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Role of Defects in III-Nitride Based Electronics

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Role of Defects in III-Nitride Based Electronics

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Abstract

The LDRD entitled "Role of Defects in III-Nitride Based Devices" is aimed to place Sandia National Laboratory at the forefront of the field of GaN materials and devices by establishing a scientific foundation in areas such as material growth, defect characterization/modeling, and processing (metalization and etching) chemistry. In this SAND report we summarize our studies such as i) the MOCVD growth and doping of GaN and AlGa_N, ii) the characterization and modeling of hydrogen in GaN, including its bonding, diffusion, and activation behaviors, iii) the calculation of energetics of various defects including planar stacking faults, threading dislocations, and point defects in GaN, and iv) dry etching (plasma etching) of GaN (n- and p-types) and AlGa_N. The result of the first AlGa_N/GaN heterojunction bipolar transistor will also be presented.

Key Words: Wide bandgap semiconductors, GaN, AlGa_N, hydrogen, defects

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I. Introduction

Wide bandgap III-Nitride semiconductors are extremely promising materials for compact, high-power, high-frequency amplifiers required for future satellite cross and up/down links, and for the robust microelectronics required for future severe environment national security applications. Due to the absence of native (homoepitaxial) substrates, defects, including point, line, and planar defects, are found to exist abundantly in GaN as a consequence of mismatched heteroepitaxy. These defects frequently interfere with the intrinsic material properties of GaN and ultimately limit the performance of electronic and optoelectronic devices. In the midst of application-orientated GaN efforts both within and outside Sandia, this LDRD is intended to provide a scientific base for understanding the roles of defects in GaN. Our approach can be categorized into three sub-fields: 1) establishing a strong metal-organic chemical vapor deposition (MOCVD) facility capable of producing device-quality GaN yet flexible enough to participate in scientific investigations, 2) applying various microscopic probes (some are unique only at SNL) to characterizing the electrical/electronic, optical, and structural properties of defects in GaN, and 3) performing state-of-the-art first principle calculation of energetics of defects in GaN. Ultimately we expect that the computational effort will produce insight on defects and be coupled to the experimental findings.

II. Metal-Organic Chemical Vapor Deposition of III-Nitride

A. MOCVD growth of GaN

Metal-organic chemical vapor deposition (MOCVD) of wide bandgap group III-nitrides has received much attention because of the demonstration¹ of blue light emitting diodes, blue laser diodes, and other optoelectronic devices. The preparation of device quality GaN on sapphire is enabled by a "two-step nucleation" procedure proposed by Amano et al.² in 1986. These authors suggested that the GaN surface underwent several morphological transitions during the two-step process including the generation of nucleation crystallites in a LT buffer layer, the formation of islands through high-temperature (HT) growth, the coalescence of these islands, and, finally, a quasi-two-dimensional (2D) growth.² The low-temperature (LT) buffer reportedly increased the density of nucleation sites and promoted the lateral growth of GaN.³ Nakamura et al.⁴ reported the first *in-situ* monitoring of the surface evolution during GaN growth using the output from an infrared (IR) pyrometer as an approximate indication of surface roughness. The observed decay and recovery of the IR transmission during the initial HT growth was supportive of Amano et al.'s model of growth evolution. Wickenden et al.⁵ observed that the degree of crystallinity of the LT buffer increases during the temperature ramp and anneal. George et al.⁶ and Wu et al.⁷ employed transmission electron microscopy (TEM) and atomic force microscopy (AFM) to examine the as-deposited and thermally-annealed LT buffer layers. Qualitatively the two reports made similar observations that the average grain size and root-mean-square (RMS) roughness of the GaN buffer layers increased at the end of the ramp/anneal stage.

Although most investigators believe that the LT buffer layer plays a deterministic role in the growth of high quality GaN, the lack of *in-situ* diagnostics in MOCVD reactors prevents a direct probing of surface evolutionary processes during growth; the precise effects of the LT buffer layer on the subsequent (HT) GaN growth and material properties remain elusive. To address this deficiency, we have implemented a real-time *in-situ* optical reflectometer capable of extracting information⁸ about growth rate, alloy composition, and of providing a qualitative measure of surface roughness in our high-speed rotating disc reactor (RDR). The information on morphological evolution enables the exploration of parameter space and provides a link between the growth parameters and the resulting material properties.

While the growth evolution is affected by the parameters reported in the literature, namely the thickness of LT buffers, the temperatures for LT and HT growth, V/III ratio, and growth rate, we have discovered that the concentration of hydrogen (H_2) carrier has a much more pronounced effect which has not been previously addressed. It is shown here that a higher H_2 concentration tends to produce a nucleation template with larger crystallites (and lower spatial densities), therefore causing significant surface roughening during HT nucleation but eventually leads to a lower defect density. A model of morphological evolution pertinent to GaN material quality is proposed by correlating reflectance transients with nucleation morphology.

The growth of GaN was carried out in an inductively-heated RDR. Ammonia (NH_3) and trimethylgallium (TMGa) were used as precursors. H_2 was used as the carrier gas and as a make-up flow required to maintain a matched laminar flow pattern in the RDR.⁹ The growth temperature was monitored by an IR pyrometer and calibrated by the melting of Ge (at 934°C). C-plane (0001) sapphire substrates were degreased and thermally cleaned *in situ* in H_2 at 1100°C. The temperatures for the deposition of the LT buffer layers and HT growth were fixed at 560°C and 1075°C, respectively. The susceptor was rotated at 1200 rpm. The flow rates of TMGa and NH_3 were 130 μ mole/min and 6.0 l/min, respectively. A normal-incidence reflectometer ($\lambda=550$ nm) was implemented using a tungsten lamp as a white light source. A lock-in amplifier was employed to suppress signals due to the radiation from the heated susceptor. Ti/Al was evaporated as metal contacts (annealed at 500°C for 5 sec in N_2 gas) for Hall measurements. (0002) symmetric x-ray diffraction rocking curves were used to assess structural quality. A Digital Instrument Nanoprobe III AFM was employed to study the microscopic surface morphology.

B. In-situ Monitoring Using Optical Reflectance

A typical trace of both reflectance intensity (solid line) and growth temperature (dashed line) is shown in Figure 1. The two-step GaN growth on sapphire proceeds through several distinct stages (highlighted by white and gray background): (i) LT buffer deposition (reflectance rises due to an increase of refractive index), (ii) temperature ramp and morphological transformation, (iii) HT deposition, lateral growth, and surface roughening (a dip in the reflectance intensity), (iv) island coalescence (the amplitude and intensity of oscillations increases), and (v) quasi 2D growth (the surface becomes optically smooth). With the use of *in-situ* reflectance monitoring, the effect of various growth parameters on the morphological evolution, in particular the extent of initial HT

roughening (stage (iii)) and the rate of subsequent recovery (stage (iv)), can be investigated. Qualitatively, a higher HT nucleation temperature and a higher NH_3 flow (at a fixed TMGa flow rate) tend to promote lateral growth, therefore reducing the amount of initial roughening (stage (iii)) and increasing the recovery rate (stage (iv)). A thinner buffer layer thickness (down to about 150 Å) generally leads to a reduced roughening and fast recovery. We note that the effects these parameters have on the GaN material properties have been reported.¹⁰

Figure 1. Absolute reflectance (solid line) and temperature (dashed line) traces recorded during a typical growth of GaN on sapphire.

C. The Effect of Hydrogen on the Nucleation of GaN

Somewhat surprisingly we have observed that H_2 carrier gas exerts a much stronger influence on the growth and material quality; a non-optimized H_2 concentration essentially precludes, at least under our growth environment, a "high-quality" GaN growth regardless of the variations from other parameters. Figure 2 shows reflectance traces from three growths of GaN on sapphire; nominally the same growth conditions were employed except the partial pressure and therefore flow rate of H_2 were systematically varied (see Table I). (The total reactor pressure, the sum of NH_3 and H_2 partial pressures, varies accordingly. Computer modeling indicated that the fluid flow is quite similar in all cases.)

The reflectance transient of sample B (see Figure 2b) represents our baseline conditions and can be taken as a reference trace with the distinct stages of growth evolution readily described by the two-step process (see Figure 1). By reducing the H_2 flow and partial pressure to 3.8 slm and 38 Torr (sample A), respectively, while keeping everything else the same, the initial roughening is completely removed (Figure 2a). (We note that neither growth temperatures nor V/III ratios could significantly alter or increase the initial

roughening in Figure 2a.) In contrast, by increasing the H_2 flow and partial pressure to 9.6 slm and 105 Torr, respectively, the initial roughening is more pronounced and there is a longer recovery time for sample C (Figure 2c). All three samples showed a specular surface morphology with well-defined step edges under AFM imaging at the end of approximately 2 μm deposition. It is worth adding that in a separate study we repeated the growth of sample B but replaced most of the H_2 by N_2 and the reflectance showed a transient nearly identical to that of sample A.

Figure 2. Absolute reflectance traces from three growths with H_2 (flow rate and partial pressure) as the only variable (refer to Table I for growth parameters).

To gain further insight about the effect of H_2 , we prepared two LT GaN layers under identical reactor conditions (to sample A and B, respectively) yet with the growth

interrupted right before the HT deposition (indicated by the arrows in Figure 2a & b) so that these morphologies could be examined by AFM. A clear trend can be seen from the AFM images (Figure 3a & b) that the increase of H₂ composition during the temperature ramp and anneal leads to an increase in the surface grain size (from 0.8 to 2 μm) as well as of the RMS surface roughness (from 45 to 90 $\text{\AA}$). It is speculated that an H₂-mediated recrystallization or grain growth process occurs during the temperature ramp stage.

Figure 3. AFM images of the morphology of the nucleation layers for sample A (a) and B (b).

Table I summarizes the structural and electrical properties of the three samples described above. With little or no roughening and nearly ideal reflectance, sample A has the broadest (0002) x-ray diffraction linewidth, indicative of the presence of the highest density of dislocations with a screw component (mid to high 10^9 cm^{-2} as determined by cross-sectional TEM). The mobility of sample A is also distinctly lower. (An increase of compensation level and an increase of structural defect density are possible explanations for the difference in mobilities.)

