polytype formation in silicon carbide.

The third defect is the formation of secondary polytype inclusions within the primary polytype boule. Over the years, the formation of the different polytypes of silicon carbide has been analyzed extensively. They have been predicted to occur via either kinetically or thermodynamically controlled routes[39-41]. Kinetic considerations employ the use of screw dislocations or stacking faults to change the stacking sequence, while thermodynamic considerations are based on the configurational and vibrational entropies of the system. A unified theory has been proposed by G.R. Fisher and P. Barnes[42], which indicated that process control instabilities must first introduce crystalline defects such as screw dislocations or stacking faults, which, in turn, allow a new polytype to form. The transformation from one polytype to another may occur by two processes[31]. The first process would require the silicon carbide to be sublimed or dissolved and regrown with the new polytype structure. The second transformation mechanism only requires the rearrangement of some of the layers via shear or diffusion.
Sheer could supply the necessary translation and rotation to produce a change in a layer as long as it occurred at the center of gravity of the tetrahedron. In other words, dislocations of 1/3<10-10> would have to glide on the basal plane between the centroid and the base of the tetrahedron. Some of the observed polytype changes within 6H silicon carbide are the 6H-to-4H and the 6H-to-3C [34]. Ultimately, this defect plus the ones mentioned above will effect the surface morphology of the prepared silicon carbide wafer.

1.4 Surface Preparation of 6H-SiC(0001)

The surface preparation of SiC plays an important role in terms of the structural and electrical characteristics of the subsequently grown films. The surface chemistry and structure of the surface will depend upon the surface preparation procedure. Recent studies using reflection high energy [43] and low energy electron diffraction [44-47]; scanning tunneling [47-50] and atomic force [51-53] and low energy electron microscopies [53]; electron energy loss [46,54], Auger electron [45,46,54], and x-ray photoelectron [45] spectroscopies have provided critical microstructural, structural, and chemical information regarding the efficacy of different chemical process routes for the preparation of these surfaces. A review of the surface preparation techniques, both past and present, of the Si terminated (0001) surfaces of the 6H and 4H silicon carbide polytypes is presented in the following subsections.
1.4.1 Surface Cleaning

The as received 6H-SiC wafers from Cree, Incorporated contain a thermally grown, 0.1 µm thick silicon dioxide passivation layer. The ex-situ removal of hydrocarbon contamination from the surfaces is achieved via sequential immersions into a boiling or an ultrasonic solvent rinse of trichloroethylene, acetone, and methanol. The substrate is then dipped into a 10:1 HF solution for 10 minutes to remove the oxide, rinsed in di-ionized water rinse and blown dry with nitrogen. The cleaned surface is terminated with oxygen and hydroxide groups from the reaction with the water rinse and/or exposure to the ambient as well as fluorine [55]. The LEED exhibits a 1 x 1 pattern with broad diffraction spots that indicate a disordered surface with contamination. To completely remove the adsorbed species noted above and obtain a well ordered surface before molecular beam epitaxial growth, an in-situ clean must be conducted.

Several in-situ cleaning methods have been proposed for 6H-SiC(0001)\textsubscript{Si} surfaces[55-57]. Reported surface states for this polytype include (1x1), (3x3), (9x9), (\sqrt{3} \times \sqrt{3})R30°, and (6\sqrt{3} \times 6\sqrt{3})R30°, depending on the cleaning procedure employed. One of the first reported methods of cleaning under UHV conditions was to anneal the silicon carbide sample at an elevated temperature [56]. During thermal annealing at approximately 1000°C, oxygen is evaporated from the surface in the form of a volatile SiO compound, leaving the surface depleted of Si. Studies by Johansson et. al.[58] have estimated that approximately 2/3 of a monolayer of the top silicon is lost during annealing below 1000°C. Adachi et al.[59] have shown that below 1000°C and following the initial loss of silicon, this element is no longer depleted from the surface at longer
annealing times. Therefore, the initial conclusions drawn from an earlier experiment [56], where in any residual carbon on the surface was predicted to form a C-C bond and graphitize the surface and produce the $(\sqrt{3} \times \sqrt{3})$ R30º reconstruction may not be completely correct. The surface arrangement of atoms is not fully understood for the $(\sqrt{3} \times \sqrt{3})$R30º obtained without a silicon flux. One model predicted by Johansson et.al. [58] envisions a trimer arrangement of C atoms above the 2 second bilayer and below the Si adatoms on the surface. However, further research needs to be conducted to determine the mechanism and chemistry involved in the formation of this reconstruction.

Upon higher temperature annealing, the $(\sqrt{3} \times \sqrt{3})$R30º surface will transform to $(6\sqrt{3} \times 6\sqrt{3})$R30º surface state, which has been shown [54] to contain much more carbon than the $(\sqrt{3} \times \sqrt{3})$R30º state. In the $(6\sqrt{3} \times 6\sqrt{3})$R30º reconstruction, silicon atoms have been predicted to diffuse from deeper bilayers and evaporate from the surface[59]. The occurrence of the $(6\sqrt{3} \times 6\sqrt{3})$R30º reconstruction is an indication of over annealing and is undesired; it will not be further discussed. For more information regarding the graphitization of the SiC surface, the reader is referred to references [58-60].

To avoid the depletion of silicon and subsequent graphitization of the surface, several procedures have been proposed to remove the oxygen via a chemical reaction or replacing the depleted silicon with silicon from an external source. Two such procedures exposed the surface to either a Ga flux [57] or a silicon flux[32,46,48,49,61-63]. In the case of the former, the Ga atoms reacted with the oxygen on the surface producing a gallium oxide, Ga₂O, which is more volatile than the silicon oxide on the surface. The reaction was studied at 900ºC, which is approximately 100ºC less than simply annealing.
the sample without a flux. However, at this low temperature residual oxygen remained on the surface. The silicon surface exposed to the Ga flux exhibited a (3 x 3) surface reconstruction after cleaning, indicating excess species on the surface.

In the latter case, the silicon flux is produced via solid source electron beam evaporation[46,48,49,61,63] or from a gas source such as silane [55]. The silicon carried away from the surface in the form of SiO is replaced by the incoming flux. The surfaces of (\(\sqrt{3} \times \sqrt{3}\))R30°, (3 x 3), (1 x 1), or (9 x 9) have been reported and depend on the amount of excess silicon on the surface and the temperature at which deposition occurred.

The two most common reconstructions for the 6H-SiC(0001)\(_{Si}\) surface are the (3 x 3) and the (√3 x √3)R30° depending on the cleaning procedure. The (√3 x √3)R30° surface state may be obtained by direct exposure to the silicon flux or by additional annealing of a 3 x 3 surface state. The accepted √3 x √3 R30° surface state has one adatom occupying the T4 site directly above the carbon atom, as shown in Figure 1.9. Auger results on 4H from Starke et.al. [32] have shown a peak-to-peak ratio of silicon to carbon to be approximately 2.2 for the (√3 x √3)R30° surface indicating excess silicon on the surface. Surface coverage of silicon has been predicted to be approximately 1/3 of a monolayer of excess silicon [48].

Figures 1.10, 1.11, and 1.12 show three possible atomic arrangements of adatoms on the surface for the 3 x 3 reconstruction. The first model shown in Figure 1.10 was proposed by Kaplan which consists of a dimer-adatom-stacking fault (DAS) model in which two adatoms rest on a layer of six silicon atoms that are above a layer of eight more silicon atoms[46]. Other models presented by Kulakov et al. [49] and Li and
Tsong.[48] have refined this model, but with different results. The model from Kulakov et al., shown in Figure 1.11, shows a structure, which consists of a single adcluster and is composed of eleven atoms. The validity of this model has been supported by X-ray photoelectron diffraction work by King et al. [64]. The second model proposed by Li and Tsong, shown in Figure 1.12, does not agree with the previous models. They propose a four-atom silicon tetrahedron on the surface based on STM results. The surface coverage is described as having a complete bilayer of silicon on the surface with additional adatoms of silicon.

The (\sqrt{3} \times \sqrt{3})R30° surface state may be obtained by additional annealing of the 3 x 3 surface to remove excess silicon. During annealing, 1 x 1 intermediate surface reconstruction has been observed due to loss of silicon from the surface[55].

Another method for cleaning the surface is sputtering/ion bombardment by highly energetic argon ions[65,66]. Incomplete removal of the residual oxygen was reported [65]. Surface damage due to the energy of the ions, may also occur. Lin et al. [67] and King et al. [55] have reported the use of hydrogen plasmas for the removal of hydrocarbons; however this process was not effective for the complete removal of oxygen. Etching has also been employed to prepare and remove damage from the surface, as described below.

1.4.2 Etching of SiC

As stated above, the surface of the silicon carbide, as stated above, contains many scratches from the polishing procedures and may also contains several disordered bilayers. These damaged regions directly affect the microstructure of the epitaxial films
grown on the surfaces. The cleaning procedures described above only affects the first few bilayers of the surface and do not remove disordered layers. Etching of the surface can be used for the removal of both contamination and damaged layers that are on the order of nanometers and for the patterning of devices. As discussed in the cleaning section, silicon is easily removed from the surface via annealing under ultra high vacuum conditions. However, carbon is tenacious and not so readily removed. Several etching techniques for silicon carbide have been developed for specific applications.

Starke et al. [68] have proposed a procedure to remove surface damage in which the surface is oxidized, cleaned with aqua regia, rinsed in acetone and again etched in HF. Once this procedure was completed and the sample placed in vacuum, a sharp LEED pattern, indicating a well-ordered surface was evident.

Other etching methods involve annealing the wafer to 1900°C [50,69] or annealing the wafer while exposing of the surface to either a gas mixture of hydrogen and HCl [70,71] or to hydrogen gas [72]. Polishing scratches are removed and replaced with steps. In the case of sublimation etching, the step heights are non unit cell height [69]. In the hydrogen etching, the surface is covered with steps that have unit cell heights. The details and results of the hydrogen etching procedure will be discussed in Chapter 3.

Other etching techniques that have been used for device fabrication, include plasma etching, photoelectrochemical etching, and reactive ion etching (RIE) which use a plasma in tandem with sputtering. The RIE process exposes the surface to species such as CF4, SF6, CBrF3 or CHF3 mixed with oxygen which react with the carbon and silicon [73,74]. For faster etching rates, electrochemical etching and photoelectrochemical
etching with HF:NH₄F [75] may be employed. These processes produce RMS roughness values on the order of mechanical polishing and are not ideal for the growth of III-Nitrides.
1.5 References


F. C. Frank, Philosophical Magazine **42** (1951).


60 K. Miyoshi and D. H. Buckley, Applications of Surface Science 10, 357-376 (1982).


Table 1.1 Physical Properties of Selected SiC Polytypes, AlN, and GaN

<table>
<thead>
<tr>
<th></th>
<th>6H-SiC</th>
<th>2H-AlN</th>
<th>2H-GaN</th>
<th>4H-SiC</th>
<th>3C-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant: a (Å)</td>
<td>3.08</td>
<td>3.112</td>
<td>3.189</td>
<td>3.076</td>
<td>3.083</td>
</tr>
<tr>
<td>Lattice Constant: c (Å)</td>
<td>15.12</td>
<td>4.982</td>
<td>5.185</td>
<td>10.046</td>
<td>7.55</td>
</tr>
<tr>
<td>Structure</td>
<td>Wurtzite</td>
<td>Wurtzite</td>
<td>Wurtzite</td>
<td>Wurtzite</td>
<td>Zinc-blende</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>3.0</td>
<td>6.2</td>
<td>3.4</td>
<td>3.263</td>
<td>2.390</td>
</tr>
<tr>
<td>Electron Affinity (eV)</td>
<td>3.5</td>
<td>≤ 0 to 1</td>
<td>3.4</td>
<td>-----</td>
<td>-----</td>
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<td>Coefficient of Thermal</td>
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<td>4.15 x 10^{-6}</td>
<td>5.59 x 10^{-6}</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Expansion (a-axis) (/K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coefficient of Thermal</td>
<td>4.68 x 10^{-6}</td>
<td>5.27 x 10^{-6}</td>
<td>7.75 x 10^{-6}</td>
<td>-----</td>
<td>-----</td>
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<tr>
<td>Expansion (c-axis) (/K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>4.9</td>
<td>2.5</td>
<td>1.3</td>
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<td>-----</td>
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<tr>
<td>(W/cm-K)</td>
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Table 1.2 Observed growth modes of GaN and AlN on 6H silicon substrates using different growth methods

<table>
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<tr>
<th>Buffer</th>
<th>Process</th>
<th>Result</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>AlN</td>
<td>MOVPE</td>
<td>Step Flow [76]</td>
</tr>
<tr>
<td>GaN</td>
<td>AlN</td>
<td>ECR-MBE</td>
<td>3D growth [22]</td>
</tr>
<tr>
<td>GaN</td>
<td>None</td>
<td>ECR-MBE</td>
<td>3D growth [15,16]</td>
</tr>
<tr>
<td>GaN</td>
<td>AlN</td>
<td>RF-MBE</td>
<td>2D growth [14]</td>
</tr>
<tr>
<td>GaN</td>
<td>None</td>
<td>RF-MBE</td>
<td>3-D nucleation [14]</td>
</tr>
<tr>
<td>GaN</td>
<td>AlN</td>
<td>GS-MBE</td>
<td>SK Growth - Low Temp. [21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2D Growth - &gt;800°C [77]</td>
</tr>
<tr>
<td>GaN</td>
<td>H2 etched SiC</td>
<td>RF-MBE</td>
<td>2D - Low Temp. 3D- High Temp. [77]</td>
</tr>
<tr>
<td>GaN</td>
<td>H2 etched SiC</td>
<td>SSJ or RF</td>
<td>3D growth [53]</td>
</tr>
<tr>
<td>AIN</td>
<td>None</td>
<td>ECR-MBE</td>
<td>2D growth [15]</td>
</tr>
<tr>
<td>AIN</td>
<td></td>
<td>ECR-MBE</td>
<td>On Axis: SK mode [78]</td>
</tr>
<tr>
<td>AIN</td>
<td></td>
<td>ECR-MBE</td>
<td>Off axis: Island like growth [78]</td>
</tr>
<tr>
<td>AIN</td>
<td>GaN</td>
<td>GS-MBE</td>
<td>FM/Layer by layer [21]</td>
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Table 1.3 Observed growth modes of GaN and AlN on sapphire substrates using different growth methods

<table>
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<tr>
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</tr>
<tr>
<td>None</td>
</tr>
<tr>
<td>L.T. GaN</td>
</tr>
<tr>
<td>MOCVD</td>
</tr>
<tr>
<td>3D on no buffer</td>
</tr>
<tr>
<td>2D on L.T. GaN buffer</td>
</tr>
<tr>
<td>[17]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>Nitride surface w/ LT GaN</td>
</tr>
<tr>
<td>MOVPE</td>
</tr>
<tr>
<td>2D Growth</td>
</tr>
<tr>
<td>3D Growth (over nitrided)</td>
</tr>
<tr>
<td>[20]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>Nitride surface w/ LT GaN</td>
</tr>
<tr>
<td>ECR-MBE</td>
</tr>
<tr>
<td>Island, 3D or 2D Growth</td>
</tr>
<tr>
<td>Dependent on ECR power</td>
</tr>
<tr>
<td>[19]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>AlN</td>
</tr>
<tr>
<td>ECR-MBE</td>
</tr>
<tr>
<td>SK mode</td>
</tr>
<tr>
<td>[16]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>None</td>
</tr>
<tr>
<td>ECR-MBE</td>
</tr>
<tr>
<td>SK Growth</td>
</tr>
<tr>
<td>[15]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>L.T. GaN</td>
</tr>
<tr>
<td>RF-MBE</td>
</tr>
<tr>
<td>2-D Mode (500ºC)</td>
</tr>
<tr>
<td>Step flow mode (600ºC)</td>
</tr>
<tr>
<td>[79]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>AlN</td>
</tr>
<tr>
<td>RF-MBE</td>
</tr>
<tr>
<td>(620º-720º) SK mode</td>
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<tr>
<td>[80]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>Nitrided</td>
</tr>
<tr>
<td>RF-MBE</td>
</tr>
<tr>
<td>2D growth enhanced at lower temperatures</td>
</tr>
<tr>
<td>[18]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>L.T. GaN</td>
</tr>
<tr>
<td>GS-MBE</td>
</tr>
<tr>
<td>2-D Mode (680ºC)</td>
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<tr>
<td>[81]</td>
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<td>AlN</td>
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<tr>
<td>None</td>
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<td>ECR-MBE</td>
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<td>2D growth</td>
</tr>
<tr>
<td>[15]</td>
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<tr>
<td>AlN</td>
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<tr>
<td>GaN</td>
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<tr>
<td>GS-MBE</td>
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<tr>
<td>2D growth</td>
</tr>
<tr>
<td>[21]</td>
</tr>
<tr>
<td>GaN</td>
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<tr>
<td>ALE and MSE</td>
</tr>
<tr>
<td>Enhanced 2D growth</td>
</tr>
<tr>
<td>[82]</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>L.T. GaN</td>
</tr>
<tr>
<td>CBE</td>
</tr>
<tr>
<td>2D growth</td>
</tr>
<tr>
<td>[83]</td>
</tr>
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</table>

Table 1.4 Observed growth mode of GaN on GaN using RF-MBE

<table>
<thead>
<tr>
<th>Observed Growth Modes of GaN</th>
</tr>
</thead>
<tbody>
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<td><strong>Homoepitaxial Growth</strong></td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>GaN</td>
</tr>
<tr>
<td>RF-MBE</td>
</tr>
<tr>
<td>2D Growth</td>
</tr>
<tr>
<td>[84]</td>
</tr>
</tbody>
</table>
Figure 1.1. Wurtzite structure of GaN and AlN. The structure may be considered as two interpenetrating hexagonal lattices with the group III occupying sites on one hexagonal unit cell and the group V on the other.
Figure 1.2. The three different growth modes for epitaxial films on a substrate. a. Frank-van der Merwe (2-dimensional), b. Volmer-Weber (3-dimensional), c. Stranski-Krastanov (combination of a and b).
Figure 1.3. Top view of the molecular beam epitaxy chamber used in the research of this dissertation and located at Duke University. It contains three Knudsen cells for the group III sources and a nozzle for the group V ammonia source.
Figure 1.4. Schematic drawing showing the step-wise dissociation of ammonia on a surface.
Figure 1.5. Equilibrium phase diagram of the C-Si system. Note that SiC is the only stable compound at one atmosphere pressure.
Figure 1.6. (a) Basic unit cell of silicon carbide. The distance between the carbon and the silicon atoms, a, is approximately 1.89 Å and between the silicon atoms, b, is 3.08 Å. (b) The two configurations of silicon and carbons atoms, rotated 180°.
Figure 1.7. Possible stacking orientations of atoms in a close packed hexagonal structure.

In plane above the plane

above the plane
In plane
Figure 1.8 Stacking sequence for the 3 main polytypes of silicon carbide

a. 6H, b. 4H, c. 3C
Figure 1.9. Adatom placement for the $\sqrt{3} \times \sqrt{3} \text{ R}30^\circ$ reconstructed surface [63].
Figure 1.10 Dimer-adatom-stacking fault (DAS) structure proposed by Kaplan [46] for the 3 x 3 reconstructed surface.
Figure 1.11. 3 x 3 surface structure proposed for SiC by Kulakov et. al. [49].
Figure 1.12. 3 x 3 surface structure proposed for SiC by Li and Tsong [48].
2 \hspace{1em} \textbf{Equipment and Procedures}

2.1 \hspace{1em} \textit{Introduction}

The growth of AlN and GaN thin films and the surface morphology and atomic structure of nitrogen doped, n-type 6H-SiC(0001)\textsubscript{Si} wafers before and after various surface preparation techniques were investigated. The experimental results presented in the subsequent chapters were obtained using the equipment and experimental procedures described in the following subsections. The hydrogen etching of the 6H-(0001)\textsubscript{Si} silicon carbide was performed in a custom designed, stand-alone system. The samples were then transferred to the Integrated Growth and Analysis system for the conduction of controlled cleaning studies under ultra-high vacuum (UHV) conditions to avoid contamination. The growth of the nitrides was conducted in the Nitride Growth and Characterization System located at Duke University. A detailed description of each system and the equipment employed is presented below.

2.2 \hspace{1em} \textit{Hydrogen Etching Chamber}

The removal of the scratches and damaged layers from polishing can be removed by etching in a hydrogen atmosphere at elevated temperatures of approximately 1600 °C for 20 minutes at 1 atm. This process has been shown to leave a flat surface with unit cell height steps \([1-5]\). Figure 2.1 shows a schematic of the chamber used for the hydrogen etching of the silicon carbide wafers. The bottom section is composed of stainless steel,
and contains ports and feedthroughs for the vacuum, electrical and mechanical connections and the vacuum gauges. The system is evacuated with a Barodyne 3 stage diaphragm pump that has a pumping speed of 18 l/s. The base pressure in the system is below 1 torr. The pump is connected through two ports, 180° apart, to assist in creating uniform flow over the samples. Pressure is monitored using a Baratron gauge with a maximum reading of 1000 Torr. Additional ports on the base flange are available for a diffusion or turbo pump, if a lower base pressure is required. The base flange of the chamber also contains 5 feedthroughs for the electrical, mechanical, and thermocouple connections.

