GaN: DEFECT AND DEVICE ISSUES

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ABSTRACT

The role of extended and point defects, and key impurities such as C, O and H, on the electrical and optical properties of GaN is reviewed. Recent progress in the development of high reliability contacts, thermal processing, dry and wet etching techniques, implantation doping and isolation and gate insulator technology is detailed. Finally, the performance of GaN-based electronic and photonic devices such as field effect transistors, UV detectors, laser diodes and light-emitting diodes is covered, along with the influence of process-induced or grown-in defects and impurities on the device physics.
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I. INTRODUCTION

Current GaN-based device technologies include light-emitting diodes (LEDs), laser diodes and UV detectors on the photonic side and microwave power and ultra-high power switches on the electronics side.\(^{(1)}\) The LED technology is by now relatively mature, with lifetimes of blue and green emitters apparently determined mostly by light-induced degradation of the polymer package that encapsulates the devices.\(^{(2)}\) The main trends in this technology appear to be optimization of optical output efficiency and solving the polymer package degradation issue. For the laser diodes one of the main lifetime limiters was p-ohmic metal migration along dislocations to short out the GaN p-contact layer by spiking all the way to the n-side of the junction.\(^{(3,4)}\) This is exacerbated by the generally high specific contact resistance (R\(_C\)) of the p-ohmic contact and the associated heating of this area during device operation. The advent of lower threshold devices and the dislocation-free GaN overgrowth of SiO\(_2\)-masked regions has allowed achievement of laser lifetimes over 10,000 hours.\(^{(5)}\) Facet formation on the laser has been achieved by dry etching, cleaving, polishing and selective/crystallographic growth. In structures grown on Al\(_2\)O\(_3\) both contacts must be made on the top of the device and hence dry etching is necessary to expose the n-side of the junction. Fabrication of UV detectors is relatively straightforward and the main issue seems to be one of improving material purity and quality.

For electronic devices for microwave power applications, the main process improvements are needed in the areas of low R\(_C\) n-ohmic contacts (the requirements are more stringent than for photonic devices, with R\(_C\) \(\leq\)10\(^{-7}\)\(\Omega\)cm\(^2\) being desirable), stable and reproducible Schottky contacts, and low damage dry etching that maintains surface stoichiometry. For the proposed high power switches (capable of 25 kA with 3kV-voltage standoff) there are a number of
possible device structures, including thyristors and several types of power MOSFET. A schematic of the latter is shown in Figure 1. In this case, critical technologies include high implant activation efficiency, gate insulator, trench etching for capacitor formation and high temperature/high current stable ohmic contacts.

Recent progress in the development of dry and wet etching techniques, implant doping and isolation, thermal processing, gate insulator technology and high reliability contacts is first reviewed. Each selectivities up to 10 for InN over AlN are possible in Inductively Coupled Plasmas using a Cl₂/Ar chemistry, but in general selectivities for each binary nitride relative to each other are low (<2) because of the high ion energies needed to initiate etching. Improved n-type ohmic contact resistances are obtained by selective area Si⁺ implantation followed by very high temperature (>1300°C) anneals in which the thermal budget is minimized and AlN encapsulation prevents GaN surface decomposition. Implant isolation is effective in GaN, AlGaN and AlInN, but marginal in InGaN. Candidate gate insulators for GaN include AlN, AlON and Ga(Gd)Oₓ, but interface state densities must still be decreased to realize state-of-the-art MIS devices.

Many outstanding reviews on GaN materials and devices have appeared previously⁶⁻¹⁴, so we will focus on processing and the influence of defects and impurities on devices.

II. PROCESSING

A. Ohmic and Schottky Contacts

(i) Schottky Contacts

There are still large variations in barrier heights reported by different workers for standard metals on GaN. Pt appears to produce the highest consistent values (~1.0-1.1 eV) with Ti producing the lowest (0.1-0.6 eV). The variability appears to result from the presence of
several transport mechanisms, and to materials and process factors such as defects present in these films, the effectiveness of surface cleans prior to metal deposition, local stoichiometry variations, and variations in surface roughness which could affect uniformity of the results. New work on silicides shows promise. For Schottky contacts Pt appeared to be stable to approximately 400°C for 1h, while PtSi was somewhat more stable (500°C) 1h), and also had barrier heights of ~0.8 eV.