Table I. Growth parameters and characterization results of Samples A-C

Sample	H ₂ flow rate	Pressure (H ₂)	Pressure (total)	μ (cm ² /V-sec)	n (cm ⁻³)	x-ray FWHM
A	3.8 slm	38 Torr	100 Torr	227	1.34×10^{17}	350"
B	7.6 slm	78 Torr	140 Torr	512	1.42×10^{17}	300"
C	9.6 slm	105 Torr	170 Torr	435	2.57×10^{17}	290"

A growth model of GaN on sapphire can be inferred from a combination of these *in-situ* and *ex-situ* characterizations. The deposition of the LT GaN buffer layer and subsequent ramp/anneal serve to prepare a nucleation template. In our case the amount of H₂ can very effectively modify the nuclei distribution. Twisting and tilting conceivably could occur among the nuclei in order to accommodate the strain energy. The result is the formation of low-angle twist and tilt boundaries during and after island coalescence. AFM shows (Figure 3a) that sample A has a smaller grain size and a higher nuclei density. Based on a model of surface evolutionary selection,¹¹ one would expect that it takes less time for the island coalescence to occur and the surface will never reach a high degree of roughness. Sample B and C, on the other hand, have larger grain sizes (and lower nuclei densities, see Figure 3b); individual islands are allowed to develop (which means an increased surface roughening) before they start to coalescence. With larger grain sizes, *lower nuclei densities*, and a rougher nucleation morphology, the templates of sample B and C counter-intuitively lead to an increased volume of defect-free columnar domains, a lower density of dislocations associated with the domain boundaries, and improved structural and electrical properties.

D. Growth of AlGaN

GaN is known¹² to exhibit a high equilibrium nitrogen vapor pressure at temperatures typically employed (1000 to 1100°C) during the MOCVD process which demands the supply of a substantial amount of ammonia (NH₃) to minimize the loss of surface nitrogen. However, a high partial pressure of NH₃ in the reaction chamber enhances the formation of the Lewis acid-base complexes (adducts) between NH₃ and metal-organic molecules (such as *trimethylgallium*, TMGa) in the gas phase. Gas-phase pre- (or parasitic) reactions often complicate the growth chemistry by adding extra steps in or even diverting precursor dissociation on the deposition surface.¹³ In many cases such gas-phase pre-reactions can also cause the depletion of reactants when large oligomers resulting from adduct decomposition and having with low vapor pressures can not be transported efficiently in the vapor stream.

So far, most of the efforts in III-nitrides have focused on visible (blue and green) light emitters employing InGaN as the active layers. The AlGaN alloy system serves a dual purpose in ultraviolet (UV) optoelectronics and power electronics. Gas-phase interactions during organometallic vapor phase epitaxy (OMVPE) between NH₃ and the two most commonly employed group III metal-organic precursors, TMGa and

trimethylaluminum (TMAI), need to be understood. Thon and Kuech¹⁴ studied the gas-phase reaction of TMGa with NH₃ and observed a rapid (< 1 sec) formation of adduct compound, (CH₃)₃Ga:NH₃. Decomposition products related to a possible oligomer product, such as [(CH₃)₂Ga:NH₂]_n, were suggested to result from a methane-elimination reaction. The presence of the (TMGa:NH₃) adducts, nevertheless, does not necessarily have to influence significantly the decomposition of TMGa or the incorporation of Ga as judged by the relative insensitivity of GaN growth rates versus NH₃ pressures.¹⁵

TMAI has been observed¹⁶ to react with NH₃ into a white crystalline solid at and below room temperature. Chen et al.¹⁵ showed that the Al incorporation (using TMAI) during MOCVD of AlGaIn strongly depends on the growth pressure which could be described by a bi-molecular chemical reaction. It is generally accepted that the TMAI:NH₃ pre-reaction is manifested by a reduced Al incorporation efficiency and a sub-linear relationship between the Al compositions in the gas and solid phases during the growth of AlGaIn. Various measures such as special gas-injection schemes,¹⁷ short inlet-susceptor separation,¹⁸ higher gas velocity,¹⁹ and reduced reactor pressures¹⁵ have been adopted to alleviate the pre-reaction between TMAI and NH₃ even though the information as to the degree to which gas-phase reactions occur under growth conditions has not been well-established.

In the following section we summarize our experimental findings of the cause-effect of the incorporation of Al under a range of OMVPE growth conditions. The effect of TMA:NH₃ reaction on the growth rate was studied *in situ* using an optical reflectance monitor²⁰ which enables us to delineate the susceptibility of the growth rate to pre-reactions over a wide range of gas compositions. We will show that the formation of (TMA:NH₃) adduct not only depletes TMA from the vapor state but also inhibits the incorporation of TMG (by as much as 60%).

E. In-situ monitoring during MOVPE of AlGaIn

We have reported²¹ that the *in-situ* reflectance monitor can provide information on surface roughening, growth rates, and even AlGaIn alloy compositions. During our initial attempt of growing AlGaIn, it was observed that the introduction of TMAI into the reactor (while leaving TMGa and NH₃ flow rates constant) caused an increase of the periodicity (of the reflectance oscillations) during the AlGaIn growth, implying a decrease in the growth rate.

Taking advantage of *in-situ* growth rate monitoring, we have now conducted a series of experiments aimed at illustrating the complex nature of the gas-phase reactions when both TMGa and TMAI are used with NH₃. Figure 4 shows a typical reflectance trace during a particular study of the gas-phase reactions. In this experiment, the TMGa and TMAI flow rates were fixed at around 60 μ mole/min. TMGa, TMAI, and both TMGa and TMAI were open sequentially to allow a measurement of the growth rates of GaN (region (i)), AlN (region (ii)), and AlGaIn (region (iii)), respectively, at a given gas composition (a layer of GaN was inserted after AlN growth to improve the surface morphology and verify the measured growth rate of GaN). We then changed the gas composition (partial pressures of H₂ and NH₃ independently, from region (A) to (B) in Fig. 4) and repeated the same valve operation. (The total reactor pressure equals the sum of the partial pressures of H₂ and NH₃ since TMGa and TMAI flows contribute negligible

pressures.) Such an *in-situ* probe allows a single growth run to provide the data necessary to construct three-dimensional plots of the growth rates of GaN (Fig. 5(a)), AlN (Fig. 5(b)), and AlGaN (Fig. 5(c)) versus partial pressures of both H₂ and NH₃.

Figure 4. A portion of reflectance trace during a gas-phase reaction study. Regions (i), (ii), and (iii) correspond to GaN, AlN, and AlGaN, respectively.

It is clear from Fig. 5(a) that the reported gas phase reactions between TMGa and NH₃ do not result in much (if any) of a decrease in growth efficiency when the H₂ partial pressure is less than 20 Torr. The decreased growth rate shown at higher H₂ pressure may be due to the etching of GaN by a H₂ surface reaction.²² Alternatively, this may be due to an indirect effect of decreasing the rate of the decomposition reaction²³ needed to compensate for the loss of nitrogen at high temperatures.¹² The trend of the growth rate of AlN versus NH₃ shows distinctly different behavior. An increase of NH₃ (with H₂ pressures below 20 Torr) leads to a rapid decrease of AlN incorporation. We note that the above observation is in qualitative agreement with the previous report¹⁵ of a bi-molecular reaction between TMAI and NH₃.

The growth rate of AlGaN (with both TMGa and TMAI open) is shown in Fig. 5(c). It is interesting to note that the measured growth rate of AlGaN is always less than the sum of the growth rates of the individual binary compounds. An "interaction parameter" Ω is therefore defined as $(GR_{AlGaN} / (GR_{AlN} + GR_{GaN}))$ which is plotted in Fig. 5(d). An Ω value approaching unity suggests an independent and additive incorporation of TMAI and TMGa. An Ω much less than unity implies that additional interactions

between the respective adduct compounds, either in the gas phase or on the gas-solid interface, have inhibited the incorporation of certain species. Comparing Fig. 5(b) and 5(d), one could argue that the reduction of Ω follows the general trend of the reduction of AlN growth rates (which in turn suggests an increase in gas-phase adduct reactions related to species such as $[(CH_3)_2Al:NH_2]_n$ ²⁴). Such reactions are seen to inhibit the incorporation of TMGa, down to less than 40% at an NH_3 partial pressure of 58 Torr. (It is worth noting that the results observed are dependent on the details of reactor and inlet designs.) We speculate that the reduction of TMGa incorporation is due to either a scavenging effect of $TMAI:NH_3$ adducts or their reaction products on TMGa (or $TMGa:NH_3$ adducts) in the gas phase. Alternatively, this may be due to a site-blocking effect²⁵ in which the competitive adsorption of $TMAI:NH_3$ decomposition products decreases the TMGa pre-reaction rate on the surface.

Figure 5. The measured growth rates of (a) GaN, (b) AlN, and (c) AlGaIn (from Figure 4) versus H_2 and NH_3 partial pressures. A plot of the interaction parameter Ω (refer to text for definition) versus H_2 and NH_3 is shown in (d).

Ideally the Lewis-base precursors should be separated physically for as long as possible from the Lewis-acid precursors before they reach the growth surface. Implementation of this concept, however, is often at the expense of growth uniformity over a large area due to the lack of gas mixing. The spacing between inlet and growth surface essentially determines the reaction time. In our system, the separation between the inlet and the susceptor surface is around 4". Under typical growth conditions, this amounts to a potential reaction time in the gas-phase of ~ 1 second, which serves to emphasize the facile nature of $\text{TMAl}:\text{NH}_3$ reaction. Another parameter one could vary is the partial pressures of the reactants. A lower reactor or NH_3 pressure not only reduces the chemical reaction rate but also increases the flow velocity, which in turn reduces the interaction time. It is worth noting that both thermodynamics calculations²² and kinetics arguments²⁶ suggest the need to maintain minimum values of V/III flow ratios and NH_3 partial pressures to overcome the dissociation of GaN, and possibly preserve the morphological, structural, and optical qualities.

III. Simulation of Hydrogen Behavior in p-GaN(Mg) at Elevated Temperatures

Hydrogen is introduced into GaN during MOCVD growth and is the most important impurity defect because of its effects on electrical properties. This is especially so for p-type GaN doped with Mg, where the H almost entirely suppresses p-type conduction until its removal by activation annealing. To facilitate the control of H effects we developed a unified mathematical description of the diffusion, reactions, uptake, and release of H in GaN at the elevated temperatures of growth and processing. This treatment is based on zero-temperature energies obtained from density functional theory as discussed elsewhere in this report.