Heating of the sample occurs in the top section of the chamber, which is composed of a water cooled quartz tube. The samples are placed on a tantalum strip heater that is connected to two molybdenum electrodes. The nominal dimensions of the Ta heater are 70 millimeter in length, 11 mm in width, and 0.025 mm thick. The heater is held in place by two 1.27 mm thick molybdenum plates. Gas is introduced into the system from the top through a custom designed nozzle with a flow straightener. The diameter of the nozzle is 2.5 inches and is water-cooled. The flow straightener consists of a 0.5 thick honeycomb inconel plate. The gas used for processing is a mixture of 25% hydrogen/75% helium which has a purity of 99.9998% or better to avoid contamination of the surface by impurities.

The temperature is monitored through the quartz walls using an Ultimax infrared thermometer from IRCON that operates in the wavelength range of 0.96 to 1.05 μm. Due to the quartz and water, the temperature reading is estimated to be approximately 50-60°C.
below the actual reading. An emissivity of 1.0 was assumed from the previous experimental research reported by V. Ramachandran et. al.[4]. The temperature of the silicon carbide was maintained between 1600º and 1650º C.

2.3 Integrated Analysis and Growth System

The surface cleaning and characterization of the hydrogen etched samples were conducted within the Integrated Analysis and Growth System (IAGS). As illustrated in Figure 2.2, this system consists of a 43 foot long transfer chamber with 13 individual chambers. The transfer chamber is maintained in the middle-to-high $10^{-10}$ torr range via the use of four cryopumps (Cryo-torr 8). Two stainless steel rails run the length of the transfer chamber; and the sample cart glides along the rails. The basic design of the sample cart consists of a stainless steel plate with three ports for samples and four teflon guides that run on the rails. The cart is moved along the rail using a pulley system with a stainless steel wire. Transfer rods are located at each chamber to remove the sample holders from the cart and transfer the holder into the selected chamber.

Samples are mounted on a molybdenum sample holder and a plate, as shown in Figure 2.3. The molybdenum plate is used for samples less than 1 inch in diameter. The layout was designed by Kieran Tracy. The plate contains a center hole of 0.25-0.6 inches in diameter and is surrounded by four arrays of smaller holes. The sample is held onto the plate with tantalum wires that are threaded through the smaller holes on the plate. The molybdenum plate holding the sample is fastened to the sample holder with tantalum wires. The mounted samples subsequently placed into a given system via a loadlock.
chamber that consists of a six-way cross and is evacuated using a Leybold Turbvac 360 turbomolecular pump. Samples are transferred onto the cart in the transfer line once the pressure in the load lock reaches $1 \times 10^{-7}$ torr.

2.3.1 *Auger Electron Spectroscopy (AES) and Low Electron Energy Diffraction System (LEED)*

The LEED and AES systems are mounted to the same six-way cross noted in the previous subsection, as shown in Figure 2.4. The LEED system was used to determine the surface structure and is mounted to the top flange. It consists of a Princeton reverse view, RLV 6-120, optics and is controlled by Princeton (11-020) LEED control electronics. Electrons are emitted from a thoria coated iridium filament operated at 1 mA of current with an emission current of 0.2 mA. The beam diameter of the incident electrons is less than 1 mm. The accelerating voltage was set to 4 kV; the gun voltage depends on the sample, but typically ranges between 80 – 150 eV. The diffracted electrons are imaged onto a phosphor screen and are captured using a DC120 Kodak digital camera with a resolution of 1280 x 960 pixels and 24 bit color.

An AES system is positioned opposite to the LEED in the same vacuum chamber. AES is obtained by rotating the sample 180º to face the system. This system consists of a 10-155 cylindrical mirror analyzer, a 11-010 electron gun control, and a 32-150 digital analyzer control. The primary electrons are again emitted from a tungsten filament and are focused to a spot size of 100 µm under typical operating settings[6] of accelerating voltage, 3 kV, 1 mA current though the filament and 0.3 mA emission current. The emission current and filament currents were adjusted slightly to adjust the number of
counts.

2.3.2 X-ray Photoelectron Spectroscopy (XPS)

The x-ray photoelectron spectroscopy unit consists of a Fisons-VG Scientific LTD XPS system mounted on a custom designed stainless steel chamber. Figure 2.5 shows a photograph of the XPS system. The chamber is evacuated using a CTI cryogenics Cryo – Torr 8, cryopump that maintains a base pressure of $3 \times 10^{-10}$ torr. Rough pumping is achieved via two Balzers TPU turbomolecular pumps that are connected to the UV lamp and to the chamber. The x-ray source consists of a dual anode Fisons XR3 that is powered by a Fisons 427 power supply. Magnesium and aluminum anodes with photon energies of 1253.6 eV and 1486.6 eV respectively, are available for research. In this work, only the aluminum source was employed.

A Fisons Clam II electron energy analyzer with a dual element transfer lens is used to collect the electrons. The analyzer has a 100 mm radius with a 4 mm slit for collection. In this research, the system was operated in the constant analyzer energy (CAE) mode with a pass energy of 50 eV for survey scans and 20 eV for detailed scans. Control of the system was achieved via VGX900 software, which allows the user to set the scanned energy ranges and the desired pass energy for each individual scan. Typically, one survey scan was conducted, and several detailed scans of specific peaks were obtained. To assure the calibration accuracy of the collected spectrums, a gold standard was analyzed every few months.
2.3.3 *Gas Source Molecular Beam Epitaxy System (GSMBE)*

The GSMBE system consists of a custom designed chamber that is used for both the growth and the cleaning of the III-Nitrides and silicon carbide. Figure 2.6 shows a digital image of the system. The system is evacuated using a Leybold Turbovac 360 CSV backed by an Edwards E2M18 dual stage rotary vane pump. When samples are not being analyzed, a 500 liter/second Varian ion pump, model 921-0038, is opened to the chamber for additional pumping on the system. The combination of the pumps brings the system background pressure into the high $10^{-10}$ torr range. The third pump on the system is a Varian Associates titanium sublimation pump, model 922-0032. This pump was used to help reduce the pressure after a run involving ammonia or after venting the chamber. A fourth indirect pump on the system is the cryopanel. During growth and cleaning runs in this research, the cryo panel was cooled using liquid nitrogen and is used to protect the knudsen cells (k-cells) from the ammonia environment. The cryo panel also assists in removing contamination from the system during outgassing and annealing of the samples.

For uniformity, the heater assembly in the GSMBE was designed in the manner used for the heaters in the other chambers on the transfer line. The sample is heated by placing the sample holder over a 0.5 mm diameter tungsten coil resistive heater, as shown in Figure 2.7. Radiative heating in the infrared and visible ranges is produced by the coil. Silicon carbide is transparent to wavelengths in these regions. Therefore, the backside of every sample was coated with tungsten using a RF sputtering system. The heater is controlled with an Eurotherm 818 controller in tandem with an 831 SCR solid
state relay. The Eurotherm 818 allows programming of the controller for specific heating and cooling profiles. During processing, the temperature of the samples used in this research was monitored using an IRCON Ultimax Optical Pyrometer, as described above, with an emissivity setting of 0.5.

Gases were introduced into the system for the growth or cleaning of the wide band gap semiconductors though two dosers (Figure 2.7). The first doser enters the system directly across from the sample and was used exclusively for the ammonia gas employed for the growth and cleaning of the III-nitride samples. Blue ammonia from Solkatronics was used, which has an advertised purity of 99.99994%. The ammonia was passed through a Pall Gaskleen ammonia purifier before entering the system. The doser was positioned approximately 2 inches away from the sample. The flow rate was controlled via a leak value, and the pressure in the system was monitored using a Granville Philips Ion Gauge with a thoria coated filament. Typical operating pressures for growth and cleaning of the III-nitrides were between $1 \times 10^{-4}$ to $1 \times 10^{-6}$ torr. The second doser, positioned at a slight angle to the substrate, was used to deliver silane to the system for the cleaning of the silicon carbide surfaces. Silane cleans employed 99.995% pure silane obtained from Mattheson. During silane cleaning, the pressure of the system was maintained at $1 \times 10^{-6}$ torr. The second doser could also deliver ethylene for the cleaning of the carbon face of silicon carbide [7].

For the growth of III-Nitrides, the GSMBE system contained three EPI Knudsen cells. A single filament "cold lipped" k-cell was used for the evaporation of aluminum [8]. This minimized the creep of aluminum over the lip and onto the tantalum
heat shielding. A second modification to the k-cell was the insertion of a second crucible with an open bottom. The cooled second crucible also caused solidification of most of the creeping aluminum before it could react with the tantalum shielding. The aluminum source was 99.9998% pure. A dual filament k-cell was used for the evaporation of gallium. In this design, a second filament was placed around the top of the crucible to minimize the gallium condensation on the lip and consequent spattering onto the sample during growth. Crucibles for both systems were 25 cc and made of pyrolytic boron nitride. The k-cells were controlled using a Eurotherm 818 controller in tandem with a 831 SRC solid state relay. The system was equipped with a Sycon STM-100 crystal rate monitor to monitor the growth rate.

2.3.4 Solid Source Molecular Beam Epitaxy Chamber

Where contamination from the residual gases in the GSMBE chamber had to be minimized, the solid source molecular beam epitaxy (SSMBE) chamber was used to anneal the samples. The SSMBE is shown in Figure 2.8. Since the system used solid silicon and germanium as its sources, the chamber was not contaminated by ammonia as in the GSMBE chamber. The chamber base pressure of $3 \times 10^{-10}$ torr was maintained though the use of a Perkin Elmer ion pump and CTI Cryo-Torr 8, cryogenic pump. The heater assembly and temperature monitoring set-up were the same as in the GSMBE.
2.4 Nitride Growth and Characterization System

The Nitride Growth and Characterization system is located within the Free Electron Laser (DFEL) at Duke University. Figure 2.9 shows the general layout of the system in the Keck Building of the FEL. The system has been designed to allow substrate cleaning and thin film growth via molecular beam epitaxy or e-beam evaporation. The samples can then be transferred in-situ for characterization via the AES system or the photo-emission electron microscope (PEEM). The DFEL provides a high power, ultraviolet light source that can be tuned for PEEM characterization of surfaces.

2.4.1 Photo-Emission Electron Microscope (PEEM)

The PEEM was designed and built by ELMITEC Elektronenmikroskopie GmbH. A layout of the PEEM is shown in Figure 2.10. The system consists of two main vacuum chambers separated by a special gate valve. The main chamber contains the sample cartridge manipulator and the ports for sample loading, and growth and monitoring equipment. The main chamber is evacuated via a Varian 75 l/sec ion pump and a Titan (Ti) sublimation pump which achieve a base pressure below $2 \times 10^{-10}$ torr. Typical operating pressures during analysis and heating are in the mid $10^{-9}$ to $10^{-8}$ torr range. The main chamber has 6 ports for in situ growth of thin films. The present arrangement has a titanium filament on one port and a four-pocket electron gun on another port. Sources present within the latter include titanium, platinum, and silicon.
As shown in Figure 2.11, the sample holder is fully integrated, and consists of the entire heating assembly including the thermocouple and all electrical connections. The samples are mounted to the sample holder using a molybdenum ring and a special molybdenum cap. The cap holds the sample in place and has three different designs. The cap may either contain a 7 mm diameter hole for large samples or a 4 mm diameter hole for small samples. The third design allows for reflection high energy electron diffraction analysis. The cap consists of a 7 mm diameter hole in addition to four slots cut from the corners for the incident and diffracted high energy electron beam. If the sample requires heating, the sample is either mounted on a molybdenum plate or tungsten is deposited on the backside of the wafer.

The second primary component of the microscope is the imaging section, which contains the magnification lenses, the microchannel plates and the phosphorus screen. This section is evacuated using a Varian 20 l/sec ion pump and a Ti sublimation pump and is also maintained in the low $10^{-10}$ to $10^{-11}$ torr range. The entire system also contains a Balzers 60 l/sec turbomolecular pump with a diaphragm backing pump for initial rough pumping and venting of the entire microscope. Through the use of the special gate valve, the lens column in differentially pumped to allow growth in the main chamber.

The electron optics in the PEEM are composed of the imaging column and the magnetic objective lens. The former consists of 4 lens used to magnify and project the electrons. Each lens consists of 40 or more coils. Focusing and magnification occur by changing the current to the coils. The objective lens allows imaging of both the image plane and the back focal plane. All of the electrons emitted in the same direction from
any point on the surface are included in the back focal plane. The back focal plane is used to align the sample with the lens column.

The emitted electrons from the surface are accelerated towards the anode using a field of 10 V/µm. The objective lens is an immersion lens and focuses the electrons to the first intermediate image at the position of the center of the gate valve between the objective lens and the imaging column. From the objective lens, the electrons pass down the imaging column through the transfer lens, a variable aperture, the field lens, and the intermediate lens, which achieve magnifications between 200x and 100,000x. The electrons are then passed through two more intermediate images before passing through a double gap projector lens and subsequently striking the microchannel plate. The aperture is inserted into the conjugated diffraction plane of the objective lens and uses a variable diameter of 50, 70, and 100 µm. The image is captured from a phosphor screen a charge couple device (CCD) camera.

The PEEM has two main sources of UV photons. The first source is a ORIEL 100 W mercury discharge lamp. The lamp produces a continuous spectrum with the peak intensity occurring at 4.9 eV with a maximum cut-off photon energy of 5.1 eV. The UV light is focused onto the sample at a 16º angle using quartz which has a cut off wavelength off approximately 6.8 eV.

The second source of photons for the PEEM is the free electron laser (FEL). A schematic of the free electron laser facility is shown in Figure 2.12. The DFEL can be operated in two modes, spontaneous and lasing. The FEL has two sections, the linear accelerator and the storage ring[9]. Electrons are initially accelerated in the linear
accelerator and then injected into the 1 GeV storage ring at the beginning of the north section. The electrons travel around the ring to the south straight section where they pass through the OK4-FEL. The latter is an optical klystron with two wigglers, electromagnetic undulators, and a buncher. The OK4-FEL uses the magnetic fields emanating from the wigglers to change the electron path and therefore emit a photon. By changing the strength of the field or the energy of the electron beam, the photon energies may be changed. A typical output spectrum from spontaneous emission of the OK4-FEL at 6.0 eV is shown in Figure 2.13. The full width at half maximum is approximately 1% of the beam energy in this case. The typical operating range for the PEEM is between 5.0 eV and 6.3 eV (with up to 6.8 eV being demonstrated) but has a range of 3 eV to 10 eV.

The FEL may also be operated in lasing mode by the insertion of two mirrors along the south section of the storage ring. These mirrors create an optical cavity approximately 53.73 meters long. Lasing has been demonstrated at 5.16 eV and more recently at 211 nm, which currently is the world record. The linewidth for 5.16 eV operation is approximately $\Delta E/E = 10^{-4}$. The lasing mode was not used for any experiments presented in subsequent sections.

The photon beam created at the OK4-FEL travels along the southern section of the storage ring. A periscope in the line directs the beam to the PEEM through a viewport to the ex situ optics. The exiting beam is approximately 2.5 inches in diameter with a variation in photon energies across the spot[10]. The exiting beam is passed through a 1 m focal length lens. Focusing adjustments due to variations in the wavelength of the photons are made using the lens position which is mounted on a stage
capable of motion in the x and y directions. After the lens, the beam is then passed through an aperture to select only the narrow distribution of photon energies in the center of the beam[10]. To assist in the focusing and adjustment of the beam, an additional mirror is placed in the path. When photon energies greater than 6.3 eV were used, the optics are covered with a nitrogen blanket.

2.4.2 Growth System

The growth system is a custom designed stainless steel chamber constructed at MDC. The system may be used for either the molecular beam epitaxial growth of III-nitrides or the deposition of metals and semiconductors via electron beam evaporation. Figure 2.14 shows a digital image of the chamber. The system is attached directly to the Auger electron spectroscopy system and is separated by a 6” gate valve.

The sample is mounted to the same sample holder that is employed in the PEEM analysis (Figure 2.11). The sample is mounted directly onto a molybdenum plate and held in place using a molybdenum RHEED cap. The backside of the samples are also coated with tungsten using an RF sputtering chamber for temperature uniformity. Sample heating is achieved by both thermionic heating from a tungsten filament and electron beam heating. Heating to approximately 400°C may be achieved by adjusting the filament current for thermionic heating. The current is supplied by a Sorensen XT Series DC power supply that provides up to 3A at 20 V. Heating via electron bombardment is used to obtain temperatures to 1600°C. The bombardment voltage is controlled via a Bertan 825 high voltage supply with a maximum voltage of 1500 V.
The growth of the III-Nitride films occurs via reactive molecular beam epitaxy. The system contains three EPI Knudsen cells for gallium, aluminum, and indium solid sources. The k-cells are controlled using a Eurotherm 818 controller in tandem with an 831 SCR solid state relay. “Blue Ammonia” from Solkatronics is used as the nitrogen source. The gas passes through an additional Millipore Microwafer purifier to remove oxygen and water vapor from the gas before entering the system. The ammonia flow is controlled using a leak valve from Granville Philips. A Granville Philips ion gauge is used to monitor the ammonia flow through measurement of the background pressure from $1 \times 10^{-5}$ to $1 \times 10^{-6}$ torr. The growth of the III-nitrides is monitored using a reflection high-energy electron diffraction system. The electron source is a EK-20-R electron gun operated at 20 kV and 1.5 amps. The diffracted electrons hit a phosphorus screen, and the image is captured using a CO-HV high performance CCD camera.

A four pocket electron beam gun from Thermionics, model number 100-004 is used for the evaporation of various materials. The materials present for evaporation are silicon, platinum, germanium, and nickel. The deposition rate is monitored using a Sycon Instruments STC-200 deposition rate controller.

The chamber employs three pumps to reach UHV conditions. The first pump is a TMU turbomolecular drag pump from Balzers, which is employed during processing. The pump possesses a second port at its base to allow nitrogen to be flowed over the bearing during processing with ammonia. The pump is backed by an MD4T diaphragm pump. Both pumps are controlled with a TCP 380 controller. In addition to the turbomolecular drag pump on the main chamber, the RHEED gun is differentially
pumped using a TMU064 turbomolecular pump backed by an MZ2D diaphragm pump which keeps the RHEED system under UHV conditions during nitride growth with ammonia. The final pump on the system is a 480 l/s Physical Electronics ion pump, controlled by a Digital 500 ion pump power supply and system control. The combination of the turbomolecular drag pump and the ion pump maintain the system pressure below \(2 \times 10^{-10}\) torr.

2.4.3 Auger System

The Auger Electron Spectroscopy system is identical to the one described above for the IAGS. The system consists of an 11-010 electron gun, a 32-150 Digital analyzer control, and a 10-155 cylindrical mirror analyzer. The AES system is operated at filament current of 2 mA and an emission current of 1.7 mA at 3 kV.

2.5 Experimental Procedure

2.5.1 Ex-Situ Processing

In these experiments, on-axis, n-type 6H-SiC(0001)\(_\text{Si}\) wafers obtained from Cree Incorporated were diced into 1 cm x 1 cm samples. To remove the wax from the dicing operation, each diced sample was cleaned by boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent. The samples were subsequently dipped into a 10:1 HF acid solution for 10 minutes to remove a 500 -1000 Å thermally grown silicon oxide film from the polished surface. The samples were rinsed in de-ionized water for at least 10 seconds. Upon removal from the water, the samples were blown dry with
nitrogen and immediately mounted onto a Ta strip heater and introduced into the hydrogen etching system.

The hydrogen etching parameters depended upon the doping of the wafer. All samples were etched using a 25% hydrogen/75% helium mixture with a flow rate of 8 slm for 20 minutes at 1 atmosphere. The temperature of the SiC wafer, however, varied between 1500º-1520ºC for highly doped samples to 1610ºC to 1640º C for lightly doped samples. The temperature was measured using an infrared pyrometer with an emissivity setting of 1.0. The range in temperatures for each sample was related to the location of the silicon carbide in contact with the heater. The SiC also reacted with the heater to form a thin layer of tantalum silicide(s). The samples were rapidly cooled while maintaining the 8 slm flow rate and the 1 atm pressure in the system. The system was then evacuated below 1 torr and vented using argon. The samples were removed for AFM characterization. Scans of 2, 5, 10 µm were conducted in the AFM on three-to-four areas of the surface using a Park Scientific Instruments Autoprobe M5 atomic force microscope with either a D, E, or F silicon nitride tip.

After AFM analysis, the samples were then cleaned using acetone and methanol to remove the glue, and tungsten was deposited on the unpolished (000-1) back of each substrate. After deposition, the pieces were again cleaned by boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent to remove any new contamination. The samples were rinsed in de-ionized water for at least 10 seconds, blown dry with dry nitrogen and mounted to a molybdenum sample holder. The samples were then
introduced via the load lock into either the integrated analysis and growth system or the nitride growth and characterization system.