The diffusion flux of H in GaN is given by

$$\Phi_{\text{dif}} = -D^0 \frac{\partial}{\partial x} [H^0] - D^+ \frac{\partial}{\partial x} [H^+] - D^- \frac{\partial}{\partial x} [H^-] - \left(D^+ [H^+] - D^- [H^-] \right) \left(\frac{1}{kT} \right) \frac{\partial}{\partial x} (E_f - E_v) \quad (1)$$

where the brackets denote concentration, E_f is the Fermi energy, and E_v is the energy of the valence-band edge. Equation (1) takes account of differing diffusion rates for the three charge states, and the final term on the right-hand side describes driven migration due to spatial variation of the Fermi level. We assume rapid local equilibration among the states of the H at any location, which is believed appropriate for the temperatures $>400^\circ\text{C}$ of concern here. One then has

$$\frac{[H^+]}{[H^0]} = \exp \left(\frac{G_H^{+0} - E_f}{kT} \right) \quad (2)$$

and

$$\frac{[H^0]}{[H^-]} = \exp \left(\frac{G_H^{0-} - E_f}{kT} \right) \quad (3)$$

where the quantities G_H are bandgap levels associated with the electronic transitions. The concentration of H_2 molecules in the lattice is given by

$$\frac{N_h [H_2]}{[H^0][H^0]} = \exp \left(\frac{G_{H_2}^0}{kT} \right) \quad (4)$$

where N_h is the atomic density of GaN and $G_{H_2}^0$ is the change in the nonconfigurational part of the Gibbs free energy arising from the combination of two neutral H atoms. State populations relating to the Mg acceptor are calculated from the equilibrium relations

$$\frac{N_h [\text{MgH}]}{[\text{Mg}^-][\text{H}^+]} = \exp\left(\frac{G_{\text{MgH}}^-}{kT}\right) \quad (5)$$

and

$$\frac{[\text{Mg}^0]}{[\text{Mg}^-]} = \exp\left(\frac{G_{\text{Mg}}^0 - E_f}{kT}\right) \quad (6)$$

where MgH is the aforementioned neutral complex and the quantities G are again changes in nonconfigurational Gibbs free energy associated with the reactions. The hole concentration is

$$[h^+] = \int_{-\infty}^{E_v} N_{\text{val}}(E) F_h(E) dE \quad (7)$$

where N_{val} is the density of states in the valence band and F_h is the Fermi distribution function for holes. An analogous equation gives the electron concentration. The description is completed by imposing charge neutrality at all locations. This is exact for a uniform system but only approximate when the concentrations of charged species vary with depth. Finally, equilibrium with external H_2 gas is included through the solubility equation

$$[\text{H}^0]^{\text{eq}} = N_h (P_{\text{gas}}^*)^{1/2} \exp\left(-\frac{G_{\text{sol}}^0}{kT}\right) \quad (8)$$

where P_{gas}^* is the fugacity of the gas. We choose to express this relationship in terms of the neutral H state simply to avoid an explicit dependence on Fermi level. The above system of equations is solved numerically.

The parameters in Eqs. (1)-(8) are mostly evaluated using results from density functional theory for wurtzite GaN as discussed elsewhere in this report. With a H atom in vacuum taken as the reference state, we find an energy of +0.34 eV for interstitial H^0 , -2.67 eV for H^+ when $E_f = E_v$, +1.52 eV for H^- when $E_f = E_v$, and -1.40 eV per atom for interstitial H_2 . The formation of the neutral Mg-H complex from Mg^- and H^+ has a binding energy of 0.70 eV. The zero-temperature dissociation energy of the H_2 molecule in vacuum is taken to be 2.28 eV, the value for the deuterium isotope. The ionization level for the Mg acceptor is taken from experimental studies to be $E_v + 0.16$ eV.²⁷ The diffusion activation energies obtained from density functional theory are 0.5 eV for H^0 , 0.7 eV for H^+ , and 1.7 eV for H^- ; the corresponding prefactors are equated to $0.001 \text{ cm}^2/\text{s}$, a representative value for interstitial solutes. Finally, the densities of states for the valence and conduction bands are also evaluated using density functional theory.

The free energies of reaction G appearing in Eqs. (1)-(8) vary appreciably with temperature, so that values appropriate for the elevated temperatures of interest here differ from those obtained for 0 K using density functional theory. Effects giving rise to

this variation include thermal expansion, the temperature dependence of the Gibbs free energy of H_2 gas, and the enthalpy and entropy arising from H vibrations. The first of these effects is neglected in the present treatment. Full account is taken of the second through the use of published thermodynamic tables for deuterium gas.²⁸ Vibrational effects are taken into account only for those H states that dominate in p-type GaN(Mg), H^+ and the Mg-H complex. As discussed elsewhere in this report, density functional theory reveals two nearly degenerate energy minima of H^+ , one at the N antibonding site oriented away from the c-axis, and the other at the c-axis bond-center position. The vibrational rates for deuterium at the antibonding site are computed to be 2100 cm^{-1} (stretch) and 599 cm^{-1} (wag), while for the bond-center site we find 2418 cm^{-1} (stretch) and 355 cm^{-1} (wag). The Mg-H complex has a single stable configuration in which the H is at a N antibonding site diagonally opposite from a Mg neighbor along a bond direction tilted from the c-axis. The vibrational rates of this H are taken to be the same as for the N antibonding site in the absence of the Mg. The vibrational contributions to enthalpy and entropy are then evaluated within the harmonic approximation.²⁹

The solid line in Figure 1 gives the solubility of deuterium (D) in GaN(Mg) at 700°C as predicted by the theoretical model. Also shown are experimental results for MOCVD GaN(Mg) on sapphire that was first activated by vacuum annealing for 1 hour at 900°C and then heated in D_2 gas at 700°C . The D concentration was measured using the ion-beam-induced nuclear reaction $^2D(^3He,p)^4He$.³⁰ That the introduced D behaved as expected within the host matrix was evidenced by IR spectroscopy, which exhibited the absorption near 2320 cm^{-1} ascribed to the Mg-H center,³¹ and also by electrical measurements in similarly treated specimens, which showed an increase in room-temperature resistivity from 3 to $14,000\ \Omega\text{-cm}$. In the model calculation the concentration of electrically active Mg acceptors was equated to $2.4 \times 10^{19}\text{ cm}^{-3}$, somewhat below the total Mg concentration of $\sim 5 \times 10^{19}\text{ cm}^{-3}$ measured by secondary-ion mass spectrometry, and compensating shallow donors were introduced at a concentration of $0.4 \times 10^{19}\text{ cm}^{-3}$. These plausible choices were made to achieve simultaneous agreement with the observed saturation of D uptake at $\sim 2 \times 10^{19}\text{ cm}^{-3}$ and with the hole concentration of $\sim 4 \times 10^{17}\text{ cm}^{-3}$ measured at room temperature before the introduction of D. All other parameters were independently evaluated as discussed in the preceding section.

The horizontal displacement between theory and experiment in Fig. 6 provides a stringent test of the mechanistic assumptions and computed H energies of the theoretical model. Interpretation of the comparison is facilitated by applying a single offset to all of the D energies in the solid relative to the energy of atomic D in vacuum so as to produce agreement with experiment. The result, given by the dashed line in Fig. 6, is achieved by reducing the D energies in the solid by 0.18 eV. We consider this shift to lie within the combined uncertainties of the predictions of density functional theory, and this tends to support the validity of the model. Moreover, thermal expansion of the GaN lattice at 700°C can be expected to reduce the energies of interstitial D, so that inclusion of this neglected effect would possibly reduce the disparity.

Figure 6. Solubility of D in GaN(Mg) at 700°C as a function of D₂ fugacity from theory and experiment.

We also used the theoretical model to treat thermal release of D from GaN(Mg), initially under the assumption of no permeation barrier at the surface. This yielded a much greater release rate than is observed. In the case of isothermal vacuum annealing at 700°C, for example, the predicted release rate exceeded the experimental value by more than 6 orders of magnitude. Similarly large disparities were found for uptake from D₂ gas. This leads us to hypothesize that the surface of p-GaN(Mg) is in fact a substantial barrier. We provisionally formulate the barrier effect in the conventional manner by assuming that there is rapid equilibration between solution and surface sites and that the rate-determining step is recombinative desorption for release and dissociative adsorption for uptake. One then has for the surface flux

$$\Phi_{\text{sur}} = \Phi_0^{\text{in}} P_{\text{gas}}^* (1 - \theta_{\text{sur}})^2 \exp\left(-\frac{E_{\text{ads}}}{kT}\right) - \Phi_0^{\text{out}} (\theta_{\text{sur}})^2 \exp\left(-\frac{E_{\text{des}}}{kT}\right) \quad (9)$$

with

$$\frac{\theta_{\text{sur}}}{1 - \theta_{\text{sur}}} = \frac{[H^0]}{N_h} \exp\left(\frac{E_{\text{sur}}^0}{kT}\right) \quad (10)$$

where θ_{sur} is the fractional occupation of surface sites. The uptake term is parameterized using two experimentally observed atomic fluxes, $\sim 3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ for 700°C and a D₂ pressure of 0.013 bar; and nearly the same value of $\sim 3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ for 500°C and a pressure of 0.88 bar. This yields $E_{\text{ads}} = 1.36 \text{ eV}$ and $\Phi_0^{\text{in}} = 2.3 \times 10^{20} \text{ cm}^{-2}\text{s}^{-1}$. In the release term, the desorption activation barrier E_{des} is estimated to be 1.8 eV from

published surface desorption studies in ultrahigh-vacuum.³² Finally, the remaining

Figure 7. Isothermal release of D from GaN(Mg) at 800°C from theory and experiment.

parameters E_{sur}^0 and Φ_0^{out} are evaluated by requiring that the solubility relation given by Eq. (8) be satisfied when $\Phi_{\text{sur}} = 0$ in Eq. (9).

In Fig. 7, the predictions of the above treatment are compared with experimental measurements of isothermal release into vacuum at 800°C. Two aspects of the comparison are noteworthy. First, the second-order release kinetics of Eq. (2) imply that, after the residual concentration of D has become small enough to have little influence on the Fermi level, the reciprocal of retained D concentration should vary linearly with time. It is evident from the figure that the experimental data conform accurately to this prediction. The second test is simply the degree to which the magnitudes of the predicted and measured release rates agree. The difference at 800°C is seen in Fig. 7 to be less than a factor of 2.

Figure 8 shows predictions of the theoretical model for D release from initially saturated GaN(Mg) during isothermal annealing along with the resultant increase of hole concentration at 300 K. Release data for 700 and 800°C are included for comparison and are semiquantitatively consistent with the modeling.

The semiquantitative agreement found in this study between the predicted and measured solubilities of D in GaN(Mg) generally supports the H configurational energies obtained using density functional theory and suggests that additional H states within the matrix need not be invoked for the elevated temperatures investigated. Our combined theoretical and experimental results on uptake and release are indicative of a surface permeation barrier that is characterized by second-order release kinetics.

Figure 8. Predicted isothermal release of D from GaN(Mg) and associated increase of hole concentration at 300 K.

Our modeling with the inclusion of the surface barrier replicates a feature of the thermal activation of GaN(Mg) that has been considered anomalous, namely, large increases in hole concentration after annealing at temperatures as low as 500°C notwithstanding the retention of substantial H to 800°C and above. The relevant insight is that, in the presence of a surface barrier with the properties formulated in this work, the H release rate varies relatively modestly with temperature while decreasing rapidly as a function of remaining H concentration, as can be seen from Fig. 8. As a consequence of

these properties, H release and the associated electrical activation can extend over several hundred °C in an isochronal anneal sequence.

In our view, the modeling approach discussed herein has the potential to provide quantitative prediction of H behavior at temperatures above about 400°C where local equilibrium among the states of the H can be assumed, although such accuracy is still to be demonstrated. An important remaining area of uncertainty is the surface barrier, whose properties may, for example, depend on temperature and ambient atmosphere. At lower temperatures where the activated transitions between H states are not all rapid, the simplifying assumption of local equilibration should give way to a full treatment of individual reaction rates.

IV. Theoretical Studies of Stacking Faults in AlN, GaN and InN, and Edge Dislocations in GaN

Transmission electron microscopy studies indicate that epitaxial GaN films contain numerous extended defects including grain boundaries, dislocations and stacking faults.^{33,34,35,36,37,38} In general, defect densities tend to be largest near the film/substrate interface due to lattice and thermal mismatch, and decrease with increasing film thickness. Stacking faults, for example, are often observed near the interfacial region^{37,39} although they have also been seen in bulk GaN samples.⁴⁰ Away from the interfacial region, threading dislocations aligned parallel to the growth direction are typically observed with densities between 10^8 and 10^{10} per cm^2 , and studies indicate that their Burgers vectors are either the *a* lattice vector (edge type), the *c* lattice vector (screw type), or the sum of these (mixed type).^{34,41,42} In spite of the large numbers of extended defects, it is possible to fabricate highly efficient light-emitting diodes from epitaxial GaN films.⁴³ This is especially surprising given that equal defect densities in other III-V films would preclude device operation. Several theories have been proposed for the insensitivity of GaN films to extended defects, and a central unanswered question is whether or not threading dislocations produce defect levels in the band gap. To answer this question, we have studied the properties of an edge-type dislocation in GaN using first-principles theoretical techniques. In addition, we have used the same techniques to determine the energies of basal-plane stacking faults in GaN.

The theoretical techniques used in these studies were based on the Kohn-Sham formulation of density-functional theory, which requires the self-consistent solution of a set of single-electron eigenvalue equations.^{44,45,46} *Ab initio* pseudopotentials were used to describe electron-ion interactions^{47,48} and the Kohn-Sham functions were expanded in a plane-wave basis.^{49,50,51} Additional details related to pseudopotentials, basis sets, Brillouin-zone sampling, and convergence tests can be found elsewhere.^{52,53} All of our calculations were performed for the wurtzite structure which is the ground-state for GaN and the structure commonly found in epitaxial films. We first examine trends in the energies of basal-plane stacking faults in AlN, GaN and InN. (Like GaN, AlN and InN have the wurtzite ground-state structure and are often alloyed with GaN to fabricate device structures.) We then consider threading edge dislocations in GaN, examining the formation energies and defect energies for a set of possible core structures, and how the formation energies depend on doping and growth stoichiometry.

A. Stacking faults in AlN, GaN and InN:

The wurtzite (2H) structure is characterized by the stacking sequence ...ABABABAB... along the [0001] direction perpendicular to the basal plane. In this notation, each letter stands for an ordered pair of cation and anion layers separated by distance uc where c is the lattice constant along [0001] and u is an internal parameter roughly equal to 0.375. (For simplicity, we refer to this ordered pair as a layer.) A particular letter refers to the atoms being placed at one of three different positions in the basal plane. In this regard, the wurtzite structure is distinguished by a stacking sequence with a repeat period of two layers, whereas the more common zinc-blende (or sphalerite) structure has the sequence ...ABCABCABC... with repeat period three along the corresponding [[111] direction. A basal-plane stacking fault is simply a disruption in the usual stacking sequence. In the wurtzite structure, there are three types of faults denoted I_1 , I_2 and E.⁵⁴ The I_1 (intrinsic) fault has stacking sequence ...ABABCBCB... with a single unit of sphalerite stacking inserted into the wurtzite stacking sequence, the I_2 (intrinsic) fault has stacking sequence ...ABABCACA... containing two units of sphalerite stacking, and the E (extrinsic) fault has stacking sequence ...ABABCABAB... containing three sphalerite units.

A stacking-fault energy is defined as the difference in energy between faulted and unfaulted structures. This energy difference is typically given in terms of either a unit area in the basal plane or the area of a primitive unit cell in which case it is referred to as a reduced stacking-fault energy. In this study, stacking-fault energies were obtained using an approach employed previously by Cheng *et al.*⁵⁵ to study polymorphism in SiC. In this approach, the energy of a (periodic) sequence of N layers is cast in the form of a 1-dimensional Ising-type model

$$NE = NE_0 - \sum_{i,n} J_n \sigma_i \sigma_{i+n} \quad (11)$$

where E_0 is a reference energy, J_n is the interaction energy between n^{th} neighbor layers, and the summations are over all N layers. The spin parameters, σ , are defined in terms of the ordering between adjacent layers with AB, BC and CA pairs assigned a value of +1, BA, CB and AC pairs assigned a value of -1, and assignments made moving from left to right through a stacking sequence. In practice, interactions beyond a certain range are neglected, limiting the summation over n above. Cheng *et al.*,⁵⁵ for example, retained interactions only up to third-neighbor layers and we have done the same. With this stipulation, the I_1 , I_2 and E energies are given by the expressions $(-2J_1 + 4J_2 - 6J_3)$, $(-4J_1 + 4J_2 - 4J_3)$ and $(-6J_1 + 4J_2 - 6J_3)$, respectively.

Layer-layer interaction energies were determined from density-functional-theory calculations for the 2H, 3H, 4H and 6H polytypes. In these calculations, lattice constants in the basal plane and the separations between adjacent layers were fixed at the relaxed values found for wurtzite. Because of this, we use the notation 3H for the three-layer unit cell instead of 3C which denotes the fully relaxed cubic structure. The model energies per layer for these polytypes are

$$E_{2H} = E_0 + J_1 - J_2 + J_3 \quad (12)$$

$$E_{3H} = E_0 - J_1 - J_2 - J_3 \quad (13)$$

$$E_{4H} = E_0 + J_2 \quad (14)$$

$$E_{6H} = E_0 - \frac{1}{3}J_1 + \frac{1}{3}J_2 + J_3 \quad (15)$$

and interaction energies were extracted from suitable combinations, substituting density-functional energies on the left-hand sides. The resulting layer-layer interaction energies are given in Table II. We note that interactions between nearest-neighbor layers are at least 15 times larger in magnitude than between second-neighbor layers. This dominance is in contrast to results obtained earlier for SiC in which the nearest-neighbor interaction was about twice the second-neighbor value.⁵⁵ We also note that the nearest-neighbor interactions are negative for the nitrides. This result, together with the dominance of the nearest-neighbor interactions, indicates that the ordering of the polytype energies was 2H, 4H, 6H, and 3H in the density-functional calculations going from lowest to highest for the unrelaxed structures. As shown below, however, the same ordering holds for the fully relaxed structures.

	AlN	GaN	InN
J_1	-27.45	-5.83	-12.43
J_2	-0.17	-0.36	+0.81
J_3	+0.05	-0.04	+0.28
E_{I1}	54	10	26
E_{I2}	109	22	52
E_E	164	34	76

Table II. Interaction energies and wurtzite reduced stacking-fault energies (in meV). To convert the reduced energies to mJ/m², multiply by 1.95 for AlN, 1.86 for GaN and 1.53 for InN.

The wurtzite stacking-fault energies are given in Table II. For each compound, the energies of the I_2 and E faults are two and three times larger, respectively, than the I_1 value. This relationship is expected from dominance of the nearest-neighbor interactions together with the expressions for the stacking-fault energies. In addition, we note that it corresponds to the I_1 , I_2 and E faults containing one, two and three sphalerite units. In comparing results among the three compounds, the stacking-fault energies are seen to be largest for AlN and smallest for GaN. As will be shown below, this ordering is consistent with the relaxed wurtzite/zinc-blende energy differences for these compounds. That is, the energy difference is largest for AlN and smallest for GaN. To test the accuracy of the model results, we directly calculated the energy of an E-type fault in AlN using unit cells containing up to nine layers. The converged value (with respect to separation of repeated faults) was within 2% of the model value verifying the accuracy of the model. We also

examined the effect of relaxation perpendicular to the stacking direction for the case of the E-type fault. Allowing full relaxation of the layer separations and cation-anion separations within each layer lowered the stacking-fault energies by less than 5%.

There have been at least two attempts to estimate stacking-fault energies in the group-III nitrides based on experimental measurements. Suzuki *et al.* utilized high-resolution TEM to observe lattice defects in AlN, GaN and InN.⁵⁶ From the spacing between Shockley partial dislocations in AlN and InN, they estimated reduced I_2 energies of 115 ± 36 meV for AlN and 27 ± 6 meV for InN. Our AlN value is within 5% of their estimate, but our InN value is twice theirs. Isolated Shockley partials were seen in GaN, but no pairs were seen from which spacings could be measured. The only other estimated value we are aware of is 2 meV for I_2 in AlN by Delavignette *et al.*⁵⁷ This value differs significantly from our result and the estimate of Suzuki *et al.*

As noted above, the unrelaxed 4H and 6H energies were found to be lower than the unrelaxed 3H energy in the density-functional calculations. In Table III we give density-functional energies for the fully relaxed 4H, 6H and 3C structures with respect to the relaxed wurtzite energy. The resulting wurtzite/zinc-blende energy differences are close to the values obtained previously by Yeh *et al.*⁵⁸ and the relaxed 4H and 6H energies fall between the wurtzite and zinc-blende values. In retrospect, this result is perhaps not surprising since the 4H and 6H structures can be thought of as having combinations of wurtzite and zinc-blende stacking. However, this simple correspondence might not necessarily hold were it not for the dominance of nearest-neighbor interactions in the nitrides.