2.5.2 In Situ Surface Preparation and Characterization: T-line.

The etched SiC pieces were transferred from the load lock via the transfer line to a chamber containing both the low energy electron diffraction system and the Physical Electronics #10-155 AES system for initial surface characterization. To compliment the Auger analysis and to determine the character of the surface bonding, the samples were then transferred to the X-ray photoemission electron spectroscopy system. Upon completion of the initial characterization, the samples were transferred to additional chambers for cleaning.

The first study consisted of transferring each sample to the gas source molecular beam epitaxy chamber with a base pressure of $2 \times 10^{-9}$ torr for a silane clean. The flux was controlled through a leak valve, however, it was not directly measured. The surface exposure was estimated at $5 \times 10^{-6}$ Langmuirs, as measured with a remote ion gauge. The sample temperature was ramped at 30º/minute to 1030ºC, as measured by the C type thermocouple in the heater. This corresponded to a surface temperature of approximately 1030ºC, as measured with an optical pyrometer with an emissivity of 0.5. Silane was introduced into the system when the thermocouple read 960ºC. Each sample was then ramped to 1030ºC, held for 10 minutes, and cooled at 40º C/min. The silane was turned off at ~ 650ºC. Upon completion of the silane clean, each sample was transferred to the
LEED and Auger systems for analysis. The sample was then removed from the system and AFM scans were conducted using a silicon nitride tip.

In the second annealing study, each sample was transferred to a solid source molecular beam epitaxy chamber, which had a base pressure of $2 \times 10^{-10}$ torr. The sample was ramped at $40^\circ C/min$ to $1030^\circ C$, as measured by the optical pyrometer and using an emissivity of 0.5. The sample was held at temperature for 15 minutes. The temperature was decreased at $40^\circ C/min$. The sample was then removed from the SSMBE chamber and transferred to the LEED and Auger for characterization. After analysis the sample was removed from the system for AFM studies.

The final set of experiments conducted in the IGCS consisted of exposing the silicon carbide to a silane clean and annealing the sample for 15 minute at $1030^\circ C$ in the GSMBE chamber. Once cleaned, the samples were transferred to the LEED and Auger chamber for surface analysis. The samples were then removed from the system for AFM imaging.

2.5.3 In Situ Surface Preparation and Characterization: Nitride Growth and Characterization System

After the tungsten deposition, the hydrogen etched SiC pieces were transferred to Duke University. The samples were exposed to a 10 minute HF vapor cleaning using a buffered oxide etch from Fisher Scientific. The samples were then placed into the load lock and passed to the transfer chamber. The sample was transferred into the MBE chamber for cleaning. As-loaded RHEED was conducted to verify the orientation of the silicon carbide surfaces. Samples were cleaned by annealing above $1030^\circ C$ for 15
minutes. The temperature was monitored using the IRCON infrared optical pyrometer with an emissivity of 0.5. The samples were ramped manually, and the pressure in the system was maintained below $1 \times 10^{-8}$ torr. RHEED analysis was conducted as the sample temperature was ramped up and held constant, and after ramping down. The process was repeated until a $\sqrt{3} \times \sqrt{3} \text{R30}^\circ$ reconstructed surface was obtained. The temperature of the sample was then decreased to the growth temperature.

The growth of gallium nitride was conducted in the GSMBE chamber located at the DFEL. The hydrogen etched samples were mounted to the PEEM sample cartridge using a molybdenum plate and held into place using the RHEED cap. The samples were then loaded directly into the load lock. Once the load lock reached $1 \times 10^{-7}$ torr, the samples were transferred into the MBE chamber. The temperature was raised manually, always keeping the background pressure below $2 \times 10^{-8}$ torr. The samples were annealed at 1030ºC for 15 minutes. The RHEED pattern showed a 3 fold pattern in the $\langle 11\overline{2}0 \rangle$ and a 1 fold pattern in the $\langle 1\overline{1}00 \rangle$ indicating a $\sqrt{3} \times \sqrt{3}$ R30º reconstructed surface. The temperature was then lowered to the growth temperature. Specifics of the procedure will be presented in each chapter. Ammonia was introduced into the system first and allowed to stabilize. The shutter to the group III element was then open and the growth was monitored using the RHEED. The samples were cooled manually under the flow of ammonia. Once the temperature was reduced below 500ºC, the ammonia flow was terminated. When the sample reached below 150ºC as read by the OMEGA controller, and the system pressure was $1 \times 10^{-7}$ torr, the sample was transferred to the AES system.
for characterization. The samples were then either removed from the system for AFM imaging or transferred to the PEEM.

Using the equipment and procedures described above, the growth of AlN and GaN were characterized on the hydrogen etched 6H(0001)$_S$ silicon carbide substrates. The results will be compared to chemically etched samples that will be exposed to similar growth and cleaning procedures. In the next chapter, PEEM and AFM results for the cleaning and etching processes will be presented. The RHEED and AFM results from nitride growth will be presented in subsequent chapters.
2.6 References

Figure 2.1 Schematic drawing of the silicon carbide hydrogen etching chamber.
Figure 2.2 Layout of the Integrated Growth and Analysis System. Figure courtesy of Edward Hurt and Kieran Tracy.
Figure 2.3 Sample holder and molybdenum plate used in the IGAS

(a) Molybdenum Sample Holder

R 0.45"

R 0.51"

R 0.59"

(b) Molybdenum Plate w/ sample

SiC sample

1” Diameter

Figure 2.3 Sample holder and molybdenum plate used in the IGAS
Figure 2.4 Low energy electron diffraction (1) and Auger electron spectroscopy (2) systems mounted to a six-way cross (3).
Figure 2.5 X-ray Photoelectron Spectroscopy system on the IGAS
Figure 2.6: Gas Source Molecular Beam Epitaxy Chamber attached to the IGAS
Figure 2.7: Heater configuration and gas flow schematic of the GSMBE. Figure courtesy of Kieran Tracy.
Figure 2.8: Solid Source Molecular Beam Epitaxy chamber attached to the IGAS
Figure 2.9 Layout of the Nitride Growth and Characterization System at Duke University.
Figure 2.10 The Photo Emission Electron Microscope
Figure 2.11 Sample Holder for the PEEM and MBE on the NGCS
Figure 2.12 Storage ring for the OK-4-FEL located at Duke University.
Figure 2.13 6.0 eV spectrum using the OK4-FEL in spontaneous mode
Figure 2.14 GSMBE with the NGCS at Duke University
3 Surface Preparation of 6H-SiC(0001) using Hydrogen Etching

3.1 Abstract

The surface morphology of hydrogen etched, nitrogen doped, n-type 6H-SiC(0001)Si wafers before and after various in-situ cleaning techniques were investigated using atomic force microscopy (AFM), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), Nomarski interference optical microscopy, and low energy electron diffraction (LEED).

In the first study, AFM and optical microscopy images of these surfaces showed that wafers with net ionized carrier concentrations of approximately $2.5 \times 10^{18} \ (N_D-N_A)/cm^3$ exhibited more surface features due to defects intersecting the surface than wafers that had net ionized carrier concentrations of $\leq 5.8 \times 10^{17} \ (N_D-N_A)/cm^3$. The surface morphology of all the samples showed regions exhibiting half unit cell high steps, which were attributed to stacking faults in the wafer. Observations using LEED and AES showed that etched silicon carbide wafers exhibited a reconstructed $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface structure with a silicon oxide layer on the surface when the sample was immediately introduced into vacuum after hydrogen etching. Analysis via XPS indicated a 4:1 ratio of oxygen to silicon in the oxide.

In the second study, the characterization of various in-situ cleaning techniques was investigated. Auger electron spectroscopy characterization of a hydrogen etched sample after annealing at 1030°C in ultra high vacuum established the removal of oxygen from
the surface to below detection limits with an uncorrected silicon-to-carbon peak-to-peak height ratio of 1.7. Low energy electron diffraction displayed a sharp \((\sqrt{3} \times \sqrt{3})R30^\circ\) diffraction pattern after annealing indicating a well ordered surface. Exposure of the etched wafers to a chemical vapor clean (CVC) using a silane flux produced a \((3 \times 3)\) surface reconstruction as identified by LEED. Characterization via AES of these samples showed that the oxygen had been removed to below the detection limits of this technique and an uncorrected silicon-to-carbon peak-to-peak ratio of 3.9. Atomic force microscopy results showed silicon islands randomly distributed across the surface. Upon further annealing of the CVC surface for an additional 10 minutes at 1030ºC, the surface structure changed to a disordered \(1 \times 1\) surface as indicated by LEED and the AES silicon-to-carbon peak-to-peak height ratio dropped to 3.4.

### 3.2 Introduction

The number of defects present in epitaxially grown III-Nitride semiconductors is dependent, in part, upon the surface quality of the substrate, since defects at the interface may propagate into the film. Of the approximately 250 different polytypes of silicon carbide, the 6H structure has gained the most interest for the epitaxial growth of III-nitrides for microelectronic device fabrication due to its high electrical and thermal conductivity and its commercial availability as large single crystal wafers. However, the as-received 6H-SiC(0001)\(_{\text{Si}}\) wafers contain many polishing scratches which can lead to defects such as stacking mismatch boundaries in the grown films[1]. To reduce the
number of defects and increase the efficiency and lifetime of the devices, these damaged and scratched layers on the surface must be removed.

The removal of the scratches and damaged layers from the surface of SiC is difficult due to its hardness and chemical inertness of the material. However, several etching techniques have been developed, including submergence in a bath of molten salts such as KOH or NaOH [2], sublimation etching [3], and exposure to HCl/H₂ vapors at elevated temperatures [4]. The first method will selectively etch defects on the surface while the second two methods do not produce surfaces with unit cell height steps and can lead to surface roughening with etch pits [3,4]. To reduce the number of stacking mismatch boundaries in subsequently grown films, a stepped surface with unit cell heights is necessary.

Etching in a hydrogen atmosphere at an elevated temperature of approximately 1600 ºC has been shown to leave a flat surface with unit cell height steps [4-8]. These surfaces have morphologies ranging from hexagonal etch pits to arrays of parallel steps. Previous LEED results have shown a \((\sqrt{3} \times \sqrt{3})R30^\circ\) surface reconstruction after etching which has been attributed to the growth of a silicon oxide layer on the surface [9]. This oxide layer must be removed for the growth of III-Nitride epitaxial films. Previous research concerned with in-situ cleaning procedures, such as annealing with and without a silicon flux, have addressed the surface structure and the removal of the surface contamination on un-etched surfaces. Approaches for cleaning of the stepped structure of etched surfaces has not been fully examined. Only recently has the surface cleaning to remove oxygen and hydrocarbons from the hydrogen etched wafers via annealing been
addressed by Bernhardt et al. [9]. In their study, they observed via AES the disappearance of oxygen from the surface at 1000°C after a 30 minute anneal.

In this work, the effect of n-type, nitrogen doping levels in the silicon carbide on the surface morphology and the effectiveness of various cleaning procedures on the hydrogen etched surface have been investigated. The surface morphology and structure were characterized using a variety of techniques including atomic force microscopy, low energy electron diffraction, scanning electron microscopy, and Auger electron spectroscopy.

3.3 **Background**

As noted above, the as-received substrates contain many polishing scratches that vary in width and depth and lead to non-unit cell height atomic steps on the surface. Due to these steps, regions on the surface have different terminations of the 6H-SiC unit cell due to its 6 bi-layer structure, as shown in Figure 3.1a. In region 1, the stacking sequence at the surface could be \( \ldots C'AB' \), while in region two, the surface termination sequence could be \( A'B'C \). Due to the change in the stacking sequence at the surface, these regions may lead to stacking mismatch boundaries in the subsequently grown III-Nitride films. For example, an island of AlN or GaN nucleated in region 1 may have a stacking sequence of \( \ldots ABAB \ldots \), while a similar island nucleated in region 2 will exhibit a \( \ldots BCBC \ldots \) stacking sequence, as illustrated in Figure 3.1b. Upon coalescence of these two islands a stacking mismatch boundary occurs at the step edge. Etching the surface in
a hydrogen environment eliminates these bi-layer steps and replaces them with unit cell height steps that exhibit the same stacking sequence at the surface.

Research regarding the etching of both the carbon and silicon face of hexagonal SiC using hydrogen was first conducted in 1965 by Chu and Campbell[5]. They found that exposure of the surface to a hydrogen atmosphere at 1600ºC produced etching at reasonable rates of approximately 0.3 µm/min at 1600ºC and yielded smooth surfaces as seen in an optical microscope. They proposed that exposure of the SiC to hydrogen shifts the chemical equilibrium toward the formation of silicon vapor and hydrocarbons.

The estimated vapor pressure for silicon above silicon carbide at 1600ºC is 4.6x10^{-6} atm [10]. Since the combined partial pressures of the silicon carbide gases, SiC_2 and Si_2C, is approximately 6x10^{-7} atm at 1600ºC [10] and is smaller than that of the silicon, the silicon carbide will dissociate at the elevated temperatures [11]. Kumagawa et al. [11] using calculated free energies predicted that the dissociation process of the SiC leaves liquid silicon and solid carbon on the surface. The liquid silicon then vaporizes, leaving carbon on the surface that is then removed via the formation of hydrocarbons.

Table 3.1 lists several chemical equations along with the free energy of formation or reaction calculated from HSC software that can be used to describe the etching process. As shown in the Table, hydrogen gas dissociation into atomic hydrogen and the formation of hydrocarbons at these temperatures exhibits a positive change in free energy. As seen in the last set of equations in Table 3.1, for etching to occur under equilibrium conditions atomic hydrogen must be present. Therefore, the silicon is removed from the surface via evaporation and per these equations via silane formation in
the temperature range of 1500ºC to 1800ºC. The carbon on the surface is removed via
the formation of hydrocarbons.

Atomic hydrogen may be produced by the catalytic action of the susceptor. Investigations by Harris et.al.[7] showed that a susceptor constructed of molybdenum increased the etching rate of the silicon carbide; the use of tungsten, tantalum, and tantalum silicide resulted in approximately the same etching rates, which was lower than the etching rate of the molybdenum. This was attributed to the fact that molybdenum acts as a better catalyst for the hydrogen dissociation. Moore et al.[12] showed that the measured hydrogen ion (H\(^+\)) current for a molybdenum susceptor at 1712ºC and a partial pressure of 2.7x10\(^{-5}\) torr was measured at \(\sim 8 \times 10^{-13}\) Amps. For a tungsten susceptor at 2175ºC and a pressure of 7.0 x 10\(^{-5}\) torr, the measured H\(^+\) current was 1.2 x 10\(^{-12}\) Amps. These numbers are greater than the hydrogen ion current measured at 677ºC which was 1 x 10\(^{-13}\) Amps. The tungsten assisted with the dissociation, but produced almost the same rate, slightly higher, for a 400ºC increase in temperature. Their results had also showed that as the pressure of H\(_2\) increased so did the measured H\(^+\) current for the tungsten susceptor.

The amount of atomic hydrogen available is one of the main components in producing flat, stepped surfaces. Silicon carbide annealed in an argon environment produces a black graphite layer, which inhibits subsequent silicon evaporation and the etching process [11]. However, in hydrogen atmospheres in concentrations as low as 5%, flat surfaces with atomic steps can be produced. Experiments have shown that a minimum linear velocity of hydrogen of 4.25 cm/sec is necessary to produce a flat
surface with unit cell height steps on the surface [11], lower flow rates results in a rough, macro-stepped morphology.

The rate and microstructural results of hydrogen etching different polytypes of SiC substrates has also been investigated. Hallin et al [13] found that the on-axis 6H-SiC(0001) substrates produced a surface morphology with regular straight terraces with unit cell height steps. The process did not transfer well to 4H-SiC(0001) and off-axis 4H and 6H-SiC(0001) polytypes. The etched surfaces of the on-axis 4H substrates exhibited triangular defects, large step formations, and etch pits. Off-axis etching did not completely remove the scratches from the surfaces of both the 4H and the 6H polytypes. Ramachandran et al.[8] have shown that hydrogen etching of 6H-SiC(0001) produces surfaces that are faceted with steps occurring in the <1-100> directions. The observed faceting on the surface was attributed to the miscut of the silicon carbide wafer. Based on their observations, they have suggested an inverse step flow mechanism for the etching process, which utilizes the idea of higher energy steps and low energy steps, with the former being etched at a faster rate than the latter.

3.4 Equipment

3.4.1 Ex Situ Preparation

On axis, nitrogen doped, n-type 6H-SiC(0001) wafers were obtained from Cree, Incorporated and diced into 1 cm x 1 cm samples, cleaned by boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent, and dipped into a 10:1 HF acid solution to remove the 500-1000 Å thermally grown silicon oxide passivation layer from
the polished surface. The samples were rinsed in de-ionized water for 10 seconds and blown dry with nitrogen and immediately mounted onto a 1.2 cm wide by 7.5 cm long Ta strip heater and introduced into the hydrogen etching system consisting of a water-cooled quartz chamber that was subsequently evacuated to under 100 mTorr by a 3 stage Baradyne diaphragm pump. The samples were etched using a 25% hydrogen/75% helium mixture with a flow rate of 8 sdm for 20 minutes at 1 atmosphere. However, the temperature of the silicon carbide wafer, as monitored using an IRCON Umax 20 pyrometer with a emissivity of 1.0, varied from 1500°C to 1650°C, depending on the doping density, which changed the amount of absorbed radiation from the heater. Estimated transmission losses through the quartz and the water jacket were approximately 5%. At the completion of the etching, the samples were rapidly cooled while maintaining the 8 sdm flow rate and the 1 atm pressure in the system. The samples were removed for AFM characterization. Three areas of the surface were scanned using a Park Scientific atomic force microscope with a microlever "E" or "F" silicon nitride tip in contact mode.

The etched samples were cleaned using acetone and methanol, and tungsten was deposited on the unpolished (000-1) back of each substrate using a Materials Research Corporation RF sputtering system. After deposition, the pieces were again cleaned in boiling trichloroethylene, acetone, and methanol for 10 minutes in each solvent, rinsed in de-ionized water for at least 10 seconds, dried with nitrogen, and mounted to a sample holder. The samples were introduced into the Integrated Analysis and Processing Tool via load lock.
3.4.2  *In Situ Surface Preparation and Characterization.*

The etched SiC pieces were transferred from the load lock to a chamber containing both a Princeton reverse view LEED unit and a Physical Electronics #10-155 AES system for initial surface characterization. Upon completion of the initial characterization, the sample were exposed to two different cleaning processes.

In the first study, each sample was annealed under ultra high vacuum conditions in a custom-made molecular beam epitaxy chamber. The base pressure of system was approximately $2 \times 10^{-10}$ torr. The sample was ramped to a surface temperature of 1030ºC as measured by the optical pyrometer with an emissivity of 0.5 and held for 15 minutes. Characterization via AES, LEED, and AFM was conducted after the cleaning step.

The second study consisted of transferring each sample to a custom-made gas source molecular beam epitaxy chamber for chemical vapor (CV) cleaning using silane. The system base pressure ranged from the low $10^{-9}$ to high $10^{-10}$ torr. The silane entered the system and was collimated and focused through the use of a doser that contained a 13 mm diameter by 2 mm thick glass capillary with 10 micrometer pores. The flux was controlled via leak valve and was not directly measured. The surface exposure was estimated at 5 Langmuirs (1L = $10^{-6}$ torr sec) as measured with a remote ion gauge. The sample temperature was ramped at 30º/minute to 960ºC at which time the silane was introduced into the system. The sample was then ramped to 1030ºC and held for 10 minutes. The sample was cooled at 40ºC and the silane flow was shut off at 650ºC. After cooling to near room temperature, characterization via LEED and AES was then conducted. AFM scans were obtained after the samples were removed from the system.
During the third study, each sample was exposed to a CV clean using silane, as described in the second study, but was followed by an additional 10 minute anneal at 1030°C. Each cleaned sample was transferred to the LEED and Auger chamber for in-situ surface analysis. The samples were then removed from the system and the cleaned surface was characterized by AFM.

### 3.5 Results: Hydrogen Etching

#### 3.5.1 Hydrogen Etching

##### 3.5.1.1 Initial Etching Attempts

Observations of the as-received silicon carbide surface via AFM revealed a large number of scratches, as seen in Figure 3.2, which are attributed to the polishing process. The scratches occurred in random directions with some scratches up to 10 nm deep and 300 nm wide. The surface RMS roughness value was approximately 12 Å. Other features observed using an optical microscope, but not shown here, included micropipes and pits.

The initial attempts at hydrogen etching were plagued by non-uniform surfaces. Throughout the qualification of the system, removal of the polishing scratches was usually achieved under a wide variety of etching conditions; however, the attainment of an atomically flat surface was difficult.