	AlN	GaN	InN
4H	24	5	11
6H	31	7	15
3C	45	11	23

Table III. Total energies (in meV per cation-anion pair) with respect to wurtzite.

To summarize this section, we determined stacking-fault energies for wurtzite AlN, GaN and InN using an Ising-type model together with effective layer-layer interactions obtained from density-functional-theory calculations. The fault energies were found to be largest for AlN and smallest for GaN consistent with their calculated wurtzite/zinc-blende energy differences. Relaxed energies were also determined for the 4H and 6H structures and they were found to fall between the wurtzite and zinc-blende values.

B. Threading edge dislocations in GaN

Based on the impressive performance of nitride-based light-emitting diodes, Lester *et al.*⁶³⁸ suggested early on that threading dislocations might not be efficient

minority-carrier recombination sites in GaN. Recent cathodoluminescence studies, however, indicate that dislocations do limit the efficiency of band-edge luminescence,^{59,60} and may also contribute to the broad yellow luminescence commonly observed in undoped and *n*-type material.⁶¹ In addition, both scanning-capacitance microscopy (SCM)⁶² and analysis of the dependence of transverse mobility on free-carrier concentration⁶³ suggest that dislocations behave as electron traps in *n*-type GaN. While experimental studies of dislocations are ongoing, theoretical studies have also begun to provide important information on these defects. In a recent theoretical study on charge-neutral edge and screw dislocations in GaN, Elsner *et al.*⁶⁴ found that the lowest energy structures were electrically inactive having filled or unfilled levels lying near the band edges. In this study, we examine both neutral and charged edge dislocations in GaN. Briefly, we find that formation energies for a set of four candidate core structures depend strongly on the Fermi level. This dependence, due to the presence of defect levels in the gap, plays an important role in determining the most stable dislocation core structure.

Our calculations utilized a 112-atom supercell containing two edge dislocations of opposite sign in order to maintain periodicity perpendicular to the [0001] direction. We considered four candidate dislocation core structures as described in Fig. 9. The full- and open-core structures are stoichiometric having equal numbers of gallium and nitrogen atoms, whereas the Ga- and N-vacancy structures are non-stoichiometric. Because of this, formation energies for the Ga- and N-vacancy structures will depend on the stoichiometry during growth, that is, on whether growth takes place under gallium- or nitrogen-rich conditions.

Relaxed structures and their total energies were obtained from density-functional calculations. Using these total energies, formation energies were then derived using the expression⁶⁵

$$E^f(q, E_F) = E_{\text{tot}}(q) - n_{\text{Ga}}\mu_{\text{Ga}} - n_{\text{N}}\mu_{\text{N}} + qE_V + qE_F. \quad (16)$$

Here, E^f is the formation energy, E_{tot} is the energy of the defect cell, n_{Ga} (n_{N}) is the number of gallium (nitrogen) atoms in the supercell and μ_{Ga} (μ_{N}) is the corresponding chemical potential, q is the charge state of the defect, and E_V is the energy of the valence-band maximum in bulk GaN including a supercell-dependent shift.⁶⁵ E_F is the Fermi level defined to be zero at the bulk valence-band maximum and have a maximum value equal to the measured energy gap, 3.48 eV. We note that the charge states and formation energies referred to above are given per supercell length (the c lattice parameter) along the dislocation line direction. In addition, the gallium and nitrogen chemical potentials depend on the stoichiometry during growth and we consider the two limiting cases of gallium-rich and nitrogen-rich conditions. Under gallium-rich conditions, μ_{Ga} is the (calculated) total energy of bulk gallium and μ_{N} is set equal to $\mu_{\text{GaN}} - \mu_{\text{Ga}}$ where μ_{GaN} is the energy of bulk GaN. Under nitrogen-rich conditions, μ_{N} is taken as half the (calculated) total energy of N_2 and μ_{Ga} is set equal to $\mu_{\text{GaN}} - \mu_{\text{N}}$.

Figure. 9. Plot of the relaxed atom positions for the charge-neutral *full-core structure* showing the super-cell boundaries. Gallium atoms are shown as larger circles and nitrogen atoms as smaller circles. One dislocation is located at the center of the supercell and the other is shared among the four corners of the supercell. The *open-core structure* was formed by removing the column of low-coordination atoms located near the center of the supercell and the *Ga-vacancy structure* (*N-vacancy structure*) was formed by removing just the low-coordination gallium (nitrogen) atoms.

Plots of formation energy vs. Fermi level for the four candidate structures are shown in Fig. 10. Note that for a particular Fermi level, we only display the plot corresponding to the charge-state having the lowest formation energy (the charge-state is given by the slope of the plot). The full-core structure, for example, is predicted to be in a neutral charge-state when the Fermi level is below 2.7 eV and in a 2^- charge-state when the Fermi level is above that. The transition from the neutral to 2^- charge-state is due to the presence of a defect level in the gap. Overall, formation energies for the four structures display a pronounced dependence on Fermi level. In addition, the effect of growth stoichiometry on the Ga- and N-vacancy-structure formation energies can be seen by comparing Figs. 2a and 2b: Formation of the Ga-vacancy structure is favored under nitrogen-rich (gallium-poor) conditions, whereas formation of the N-vacancy structure is favored under gallium-rich (nitrogen-poor) conditions. Under nitrogen-rich growth conditions (Fig. 2a), the Ga-vacancy structure is predicted to be the most stable in *n*-type material, the full-core structure is most stable in *p*-type material, and either the full-core or Ga-vacancy structure will be most stable in undoped material depending on the Fermi level. In *n*-type material, the Ga-vacancy structure will behave as an electron trap yielding a negatively charged dislocation. The full-core structure, on the other hand, will be charge-neutral in *p*-type or undoped material. For completeness, we note that a dislocation density of 10^{10} cm^{-2} corresponds to 2×10^{17} defect sites per cm^3 . A high density of dislocations in *n*-type material may therefore cause significant compensation of the donor species.⁶³ Under gallium-rich growth conditions (Fig. 10b), the N-vacancy

structure is predicted to be most stable except for the case of *n*-type material. Here, all four structures have similar formation energies within the uncertainty in these calculations and a dislocation will likely display a mixture of the four core structures. Regardless of the details of the core structure, a dislocation in *n*-type GaN grown under gallium-rich conditions will behave as an electron trap and accumulate electrons. This result is consistent with the recent SCM study by Hansen *et al.*,⁶⁴ and an analysis of the dependence of transverse mobility on carrier concentration in *n*-type GaN by Weinmann *et al.*⁶³ (We examine the phenomenon of charge accumulation in more detail below.) In addition, we predict that a edge dislocations in *p*-type material will act as hole traps. Corresponding measurements have not yet been performed for *p*-type GaN.

Among the four core structures examined, several exhibited pronounced structural changes when of one or more electrons were added. Adding two electrons to the full-core structure, for example, produced a noticeable tilt in the Ga-N bond angles of the two pairs on the upper side of the dislocation core (see Fig. 11). This behavior is likely due to a repulsive interaction between the negatively charged nitrogen atoms in these pairs and the gallium atom at the dislocation core which has a filled lone-pair state in the 2⁻ charge-state. (The lone-pair state on the gallium atom is unfilled in the neutral charge-state in agreement with the results of Elsner *et al.*⁶⁴) In the Ga-vacancy structure, the nitrogen atom at the dislocation core moved 0.6 Å along the [0001]-direction as three electrons were added starting from the neutral charge-state. This displacement is likely due to the large electron affinity of the nitrogen atom: In the neutral charge state it resides close to the surrounding gallium atoms, but as electrons are added it moves back to its normal position in the lattice. A similar displacement occurred for the low-coordination gallium atom in the N-vacancy structure although the magnitude was only 0.2 Å.

To summarize this section, we have determined the relaxed core structures and the formation energies for neutral and charged edge dislocations in GaN as a function of Fermi level and growth stoichiometry. Formation energies for the four candidate structures show a pronounced dependence on Fermi level and on growth stoichiometry for Ga- and N-vacancy structures. As a result, threading edge dislocations in GaN should exhibit a variety of core structures depending on the amount and type of doping in the surrounding material, and on the stoichiometry during growth. Dislocations in *n*-type material should behave as electron traps and therefore be negatively charged. This result is consistent with the recent SCM study by Hansen *et al.*,⁶² and an analysis of the dependence of transverse mobility on carrier concentration in *n*-type GaN by Weinmann *et al.*⁶³

Figure. 10. Plots of the formation energy versus Fermi level under (a) nitrogen-rich and (b) gallium-rich conditions.

Figure. 11. Plots of the region near the dislocation core for the relaxed full-core structure in the (a) neutral and (b) 2⁻ charge states. In the 2⁻ charge-state, the Ga-N bond of the pair located above and to the right (and left) of the low-coordination atoms displays a pronounced tilt as compared with the neutral charge-state.

C. Theoretical Studies of Hydrogen in Wurtzite and Zinc-Blende GaN

Hydrogen is a common impurity in GaN films grown via metalorganic vapor-phase deposition where it is introduced either from the source compounds or from H₂ when used as a carrier gas.⁶⁶ Hydrogen may also be introduced after growth for purposes of device isolation,⁶⁷ as a byproduct of various processing steps,⁶⁶ or simply to study its annealing behavior.^{66,68} Understanding the annealing behavior of hydrogen in GaN is particularly important because it has been found that either low-energy electron-beam irradiation⁶⁹ or a post-growth anneal⁷⁰ is needed to dissociate Mg-H complexes and activate *p*-type doping in MOCVD-grown material. Moreover, hydrogen is retained in GaN up to a temperature of approximately 900°C, and is therefore expected to play a significant role in nearly all processing stages of GaN-based devices.⁷¹

Because of its importance to emerging nitride-based technologies, hydrogen in GaN has been the focus of a number of recent experimental and theoretical studies. (See chapters 6 and 11 in Ref. 66 for reviews of theoretical and experimental work in this area.) Many questions remain unanswered, however, regarding topics such as the annealing behavior of hydrogen and its interaction with point and extended defects. A starting point for answering these questions can be provided by theoretical studies of hydrogen in defect-free GaN. Neugebauer and Van de Walle (NVdW) performed such a study for zinc-blende GaN.^{72,73} They found several interesting features including a large negative-U effect and a preference for the nitrogen anti-bonding site by H⁺ instead of the bond-centered site favored in other semiconductors. Based on their previous studies of native point defects in GaN,⁷⁴ they also suggested that hydrogen should display similar behavior in the more technologically relevant wurtzite structure. However, there are notable differences in the two crystal structures that could affect interstitial hydrogen. The lower symmetry of wurtzite, for instance, results in there being two different Ga-N bond lengths and bond angles. This could affect the relative stabilities of anti-bonding and bond-centered sites. An even more noticeable difference is revealed by examining

the two crystal structures on a length scale larger than their bond lengths. As shown in Fig. 12, the wurtzite structure has three-fold symmetric (trigonal) channels oriented along the [0001] direction (*c*-axis) and extending through the length of the crystal. In zinc blende, the analogous trigonal channels are oriented along $\langle 111 \rangle$ directions, but are blocked at intervals of 7.8 Å by a pair of gallium and nitrogen atoms.