Figure 3.3a shows an SEM image of an initial etching attempt in which a flow rate of 4 slm of a 5% hydrogen / 95% helium mixture was used. This flow rate produced a linear velocity of hydrogen of approximately 2.1 cm/s across the sample surface. The
surface is decorated with depressions that appear to merge together at a single level. As seen if Figure 3.3b, a 9000x magnification image of the bottom of one of the depressed regions reveals that sub-micron size islands are evident. The islands are attributed to excess silicon in these regions. Atomic force microscopy results of the surface revealed that unit cell height steps were still evident.

A second problem that was initially encountered was the evolution of micromasking on the surface, as shown in Figure 3.4. This 30 µm x 30 µm, 3-dimensional AFM image shows tall columnar structures scattered randomly across the surface. The width of the columns ranged from 3500 - 5000Å, and the height ranged from 100-1000Å. From the highest column, the etching rate for the process was estimated to 100 Å/minute. Micromasking effects were minimized by reduced exposure to the environment after ex-situ cleaning and a reduction in the amount of volatile oxide in the system. The effect was almost completely removed, once the a tungsten sample platter was employed in the etching process.

A third problem encountered during etching occurred in samples with an ionized carrier concentration of $2.5 \times 10^{18} \text{ cm}^{-3}$. The etching procedure used for samples with ionized carrier concentrations of $\leq 5.8 \times 10^{17} \text{ cm}^{-3}$ did not work with the more highly doped samples. Figure 3.5 shows a 10 µm atomic force microscopy scan of a wafer that was etched at 1610 - 1640ºC for 20 minutes. The surface RMS roughness value is 2.5 Å with a step height that varies between 3 - 6 Å with surface undulations, and which produced a peak-to-valley height of approximately 19.2 Å. Lowering the temperature by approximately 100ºC produced unit cell height steps.
3.5.1.2 Surface Morphology and Defects

As shown in Figure 3.6, the surface morphology of the etched samples with a doping density of approximately $4.8 \times 10^{17}$ was different from samples with a doping density of approximately $2.5 \times 10^{18} (N_D - N_A)/\text{cm}^3$. Figure 3.6a shows a 200x optical microscope image obtained using a Nomarski filter of the lower doped sample after hydrogen etching. The differences in gray level are due to the reflections of light from the smooth surface. The surface appears very smooth with a few hexagonal structures occurring around several micropipes; however, these were too small to obtain a higher magnification image showing the stepped structure of the SiC around the defect using the optical microscope. Figure 3.6b shows a 200x image obtained with an optical microscope with a Nomarski interference filter. The higher doped sample surface appears to be covered with pyramidal structures distributed across the entire wafer. The density of the defects was not uniform across the surface. Samples taken from the edge of the wafer exhibited a higher density of defect structures.

Figure 3.7 shows a typical 30 µm x 30 µm AFM image of a hydrogen-etched surface from a sample doped $\leq 5.8 \times 10^{17} (N_D - N_A)/\text{cm}^3$. The surface shown in Figure 3.7a, contains two distinct regions with different step heights and widths. The first region has a unit cell step height of approximately 15 Å and a step width of 0.3 µm indicating a 6H unit cell step. The second region shows varying step heights and widths with the former averaging 6Å high and the latter varying due to the curvature of the region. The inset in Figure 3.7a shows a 5 µm x 5 µm image of the transition from the steps with unit cell heights to steps with half unit cell heights, a faulted region. In some cases, the
additional plane in the defect has been observed to extend into the 6H region, as shown in
Figure 3.7b. The edges of the defect region are curved but appear to be at an angle of
approximately 58° +/- 2° to the 6H step edges. The step edges in the defect region occur
at approximately 45° to the <1-100> 6H step direction; however they are curved.

Figure 3.8 shows two AFM images from the samples with a doping density of
2.5 x 10^{18} (N_D - N_A)/cm^3. In Figure 3.8a, three distinct regions are evident: (1) a region
where a micropipe or screw dislocation intersects the surface, (2) a region containing step
heights of approximately 6 Å, and (3) a region that exhibits the 6H unit cell height steps.
A more detailed image of the micropipe intersecting the surface is displayed in Figure
3.8. These types of defects consistently appeared in the samples with the higher doping
densities.

3.5.1.3 In Situ Surface Cleaning

Figure 3.9 shows the XPS spectra of an as-loaded hydrogen etched surface. A
summary of the peak positions and intensities is given in Table 3.3. The silicon peak
may be de-convoluted into two peaks attributed to a Si-O bond indicated by the peak at
binding energy of 102.2 eV and a Si-C bond at a binding energy of 101.4. A single
oxygen peak may be seen at 534.3 indicating bonding to silicon [14]. The carbon peak,
not shown, was de-convoluted into two peaks at 285.7 eV and at 283.5 eV. The former
peak was attributed to hydrocarbons from the cleaning process and the latter to the Si-C
bond. The as-loaded AES spectra shown in Figure 3.10a revealed peaks for silicon,
carbon, and oxygen. Table 3.2 summarizes the positions and peak-to-peak ratios of the
carbon KLL and silicon LVV based on the spectra in Figure 3.10. The silicon-to-carbon ratio which is not corrected for sensitivity factors of an as loaded sample is approximately 0.6.

The LEED pattern of the as-loaded surface varied between a (1 x 1) or (√3 x √3)R30° pattern depending on the ex-situ surface preparation. Samples inserted directly into the vacuum without ex-situ cleaning or analysis exhibited a strong (√3 x √3)R30° pattern, as shown in Figure 3.11a. If the sample was cleaned with solvents, hydrocarbons were deposited on the surface, changing the LEED pattern to a 1 x 1 pattern. In-situ cleaning of the hydrogen etched surface was conducted to verify that present cleaning processes did not damage or vary the stepped surface structure.

Auger electron spectroscopy of the samples annealed for 15 minutes at 1030°C showed that oxygen had been removed below the detection limit. Temperatures below 1000°C were shown to be ineffective for the complete removal of the silicon oxide. The uncorrected silicon-to-carbon peak-to-peak height (pph) ratio was between 1.6 and 1.7, depending on the sample. This value is obtained for the (√3 x √3) R30° surface, which is shown in Figure 3.11b. Analysis via AFM of the sample before and after the annealed showed that the RMS roughness had not changed within the experimental error. Figure 3.12a and b shows the before and after AFM images of the annealed sample.

The as-loaded samples that were exposed to the CV clean using silane showed a sharp 3 x 3 LEED pattern with a dark background, as shown in Figure 3.11c, indicating an ordered surface. From the AES spectra, the uncorrected silicon-to-carbon pph ratio was calculated to be 3.9, as described above. Annealing the 3 x 3 surface for an
additional 10 minutes at 1030ºC caused the LEED pattern to change to a 1 x 1 structure with an additional ring appearing (Figure 3.11d). The AES spectra showed an uncorrected Si/C pph ratio of 3.4, indicating some loss of silicon. As shown in Figure 3.12c and d, the AFM results showed the formation of silicon islands on the surface after the silane clean. These are attributed to the deposition of excess silicon. The islands had a height ranging from 26 - 112Å and a width of 500-1000Å. After the additional 10 minute anneal, the island size decreased in height to 20 - 50 Å, but the width increased to 1500-2500Å. There appeared to be no effect on the step structure of the surface.

3.6 Discussion

3.6.1 Initial attempts: Surface Morphology

The effect of the linear flow velocity on the morphology of the etched silicon carbide may be considered from both thermodynamic and kinetic viewpoints. As shown in Figure 3.3a, the use of a low linear flow velocity of H₂ to etch the SiC(0001) surfaces resulted in a relief type morphology with steps on the surface without producing a black carburized film. This indicates that sufficient atomic hydrogen was present to remove carbon via the formation of hydrocarbons. The islands at the bottom of the depressions on the surface, shown in Figure 3.3b, indicate that silicon removal was a limiting factor to producing a flat surface and that the flow of hydrogen plays a role in its removal. Kumagawa et.al. [11] reported on a similar surface morphology for 6H-SiC samples etched using a low velocity of hydrogen flow. They did not report on the formation of islands as observed in our SEM image (Figure 3.3b). Differences between the two
processes included the methods of manufacturing of the 6H-SiC, the etching temperatures, and the percentages of hydrogen used for the etching process. For example, in the experiments of Kumagawa et al. a 100% hydrogen gas was used; whereas, in these experiments a 5% hydrogen/95% helium mixture was used. This should exaggerate the effect of the low flow velocity of the hydrogen gas due to a reduction in the number of hydrogen atoms impinging on the surface per unit time.

As indicated in the last set of equations in Table 3.1, atomic hydrogen plays a thermodynamic role in the removal of both carbon as hydrocarbons and silicon as silane from the surface, if equilibrium conditions exist. However, as shown in the Table, the formation of atomic hydrogen from hydrogen gas exhibits a positive free energy. As noted above, the molybdenum and tungsten act as a catalysis for the thermal dissociation of the hydrogen gas. Moore et al. [12] had proposed that the H$_2$ molecule is adsorbed as two adjacent atoms and can depart independently from the surface at sufficiently high temperatures. This process could produce the necessary atomic hydrogen for the above reactions. When the flow velocity is low, an inadequate amount of hydrogen impinges upon the surface per unit time to effectively remove both the free silicon and free carbon. Also, kinetically, without the higher flow rate, the bi-products of the etching process such as evaporated silicon are not transported away from the surface and may re-deposit. The critical linear velocity as observed by Kumagawa et.al.[11] was 4.25 cm/sec. Increasing the velocity in the present experiments to this level, the surface morphology changed from the rough, relief type morphology seen in Figure 3.3a and b to a flat surface without the silicon islands. This may also help to explain the differences in processing
parameters encountered, in the literature since the different research groups only report flow rate instead of linear flow velocities.

The other problem encountered with the etching process was the development of 3-6 Å steps across the samples that had doping densities around \(2.5 \times 10^{18} \frac{N_D - N_A}{cm^3}\). As discussed in the Results section, this step height was observed when the etching procedure developed for lightly doped was employed. This effect may be attributed to overetching due to the darker color wafers. During etching, since SiC is transparent to IR radiation, the pyrometer is measuring the temperature of the heater behind the sample. As the wafers having the lower nitrogen doping are etched, a reduction in the scattering of the photons at the surface occurs due to the removal of scratches. This resulted in a higher temperature reading. The temperature was continuously lowered to maintain a reading around 1600ºC. However, the higher nitrogen doped wafers did not exhibit this change in scattering as the scratches were removed due to their overall darker color. Therefore, temperature adjustments were not made and the sample was held at the higher temperature during the entire run. When both types of samples were run at the same time at a sample platter temperature of 1600ºC, both exhibited a unit cell high stepped morphology.

### 3.6.2 Surface Morphology and Defects

Hydrogen etching of the 6H-SiC(0001)\(_S\) surfaces generally produces atomic steps with a height of 15 Å. However, as was shown in Figure 3.7 and Figure 3.8, areas of the surface, independent of doping density, contain defective regions such as faulted regions.
that contain varying step heights or hexagonal structures intersecting the surface. As stated in the results, the average measured step height was 6 Å in the faulted region and noting that there is an effect on the measured height from the tip diameter in the AFM, this number corresponds to approximately half the unit cell height of 6H silicon carbide and to the unit cell height of the 3C structure. Intrinsic faults in the silicon carbide wafer may produce this zincblende or cubic arrangement [15]. Therefore, this splitting of the steps is attributed to etching in a faulted region on the basal plane.

In the AFM image in Figure 3.7, the edges of the steps with half unit cell height steps, run along one side of a facet on the surface with the partial dislocations following along the ridge and valley. Ramachandran et.al. [8] have proposed an inverse flow mechanism for the etching process in which two types of steps may form, one being of lower energy than the other. The etching process causes the disappearance of the higher energy steps. When a stacking fault occurs, due to the atomic rearrangement, a region is formed that produces half steps with same stacking sequence and therefore the same energy. Based on stacking sequences of the 3C and 6H structures, steps terminated with the CBA stacking sequence have the lower energy. As noted in the results section, these steps were measured at 45° to the step edges. However, due to the undulations on the surface, the miscut of the wafer, and AFM processes, this angle is most likely to be 60°, indicating a rotation in the stacking sequence as predicted by Figure 3.13 [16].

As noted in the optical microscope images in Figure 3.6, the higher the doping level in the substrate, the more hexagonal structures were present at the surface for a hydrogen etched wafer. Okamoto et al. [17] showed for sublimation grown SiC with
Acheson seeds from 6H bulk single crystals, that as the carrier concentration increased the etch pit densities increased. In their experiments as the carrier concentration was increased from $5 \times 10^{17} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$ the etch pit density, which is related to the defect density, increased from $\sim 2 \times 10^4 \text{ cm}^{-2}$ to $\sim 7 \times 10^4 \text{ cm}^{-2}$. The increase was attributed to an increase in subgrain boundaries. Glass et al. [18] showed that samples grown by the modified-Lely method also exhibited domain boundaries with high dislocation densities. Therefore, an increase in the doping level, resulted in an increase in the number of dislocations present in the wafer.

3.6.3 Surface Cleaning

The preparation of an atomically clean surface is important to reduce the number of defects in subsequently grown films [19]. As discussed in the Results section, the AES spectra of the as-loaded sample indicated the presence of bonding between the Si\textsubscript{LVV} and O\textsubscript{KLL} as indicated by the two peaks located around 65 eV [9]. Based on the intensities of the Si-O peak in the silicon spectrum and the oxygen peak from XPS, as given in Table 3.3, the stoichiometry of the silicon oxide layer is calculated to be four oxygen atoms to every silicon atom. Bernhardt et.al. [9] have proposed an Si\textsubscript{2}O\textsubscript{3} silicate overlayer on the (0001) surface based on quantitative LEED analysis with Si atoms having either an SiO\textsubscript{4}, SiC\textsubscript{3}O, SiC\textsubscript{3}H coordination. The additional bonding structures would contribute to the different conclusions reached by XPS observations in this study.

The removal of this oxide required a higher annealing temperature than for un-etched samples, the latter of which the oxide was desorbed at 950°C. The AES analysis of
the peak intensities after annealing without a silicon flux indicated a silicon-to-carbon pph ratio of 1.6 which is lower than the reported value of 2.21 for the cleaning of 4H-SiC in a silicon flux [20], but higher than the ~1.0 value reported for unetched samples annealed at 1000º C [21]. This value is also greater than the ratio of 1.0, which had been calculated when unetched samples had silicon deposited on the surface at room temperature followed by subsequent annealing [22]. Work done by Johansson et.al. [23] have shown that annealing unetched samples at 950ºC will reduce the amount of silicon on the surface to 1/3 of a monolayer. Analysis of the annealed AES spectrum gives a pph ratio of 0.7 when sensitivity factors are taken into account. The AES spectra of the carbon peak did not indicate a graphitized surface [24], which has been reported at higher annealing temperatures. Annealing for longer times, up to 30 minutes at 1030ºC, did not significantly change the silicon-to-carbon ratio, indicating that the only silicon loss from the surface occurred during the evaporation of the volatile silicon oxides. Atomic force microscopy before and after the annealing process did not show a significant change in the step height or morphology of the surface. Based on the analysis of both large area scans and small area scans, the RMS roughness value did not change.

To reduce the problem of silicon loss during annealing, cleaning the surface in a silicon flux has been proposed [25]. In the present experiments, the silane flux was reduced by a factor of 100 under that which was previously reported [21]. The LEED patterns showed a strong 3 x 3 pattern with no background noise, again indicating an ordered surface. The silicon-to-carbon ratio of 3.9 is in the range of reported values[20,21], 3-5, for the 3 x 3 reconstruction. The difference in values may be
attributed to the different methods of surface preparation. The excess silicon on the surface produced silicon islands that nucleated randomly across the surface. There did not appear to be preferential nucleation at the step edges. The observed critical thickness for the SK growth of the islands was found to gradually decrease with increasing temperature [26]. At temperatures less than 625º silicon islands have been observed to form at a total coverage of silicon of 2.2 monolayers. The predicted models for the development of the 3 x 3 reconstruction employ the formation of at least two layers of silicon atoms on the surface [25,27,28]. Due to the increased mobility of silicon and the decrease in critical thickness at the cleaning temperatures, the CV cleaning process consistently leads to the development of islands when obtaining the (3 x 3) surface state.

When the 3 x 3 reconstructed surface was annealed at the higher temperatures, the pph ratio of the silicon-to-carbon, slightly decreased due to the evaporation of silicon from the surface. The LEED pattern also changed to a 1 x 1 pattern with an additional ring forming which is attributed to a disordering due to this silicon loss. Previous research on un-etched surfaces indicate that further annealing should result in further loss of silicon from the surface resulting in a \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern [21]. Subsequent III-Nitride growth on surfaces with any excess silicon has led to the formation of silicon nitride and was not further investigated [29].

3.7 Summary

The effect of net carrier concentrations in the silicon carbide substrates on the surface morphology of samples etched in flowing H₂ gas at elevated temperatures has
been characterized. Comparison of the surface morphology of substrates with net carrier concentrations of $2.5 \times 10^{18} \text{(} N_D - N_A \text{)} / \text{cm}^3$ to substrates with a net carrier concentrations of $\approx 5 \times 10^{17} \text{(} N_D - N_A \text{)} / \text{cm}^3$ exhibited a surface morphology with hexagonal structures distributed across the surface on the former and a flat surface on the latter. The increase in the number of hexagonal structures is attributed to an increase in the dislocation density associated with the higher doping levels of the substrate. The observed planar defects contained a 3C stacking sequence which produced half unit cell high steps.

The cleaning of the surface with or without a silicon flux does not affect the unit cell height structure. Thermal desorption of the silicon oxide layer has been found to leave the surface slightly depleted of silicon as compared to annealing with a silicon flux. Auger electron spectroscopy analysis and LEED analysis of the surface after thermal desorption of the silicon oxide layer did not indicate the formation of a graphitic layer at our annealing temperatures and showed a strong ($\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. This indicated a well ordered surface structure. Cleaning with a silane flux produced a 3 x 3 LEED pattern. However, AES showed an increase in the silicon-to-carbon ratio and AFM showed that the excess silicon on the surface had formed islands. Additional annealing of the surface produced a 1 x 1 LEED pattern with the formation of an additional ring, indicating a disordering of the surface. Analysis via AES indicated a drop in the amount of silicon on the surface, however AFM confirmed that islands were still present. All methods resulted in an oxide free surface for the subsequent processing. Due to the island formation of silicon on the silicon carbide, the best surfaces were cleaned via
annealing and produced a flat atomically clean, well ordered surface for the subsequent growth of III-Nitride films.
References


Table 3.1. Change in Free Energy for Potential Reactions during the hydrogen etching of 6H-(0001) surfaces.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>D G (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1500 °C</td>
</tr>
<tr>
<td>H₂(g) = 2H(g)</td>
<td>57.5</td>
</tr>
<tr>
<td>2C + H₂(g) = C₂H₂(g)</td>
<td>30.8</td>
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<tr>
<td>2C + 2H₂(g) = C₂H₄(g)</td>
<td>43.7</td>
</tr>
<tr>
<td>2C + 3H₂(g) = C₂H₆(g)</td>
<td>66.3</td>
</tr>
<tr>
<td>Si = Si(g)</td>
<td>46.0</td>
</tr>
<tr>
<td>Si = ½Si₃(g)</td>
<td>64.0</td>
</tr>
<tr>
<td>Si + 2H₂(g) = SiH₄(g)</td>
<td>48.1</td>
</tr>
<tr>
<td>SiC = Si + C</td>
<td>13.8</td>
</tr>
<tr>
<td>SiC = Si + C(g)</td>
<td>118.6</td>
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<tr>
<td>2SiC + 3H₂(g) = 2Si(g) + C₂H₆(g)</td>
<td>185.9</td>
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<td>2SiC + 2H₂(g) = 2Si(g) + C₂H₄(g)</td>
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<td>48.2</td>
</tr>
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<td>2SiC + 6H(g) = 2Si(g) + C₂H₆(g)</td>
<td>13.3</td>
</tr>
<tr>
<td>Si + 4H(g) = SiH₄(g)</td>
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<tr>
<td>2C + 4H(g) = C₂H₄(g)</td>
<td>-71.3</td>
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<tr>
<td>2SiC + 10H(g) = 2SiH₄(g) + C₂H₂(g)</td>
<td>-173.6</td>
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Table 3.2. Peak positions and Peak to Peak height (pph) ratios data for various 6H-SiC(0001) hydrogen etched surfaces.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silicon (LMM) position (eV)</th>
<th>Si&lt;sub&gt;p-p&lt;/sub&gt; height</th>
<th>Carbon (KLL) position</th>
<th>C&lt;sub&gt;p-p&lt;/sub&gt; height</th>
<th>Si/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. As loaded</td>
<td>87.5</td>
<td>316</td>
<td>270</td>
<td>523</td>
<td>0.6</td>
</tr>
<tr>
<td>b. (√3x√3) R30º</td>
<td>91.5</td>
<td>649</td>
<td>271</td>
<td>390</td>
<td>1.7</td>
</tr>
<tr>
<td>c. 3 x 3</td>
<td>90.5</td>
<td>1354</td>
<td>270.5</td>
<td>348</td>
<td>3.9</td>
</tr>
<tr>
<td>d. 1 x 1</td>
<td>90.5</td>
<td>1341</td>
<td>270</td>
<td>389</td>
<td>3.4</td>
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</tbody>
</table>
Table 3.3. Summary of As-loaded XPS Si2p, O1s, and C1s data (uncorrected for sensitivity factors) for 6H-SiC(0001)Si hydrogen etched surfaces.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (eV)</th>
<th>FWHM</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 1</td>
<td>101.4</td>
<td>1.266</td>
<td>1213.6</td>
</tr>
<tr>
<td>Peak 2</td>
<td>102.2</td>
<td>1.0</td>
<td>203.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>532.9</td>
<td>1.89</td>
<td>1587.2</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 1</td>
<td>283.5</td>
<td>1.1</td>
<td>1216.8</td>
</tr>
<tr>
<td>Peak 2</td>
<td>285.7</td>
<td>2.2</td>
<td>1861.9</td>
</tr>
</tbody>
</table>
Figure 3.1. (a) Cross-sectional schematic of 6H-SiC(0001) showing a non-unit cell height step. (b) Top view of the stacking mismatch boundary formed by the two different stacking sequences on either side of the step from[30].
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Comparison of Auger Data for various Cleaning methods

Figure 3.10. AES survey spectra from a hydrogen etched 6H-SiC(0001) surface. (a) As-loaded, (b) $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructed surface via thermal annealing, (c) 3 x 3 reconstructed surface via a Silane clean, and (d) a 1 x 1 after annealing the 3 x 3.
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4 Photo-Emission Electron Microscopy (PEEM) of Cleaned and Etched 6H -SiC(0001).