Figure 12. a) View of the zinc-blende structure along the [111] direction. b) View of the wurtzite structure along the [0001] direction (*c*-axis). Gallium atoms are shown as larger empty circles and nitrogen atoms as smaller filled circles.

In order to study the behavior of hydrogen in wurtzite GaN and to investigate the structural differences outlined above, we performed charge-state calculations for hydrogen in wurtzite and zinc-blende GaN. These calculations were performed using periodically repeated 72-atom wurtzite and 64-atom zinc-blende supercells. Test calculations using a 32-atom zinc-blende supercell were also performed to check the convergence of the 64-atom-cell results. No differences were found. Further details of these calculations are available elsewhere.⁷⁵

Structures containing hydrogen were relaxed until the forces on each atom were less than 50 meV/Å. Formation energies were then obtained using the expression⁶⁵

$$E^f(q, E_F) = E_{\text{tot}}(q) - n_{\text{Ga}} \mu_{\text{Ga}} - n_{\text{H}} \mu_{\text{H}} + qE_V + qE_F. \quad (17)$$

Here, E^f is the formation energy, E_{tot} is the energy of the supercell containing hydrogen, $n_{\text{GaN}}\mu_{\text{GaN}}$ is the energy of the supercell without hydrogen, n_{H} is the number of hydrogen atoms and μ_{H} is the hydrogen chemical potential, q is the charge state of the supercell, and E_{V} is the energy of the valence-band maximum in bulk GaN including a supercell-dependent shift.⁶⁵ E_{F} is the Fermi level defined to be zero at the bulk valence-band maximum and to have a maximum value equal to the measured energy gap (3.25 eV for zinc blende and 3.48 eV for wurtzite). For μ_{H} , we used -0.90 eV which is the calculated spin-polarized energy of a hydrogen atom. Formation energies are thus given with respect to hydrogen atoms in the gas phase. To reference instead to H_2 in the gas phase, add 2.31 eV to the formation energies corresponding to the calculated binding energy of H_2 including the zero-point vibrational contribution. Many possible sites for interstitial hydrogen were investigated and formation energies for the three species, H^+ , H^0 , and H^- , were calculated at each site. We also studied supercells containing two hydrogen atoms, in both associated (H_2) and unassociated (2H^+) configurations. In the latter case, the goal was to examine the likelihood of H^+ clustering in p -type material. We first describe our results for cells containing one hydrogen atom, and then discuss results for cells containing an additional hydrogen atom.

Due to the large difference in electronegativity between nitrogen and gallium, the bonding in GaN is partly ionic in nature. This ionicity is expected to have significant impact on the formation energies and stable lattice sites of the charged species, H^+ and H^- . NVdW,^{72, 73} for example, found that H^+ in zinc-blende GaN prefers to remain near the negatively charged nitrogen atoms whereas H^- sits as far as possible from nitrogen atoms. We find similar results for hydrogen in wurtzite GaN, but we also find noteworthy differences in the stable lattice sites between wurtzite and zinc blende. The most significant difference is in the lattice site of H^+ . In zinc blende, the nitrogen anti-bonding (AB_{N}) site is more stable than the bond-centered (BC) site by 0.26 eV. Due to its lower symmetry, there are two types of nitrogen-anti-bonding and bond-centered sites in the wurtzite structure. We refer to these as $\text{AB}_{\text{N},\parallel}$ and $\text{BC}_{\parallel}$ when the N-H^+ direction is parallel the c -axis, and $\text{AB}_{\text{N},\perp}$ and $\text{BC}_{\perp}$ when the N-H^+ direction is roughly perpendicular to the c -axis. The $\text{AB}_{\text{N},\perp}$ and $\text{BC}_{\parallel}$ sites have the same formation energy, the $\text{BC}_{\perp}$ site is 0.16 eV higher, and the $\text{AB}_{\text{N},\parallel}$ site is an additional 0.03 eV higher. Our results therefore indicate that the $\text{BC}_{\parallel}$ site is stable in wurtzite, but unstable in zinc blende. We attribute the stability in wurtzite to an increased flexibility for relaxing bond angles between the nearby gallium and nitrogen atoms. In particular, placing H^+ in a bond-centered site causes the nearby gallium atom to relax into a planar configuration with its remaining three nearest-neighbor nitrogen atoms radically changing the Ga-N bond angles. As shown in a previous study of zinc-blende and wurtzite GaN elastic properties,⁷⁶ the wurtzite structure is more easily able to relax its bond angles than zinc blende. (See also Ref. 77 and Chap. 6 in Ref. 66.)

The most stable site for H^- is also different in wurtzite and zinc blende. In zinc blende, H^- is stable at the gallium anti-bonding (AB_{Ga}) site, although the tetrahedral gallium ($\text{T}_{\text{d,Ga}}$) site is only 0.08 eV higher in energy. In wurtzite, the stable site is at the center of the trigonal channel (see Fig. 12), 0.66 Å from a plane of gallium atoms and roughly halfway between two planes of nitrogen atoms. The wurtzite analog to the zinc-blende $\text{T}_{\text{d,Ga}}$ site has a formation energy 1.76 eV higher than the trigonal site due to the presence of a nearby nitrogen atom. In general, the extended trigonal channel is an

important structural feature distinguishing wurtzite from zinc blende. As noted above, the trigonal channel in zinc blende is blocked at intervals of 7.8 Å by a pair of gallium and nitrogen atoms. This blockage might also be expected to affect the diffusion barrier of H⁻ in zinc-blende GaN. In wurtzite, a likely diffusion path for H⁻ is along the center of the trigonal channel. Based on calculations for this path, we estimate the diffusion barrier to be 1.6 eV. The analogous path in zinc blende is from a T_{d,Ga} site to a tetrahedral nitrogen (T_{d,N}) site, and then to a different T_{d,Ga} site. The energy barrier for this path is estimated to be 1.9 eV, about 20% higher than the wurtzite result. We note that both of these values are significantly lower than the 3.4 eV given by NVdW.^{72,73} In particular, we do not see the sharp rise in energy shown in Fig. 1b of Ref. 73 near the midpoint of the path described above. The much smaller diffusion barriers found in this study imply that H⁻ will have noticeable mobility in GaN at growth and processing temperatures. A barrier of 3.4 eV, on the other hand, implies that H⁻ is practically immobile at these temperatures.

Due to its neutrality, NVdW found that the formation energy of H⁰ in zinc-blende GaN was insensitive to position.^{72,73} We find the same insensitivity for H⁰ in zinc-blende and wurtzite GaN. However, the formation energy of neutral H₂ is very sensitive to position and the stable sites are also quite different in the two crystal structures. In wurtzite, the stable site is at the center of the trigonal channel with the H-H bond parallel to the c-axis. One of the hydrogen atoms sits 0.45 Å from a plane of gallium atoms, the other sits 0.77 Å from a plane of nitrogen atoms, and the H-H bond length is 0.76 Å. In zinc blende, H₂ sits near a T_{d,Ga} site in the trigonal channel with the H-H bond parallel to a <111> direction. One hydrogen atom sits 0.12 Å from a plane of gallium atoms, the other sits 1.09 Å from a plane of nitrogen atoms, and the H-H bond length is again 0.76 Å. In wurtzite, H₂ is located roughly equidistant between planes of gallium and nitrogen atoms. H₂ cannot sit at this same position in zinc blende because a nearby gallium atom is blocking the trigonal channel. As a result, the H₂ formation energy in wurtzite is 0.56 eV lower than in zinc blende. The increased stability in wurtzite is likely due to a polarization of the molecule, and the resulting attractive dipole interaction with the three nearby Ga-N pairs lining the trigonal channel. Polarization is not effective in zinc blende because the gallium atom blocking the trigonal channel has the same charge as the nearby hydrogen atom.

In Fig. 13, we plot formation energies for the most stable sites in zinc blende and wurtzite as a function of Fermi level. The two plots are similar to each other and to the plot shown earlier by NVdW.⁷³ Both plots in Fig 13, for example, display large negative-U values of -1.8 eV for wurtzite and -2.2 eV for zinc blende, similar to the -2.4 eV reported by NVdW. (The U value is defined as the difference in crossing points of the H⁰/H⁻ and H⁺/H⁰ formation energies.) Our H₂ formation energies are also roughly 0.7 eV lower than the value found by NVdW. The relatively low formation energy for H₂ may have important consequences for the behavior of hydrogen in GaN. Its value, given per atom in the plot, is lower than those of H⁺ and H⁻ when the Fermi level lies near the middle of the gap. This will not be significant in material where the hydrogen concentration is small compared to those of other impurities, or native defects. However, in cases where the hydrogen concentration is large (such as in hydrogen-implanted material), hydrogen can become the dominant impurity, pinning the Fermi level near the middle of the gap and yielding a non-negligible concentration of H₂. Another situation

where the low formation energy may become significant is in the growth of magnesium doped *p*-type material. Hydrogen acts like a donor in *p*-type material and will therefore compensate magnesium, lowering its formation energy. This compensation, however, tends to shift the Fermi level toward the middle of the gap where H_2 can begin to form, limiting the concentration of H^+ .⁷⁸

Figure 13. Formation energies (per hydrogen atom) versus Fermi level in a) zinc-blende, and b) wurtzite GaN. *P*-type material corresponds to small values of the Fermi energy and *n*-type material to large values.