4.1 Abstract

The surface structures of both cleaned and hydrogen etched 6H-SiC(0001)\textsubscript{Si} wafers have been investigated using photo emission electron microscopy (PEEM). In the first study, the SiC wafers were exposed to different cleaning processes to obtain surfaces with a ($\sqrt{3} \times \sqrt{3}$)R30° or a 3 x 3 diffraction pattern. The PEEM images, obtained using either a mercury arc lamp or the Duke University free electron laser (DFEL) as the photon source revealed that the reconstructed surfaces cleaned with 10 Å of silicon evaporated onto the SiC substrate at 27°C in 10\textsuperscript{-10} torr vacuum were non-uniform and exhibited silicon islands. By contrast, uniform surfaces were achieved on samples annealed at 900°C for 10 minutes at 10\textsuperscript{-9} torr. In the second study, characterization of a hydrogen etched surface using the PEEM with the DFEL as the photon source revealed a high density of dislocations and a stepped surface structure for wafers with carrier concentrations of 2.8 x 10\textsuperscript{18} (N\textsubscript{D}-N\textsubscript{A}) cm\textsuperscript{-3}. 
4.2 Introduction

The surface preparation of SiC plays an important role in terms of the density of defects generated in epitaxially grown films[1] and the electrical characteristics of subsequently fabricated devices[2]. Recent reflection high energy[3] and low energy electron diffraction[4-8], scanning tunneling [7-11] and atomic force[11-13] microscopies, low energy electron microscopy [14], electron energy loss spectroscopy[6,8], and Auger electron[5-8] and x-ray photoelectron[5] spectroscopy studies have provided critical microstructural, structural, and chemical information regarding the efficacy of different chemical process routes for the preparation of these surfaces. Two generic preparations that have generated considerable interest are surface cleaning and hydrogen etching. The surfaces of 6H-SiC(0001)$_{Si}$ using a Si flux and annealing can be prepared to exhibit surface diffraction patterns of $3 \times 3$, $(\sqrt{3} \times \sqrt{3})R30^\circ$, $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ or $1 \times 1$ [5-7]. The structures of $(\sqrt{3} \times \sqrt{3})R30^\circ$ or $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ patterns have been observed for surfaces annealed without a silicon flux [15,16]. Hydrogen etching of 6H-SiC(0001)$_{Si}$ surfaces removes the polishing scratches and replaces them with atomic steps that have a unit cell height[11-13]. These single unit cell steps apparently eliminate stacking mismatch boundaries[13,17] associated with the growth of 2H-AlN and 2H-GaN. A complimentary method to characterize these surfaces is through photo-electron emission microscopy using an intense and/or tunable UV source.
In the research associated with this paper, PEEM was used to examine the (0001)_{Si} surfaces of cleaned or etched 6H-SiC. In general, different surface preparations produce different atomic arrangements and structures on the surface that affect both the photo-threshold energy and the topography, and, therefore, provide two different contrast mechanisms for imaging the surface with the PEEM. The first set of experiments exploited these differences in photo-threshold energies to achieve observations of the surfaces of 6H- SiC(0001)_{Si} before and after cleaning. In the second set of experiments the stepped surface structures produced by hydrogen etching on 6H-SiC(0001)_{Si} wafers were imaged in the PEEM using the topographic differences of the steps to achieve contrast imaging. The following sections provide the experimental details as well as the results and a summary of these investigations.

4.3 Experimental Procedure

4.3.1 Ex Situ Preparation

The samples used in the cleaning experiments consisted of 9 mm x 9 mm pieces diced from n-type 6H-SiC(0001)_{Si} wafers obtained from Cree Incorporated. Prior to processing in vacuum, the as-received samples were dipped into a 10:1 HF acid solution to remove the silicon oxide from the polished surface. Tungsten was then deposited on the unpolished (000-1) back of each substrate to assist in radiative and electron bombardment heating (see below). After deposition, the pieces were cleaned by boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent. The samples were then placed over a 10:1 HF buffered oxide etch to remove the remaining oxide [18].
The hydrogen etched samples were prepared at Carnegie Mellon University. Detailed descriptions of the etching process and the AFM results are given elsewhere[12]. The etched samples were boiled in trichloroethylene, acetone, and methanol for 5 minutes in each solvent. Both sets of samples were then transferred through a load lock to the Nitride Growth and Characterization System (NGCS).

4.3.2 In Situ Surface Preparation and Characterization

The NGCS consists of a gas source molecular beam epitaxy system (GSMBE), an Auger electron spectroscopy (AES) system, and a PEEM, as shown schematically in Figure 4.1. Detailed descriptions of the PEEM system and its operation with the Free Electron Laser Facility are given elsewhere[19]. The SiC pieces to be cleaned were transferred from the load lock chamber into the Physical Electronics #10-155 AES system for initial surface analysis. They were subsequently transferred to the GSMBE for cleaning and RHEED studies. For the samples cleaned with silicon, each sample was exposed at room temperature to a Si flux provided by a Thermionics 4-pocket Linear Evaporation System. The surface was monitored during this exposure using a Staib Instruments NEK-1025-R reflection high energy electron diffraction (RHEED) system. Sample heating consisted of radiative heating from a tungsten filament to approximately 400ºC and electron bombardment for higher temperatures. The temperature measurements were obtained using an optical pyrometer with an emissivity setting of 0.5. For the samples cleaned without silicon, the wafer was heated at 900ºC for 10 minutes in
10⁻⁹ torr vacuum until the (√3 x √3)R30⁰ was observed. The samples were then returned to the AES system for analysis of the reconstructed surface, and transferred to the PEEM for observation using a mercury arc lamp with a high energy cut-off at ≈5.1 eV or the free electron laser in spontaneous mode with a photon energy of 6.0 eV. The hydrogen etched samples with carrier concentrations of 2.8 x 10¹⁸ cm⁻³ were transferred directly to the PEEM without in situ surface preparation. The hydrogen etched samples with a carrier concentration of 5.11 x 10¹⁷ cm⁻³ were annealed for 15 minutes at 1030°C in the GSMBE before loading into the PEEM.

### 4.4 Results and Discussion

#### 4.4.1 Surface Cleaning of SiC

Figure 4.2a, shows the PEEM image of an ex-situ prepared 6H-SiC(0001) sample in the as-loaded condition. The image shows uniform emission across the sample. The RHEED pattern shown in Figure 4.3a shows a 1 x 1 diffraction pattern along the <11-20> and <1-100> directions. Auger spectroscopy of this surface showed a strong oxygen peak with a silicon-to-carbon peak-to-peak height (pph) ratio of 0.6.

As noted in the previous section, to obtain a (√3 x √3)R30⁰ surface structure without a silicon flux, the sample was heated at 900°C for 10 minutes in 10⁻⁹ torr vacuum. RHEED of the surface exhibited a 1x pattern in the <11-20> and a 3x pattern in the <1-100>, as shown in Figure 4.3b. This pattern indicates a (√3 x √3)R30⁰ surface reconstruction. A PEEM image of this surface structure is shown in Figure 4.2b. The surface is bright and the emission is uniform. The (√3 x √3) R30⁰ reconstruction has an
estimated threshold energy of 5.06 eV [20], which makes the surface appear bright in the PEEM images. Previously reported values for the silicon-to-carbon pph ratio of a surface cleaned without excess silicon have been below 1.0 [21]. The uncorrected and corrected ratio for this study was 1.6 and 0.6 respectively.

The \((\sqrt{3} \times \sqrt{3})R30^\circ\) surface structure may also be obtained using excess silicon. The excess silicon is deposited to replace silicon lost from silicon oxide evaporation. Approximately 10 Å of silicon was deposited on the surface of the 6H-SiC(0001) at room temperature followed by annealing at 830-925 °C for 30 minutes. A strong \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern may be seen in Figure 4.3c and a PEEM image of the surface is shown in Figure 4.2c. The image shows uniform emission and the presence of islands. Again, the surface appears bright due to an estimated threshold energy of 5.06 eV [20]. AFM scans confirmed the presence of islands on the surface which are attributed to excess silicon. The Auger spectrum showed a silicon-to-carbon pph ratio of 2.4 (1.0 when corrected for sensitivity factors), which is in close agreement with the 2.21 value reported by Starke et al.[7] for the \((\sqrt{3} \times \sqrt{3})R30^\circ\) on a 4H-SiC(0001).

To obtain a 3x3 reconstruction, the SiC substrate was annealed without a silicon flux at 900 °C in the GSMBE until a \((\sqrt{3} \times \sqrt{3})R30^\circ\) RHEED pattern became evident. The silicon flux was then initiated, and the process was monitored using RHEED. Deposition was discontinued when a 3x3 pattern was obtained. A spotty pattern also appeared concurrently superimposed on the 3x3 pattern and was attributed to excess silicon islands on the surface [10]. As shown in Figure 4.3d, the 3x3 pattern remained upon cooling. A calculated silicon-to-carbon pph ratio of 4.3 (1.7 when corrected for sensitivity factors)
was obtained from the Auger spectrum in Figure 4.2d, which between the values of $>3.0$
reported by King et al.[21] and 5.2 reported by Starke et al.[7] for the 3x3 reconstruction
on 4H-SiC(0001). The difference in values is likely due to the incomplete coverage by
the Si, as observed in the PEEM image in Figure 4.2d. The bright areas indicate either a
1x1 or $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction both of which have an estimated threshold values of
5.06 eV [20]. The dark areas, which were not excited by the photons, indicate a 3 x 3
reconstruction, which has an estimated threshold energy of 6.1 eV [20]. The Auger
spectrum did not indicate the presence of oxygen on the surface.

### 4.4.2 Hydrogen Etching

The PEEM images from a hydrogen etched samples are shown in Figure 4.4 and
Figure 4.5. Figure 4.4 shows a 150 and 20 µm FOV images of a hydrogen etched wafer
with doping levels of $5.11 \times 10^{17} (N_D - N_A) \text{ cm}^{-3}$. Emission occurred uniformly from the
terraces. Two regions may be observed on the surface in Figure 4.4b. Region 1 in the
image shows terrace widths of approximately 0.3 µm. The AFM studies showed that this
region contained half unit cell height steps. Region 2 exhibits terrace widths of
approximately 0.6µm which correspond to unit cell height steps.

The PEEM images in Figure 4.5 were obtained for a hydrogen etched surface of a
wafer with a net carrier concentration of $2.8 \times 10^{18} (N_D - N_A) \text{ cm}^{-3}$. In the 150 µm field of
view PEEM image in Figure 4.5a, the surface shows a stepped structure with several
dislocations, labeled A, intersecting the surface. Figure 4.5b shows two 50 µm FOV
PEEM images. In the first image, the dislocations shown in Figure 4.5a are evident. In
the second image, a transition region between two stepped structures is observed. This region appears darker in the image. Also evident in the image is a region that appears disordered, labeled B, which does not show any steps.

Figure 4.5c, shows two 20 µm field of view images of a screw dislocation intersecting the surface and of a transition region between two different stepped structures. From the image of the dislocation, emission is associated with the bright regions, which were measured to be approximately 0.6 µm in width in the PEEM image. This value was then compared to AFM, in which a terrace width was ~0.6 µm was measured. The step height, determined by AFM, is 15 Å, which is the length of the 6H-SiC unit cell along the [0001] axis [12].

4.5 Summary

In situ RHEED monitoring of 6H-SiC(0001) surfaces during in-situ cleaning via the exposure to evaporated Si does not give a complete picture of the surface structure. A complementary and unique technique to RHEED is PEEM coupled with an intense UV light source to study the efficacy of different surface preparations of 6H-SiC(0001)Si substrates through the different threshold energies. The RHEED patterns obtained in this study showed spotty 3x3, which was attributed to excess Si, and clear (√3 x √3)R30° patterns. The PEEM images with the mercury arc lamp in this study revealed a non-uniform surface structure that was attributed to different or incomplete reconstructed regions for samples cleaned with and without silicon deposition. PEEM images revealed that samples cleaned with silicon produced islands on the surface, and samples without
silicon showed a uniform surface. The PEEM images of the hydrogen etched 6H-SiC(0001) surface showed a stepped structure with each step having the height of one unit cell (15Å). The intersections of dislocations with the surface were observed by the etched patterns around them. PEEM has been shown to be a valuable tool in the analysis of the surface due to the work function differences for the different surface preparation techniques.
4.6 References


Figure 4.1. Schematic arrangement of the Nitride Growth and Characterization System located at the Free Electron Laser Laboratory at Duke University.
Figure 4.2. PEEM images and Auger spectra of 6H-SiC (0001)\textsubscript{Si} samples. (a) A 266x image using an Hg lamp of an as-loaded SiC sample with a 1x1 reconstruction, (b) a 266x image obtained using the FEL with $h\nu = 6.0$ eV of annealed surface with a ($\sqrt{3}$ x $\sqrt{3}$)R30° RHEED pattern, (c) A 266x using Hg lamp of a different sample after a ($\sqrt{3}$ x $\sqrt{3}$)R30° RHEED pattern had been obtained with excess silicon, and (d) A 800x using an Hg lamp after a 3x3 RHEED pattern had been obtained with a superimposed spotty pattern produced by the presence of Si islands. The dark spots in (b) and (c) are due to channel plate damage.
Figure 4.3. RHEED pattern for 6H-SiC(0001)$_{Si}$ along the <1-100> and <11-20> directions for (a) an as-loaded surface, (b) after annealing to produce a (3 x 3)R30° surface reconstruction without a silicon flux, (c) after annealing with excess silicon to produce a (3 x 3)R30° surface reconstruction, and (d) (3 x 3) surface reconstruction.
Figure 4.4. PEEM images of an hydrogen etched, on -axis 6H-SiC (0001) wafer with a net ionized carrier concentration of $5.11 \times 10^{17} \ (N_D-N_A) \ cm^{-3}$ using spontaneous emission of the FEL at 5.85 eV as the excitation source. a) 150 µm F.O.V. b) 20 µm F.O.V. The four dark spots are due to channel plate damage.
Figure 4.5. PEEM images of an etched, on-axis 6H-SiC (0001) wafer with a net ionized carrier concentration of $2.8 \times 10^{-18} (N_D-N_A) \text{cm}^{-3}$ using spontaneous emission of the FEL at 5.95 eV as the excitation source. a) 150 µm F.O.V. b) 50 µm F.O.V. c) 20 µm F.O.V.

5.1 Abstract

The initial growth of AlN and GaN thin films on 6H-SiC(0001) substrates previously etched in flowing 25%H$_2$/75%He at approximately 1600°C for 15 minutes was investigated using photo-electron emission microscopy (PEEM), atomic force microscopy (AFM), and reflection high energy electron diffraction (RHEED). Etching resulted in a surface containing unit cell high and one-half unit cell high steps. PEEM results showed that AlN films nucleated immediately and coalesced, except in areas of the substrate surface containing half unit cell height steps. Bright spots were observed from pits in these areas of the films. GaN films grown at 700°C and 800°C exhibited three-dimensional growth along the steps. The coalescence of the former depended upon the step structure and the latter exhibited coalescence after 5 minutes of growth. The GaN grown at 700°C showed that regions with the half unit cell height steps exhibited long voids in the film.
5.2 Introduction.

The binary system of gallium nitride (GaN) and aluminum nitride (AlN) form a complete solid solution with a bandgap range from 3.4 eV to 6.2 eV. The development of thin films of these materials, their alloys and associated device structures has matured sufficiently to allow their use in commercial applications including blue, green and violet light emitting diodes and blue emitting laser diodes [1]. Due to their strong atomic bonding, they are also candidate materials for high-frequency and high-power applications such as high electron mobility field effect transistors. AlN is being used as a buffer layer and potentially as an insulator for SiC-based metal-insulator-semiconductor structures [2]. However, the dislocation density in heteroepitaxial thin films of these materials, even for high brightness LED’s, is on the order of $10^{10}$ cm$^{-2}$ [3].

The primary drawback to epitaxial growth of these materials is the lack of suitable GaN and/or AlN substrates. Innovative growth techniques including lateral epitaxial overgrowth and pendo-epitaxy have resulted in substantial reductions in defect densities in GaN and AlGaN films grown by MOCVD [4,5]. A reduction in the density of planar defects including stacking mismatch boundaries has also been observed in films grown on hydrogen etched substrates [6]. The hydrogen etching process removes the surface layers and the associated damage due to polishing and creates an atomically smooth surface with steps having primarily unit cell heights [7-10]. To improve the lifetime and efficiency of III-nitride devices, a thorough understanding of the factors that effect growth and consequent defect formation must be investigated. The unique combination
of a molecular beam epitaxy (MBE) chamber in tandem with a photo-electron emission microscope may be used to obtain a better understanding of the growth of thin films.

The initial growth of III-Nitrides on cleaned and/or hydrogen etched 6H-SiC has been studied using x-ray photoemission spectroscopy [11], low energy electron microscopy [12], low energy electron diffraction [12], atomic force microscopy [13], and reflection high energy electron diffraction [13]. Two-dimensional growth of AlN(0001) has been observed on unetched surfaces of 6H-SiC(0001) [11]. GaN(0001) deposited directly on unetched SiC substrates previously annealed at 600ºC and exposed to a plasma activated nitrogen flux exhibited three-dimensional growth [11]. GaN films grown using an RF plasma source on hydrogen etched surfaces exhibited two-dimensional growth at low temperatures below the critical thickness and three-dimensional growth at higher temperatures [13]. Low energy electron emission studies showed that the nucleation of GaN on hydrogen etched surfaces occurred along the step edges and that slow growth occurred across the substrate without full coalescence even after two hours [12].

A similar technique to LEEM, PEEM employs the photoelectric effect to image electrons emitted from the surface due to photoemission. PEEM has been utilized in the investigations of electron emission from GaN and diamond surfaces [14,15], Schottky contacts [16], surface diffusion studies of adsorbates [17], oxidation of surfaces [18], magnetic materials [19], tribo-chemical interactions [20], and thin film heteroepitaxial growth [21,22]. Morphology studies have included NiₓSi₁₋ₓ films formed by depositing nickel on strained and unstrained, n-type Si(100) substrates [21] and titanium silicide
epitaxially grown islands on Si(001) surfaces[22]. The films Ni$_x$Si$_y$ formed islands at 600°C on the bulk substrate and 700°C on the strained substrate. Island motion was observed during annealing of the latter at 1150°C. Films of III-nitride materials have been investigated as pyramidal arrays grown via organometallic vapor phase epitaxy[15]. PEEM observations showed over a 150 µm field of view uniform emission.

In this research, PEEM was used in tandem with a GSMBE for in situ determination of the initial growth modes of AlN and GaN on hydrogen etched 6H-SiC(0001) surfaces with light provided by the Duke (University) free electron laser(DFEL).

5.3 Background

Photoemission from a metal occurs when the photon energy is greater than the work function, as illustrated in Figure 5.1. Photoemission from a semiconductor occurs when photons have an energy greater than the sum of the bandgap and the electron affinity which is called the photo-threshold energy, as illustrated in Figure 5.1b. Table 5.1 lists several metals and their workfunctions as well as wide band gap materials and their bandgaps, electron affinities, and photo-threshold energies.

Photoemission from solids may be described by a three step process proposed by Bergland and Spicer [23,24]. The emission of electrons is considered to be a volume process of which the first step is their optical excitation to higher energies into the conduction band. In the second step, the electron transits to the surface. In transiting to the surface, the electrons may be scattered due to various interactions. In inelastic
scattering, the electrons will lose (or gain) energy via electron-electron, electron-ion, electron-plasmon, and/or electron-phonon interactions. These interactions change the energy of the escaping electrons, which can contribute to chromatic aberrations in the PEEM. The electrons imaged by PEEM have emitted from within one mean free path of the surface, however, some of those electrons may have originated and migrated from deeper in the bulk.

Figure 5.2 shows the universal curve taken from *Physics at Surfaces* by A. Zangwill [25] for the electron inelastic scattering mean free path. In the experiments described in the following sections, the employed photon energies ranged between 5 and 6 eV. The result was an inelastic electron mean free path of 70 – 100 Å. The estimated penetration depth of the photons is given by the attenuation length, $l$, which is calculated using the equation

$$l = \frac{1}{\alpha} \quad (\text{m}) \quad (5.1)$$

where $\alpha$ is the absorption coefficient in m$^{-1}$. The absorption coefficient is given by the imaginary part of the refractive index through the equation

$$\alpha = \frac{4\pi E}{c h} k \quad (5.2)$$

where $E$ is the photon energy, $h$ is Plank's constant in eV-s, and $k$ is the extinction coefficient (the imaginary part of the index of refraction). For a photon energy of 6.0 eV (5 eV) with an extinction coefficient of approximately 1 (0.5) [26], the penetration depth...
for GaN is calculated to be approximately 160 Å (400 Å). Using the same calculation for AlN with an extinction coefficient obtained from RF deposited AlN [27], the penetration depth has been calculated to be greater than 2500 Å for photons having an energy of 6.0 eV. Therefore information from the photo emission process may be collected up to 100Å into the sample in the case of GaN and AlN.

In the last step, the electron must overcome the surface potential barrier and be emitted into vacuum. The electrons experience a change in the potential at the surface that varies from that of the bulk potential to a constant external value. This change is dependent upon (1) the surface dipole that is the difference in electrostatic potential between the bulk and vacuum, and (2) the short range Coulomb interactions. A more unified approach to the photoemission process uses the wavefunctions of the emitted electrons. However, this approach is not convenient, and is mostly qualitative in its present form and will not be discussed.

5.4 Experimental Procedures

5.4.1 Overview of the Growth and Characterization System

The MBE growth of the GaN and the AlN films was conducted in the Nitride Growth and Characterization System (NGCS) located at Duke University. The NGCS consists of a load lock, the gas source molecular beam epitaxy system (GSMBE), an Auger electron spectroscopy (AES) system, and a PEEM connected to each other via a six-way cross. A schematic drawing of this system is shown in Figure 2.8.
The growth of the III-Nitride films was achieved using molecular beam epitaxy. The system contains three EPI Knudsen (k) cells for gallium, aluminum, and indium solid sources. The temperature of the k-cells were controlled using a Eurotherm 818 controller in tandem with an 831 SCR solid state relay. High purity “blue" ammonia* was used as the nitrogen source. The ammonia flux was controlled using a leak valve** and was not directly measured. A remote ion gauge** was used to monitor the ammonia flow to achieve a growth pressure of $1 \times 10^{-5}$ to $1 \times 10^{-6}$ torr. A custom made nozzle resulted in a higher pressure in front of the sample. The growth of the III-nitrides was monitored using a Staib Instruments reflection high-energy electron diffraction system.

5.4.2 Film Growth

Wafers of 6H- SiC(0001)$_{Si}$ were used in the growth studies. Prior to loading into the NCGS, each sample was dipped for 10 minutes in a 10% HF solution to remove the thermally grown oxide, etched for 20 minutes at ~1600° C at 1 atmosphere in a 25:75 H$_2$/He mixture (by weight), coated on the unpolished (000-1) side with tungsten using an RF sputtering system, chemically cleaned via boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent, and exposed to HF vapor for 15 minutes to remove the residual oxide [28].

A molybdenum plate was placed behind the SiC wafers in a sample holder

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*Solkatronic Chemicals, Morrisville, PA 19067

**Granville Phillips (Helix Corporation), Longmont, CO 80503-9501
specifically designed for the PEEM to achieve uniform heating across the wafer. The wafers were cleaned via annealing in the MBE system. Oxygen and hydrocarbons were removed from the surface of each wafer during an increase in the wafer temperature to 1030°C while maintaining a system pressure below $<10^{-8}$ torr. The wafers were then held at 1030°C for 15 minutes. The temperature of the wafers was monitored using an optical pyrometer with an emissivity setting of 0.5. The surface crystallography was monitored using reflection high-energy electron diffraction (RHEED) with a 20 kV beam. A 3x pattern along the $<1-100>$ direction and a 1x pattern along the $<11-20>$ direction were exhibited on the phosphor screen after annealing, as shown in Figure 5.3. These RHEED patterns indicate of $(\sqrt{3} \times \sqrt{3})R30°$ reconstructed surface. The AES of the cleaned surfaces showed a silicon-to-carbon peak-to-peak height (pph) ratio uncorrected for sensitivity factors of 1.6 - 1.7; the surface concentration of oxygen was below the detection limits of this technique.

The sample temperature was subsequently adjusted to the growth temperature. Table 5.2 lists the growth conditions used in this study. Once the system was stabilized, the group III species was introduced followed by the group V species, allowing growth to begin. The growth rates of AlN and GaN were ~ 0.1 Å/second ~0.3 Å/second, respectively. The AlN growth runs lasted from 30 seconds for the analysis of the initial growth mode to 15 minutes to obtain complete coverage of the surface. Films of GaN were deposited from two minutes for analysis of the initial growth mode, to 5 minutes to obtain complete coverage of the surface. Upon completion of the growth, the group III
source was shuttered, the temperature was lowered manually and the ammonia source was shut off at a sample temperature less than 400ºC.

5.4.3 Analysis Systems

The initial growths of the AlN and the GaN thin films were studied using the PEEM with a Hg arc lamp or in tandem with UV excitation from the DFEL Laboratory. The PEEM* consists of two main vacuum chambers separated by a special gate valve. The main chamber contains the sample cartridge manipulator along with the growth and the monitoring equipment. The sample holder is fully integrated and consists of the entire heating assembly including the thermocouple and all electrical connections. The second chamber of the microscope is the imaging section or lens column, which contains the magnification lenses, the microchannel plates and the phosphorus screen. The lens column consists of a transfer lens, a field lens, a double gap projector lens, and an objective lens capable of providing 10 nm resolution. The lens column can provide magnifications from 200x to 100,000x, which corresponds to a field of view ranging from 150 µm to 1.5 µm.

Photons to the system were provided either by a 100 W mercury arc lamp with a high energy cut-off of approximately 5.1 eV or from the DFEL. Due to the broad

*ELMITEC Elektronenmikroskopie GmbH, Schacht 1, D - 38678 Clausthal-Zellerfeld, Germany
spectrum, low intensity, and low cut-off energy, the mercury arc lamp was used for beam alignment purposes during characterization of the wide band gap semiconductors.

The free electron laser consists of a 1 GeV storage ring with an OK-4 FEL optical klystron. Typical operating energies of the storage ring were 260 MeV or 500 MeV. The optical klystron consists of two electromagnetic wigglers that allow the photon energies to be adjusted from 3 eV to 10 eV. In these experiments, the photon energies were adjusted between 5.4 eV to 6.3 eV. Photons with energies above 6.3 are absorbed in the atmosphere before they can enter the system. One of the main benefits of using the FEL is the ability to adjust the photon energy during an experiment. For example, Figure 5.4 and Figure 5.5 shows a series of PEEM images of a 6H-SiC surface with partial coverage of AlN and GaN films, respectively. In Figure 5.4, the AlN film can be observed in the top half of the image. The photon energies of the FEL were adjusted from 5.2 eV to 6.3 eV to determine if a turn-on energy existed for the film. Images at 5.2, 5.5, and 6.0 eV showed a distinct boundary between the AlN and SiC. Also evident in these images is an Auger spot, which changes the work function through the deposition of hydrocarbons and oxygen. At an energy of 6.3 eV, the AlN begins to lose some contrast with the SiC, as observed in the upper right hand corner. The estimated threshold energy for AlN is 6.2 eV due to its negative electron affinity. The GaN in Figure 5.5 appeared to lose contrast with the SiC at 6.3 eV despite the fact that GaN has a photo-threshold energy of 6.8 eV, as deduced from the bandgap energy of 3.4 eV and the electron affinity of 3.4 eV.

Another benefit of using the FEL is the narrow line width of the emitted photons. Line widths are approximately 1% of the photon energy. This narrow line width reduces
the chromatic aberrations associated with a variation of electron energies. During the experiments, a storage ring current of 50 mA was used, which provided an average power of ~1.3 mW at the PEEM. A more detailed description of the system is presented in Chapter 2 or reference [31].

5.5 Results

The hydrogen etched SiC(0001) surfaces exhibited different microstructures associated with the net ionized carrier concentrations in the substrate as shown in the AFM images in Figure 5.6a and b. The respective figures show typical surfaces associated with wafers with net ionized impurity concentrations of \(\sim 2 \times 10^{18} \text{ cm}^{-3}\) and \(\sim 5 \times 10^{17} (N_D-N_A) \text{ cm}^{-3}\). Note the different regions, with unit cell height steps (labeled 1) and half unit cell height steps (labeled 2) in the two images. PEEM images for similar surfaces are shown at 50 µm and 10 µm field of view in Figure 5.7a and Figure 5.7b.

5.5.1 Gallium Nitride

Figure 5.8a and Figure 5.10a display PEEM images of the growth of GaN using GSMBE at 700ºC and 800º C, respectively. The image in Figure 5.8a shows a 50 µm field of view of a 40-50 Å thick GaN film after 2 minutes of growth obtained using the FEL with a photon energy of 6.2 eV. The bright spots are attributed to emission from the silicon carbide (threshold energy of \(\sim 5.1 \text{ eV}\)) through holes in the GaN film. These openings are ascribed to gallium droplets that formed on the surface during growth and subsequently evaporated after the Ga source was closed. The rest of the surface, which
appears darker than the openings, region A, exhibits uniform emission indicative of GaN deposition (photo-threshold energy of 6.8 eV). Though the photon energy used for this experiment was below the photo-threshold of the GaN, emission resulted from photo excitation in the silicon carbide substrate. When thicker films were deposited, as was seen in Figure 5.5c, the films appeared dark.

The PEEM image in Figure 5.8a shows regions, labeled A, of uniform emission from the surface indicating coalescence of the film. The same image also shows regions where the steps are still evident, as indicated by the arrow for the region labeled B. These lines appear brighter in the image due to the exposed SiC from incomplete coalescence of the film. A 10 µm x 10 µm AFM scan of a region similar to that shown in Figure 5.8a, is presented in Figure 5.8b and confirms these results. The latter AFM image shows that the film has grown in a three-dimensional growth mode, as shown by the height profiles in Figure 5.9. Region A of Figure 5.9b, shows an area where the film began to coalesce at the steps. In most cases the remaining openings in the film did not extend to the substrate as indicated by the height profile of Figure 5.9a. In region B, deep valleys in the film, as shown in the height profile in Figure 5.9b, were observed due to the vertical growth of the GaN.

Coalescence of the film depended upon the step structure of the hydrogen etched surface. As indicated by the arrows in region A in Figure 5.8b, coalescence of the film occurred where steps with a terrace width of approximately 0.7 µm had been etched. This step width corresponds to region 1 of Figure 5.6b, which exhibits unit cell high steps. In the non-coalesced region, region B, the steps terraces were half the width as
those in region A, as indicated by the small arrows. This corresponds to the stepped area shown in region 2 of Figure 5.7b, which exhibits one-half unit cell high steps.

Figure 5.10a shows a 5 µm field of view PEEM image for the GaN films grown at 800°C taken using the FEL with a photon energy of 6.0 eV. The image has been inverted (i.e. black ↔ white) for consistency with the AFM scan. Therefore, the light regions in the image indicate the GaN film, and the dark regions are the SiC substrate. RHEED of this film produced a spotty pattern superimposed on a (√3 x √3)R30° streaked pattern. The former resulted from the three dimensional growth of the GaN; the latter was from the SiC surface. The results presented in Chapter 6 note that exposure of the SiC(0001) having a (√3 x √3)R30° reconstruction to ammonia nitrides the surface, but the (√3 x √3)R30° diffraction remains.

As shown in the PEEM image in Figure 5.10a, growth occurred as uncoalesced islands along the steps. The 5 µm x 5 µm AFM scan shown in Figure 5.10b confirms these results. Figure 5.11 shows height profiles from the AFM image for two different regions on the surface. The nucleation of the GaN appears to have occurred at the step-terrace intersection and the growth is nearly vertical. This may also be observed in the AFM image, in which the right edge of the GaN lines appears straight and the left edge appears non-uniform due to growth across the terrace. After 5 minutes of growth at 800 °C, additional PEEM images, as shown in Figure 5.12a, indicated that the film had coalesced producing a surface with uniform emission. The film appears dark, except for some emission from the underlying silicon carbide. The 5 µm x 5 µm AFM image, Figure 5.12b showed similar results. The step edges were barely evident in both the
AFM and PEEM images as indicated by the arrow perpendicular to the steps. AFM confirmed that the islands, seen in Figure 5.12, had coalesced and formed a continuous surface with an RMS value of ~30 Å.

5.5.2 Aluminum Nitride Growth

The AlN growth was initiated with an aluminum flux. After 10 seconds of aluminum exposure, the surface exhibited a 1 x 1 RHEED pattern. Ammonia was then introduced into the system, and growth was conducted for 30 seconds. The RHEED pattern exhibited a (√3 x √3)R30° reconstruction with faint spots appearing on the primary rods. As with the GaN films, this pattern indicated that portions of the SiC substrate remained uncovered. These results were confirmed by AES. Figure 5.13 shows a series of PEEM images at different magnifications of the surface after growth. Figure 5.13a shows a 50 µm field of view (FOV) taken with FEL excitation at 5.8 eV. Two distinct emission signatures are observed, which correspond to the light and dark regions observed on the hydrogen etched surface in Figure 5.7. The results presented below indicate that these light and dark regions are a result of different coverage of the AlN.

Figure 5.13b shows a 20 µm FOV image of two regions containing AlN with different microstructures. In one region, labeled C, the AlN appears bright and exhibits uniform emission. As discussed in the Background section, the emission from the AlN surface for thin films is a result of emission of electrons excited from the underlying SiC substrate. In the other region, labeled D, non-uniform emission occurs. The 10 µm FOV PEEM image of the transition region is shown in Figure 5.13 c. This image shows that
the steps widths change from approximately 0.3 µm on the right side of the image (region D) to 0.6 µm on the left side (region C). There are a number of bright dots evident in the image. The dark lines are attributed to the steps. The dots appear in the image where the terrace widths associated with half unit cell height steps are visible and in transition regions. Figure 5.13d shows another 10 µm PEEM image of a different area that exhibits the transition from a stepped region with bright islands to a region with uniform emission where the steps are no longer evident.

Before growth, the surface structure exhibited facets and hexagonal pits similar to those seen in Figure 5.7b. As with the GaN films grown directly on the SiC, the growth of the AlN was dependent upon the stepped structure of the surface. Figure 5.14a shows a 20µm x 20 µm AFM image of a similar AlN region with a similar transition in step structure as that noted in the PEEM images. As is evident in the 2 µm x 2 µm scan of the center region in Figure 5.14b, the bright dots in the previous PEEM images may be attributed to pits that occurred at the step-terrace intersection. These pits would be expected to result in an increase in the emission due to the exposure of the SiC. The pits occurred in regions where the terrace width had decreased. The regions with full unit cell height steps did not exhibit any pits as shown in Figure 5.14c.

Figure 5.15 shows a PEEM image of an AlN film grown for 15 minutes at 1000ºC on a hydrogen etched wafer with a net ionized impurity concentration of 5 x 10^{17} cm^{-3}. The arrow indicates the directions of the steps on the surface, which are very faint, but could be detected in the PEEM image. Emission from the surface was uniform with no indication of the pits observed in the prior sample. The formation of pits only occurred at
the interface during the initial stages of growth.

5.6 Discussion

The growth of GaN directly on the etched SiC was determined to be three-dimensional in the temperature range of 700ºC - 800ºC. Nucleation of the films had occurred along the step-terrace intersection and growth occurred across the terraces. This finding is consistent with result presented Pavlovska et al.[12] who used LEEM to study the real time growth of GaN at 650ºC on hydrogen etched 6H-SiC. However, in their research, they had not obtained a continuous film by MBE growth even after 120 minutes. As noted above, the coalescence of the film grown at 700ºC depended upon the step structure of the hydrogen etched surface. The change in the film morphology could be attributed to different surface energy of the half unit cell high regions. As noted in chapter 3, the half unit cell high steps exhibit a cubic stacking sequence. The results presented above, indicate that this affects the growth and nucleation in these regions. The growth processes on the half unit cell high stepped regions may also be due to kinetic effects such as lower surface mobility in these regions.

The growth of AlN on the etched surface was determined to be two-dimensional with the film morphology following the stepped structure. This has been seen on unetched samples, as shown in Chapter 6, where the morphology of the scratched surface is observed in the AlN film. As noted above, the PEEM exhibited regions showing stepped structures with and without the bright spots from the pits in the films. The pits, which result in increased emission from the silicon carbide substrate, formed in the films
grown on the regions with half unit cell high steps. The pits were observed along the steps and may be due to energetic or kinetic processes. Films grown for 15 minutes at 1000ºC did not exhibit the pits, and the step structure of the substrate could still be faintly observed. The PEEM images also showed regions of uniform emission, as in Figure 5.13b. This has been attributed to the height variations on the surface which resulted in these regions being out of focus.

5.7 Summary

Photo-electron emission microscopy with free electron laser excitation and AFM were used to characterize GaN and AlN thin films on etched SiC. As seen by both PEEM and AFM, growth of GaN at 800ºC displayed a three-dimensional growth mode with nucleation occurring along the steps. The GaN films grown directly on the SiC substrate at 700ºC also exhibited three-dimensional growth. PEEM of the GaN films grown at 700ºC showed regions of uniform emission, bright spots attributed to holes in the film, and regions where coalescence of the film had not occurred and the steps were still visible. AFM characterization was used to confirm the film morphology and the dependence of the GaN growth on the step structure. Similar results were observed for AlN growth. PEEM images showed regions with uniform emission from coalesced films and regions exhibiting bright dots attributed to pits forming at the steps. The pits were only found in regions which had terrace widths of approximately 0.3 µm, which corresponded to half unit cell high steps. PEEM results showed that AlN films grown for 15 minutes at 1000ºC did not exhibit the bright islands associated with the pits. The
PEEM in tandem with the FEL provides a unique combination for in-situ characterization of the growth of III-Nitride thin films.
5.8 References