For wurtzite GaN, we estimated vibration frequencies for the N- H^+ stretch modes. The values are 3240 cm^{-1} for the $AB_{N,\parallel}$ site, 3120 cm^{-1} for the $AB_{N,\perp}$ site, 3680 cm^{-1} for the $BC_{\parallel}$ site, and 3480 cm^{-1} for the $BC_{\perp}$ site. As expected, the frequencies are higher for the bond-centered sites due to the repulsive interaction between the hydrogen atom and the nearby gallium atom having a broken bond. In addition, we note that these values are similar to those observed in hydrogen implanted material by Weinstein *et al.*⁷⁹ In that case, it was suggested that the frequencies corresponded to hydrogen passivating defect sites. Finally, we point out that the zero-point vibrational energy of these modes is approximately 0.2 eV. This contribution was not included in the formation energies shown in Fig. 13.

In addition to the calculations for neutral H_2 , we also considered two H^+ ions in wurtzite GaN to study the possibility of hydrogen clustering in *p*-type material. When separated by more than about 5 Å, the formation energy for the pair is roughly the sum of

the formation energies for two isolated H^+ ions, indicating that screening is effective in this system. Surprisingly, we also found several configurations, having H^+ ions bonded to the same or nearby nitrogen atoms, with formation energies equal to or lower than the sum of formation energies for isolated ions. In addition to highlighting the effectiveness of screening in this system, these results suggest that either the strain fields surrounding two H^+ ions can complement each other, lowering the total formation energy for the complex, or new bonds are being formed.

Three structures were found having formation energies lower than for isolated H^+ ions. The first has H^+ ions at consecutive $BC_{\parallel}$ sites along the $[0001]$ direction, and a new bond formed from gallium and nitrogen atoms relaxing in opposite directions due to the presence of the H^+ ions. The second structure consists of H^+ ions at $BC_{\parallel}$ and $BC_{\perp}$ sites related to the same nitrogen atom. That is, the H^+ ions were found to break two Ga-N bonds on the same nitrogen atom, a result that indicates strong reactivity for H^+ in GaN. The formation energies for these two configurations are 0.15 eV lower than for isolated H^+ ions in wurtzite GaN with the first structure likely benefiting from the formation of the new Ga-N bond and the second from complementary relaxations in the surrounding lattice. The third structure consists of H^+ ions in $BC_{\parallel}$ and $AB_{N,\parallel}$ sites in adjacent columns of atoms along the $[0001]$ direction and lying roughly in the same plane perpendicular to the $[0001]$ direction. The formation energy in this case is 0.31 eV below that for two isolated H^+ ions, with the low formation energy being due to relaxation in the surrounding gallium and nitrogen positions. While we have not considered all possible configurations with two H^+ ions nor complexes containing more than two ions, these results nevertheless suggest that hydrogen clustering may play a role in *p*-type material.

In summary, we find noteworthy differences in the formation energies and stable lattice sites of hydrogen in wurtzite and zinc-blende GaN. H^+ is equally stable at a bond-centered site and a nitrogen anti-bonding site in wurtzite GaN, but is unstable at a bond-centered site in zinc-blende GaN. This difference is attributed to the increased flexibility of wurtzite for relaxing Ga-N bond angles. Additional calculations for two H^+ ions in wurtzite GaN indicates that these ions can break two Ga-N bonds to the same nitrogen atom and, in general, can form clusters of several types. H_2 is found to have a lower formation energy in wurtzite than in zinc blende, a result that could affect the growth of *p*-type wurtzite material. In *n*-type material, we find that H^- occupies different sites, and we estimate diffusion barriers of 1.6 eV in wurtzite and 1.9 eV in zinc-blende, significantly lower than the value given previously. In general, the different results for interstitial hydrogen zinc-blende and wurtzite GaN follow from differences in the two crystal structure related to the lower symmetry of wurtzite and the existence of trigonal channels in wurtzite extending through the length of the crystal. These structural differences are also likely to have an effect on the energetics of other types of interstitial atoms in zinc-blende and wurtzite GaN and on the energetics of other interstitial atoms interacting with hydrogen.⁸⁰

V. Plasma Etching of GaN

A. ICP Etching of GaN

Due to the extensive etch requirements, unique material properties, and the ineffectiveness of wet chemically etching, plasma etching has been used almost exclusively in group-III nitride device fabrication. In particular, the utilization of high-density plasma (HDP) etch systems has contributed to the development of versatile, well-controlled etch processes. For example, GaN etch rates ranging from ~ 100 Å/min to >1 $\mu\text{m}/\text{min}$ have been reported in inductively coupled plasma (ICP) etch systems with anisotropic profiles and smooth etch morphologies. Improved HDP etch results are due to plasma densities which are 2 to 4 orders of magnitude higher than reactive ion etch (RIE) thus improving the III-N bond breaking efficiency and the sputter desorption of etch products formed on the surface. Additionally, since ion energy and ion density can be more effectively decoupled as compared to RIE, it may be possible to improve etch selectivity, better control etch rates, and reduce plasma-induced damage while maintaining critical dimensions and anisotropy.

Figure 14 shows ICP, electron cyclotron resonance (ECR), reactive ion beam etch (RIBE), and RIE GaN etch rates as a function of dc-bias. GaN etch rates obtained in ICP- and ECR-generated plasmas increased monotonically with dc-bias and were significantly faster than those obtained in either RIE or RIBE plasmas due to densities which were 1 to 3 orders of magnitude higher. GaN etches much slower in low plasma flux etch systems (RIE and RIBE) due to inefficient breaking of the group-III-N bond. HDP etch systems (ECR and ICP) not only improve the bond-breaking efficiency; but also enhance the sputter desorption of etch products from the surface. RIBE etch rates may also have been slower as compared to ECR or ICP due to lower operational pressures (0.3 mTorr compared to 2 mTorr) or the high source-to-sample separation, which reduced both the ion and neutral flux at the GaN surface.

Figure 14. GaN etch rates in RIE, ECR, ICP, and RIBE Cl_2 -based plasmas as a function of dc-bias. RIBE data was obtained in a Cl_2/Ar plasma whereas a $\text{Cl}_2/\text{CH}_4/\text{H}_2/\text{Ar}$ plasma was used in the RIE, ECR, and ICP reactors.

B. Etching of AlGaN, n-GaN, and p-GaN

Plasma chemistry has also shown a significant effect on GaN etch characteristics. In particular, BCl_3/Cl_2 plasmas have also shown encouraging results in etching GaN films. The addition of BCl_3 to a Cl_2 plasma can improve sputter desorption due to higher mass ions and reduce surface oxidation by gettering H_2O from the chamber. Combining BCl_3/Cl_2 in an ICP etch process has yielded GaN ICP etch rates ranging from a few 100 Å/min to ~8000 Å/min with highly anisotropic, smooth etch profiles. Such a versatile etch process could be used to etch a variety of nitride based devices including the fabrication of many electronic and photonic devices which require patterning of either p-n junctions or heterostructures. One of our milestones for this LDRD was to examine HDP etch characteristics for GaN films. Etch rates are shown in Figure 15 for n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ as a function of % Cl_2 in a BCl_3/Cl_2 ICP-generated plasma. As the % Cl_2 increased, etch rates for all films increased up to 80% due to higher concentrations of reactive Cl. This was confirmed using optical emission spectroscopy (OES) where the Cl^+ and Cl^0 emission intensity increased up to 80% Cl_2 . Slower etch rates observed at 100% Cl_2 , were attributed to lower Cl^0 and Cl^+ emission intensity and less efficient sputter desorption of the etch products from the surface in the absence of the heavier BCl_x ions. once again due to higher concentrations of reactive Cl. In a pure Cl_2 plasma, etch rates again decreased due to less efficient sputter desorption of etch products in the absence of BCl_3 as well as a decrease in the Cl^+ and Cl^0 emission intensity. The Al-containing films showed a much more substantial decrease in etch rate at 100% Cl_2 . In the absence of BCl_3 ,

Figure 15. n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etch rates as a function of % Cl_2 in a $\text{BCl}_3/\text{Cl}_2/\text{Ar}$ ICP plasma. Plasma conditions were: 2 mTorr pressure, 500 W ICP-source power, -250 V dc-bias, and 25°C cathode temperature.

any Al-oxides formed on the surface were not efficiently sputtered off thus lowering the etch rate and yielding rough surface morphologies.

Etch optimization also requires balancing the physical and chemical components of the etch mechanism. The physical component of the etch is often varied by controlling the ion energy and plasma density. Variations in ion energies (dc-bias) can create changes in the breaking of surface bonds, physical sputter removal of surface material, and sputter desorption of etch products from the surface. Etch rates for n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ are shown in Figure 16 as a function of dc-bias. Etch rates for all films increased as the dc-bias or ion bombardment energy increased due to improved efficiency of III-N bond breaking and more effective sputter desorption of etch products from the surface. Etch rates were less than 400 Å/min at -50 V dc-bias, then increased to >3000 Å/min at -250 V implying a threshold in ion energy for etch initiation.

Figure 16. n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etch rates as a function of dc-bias. Plasma conditions were: 2 mTorr pressure, 500 W ICP-source power, 32 sccm Cl_2 , 8 sccm BCl_3 , 5 sccm Ar, and 25°C cathode temperature.

By varying the ICP source power, the chemical (concentration of reactant neutral flux) and physical (ion flux) components of the etch mechanism can be changed. As the ion flux increases so does the efficiency of III-N bond breaking and the sputter desorption of etch products from the surface. In Figure 17, n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etch rates are plotted as a function of ICP source power. Etch rates increased for all films up to 1000W implying either a reactant limited regime

under low ICP source power, improved sputter desorption of etch products from the surface, and/or improved bond breaking under high ion flux conditions.

Figure 17. n-GaN, p-GaN, $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etch rates as a function of ICP power. Plasma conditions were: 2 mTorr pressure, 32 sccm Cl_2 , 8 sccm BCl_3 , 5 sccm Ar, -250 V dc-bias, and 25°C cathode temperature.