Table 5.1. Threshold and workfunction energies for selected metals and wide bandgap semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Reconstruction</th>
<th>Bandgap (eV)</th>
<th>Electron Affinity (eV)</th>
<th>Threshold Energy or Workfunction (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Carbide</td>
<td>3 x 3</td>
<td>3.0</td>
<td>3.2</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1 x 1</td>
<td>3.0</td>
<td>2.2</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>√3 x √3</td>
<td>3.0</td>
<td>2.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Gallium Nitride</td>
<td>3.4</td>
<td>3.4</td>
<td>(NEA)</td>
<td>6.8</td>
</tr>
<tr>
<td>Aluminum Nitride</td>
<td>6.2</td>
<td>6.2 (NEA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>---</td>
<td>---</td>
<td></td>
<td>4.06-4.28</td>
</tr>
<tr>
<td>Gallium</td>
<td>---</td>
<td>---</td>
<td></td>
<td>4.2</td>
</tr>
</tbody>
</table>
Table 5.2. Experimental setup and growth conditions for AlN and GaN growth.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film</th>
<th>Substrate Temperature (°C)</th>
<th>Ammonia Background Pressure (Torr)</th>
<th>Growth Initiation</th>
<th>Growth Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>AlN</td>
<td>900</td>
<td>$5 \times 10^{-6}$</td>
<td>Aluminum</td>
<td>30 sec</td>
</tr>
<tr>
<td>Sample B</td>
<td>AlN</td>
<td>1000</td>
<td>$5 \times 10^{-6}$</td>
<td>Aluminum</td>
<td>15 min</td>
</tr>
<tr>
<td>Sample C</td>
<td>GaN</td>
<td>700</td>
<td>$1 \times 10^{-5}$</td>
<td>Gallium</td>
<td>2 min</td>
</tr>
<tr>
<td>Sample D</td>
<td>GaN</td>
<td>800</td>
<td>$5 \times 10^{-6}$</td>
<td>Gallium</td>
<td>2 min 30 sec</td>
</tr>
<tr>
<td>Sample E</td>
<td>GaN</td>
<td>800</td>
<td>$5 \times 10^{-6}$</td>
<td>Gallium</td>
<td>5 min</td>
</tr>
</tbody>
</table>
Figure 5.1 Schematic diagrams of the photoemission process for (a) a metal, and (b) a semiconductor.
Figure 5.2. The universal curve for the inelastic mean free path of electrons [25]
Figure 5.3 RHEED pattern of an annealed surface at 1030 °C for 15 minutes along (a) <11-20> and (b) <1-100>
Figure 5.4. 150 µm FOV PEEM images of an 6H-SiC surface that is partially covered with an AlN film grown for 30 minutes. Images taken with (a) Mercury arc lamp, (b) FEL with $h\nu = 5.2$ eV, (c) FEL with $h\nu = 5.5$ eV, (d) FEL with $h\nu = 6.0$ eV and (e) FEL with 6.3 eV.
Figure 5.5. 150 µm FOV PEEM images of an 6H-SiC surface that is partially covered with an GaN film grown for 30 minutes. Images taken with (a) Mercury arc lamp, (b) FEL with $\hbar \nu = 5.0$ eV, (c) FEL with $\hbar \nu = 5.5$ eV, (d) FEL with $\hbar \nu = 5.9$ eV, and (e) FEL with $\hbar \nu = 6.3$ eV. Note the three dark spots are a result of channel plate damage.
Figure 5.6. AFM images of hydrogen etched 6H-SiC surfaces. (a) a 15 µm x 15 µm scan of a substrate doped to $2 \times 10^{18}$ cm$^{-3}$ and (b) 15 µm x 15 µm scan of a substrate doped to $\sim 5 \times 10^{17}$ cm$^{-3}$.
Figure 5.7. PEEM images of hydrogen etched 6H-SiC surfaces. (a) A 50 µm field of view of a wafer with a doping density of $\sim 2 \times 10^{18}$ cm$^{-3}$ taken with the FEL with a photon energy of 6.0 eV. (b) 10 µm field of view of a wafer with a doping density of $\sim 5 \times 10^{17}$ cm$^{-3}$ taken with the FEL with a photon energy of 5.6 eV.
Figure 5.8. GaN growth at 700 °C for 2 minutes on a hydrogen etched 6H-SiC surface. (a) a 50 µm field of view PEEM image taken with the FEL with a photon energy of 6.2 eV and (b) a 10 µm x 10 µm AFM scan showing the growth on two different stepped regions on the surface. The bright spots in the PEEM image correspond to emission from the SiC substrate through the holes in the film seen in the AFM image. The arrows indicate the steps. Height profiles for lines A and B are shown in Figure 5.9.
Figure 5.9. Height profiles for the GaN film shown in Figure 5.9. (a) Height profile for the Region A. (b) Height profile for the uncoalesced region, Region B. Valleys are evident in the film with varying depths.
Figure 5.10. GaN growth at 800°C for 2 minutes and 30 seconds on a hydrogen etched substrate. (a) a 5 µm field of view PEEM image that has been inverted (black ↔ white) taken with the FEL with a photon energy of 6.0 eV and (b) a 5 µm x 5 µm AFM scan showing the growth and nucleation on the step edges. Lines profiles A and B are shown in Figure 5.11.
Figure 5.11. Line profiles A and B for a GaN growth at 800°C for 2 minutes and 30 seconds on a hydrogen etched substrate. Nucleation appears to have occurred at the step corners and growth occurred vertically.
Figure 5.12. GaN film grown for 5 minutes at a temperature of 800ºC. (a) a 5µm field of view PEEM image taken with the FEL with a photon energy of 5.9 eV showing that steps are still evident and (b) 5 µm x 5 µm AFM scan showing the step edges on the surface.
Figure 5.13. PEEM images of the growth of AlN on hydrogen etched SiC. (a) 50 µm FOV image taken using the DFEL with a photon energy of 5.8 eV, (b) 20 µm FOV images taken using the DFEL with a photon energy of 5.8 eV, and (c) and (d) 10 µm FOV images taken using the DFEL using a photon energy of 5.9 eV. The dark spots are a result of channel plate damage.
Figure 5.14. AFM of AlN growth on hydrogen etched 6H-SiC (a) a 20 µm x 20 µm AFM image of a region similar to that in Figure 5.13b showing a transition region between two different stepped structures. (b) a 2 µm x 2 µm scan of a region with half unit cell height steps. The region displays pits along the step edges. (c) a 2 µm x 2 µm scan of a region of unit cell height steps. The film is fully coalesced in this region.
Figure 5.15. 10 µm field of view PEEM image of AlN after 15 minutes of growth taken with 5.9 eV light from the FEL. The surface exhibited very uniform emission without any indication of the bright islands seen in the previous PEEM images.
6 Surface Engineering for the Growth of AlN via Molecular Beam Epitaxy using ammonia and Chemical Vapor Deposition

6.1 Abstract

The growth of AlN via gas source molecular beam epitaxy (GSMBE) and metallorganic chemical vapor deposition (MOVPE) was studied on unetched and hydrogen etched 6H-SiC(0001) surfaces. Investigations regarding the growth of AlN films on the unetched SiC surfaces by GSMBE focused on the affect of the in situ surface cleaning techniques and growth initiation sequence on the surface morphology and crystalline quality. The surfaces were prepared with and without excess silicon deposition during cleaning. Comparisons were made between AlN films whose growth was initiated with either an ammonia or an aluminum flux on these types of surfaces. Films initiated with the former resulted in a surface morphology with island structures, which are attributed to the initial formation of a silicon nitride layer. Film growth initiated with an aluminum flux exhibited a smooth surface morphology and displayed a stepped structure. The various surface preparation techniques and growth procedures had no effect on the full with half maximum of (~360 arcsecs) of the (0002) peak of the films.

A 2 µm x 2 µm atomic force microscopy (AFM) scan of AlN films grown by GSMBE for 30 minutes at 900ºC on a hydrogen etched surface showed a smooth surface with an RMS roughness value of ~4 Å. In larger 5 µm x 5 µm scans, stepped regions were evident. Films grown at 1000 ºC had a FWHM between 150-200 arcsecs. RHEED
and AFM indicated that these films exhibited a Stranski-Krastanov type growth mode with islands forming along the step/terrace intersections. In comparison, AlN films grown via MOCVD on a hydrogen etched wafers with a doping concentration of $6.5 \times 10^{17} \text{ cm}^{-3}$ had an RMS roughness value of $\sim 4 \, \text{ Å}$ and an XRD rocking curve FWHM of $\sim 260 \, \text{ arcsec}$; which was independent of the surface structure of the hydrogen etched wafer.

### 6.2 Introduction

Aluminum nitride (AlN) is a wide bandgap semiconductor with a bandgap of 6.2 eV and the thermal conductivity of 3.2 W/cm K. It has potential applications in high-power, high-temperature electronics that operate in the acoustic or deep ultra violet wavelengths. It forms a complete solid solution with GaN to produce materials with a bandgaps range between 3.4 eV and 6.2 eV, that are used with related alloys in green and blue emitting optoelectronics devices and several types of microelectronic devices. AlN is also used as a buffer layer for the growth of GaN epitaxial films grown primarily on sapphire and $\alpha$-SiC substrates.

The conditions for growth of AlN films on 6H-SiC(0001) have been investigated for both MBE and CVD [1-5]. The initial stages of AlN films grown by molecular beam epitaxy with an ECR plasma source were found to grow layer-by-layer[3]. The investigation also showed that the silicon carbide formed a silicon nitride layer on the surface. Ebling et al.[1] found that the surface morphology of AlN films grown by RF-plasma enhanced MBE was strongly influenced by the III-V ratio. Atomically flat
surfaces had been obtained when a stoichiometric III-V ratio was used for growth. AlN grown by MBE using ammonia showed a smooth flat surface for films grown at 1100ºC [2]. In contrast, Thompson et al. [4] observed a change in the surface morphology from pseudomorphic to three-dimensional at ~640ºC for films grown via plasma source molecular beam epitaxy. One investigation into MOCVD grown AlN films, showed a quasi-two dimensional growth with an atomically flat surface when deposited on an SiC epilayer [5].

Along with the growth conditions, substrate preparation plays an important role in the density of defects in epitaxially grown films and in the fabrication of devices [6,7]. The substrates contain a 1000Å thick intentionally grown thermal oxide on the surface that must be removed prior to growth. Several in-situ and ex-situ cleaning techniques have been investigated for silicon carbide [8-14]. Ex-situ cleaning, such as dipping the wafer in TCE, acetone and methanol followed by dipping in an HF solution, result in a monolayer of oxygen and adventitious/surface carbon remaining on the surface [10,12]. Once placed under vacuum, an additional in-situ clean must be conducted to remove the remaining contamination.

Several in situ cleaning methods include thermal desorption [14], annealing in a silicon or gallium flux [8,9,11], exposure to a hydrogen plasma [13], and bombardment the surface with argon ions [15]. Annealing the sample with excess silicon has been shown produce an uncontaminated, silicon rich surface [9,16]. As discussed in Chapter 4, annealing the sample without silicon deposition, produced an atomically ordered surface with contamination levels below detectable limits. Previous research into
surfaces after thermal desorption of the oxide has suggested that this process reduces the amount of silicon on the surface [17]. The effect of these two cleaning methods on subsequently grown films has not been examined.

Another surface preparation technique that has gained interest is hydrogen etching, which removes scratches and damaged layers from the surface. Research regarding the etching of 6H-SiC using hydrogen was first conducted in 1965 by Chu and Campbell[18]. Hydrogen etching has been shown to leave the surface flat with unit cell height steps, which in the case of 6H-SiC are 15 Å high[19]. The atomic structure of the surface after etching shows a (√3 x √3)R30º LEED pattern which has been attributed to a highly oriented monolayer of silicon dioxide on the surface [20]. Bernhardt et al. [20] proposed that Si₂O₃, as measured by quantitative LEED, exists as an honeycomb overlayer which can be removed by thermal desorption at approximately 1000ºC. Prior to III-Nitride growth, this oxide layer must be removed using one of the in-situ techniques mentioned above.

In this paper, the effect of different surface preparations on the morphology and the crystalline structure of AlN films grown by GSMBE and MOCVD on 6H-SiC(0001) surfaces will be presented. Effects of the different cleaning methods and growth initiation, i.e. ammonia initiation vs aluminum initiation, will also be presented.
6.3 Experimental Procedure

6.3.1 Ex-situ Preparation and Etching

On-axis, Si-terminated, n-type 6H-SiC(0001) wafers* were diced into 1 cm x 1 cm samples: chemically cleaned by boiling in trichloroethylene, acetone, and methanol for 10 minutes in each solvent; and dipped into a 10:1 HF acid solution for 10 minutes to remove a 500 -1000 Å thermally grown silicon oxide; rinsed in de-ionized water for at least 10 seconds and dried in flowing nitrogen.

For studies on the hydrogen etched surface, the samples were immediately mounted onto a 1.2 cm wide by 7.5 cm long Ta strip heater, introduced into the water-cooled quartz chamber of a hydrogen etching system and evacuated using a three-stage diaphragm pump** to a base pressure below 100 mTorr. The samples were etched for 20 minutes at 1 atmosphere using a 25% hydrogen/75% helium mixture with a flow rate of eight slm. The temperature of the silicon carbide wafer was varied from 1550ºC to 1650º C, depending on the doping density of the wafer and monitored using an optical pyrometer† with an emissivity setting of 1.0. The samples were rapidly cooled while maintaining the same flow rate and pressure.

* Cree Incorporated, Durham, NC 27703
** Barodyn BD-20-10MT, Danielson Vacuum Products, Inc., Lisle, IL 60532
† UMAX 20, IRCON, Inc. Niles Il, 60714
6.3.2 Molecular Beam Epitaxy

Tungsten was deposited on the C-terminated face of each SiC wafer via RF sputtering to adsorb radiation during the sample heating. The Si-terminated surfaces were again exposed to the aforementioned ex-situ solvent clean followed by a 10 minute clean in HF vapor from a 30:1 buffered oxide etch and immediately introduced into the cleaning chamber and placed under vacuum.

Table 6.1 summarizes the subsequent surface preparation and cleaning techniques used for each sample. The temperature during cleaning was monitored using the IRCON infrared optical pyrometer with an emissivity setting of 0.5. The samples were ramped manually to maintain a system pressure below $1 \times 10^{-8}$ Torr. RHEED was used to monitor the surface of the sample at each step. After cleaning, the silicon carbide exhibited a three-fold pattern along the $<1\text{-}1\text{0}0>$ direction and a one-fold pattern along the $<1\text{1}2\text{0}>$, indicative of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructed surface.

The surfaces of unetched samples were prepared via two methods. In the first method, 15-18 Å of silicon was evaporated on the surface at room temperature via e-beam evaporation at $\leq 0.1$ Å/second. The wafers were subsequently annealed per Table 6.1 until a $(\sqrt{3} \times \sqrt{3})R30^\circ$ RHEED pattern was observed. In the second cleaning method, samples were only annealed at approximately 930-950°C until a $(\sqrt{3} \times \sqrt{3})R30^\circ$ RHEED pattern was observed. The temperature was subsequently adjusted to the growth temperature. The hydrogen etched samples were not exposed to Si; they were annealed for 15 minutes under UHV conditions at a higher temperature, 970-1030°C. The
temperature was subsequently adjusted to the growth temperature.

Growth of AlN was conducted in a custom MBE chamber evacuated with an ion pump and turbomolecular drag pump to a base pressure of approximately $2 \times 10^{-10}$ Torr. The films were grown at the temperatures given in Table 6.1 and ammonia pressures of $2 - 5 \times 10^{-6}$ Torr. The AlN growth was initiated on the unetched samples via exposure of the surface to a flux of either ammonia or aluminum, as shown in Table 6.1. The ammonia flux was not measured directly, but controlled via a leak value to the background pressures noted above. The aluminum flux was measured to be $\sim 0.1$ Å/sec. For the hydrogen etched samples, the growth was always initiated with the aluminum flux. Growth was conducted for 30, 60, or 90 minutes, at which point the aluminum flux was shut off. The samples were manually ramped down and the ammonia flux stopped at 400 ºC. During the growth and ramp down, the surface was monitored using RHEED. Upon reaching room temperature, AES spectra were obtained.

### 6.3.3 Metalorganic Chemical Vapor Deposition (MOCVD)

For comparison to the MBE films, AlN films were grown via MOCVD on an NCSU hydrogen etched sample with a net ionized carrier concentration of $6.5 \times 10^{17}$ cm$^{-3}$, a CMU hydrogen etched sample with a net ionized carrier concentration $2.3 \times 10^{18}$ cm$^{-3}$, and an unetched, chemically cleaned sample. The MOCVD system consists of a water-cooled vertical pancake-style quartz chamber that could be evacuated to a base pressure of $1 \times 10^{-5}$ torr. Prior to growth, the samples were annealed at 1274 ºC for 15 minutes under a flow of 3 slm of hydrogen, to evaporate any residual oxide from the
surface. Trimethylaluminum (TMA) was used as the Al source and ammonia as the nitrogen source. AlN growth was conducted for 30 minutes at a sample platter temperature of \( \approx 1274 ^\circ \text{C} \), as measured with an optical pyrometer and using an emissivity setting of 0.8. The chamber pressure was maintained at 20 torr during growth. For consistency, the AlN films were grown on the etched and unetched wafers during the same run.

6.3.4 Analysis

The MBE and MOCVD AlN thin films were characterized by both atomic force microscopy and x-ray diffraction. Atomic force microscopy\(^{(a)}\) characterization using 2 \( \mu \text{m} \times 2 \mu \text{m} \), 5 \( \mu \text{m} \times 5 \mu \text{m} \), and 10 \( \mu \text{m} \times 10 \mu \text{m} \) scans were obtained with microlever "E" or "F" silicon nitride tips operated in contact mode. X-ray diffraction (XRD) rocking curve analysis was conducted using a Philips X-Pert-MPD multipurpose diffractometer system with a 4-crystal Bartels monochromator of Ge(220) and a nickel filtered Cu anode. In this configuration, the system has a resolution for \( D_w \) of 12 arcsecs. Epitaxial films with a thickness above 300 Å may be analyzed. The rocking curves were obtained for the (0002) peak via omega or omega/2theta scans.

\(^{(a)}\) Park Scientific Autoprobe M5, ThermoMicroscopes, Sunnyvale, CA 94089
6.4 Results and Discussion

6.4.1 MBE Growth

6.4.1.1 Growth initiated with aluminum

Figure 6.1 shows the RHEED patterns along the <1-100> direction after growth of the AlN initiated with an aluminum flux on (a) a surface cleaned with evaporated silicon (Sample A), and (b) on a surface after thermal desorption (Sample B). A streaked 1 x 1 RHEED pattern was observed during growth of the sample in which growth had been initiated with the aluminum flux on a surface cleaned with deposited silicon, Sample A. During ramp down after growth, when the aluminum flux was turned off, the RHEED pattern changed to 3 fold by 3 fold, or a 3 x 3 surface reconstruction as shown in Figure 1a. This pattern is attributed to the residual silicon on the surface. The Auger spectra showed both the KLL and LMM silicon peaks, along with the aluminum and nitrogen peak, as shown in Figure 6.2. The carbon peak at ≈ 273 eV was not present, indicating that the silicon Auger signal was not coming from the silicon carbide substrate. The growth rate in this regions was approximately 3 Å/minute. For thicker films, the silicon signal disappeared.

Excess silicon on the surface has been observed to form islands and affect the subsequent growth of the AlN. Figure 6.3 shows a 2µm x 2µm AFM image of a silicon rich surface annealed at 900ºC, resulting in a to a (√3 x √3)R30º surface structure, which displays many silicon islands, Sample M. The interaction of the silicon with the AlN may have resulted in the reduced growth rate of the AlN as compared to AlN grown on
surfaces cleaned by annealing only. The excess silicon segregated to the surface, as observed in the Auger spectrum, reducing the growth rate by occupying either the Al or nitrogen sites.

On the annealed samples that had growth initiated with aluminum (Sample B), RHEED exhibited a streaky 1 x 1 pattern during growth and a 2 x 2 pattern during cool down after the ammonia was shut off. The pattern reverted back to 1 x 1 once room temperature was reached. The 2 x 2 pattern was attributed to the adsorption of excess ammonia on the surface; this pattern has been reported [21] to be unstable with respect to both contamination and temperature.

Figure 6.4a and b shows AFM images of the samples described above. As indicated by RHEED, a smooth stepped surface occurred for the samples that had growth initiated with the Al flux. The exposure time of the surface to the aluminum flux was 10 seconds for Sample A and 1.5 minutes for Sample B. The RMS roughness values for these surfaces were approximately 4 Å for the former and 9 Å for the latter. X-ray diffraction rocking curves for the AlN films produced w-2q rocking curves with FWHM of approximately 360 arcsecs, and was independent of the growth initiation method.

Growth initiated with aluminum on a hydrogen etched (Sample E) wafer resulted in a smooth surface as shown in Figure 6.5. A 5 µm x 5 µm and a 2 µm x 2 µm AFM scan of the surface showed a surface roughness of approximately 14 Å for the 5 µm x 5 µm scan and 4 Å for the 2 µm x 2 µm scan. As shown in the 5 µm x 5 µm scan, the stepped structure is still evident in some regions of the surface, resulting in the higher
RMS value. As the temperature was increased to 1000 ºC, the growth changed to a Stranski-Krastanov growth mode. RHEED exhibited a streaked 1 fold pattern with spots after growth for 90 minutes. A 2 µm x 2 µm AFM image of the surface is shown in Figure 1.6. The surface had an RMS roughness value of ≈12 Å with islands observed along the step/terrace intersections. An x-ray diffraction rocking curve along the (0002) peak had a FWHM of 150-200 arcsecs.

6.4.1.2 Growth Initiated with Ammonia

For samples whose growth was initiated with ammonia, the surface was exposed to an ammonia flux until the pressure had stabilized, at which point an aluminum flux was introduced. The same process was used on substrates with or without excess silicon on the surface, and had resulted in the same AlN surface morphology. Exposing the clean surface to ammonia, resulted in nitrogen bonding to the surface, which could not be readily detected by RHEED, but was evident in the Auger spectra. Figure 6.7a and b show the (√3 x √3)R30º RHEED pattern along the <1-100> and <11-20> directions for a clean surface before exposure to ammonia. The Auger spectra for the annealed surface before ammonia exposure is shown in Figure 6.8b and reveals that the oxygen and nitrogen levels are below the detectable limit of the Auger system. Figure 6.7c and d show the RHEED patterns for a surface after it had been exposed to ammonia for 2 minutes at approximately 960ºC. The RHEED pattern remained a (√3 x √3)R30º pattern, as shown in Figure 1.7 c and d. As discussed in chapter 3, one suggested model for the (√3 x √3)R30º proposed that the silicon adatoms sit on a trimer of carbon atoms or at the T4 site[22]. Bonding with nitrogen from the dissociated ammonia would satisfy the
silicon adatom's dangling bond, and the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction would remain. The Auger spectra in Figure 6.8c shows that after the 2 minute exposure to ammonia, nitrogen was detected on the surface. The silicon peak showed a faint additional peak around 67 eV indicating bonding of the silicon to the nitrogen. This additional peak in analogous to the peak observed at 65 eV via the formation of silicon oxide [20]. X-ray photoemission spectroscopy results, as observed in Figure 6.9 and Figure 1.10, show that residual ammonia, as low as $1 \times 10^{-8}$ torr in the system can also result in nitrogen on cleaned surfaces. Based on STM observations from Owman et al. [22], the ($\sqrt{3} \times \sqrt{3}$)R30° surface may also exhibit defect areas along the surface after annealing. These areas may lead to regions not terminated with nitrogen, which could result in different growth rates of the AlN leading to islands.