Etch profile and etch surface morphology can also be critical to the fabrication of devices where anisotropic profiles are necessary or subsequent processing steps including the formation of metal contacts, deposition of interlevel dielectric or passivation films, or epitaxial regrowth require smooth surfaces. Sidewall morphology is especially critical for dry etched laser mirrors or for buried planar devices. In Figure 18, SEM micrographs are shown for n-GaN, p-GaN, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$, etched in a BCl_3/Cl_2 ICP-generated plasma. As stated earlier, etch rates were comparable for all three films ($\sim 4500 \text{ Å/min}$) and the etch was highly anisotropic and smooth. In Figure 19, SEM micrographs are shown for n-GaN, p-GaN, $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$, and $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ in a pure Cl_2 ICP plasma. Much rougher surfaces were obtained for the Al-containing films (c and d) as compared to the a) n-GaN and b) p-GaN samples. Etch rates were also much slower for the Al-containing films (refer to Figure 15). Rough surfaces may be due to preferential etching of the lighter N-atoms resulting in a group-III rich surface or micro masking. The Al-containing films may experience micro-masking in a pure Cl_2 plasma due to either a) inefficient breaking of the Al-N bonds (the AlN bond energy is 11.52 eV/atom as compared to 8.92 eV/atom for GaN); b) Al oxidation which was not efficiently sputtered off; or c) inefficient sputter desorption of etch products from the surface. Also notice that the GaN films are neither as anisotropic or smooth when etched in pure Cl_2 as compared to the 80% Cl_2 /20% BCl_3

gas ratio. This implies that the chemical to physical components of the etch mechanism were not optimized in a pure Cl_2 plasma.

Figure 18. SEM micrographs of a) n-GaN, b) p-GaN, and c) $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etched under the following ICP conditions: 32 sccm Cl_2 , 8 sccm BCl_3 , 5 sccm Ar, 500 W ICP power, -250 V dc-bias and 2 mTorr pressure.

Figure 19. SEM micrographs of a) n-GaN, b) p-GaN, c) $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N}$ and d) $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$ etched under the following ICP conditions: 40 sccm Cl_2 , 5 sccm Ar, 500 W ICP power, -250 V dc-bias and 2 mTorr pressure.

C. ICP Etching of Devices

The BCl_3/Cl_2 ICP plasma has been used to etch several GaN based devices including the AlGaIn/GaN quantum well ultraviolet LED structure shown schematically in Figure 20a. The SEM micrograph in Figure 20b shows the LED mesa structure etched to a depth of $\sim 1.1 \mu\text{m}$ at an etch rate of $\sim 4200 \text{ \AA}/\text{min}$. In addition, GaN/AlGaIn heterojunction bipolar transistors (HBTs) and GaN junction field effect transistors (JFETs) have been fabricated using ICP Cl_2 -based plasmas with reasonable device performance.

Figure 20: a) Schematic of the GaN/AlGaIn LED structures. b) SEM micrograph of GaN/AlGaIn quantum well structure etched in the ICP under the conditions: 8 sccm BCl_3 , 32 sccm Cl_2 , 2 mTorr pressure, 500 W ICP power, and 125 W cathode rf-power with a corresponding dc-bias of -200 V

In summary, the BCl_3/Cl_2 plasma chemistry in combination with the ICP etch platform provides a very versatile etch process for the group-III nitrides. Etch rates ranging from 100 to $8000 \text{ \AA}/\text{min}$ with highly anisotropic profiles and smooth etch morphologies have been obtained. Etch processes have been optimized and applied to several photonic and electronic device applications with encouraging results. Understanding and minimizing plasma-induced damage mechanisms will become more important as device structures become more complicated and design rules shrink.

VI. AlGaIn/GaN Heterojunction Bipolar Transistors

There is a strong interest in GaN-based electronics for applications involving high temperature or high power operation, based on the excellent transport properties of the III-nitride materials system.^{81,82,83,84,85,86,87} Impressive advances in the performance of AlGaIn/GaN high electron mobility transistors continue to be reported, due in part to the formation of piezoelectrically-induced carriers in a 2-dimensional electron gas at the heterointerface.^{85,86,87} There is also interest in the development of GaN/AlGaIn

heterojunction bipolar transistors (HBTs) to meet the linearity requirements of some future electromagnetic systems, particularly for military applications where ultrawide bandwidth and linearity are key issues. In these vertical device structures, minority carrier lifetime,⁸⁸ interface quality and doping control are important factors.⁸⁵

There have been two recent reports on initial demonstrations of GaN/AlGaIn HBT operations.^{89,90} In one case, extrinsic base regions were grown by metal organic chemical vapor deposition (MOCVD) before base mesa etching to contact the collector. This was performed to overcome the high base resistance arising from the relatively low hole concentration (typically $\leq 10^{18} \text{ cm}^{-3}$) achievable in GaN (Mg).⁸⁹ Devices with $3 \times 20 \text{ } \mu\text{m}^2$ emitters produced a dc current gain at 25 °C of ~ 3 . In the other report, the active layer structure was grown by rf plasma-assisted molecular beam epitaxy (MBE) on top of an MOCVD buffer.⁹⁰ Large area (90 μm diameter) devices were fabricated by a low damage dry etch process similar to that developed for GaAs/AlGaAs HBTs. The dc gain at 25 °C was in the range 1-3, but increasing the operation temperature to 300 °C produced a gain of ~ 10 by increasing the ionization efficiency of the Mg acceptors in the base layer.

In this report we summarize the MOCVD growth of a graded emitter HBT structure, the measurement of background impurities (C, O, H) by secondary ion mass spectrometry (SIMS) since these could potentially influence doping levels and profile, and finally on the dc characteristics of the HBT devices

The layer structure is shown schematically in Figure 21, and was grown at $\sim 1050 \text{ }^\circ\text{C}$ following deposition of the GaN buffer at $\sim 550 \text{ }^\circ\text{C}$ on the c-plane Al_2O_3 substrate. The growth system has been described in detail previously,⁹¹ but in brief is a rotating (1200 rpm) disk MOCVD reactor. Ammonia (NH_3), trimethylgallium (TMGa) and trimethylaluminum (TMAI) were used as precursors, while silane (SiH_4) and bis-cyclopentadienyl-magnesium (Cp_2Mg) were employed for n- and p-type doping, respectively. High purity H_2 was used as the carrier gas. After growth the sample was annealed in the reactor at 850 °C for 20 min under 140 Torr of flowing N_2 to activate the Mg acceptors.

500 nm GaN Si-doped ($>5 \times 10^{19} \text{ cm}^{-3}$)
20 nm AlGaIn graded to GaN Si-doped ($>1 \times 10^{19} \text{ cm}^{-3}$)
800 nm AlGaIn Si-doped ($>1 \times 10^{19} \text{ cm}^{-3}$)
20 nm GaN undoped
220 nm GaN Mg-doped ($>5 \times 10^{17} \text{ cm}^{-3}$)
400 nm GaN Si-doped ($>1 \times 10^{16} \text{ cm}^{-3}$)
500 nm GaN Si-doped ($>1 \times 10^{19} \text{ cm}^{-3}$)
GaN Buffer Layer

Figure 21. Schematic of GaN/AlGaIn HBT structure.

There are two important aspects to dopant and background impurity control in HBT structures. The first is that the p-type dopant should be confined to the base region, and not spill-over into the adjacent n-type emitter, where it could cause displacement of the junction and hence the loss of the advantage of the heterostructure. Figure 22 shows SIMS profiles of the Al marker, signifying the position of AlGaIn emitter layer, and also the Mg doping profile in the adjacent base layer. It is clear that the reactor memory effect for Cp_2Mg has produced incorporation of Mg in the emitter, although the real situation is not quite as severe as it seems in the data because of "carry-over" of the matrix Al signal during the depth profiling. The fact that working HBTs can still be made on this material is due to the higher electron concentration in the emitter from the Si doping (Si ionization level is ≤ 30 meV, so that all of the Si will contribute an electron at 25 °C) relative to the hole concentration contributed by the Mg acceptors, whose ionization level is ≥ 170 meV in AlGaIn.

Figure 22. SIMS profiles of Mg in the GaN/AlGaIn structure.

The second aspect of impurity control is to minimize the concentration of O (which probably creates a shallow donor state in GaN), C (which may lead to compensated material) and H (which can passivate the Mg acceptors in the base). Figure 3 shows SIMS profiles for these elements, as well as for the intentional Si doping. Note that the C concentration throughout most of the structure is well below that of the Si, suggesting it will have no significant effect on the electrical properties of the material. The O concentration is also relatively constant and at a density well below that of the Si. It is clear that only a fraction of the oxygen is electrically active, since the base remains

p-type even though the hole concentration from the Mg acceptors could be lower than the electron concentration from the O donors if all the oxygen was active. Note that residual hydrogen still decorates the Mg doping in the base, but since a reactivation anneal was performed, the hydrogen most likely is in the form of electrically inactive molecules or larger clusters, through the reactions:

Figure 23. SIMS profiles of Si, C, O and H in the GaN/AlGaN structure.

These are in analogy with the behavior of hydrogen in other p-type semiconductors.⁹² The concentrations of oxygen and carbon in GaN are a factor of 3-5 higher than that in comparable GaAs/AlGaAs HBTs.⁹³ It remains to be established as to the relative contributions of background impurities and structural defects to degradation of gain in GaN/AlGaN HBTs.

A Gummel plot from a 90 μm diameter device operated at 300 $^{\circ}\text{C}$ is shown in Figure 24. The maximum gain is ~ 10 , similar to the previous report.⁽¹⁹⁾ In general we could not obtain common-emitter characteristics, because the resistance of the extrinsic base region is too high to achieve modulation. The performance of the HBT is dominated by this high base resistance, and the resultant high specific contact resistivity of the

ohmic metallization. At room temperature the alloyed (700 °C, 30 sec) Ni/Au is rectifying (Figure 5). However as the measurement temperature is increased the p-contact becomes ohmic, concomitant with the improved performance of the device. From separate transmission line measurements, we determined the specific contact resistivity to be in the $10^{-2} \Omega\text{-cm}^2$ range at 300 °C.

Figure 24. Gummel plot of GaN/AlGaIn HBT measured at 300 °C.

Figure 25. I-V characteristics for Ni/Au base contact at different measurement temperatures.

VII. Conclusions

Significant progress was made throughout the course of this LDRD. Most notably the following goals have been explicitly accomplished: 1) the establishment of a GaN MOCVD growth facility capable of supporting both device activities and scientific investigation, 2) the understanding of hydrogen impurity in GaN (both n- and p-types) through a combined effort of implantation, annealing, characterization, and modeling, 3) detailed calculation of defects energetics, including planar, linear, and point defects in GaN, 4) state-of-the-art processing (contacts and etching) of GaN with a high degree of anisotropy and verticality, 5) proof-of-concept electronic devices.

VIII. References

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