Figure 6.1 shows the RHEED patterns along the <1-100> direction after growth of the AlN initiated with ammonia on a (c) surface cleaned with evaporated silicon (Sample C), and (d) on a surface after thermal desorption (Sample D). Samples in images (c), and (d), in which growth was initiated with an ammonia flux, the streaked pattern showed the presence of spots indicating surface roughening or the onset of three-dimensional growth. AFM of samples (c) and (d), shown in Figure 1.4c and d, exhibited a stepped morphology with many small islands that were between 25-50Å high. Aluminum exposure to the surface before ammonia introduction mentioned previously appeared to minimize this affect.
6.4.1.3 In situ cleaning

The in situ technique used to clean the SiC surface did not have a significant affect on the crystalline structure or the surface morphology of the AlN films, as observed by comparing Figure 6.4a and b or c and d as noted above. This can be explained by reviewing the resulting surface structure of the SiC after each clean. Thermal desorption without room temperature silicon deposition produced a surface as shown in Chapter 3. Owman et al.[22] using scanning tunnelling microscopy results, predicted that silicon adatoms at either the T4 site or in a trimer arrangement with carbon atoms produced the $\sqrt{3} \times \sqrt{3}$R30° surface structure. In either arrangement, the resulting surface is ordered and is terminated with silicon. By maintaining an annealing temperature below 1030°C, the amount of silicon and the structure of the surface remained the same up to annealing times of 30 minutes. This result agrees with work by Adachi et al.[23]. Cleaning the surface with excess silicon results in a similar surface structure with silicon adatoms predicted to occupy the T4 sites{}. As the above XRD results indicate, the surfaces after the various cleaning methods did not affect the surface morphology or crystalline quality of the film.

6.4.2 Chemical vapor deposition

All films were grown for 30 minutes and were fully coalesced. Figure 6.11 and Figure 6.12 show AFM scans of the surface morphology for the unetched and hydrogen
etched surface for the wafer with a carrier concentration of $6.5 \times 10^{17} \ (N_D-N_A)/\text{cm}^3$.
respectively, after growth. The AlN on the unetched surface had an RMS roughness value of $\sim 10 \ \text{Å}$, an exhibited the polishing scratches from the underlying substrate. The AlN on the hydrogen etched surface had an RMS roughness value of $\sim 4 \ \text{Å}$ and showed the stepped structure of the substrate which for this sample was a transition region between steps with unit cell height and half unit cell height.

The surface morphologies, as observed with an optical microscope with a Nomarski interference filter, of the AlN grown on hydrogen etched wafers with two different doping concentrations are shown in Figure 6.13a and b. The AlN grown on hydrogen etched wafers with doping levels of $6.5 \times 10^{17} \ (N_D-N_A) \text{cm}^3$, the surface appeared smooth as shown in Figure 1.13a. The 40 µm x 40 µm AFM image Figure 1.14a shows a faceted surface with heights up to 150 Å. The AlN film grown on the wafer with a $(N_D-N_A)$ of $2.3 \times 10^{18} \ \text{cm}^3$ exhibited hexagonal pits in the AlN film due to the hydrogen etching of the silicon carbide substrate, as shown in Figure 1.13b. The inset in the Figure shows a 100x image of the surface before growth (note that the image is inverted from the camera). Figure 6.14 shows a 40 µm x 40 µm AFM image of the hexagonal pits. In Figure 6.15, the XRD rocking curves showed a decrease in the FWHM around the 0002 peak from 380 arcsecs for the unetched sample to 260 arcsecs for the films grown on the etched samples; the FWHM of the etched samples was independent of the doping concentration.

The decrease in the FWHM of the XRD rocking curves along the (0002) peak may be attributed to a relaxation in the film. Hydrogen etching removes the bi-layer
steps, which results in a reduction in stacking mismatch boundaries [24]. The resulting surface morphology of the MOCVD grown AlN, as observed by the optical microscope, depended upon the doping levels in the silicon carbide wafer. Okamoto et al.[25] had shown that as the doping concentration increased in 6H-SiC grown by sublimation method on 6H Acheson seeds, the number of etch pits observed on the surface also increased. Hydrogen etching of the higher doped samples resulted in an increase in the hexagonal spiral structures, which occur around micropipes and dislocations. These additional structures affected the morphology of the subsequently grown AlN films.

### 6.5 Summary

AlN films were grown via MBE on cleaned surfaces prepared with and without excess silicon. Growth had been initiated with either an aluminum or an ammonia flux. When the growth was initiated with ammonia, non-uniform nitrogen bonding is believed to result in island structures on the AlN films. The surface in between these islands exhibited a flat stepped surface, indicating two-dimensional growth. In contrast, when the AlN growth was initiated with aluminum, the surface was atomically smooth with a stepped structure, and exhibited two-dimensional growth without the formation of islands. A comparison of XRD rocking curves of the (0002) had shown that there was little difference between films grown on the surfaces cleaned with or without excess silicon.

Growth via MBE at 900°C for 30 minutes on hydrogen etched surfaces also
exhibited smooth surfaces with a measured surface RMS roughness value of ~4 Å in a 2 µm x 2 µm scan of the surface. In a 5 µm x 5 µm scan, the image showed the stepped structure of the substrate and had ~14Å RMS roughness value. These values are similar to that observed on the unetched substrates. AlN films grown at 1000ºC for 90 minutes exhibited an SK growth mode with islands forming at the step/terrace intersection. The resulting film had an RMS roughness value of ≈12 Å and a XRD rocking curve FWHM of 150-200 arcsecs along the (0002) peak.

In comparison to the MBE films, the CVD grown films exhibited a RMS roughness value of ~10 Å on unetched surfaces and ~4 Å on the hydrogen etched surfaces. The FWHM of the XRD rocking curves along the (0002) peak were 380 arcsecs and 260 arcsecs, respectively. The surface morphology as observed in a optical microscope of the AlN was improved when the AlN was grown on wafers with a net ionized impurity concentrations of 6.5 x 10^{17} cm^{-3}, which is attributed to a smoother morphology of the etched SiC substrate.
6.6 References


Table 6.1 Summary of AlN growth parameters for MBE and MOCVD grown films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Preparation</th>
<th>Growth Temp. (°C)/Time (min)</th>
<th>Silicon Carbide Cleaning Method (°C)</th>
<th>Growth Initiation Species (flux)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>Unetched</td>
<td>900 ºC 30 minutes</td>
<td>Annealed with Silicon (910 ºC)</td>
<td>Aluminum (≈0.1 Å/sec)</td>
</tr>
<tr>
<td>Sample B</td>
<td>Unetched</td>
<td>900 ºC 30 minutes</td>
<td>Annealed without Silicon (930 ºC)</td>
<td>Aluminum (≈0.1 Å/sec)</td>
</tr>
<tr>
<td>Sample C</td>
<td>Unetched</td>
<td>900 ºC 30 minutes</td>
<td>Annealed with Silicon (970 ºC)</td>
<td>Ammonia (4.5x10^-6 torr)</td>
</tr>
<tr>
<td>Sample D</td>
<td>Unetched</td>
<td>900 ºC 30 minutes</td>
<td>Annealed without Silicon (955 ºC)</td>
<td>Ammonia (5.1x10^-6 torr)</td>
</tr>
<tr>
<td>Sample E</td>
<td>Hydrogen Etched</td>
<td>900 ºC 30 minutes</td>
<td>Annealed without Silicon (970 ºC)</td>
<td>Aluminum (≈0.1 Å/sec)</td>
</tr>
<tr>
<td>Sample F</td>
<td>Hydrogen Etched</td>
<td>1000ºC 90 minutes</td>
<td>Annealed without Silicon (1030ºC)</td>
<td>Aluminum (≈0.1 Å/sec)</td>
</tr>
<tr>
<td>Sample G</td>
<td>Unetched</td>
<td>N/A</td>
<td>Annealed with Silicon (925ºC)</td>
<td>N/A</td>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Preparation</th>
<th>Growth Temp. (°C)/Time (min)</th>
<th>Silicon Carbide Cleaning Method (°C)</th>
<th>Growth Initiation Species (flux)</th>
</tr>
</thead>
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<tr>
<td>Sample G</td>
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<td>Annealed (1275 ºC)</td>
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<tr>
<td>Sample H</td>
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<td>Annealed (1275 ºC)</td>
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</tr>
<tr>
<td>Sample I</td>
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<td>Annealed (1275 ºC)</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure 6.1. RHEED patterns along <1-100> direction for AlN grown by GSMBE under a) growth initiated with an aluminum flux on a surface cleaned with excess silicon, (b) growth initiated with aluminum on an annealed only surface, (c) growth initiated with ammonia flux on a surface cleaned with silicon, and (d) growth initiated with ammonia on an annealed only surface.
Figure 6.2. Auger spectra of AlN grown by GSMBE on a silicon rich surface with aluminum flux initiation. The spectra shows both the KLL and LMM silicon peaks, along with the aluminum and nitrogen peak, but not a carbon peak.
Figure 6.3. A 2 µm x 2 µm AFM image of a 6H-SiC(0001) surface after silicon deposition and annealing at 925°C to form a (√3 x √3)R30º reconstruction. The white spots are attributed to islands of silicon formed, as determined by the Si/C ratio of 2.4.
Figure 6.4. 2 µm x 2 µm AFM scans of AlN growth by GSMBE via (a) growth initiated with an aluminum flux on a surface cleaned with silicon, (b) growth initiated with aluminum on an annealed only surface, (c) growth initiated with ammonia flux on a surface cleaned with silicon, and (d) growth initiated with ammonia on an annealed only surface.
Figure 6.5. 5 µm x 5 µm and a 2 µm x 2 µm AFM scans of an AlN grown by GSMBE on a hydrogen etched surface at 900 °C.
Figure 6.6. 2 µm x 2 µm atomic force microscopy scan of GSMBE grown AlN films at 1000°C for 90 minutes. Gray scale is 0-120Å. Growth occurred via an SK growth mode with islands formed at the step edges.
Figure 6.7. RHEED patterns for (a), (b) a cleaned (thermal desorption) surface exhibiting a \((\sqrt{3} \times \sqrt{3})R30^\circ\) surface reconstruction along the \(<1\text{-}100>\) and \(<11\text{-}20>\) directions, respectively. (c), (d) a surface exposed to an ammonia flux at 960ºC for 2 minutes along \(<1\text{-}100>\) and \(<11\text{-}20>\) directions, respectively.
Figure 6.8. Auger spectra of (a) an as-loaded sample, (b) an annealed surface exhibiting a \((\sqrt{3} \times \sqrt{3})R30^\circ\), and (c) the annealed surface exposed to 2 minutes of ammonia at 960\(^\circ\)C.
Figure 6.9. XPS spectra of the oxygen peak for (a) as loaded sample, (b) after a 5 minute anneal at 1000ºC, and (c) after an additional 10 minute anneal at 1030ºC.

Figure 6.10. XPS spectra of the nitrogen peak for (a) as loaded sample, (b) after a 5 minute anneal at 1000ºC, and (c) after an additional 10 minute anneal at 1030ºC.
Figure 6.11. AFM images of an AlN film grown via MOCVD on an unetched 6H-SiC(0001) surface, Sample G. (a) a 5µm x 5 µm scan, (b) a 10 µm x 10 µm scan
Figure 6.12. AFM images of an AlN film grown on a hydrogen etched surface via MOCVD, Sample H (a) a 5 µm x 5 µm scan, (b) a 10 µm x 10 µm scan
Figure 6.13.  Surface morphology as observed using an optical microscope with a Nomarski interference filter for an AlN film grown hydrogen etched 6H-SiC(0001) surfaces for a net carrier concentrations of (a) $6.5 \times 10^{17} \text{(N}_D-\text{N}_A\text{)} \text{ cm}^{-3}$ (Sample H) and (b) $2.3 \times 10^{18} \text{(N}_D-\text{N}_A\text{)} \text{ cm}^{-3}$ (Sample I).  The inset in Figure 6.10b shows an inverted 50x image of the SiC wafer surface before growth.
Figure 6.14. 40 µm x 40 µm atomic force microscopy images of (a) AlN grown by MOCVD on a hydrogen etched wafer with a net carrier concentration of $6.5 \times 10^{17}$ cm$^{-3}$, and (b) AlN grown by MOCVD on a hydrogen etched wafer with a net carrier concentration of $2.3 \times 10^{18}$ cm$^{-3}$. 
Figure 6.15. XRD rocking for AlN grown via MOCVD on (a) an unetched substrate with FWHM of 380 arcsecs, (b) an etched substrate with a net ionized carrier concentration of $6.5 \times 10^{17} (N_D - N_A) \text{ cm}^{-3}$; FWHM = 260 arcsecs, and (c) an etched substrate with a net ionized carrier concentration of $2.3 \times 10^{18} (N_D - N_A) \text{ cm}^{-3}$; FWHM = 260 arcsecs
7 Concluding Remarks

7.1 Summary of Results

The surface preparation of on-axis, nitrogen doped 6H-SiC(0001) substrates and the growth of AlN and GaN thin films were examined by photoemission electron microscopy, atomic force microscopy, and x-ray diffraction. The surfaces of the substrates were either hydrogen etched and thermally annealed or cleaned with and without a silicon flux and unetched (chemically etched).

Hydrogen etching removed polishing scratches from the surface of on-axis 6H(0001) wafers. However, the resulting surface morphology was dependent upon the nitrogen doping concentration of the substrate. The surfaces of wafers with nitrogen concentrations of \( \geq 2.5 \times 10^{18} \text{ cm}^{-3} \) contained hexagonal pyramids and pits. The surface typically showed three different stepped regions; (1) arrays of 6H unit cell high steps, (2) spiral step structures with unit cell heights around dislocations and micropipes and, (3) step structures exhibiting 1/2 unit cell high steps associated with stacking faults. Samples with doping concentrations of \( \leq 1.35 \times 10^{18} \text{ cm}^{-3} \) were flat, and without hexagonal structures noted above. These latter surfaces generally exhibited two types of stepped structures; (1) arrays of 6H unit cell high steps and (2) step structures exhibiting 1/2 unit cell high steps associated with stacking faults in the silicon carbide.

The surface preparation of the silicon carbide substrates was examined for both hydrogen etched and chemically etched wafers to determine the best surface for subsequent growth. Chemically etched surfaces exposed to silicon before annealing or during annealing exhibited silicon islands after cleaning for both the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) and 3
x 3 surface structures. A spotty RHEED pattern was evident for the 3 x 3 structure. Observations of the surface with the PEEM with excitation from a mercury arc lamp showed that the surfaces prepared to 3 x 3 reconstruction were non-uniform, exhibiting regions of either 1 x 1 or (√3 x √3)R30° surface diffraction. The (√3 x √3)R30° surface showed uniform emission. The images for both samples also showed the formation of silicon islands.

Chemically etched surfaces cleaned via thermal desorption also exhibited a (√3 x √3)R30° surface structure. The annealing resulted in a silicon-to-carbon ratio of 1.6, which is lower than the ratio of 2.4 obtained for samples annealed with excess silicon. PEEM observations showed uniform emission from the surface.

Hydrogen etched surfaces, which were inserted directly into the vacuum system, were found to contain a native oxide layer and exhibited a (√3 x √3)R30° surface diffraction. Thermal desorption of the oxide from these surfaces required a temperature greater than 1000°C, which is approximately 50-100°C higher than the chemically etched surfaces. The cleaned surface also exhibited a (√3 x √3)R30° surface reconstruction and Auger electron spectroscopy results showed a silicon-to-carbon peak-to-peak ratio of 1.6 and oxygen levels below the detection limits of the instrument. Annealing the hydrogen etched surface in a silane flux, resulted in a 3 x 3 diffraction pattern and the formation of silicon islands on the surface. Auger electron spectroscopy results showed a silicon-to-carbon peak-to-peak ratio of 3.9 and oxygen levels below the detection limits of the instrument. Atomic force microscopy showed islands of silicon on the surface. The stepped surface structures after these cleaning processes were un-affected. Based on
PEEM and AFM results, annealed surfaces without excess silicon were used for the growth of the III-Nitrides.

Initial growth studies of GaN and AlN on the hydrogen etched surfaces, conducted using photo-electron emission microscopy and atomic force microscopy, showed that the growth and coalescence of the epitaxial films depended upon the type of stepped structure and substrate temperature. Films of GaN deposited directly on the silicon carbide substrate at 700ºC for 2 minutes grew as three-dimensional islands. In regions where the steps were of half unit cell height (with half width), the islands formed along the step-terrace intersection, and were separated by long voids. In the regions with full unit cell height steps, the films coalesced more completely producing only small openings in the film. GaN films grown at 800ºC for 2 minutes and 30 seconds nucleated and grew vertically along the step-terrace intersection. Coalescence of the films occurred after 5 minutes, but the step edges were still evident.

AlN growth on hydrogen etched 6H-SiC also exhibited two different growth morphologies depending on the nature of the stepped regions. The AlN growth on the hydrogen etched surface exhibited pits in the regions containing half unit cell high steps. In the full unit cell height regions, the films did not exhibit any pits. Growth at higher temperatures and longer times did not exhibit any pits and showed a uniform surface as observed in the PEEM.

The surface morphology of AlN grown via GSMBE on unetched 6H-SiC was found to be dependent upon the growth initiation procedure used. Films in which growth was started with ammonia exhibited island formation on the surface. When film growth was initiated with the aluminum flux, the surface morphology was smooth and RHEED
exhibited a streaky pattern indicating two-dimensional growth. The difference in morphology is attributed to non-uniform nitrogen bonding at the interface in the former situation. The affect of surface cleaning on the FWHM of an x-ray diffraction rocking curve was also investigated. Rocking curve scans showed a value of approximately 360 arcsecs for films that were grown on substrates cleaned with or without excess silicon.

XRD rocking curve of GSMBE growth of AlN on etched 6H-SiC(0001) wafers showed a FWHM 200 arcsecs for AlN films grown at 1000°C. However, the surface of the film began to exhibit a Stranski-Krastanov growth mode with islands forming at the step/terrace intersection. The surface of the films grown at 900°C for 30 minutes exhibited a RMS roughness value of approximately 4 Å for 2 µm x 2 µm scans, which was equivalent to films grown on chemically etched surfaces. At scans of 5 µm x 5 µm, the films still appeared smooth, however some of the steps were evident and longer growth times are required for complete coverage. AlN films grown via MOCVD on unetched and hydrogen etched 6H-SiC(0001) surfaces had an RMS roughness value of 10Å for the former and approximately 4 Å for the latter. The FWHM of the XRD rocking curve along for the (0002) peak decreased from 380 arcsecs on the unetched surfaces to 260 arcsecs on hydrogen etched surfaces.

The growth, surface morphology, and crystal quality of AlN and GaN thin films depended upon the surface preparation of the substrate with the best films obtained for hydrogen etched surfaces cleaned via annealing. PEEM in tandem with the free electron laser has been shown to be a complimentary tool for the in-situ analysis of III-Nitride thin films grown by gas source molecular beam epitaxy.
7.2 Future Work

The photo-electron emission microscope in tandem with the molecular beam epitaxy chamber has proven to be a valuable tool for the in-situ characterization of the growth of III-Nitrides. One of the fundamental problems today is the formation of contacts on p-type III-Nitride films and other wide bandgap materials. Complicated structures involving three or more metals have been employed. The PEEM due to its surface sensitivity could be employed to observe the reactions occurring between thin films of the metals and the wide bandgap semiconductors. The study could include the effects of various cleaning techniques of the wide bandgap materials on the reactions.

The PEEM in tandem with the free electron laser may also be used to determine surface diffusion coefficients of the group III and group V sources under various conditions. For example, a few mono-layers of gallium could be deposited on the surface. Using a pulsed laser, an area of gallium could be evaporated from the surface exposing the underlying substrate. The sample could be heated in the PEEM and the diffusion of the gallium species could be monitored. This could be done on a variety of substrates with different surface preparations and thin films.

Future work should also include a study of the growth modes and the effect of surface preparations for Al\textsubscript{x}Ga\textsubscript{1-x}N, InN, and In\textsubscript{x}Ga\textsubscript{1-x}N alloy grown by molecular beam epitaxy using the PEEM and AFM. Through the use of the tunable free electron laser, threshold energies, and therefore compositions of the grown films could be determined in situ.