Recent reviews and studies of Schottky contact properties on GaN have appeared. The measured barrier heights in most cases are a function of the difference between the metal work function and the electron affinity of GaN. Some typical values for barrier height for different metals are 1.1 eV for Pt(19), 0.91-1.15 eV for Au(20,21), 0.6 eV for Ti(22) and 0.94 eV for Pd.(23) For Ni there is a fairly large discrepancy in reported values, ranging from 0.66 eV(24) to 0.99 eV(25). For deposition onto n-GaN (~10^17 cm^-3), rectifying behavior was observed for Pt, Ni, Pd, Au, Co, Cu, Ag, ohmic behavior for Sc, Hf, Zn, Al and V, while intermediate behavior (slightly rectifying) was obtained for Nb, Ti, Cr, W and Mo. Schmitz et al.(16) calculated from their data that the density of surface states on GaN was ~1.8x10^{13} cm^-2 eV^-1, suggesting the degree of pinning of the barrier height is less than on GaAs where the surface state density is roughly an order of magnitude higher.

A comparison of barrier height data from various sources is shown in Figure 2. In the early days of forming rectifying contacts on GaN it was often believed the Fermi level at the surface and at the metal-nitrides interface was unpinned. The data of Figure 2 shows that indeed the barrier height does vary with metal work function. The strategy is then to use a metal with a large work function on GaN (such as Pt) to form a Schottky barrier, while a metal with a low work function (such as Ti) should be selected for ohmic contacts.
The influence of the surface cleanliness is obviously most important in determining the quality of the Schottky contact. *In-situ* deposition of Ga, followed by thermal desorption under ultra-high vacuum conditions is found to produce clean GaN surfaces\(^{(34,35)}\), while *in-situ* \(\text{N}_2^+\) ion sputtering can also remove native oxides.\(^{(36,37)}\) Liu and Lau\(^{(15,38)}\) and Mohney and Lau\(^{(18)}\) have reviewed surface cleaning processes for GaN. A number of different acid solutions, including \(\text{HNO}_3/\text{HCl}, \text{HCl}/\text{H}_2\text{O}\) and \(\text{HF}/\text{H}_2\text{O}\), have been examined for removing the native oxide\(^{(39)}\), and superior current-voltage characteristics are observed for the resultant rectifying contacts.\(^{(40)}\) As on other III-V compound semiconductors, \(\text{HCl}\) and \(\text{HF}\) can significantly reduce the oxide on GaN\(^{(41,42)}\), while the bases \(\text{NH}_4\text{OH}\) and \(\text{NaOH}\) can also dissolve the oxide.\(^{(43)}\) To this point, there has been no clear demonstration of the effect of the polarity of the epilayer on the barrier height.

Mohney and Lau\(^{(18)}\) have also commented on the fact that there can be significant spatial differences in the quality of Schottky barrier contacts on a n-GaN, with diodes showing ideality factors ranging from \(<1.1\) to \(\geq1.3\) on the same wafer. While thermionic emission is clearly the dominant current transport mechanism in most diodes, tunnelling and generation-recombination may also be present. In many cases the high dislocation density in material used to date are probably responsible for most of the spatial variations.

The thermal stability of Schottky contacts on GaN is critically important for practical device operation. The thermal limits of most of the metal/GaN combinations are between 300°C and 600°C, specifically 300°C for Pt\(^{(44)}\), 400°C for Pt\(^{(45)}\), 575°C for Au\(^{(46)}\) and 600°C for Ni\(^{(18)}\). As mentioned earlier, the silicides of Pt and Ni display greater thermal stability than the pure metals.\(^{(45)}\) These contacts however may not be in thermodynamic equilibrium with the GaN, leading to formation of metal gallides and silicon nitride upon prolonged annealing.
There is little information on barrier heights on p-GaN due to the general difficulty in growing high quality p-type material and the low hole mobility. A barrier height of 2.38 eV was reported for Au on p-Ga.\(^{(47)}\)

(ii) n-Ohmic Contacts

The commonly accepted ohmic contact to n-GaN is Ti/Al, which is generally annealed to produce oxide reduction on the GaN surface. Multi-level Au/Ni/Al/Ti structures appear to give wider process windows, by reducing oxidation of the Ti layer.\(^{(48)}\) $R_C$ values of $\leq 10^5 \Omega \text{cm}^2$ have been produced on HFET devices using Ti/Al annealed at 900°C for 20 secs.\(^{(15)}\)

Both W and WSi$_x$ on n$^+$ epi GaN layers ($n \approx 10^{19} \text{cm}^{-3}$) produce reasonable contacts ($R_C \approx 3 \times 10^5 \Omega \text{cm}^2$), but extremely stable behavior\(^{(49)}\) – annealing at 1000°C led to shallow reacted regions of $\leq 100$ Å, and in junction field-effect transistor structures these contacts can withstand implant activation anneals at 1100°C.\(^{(50)}\) Reaction with the GaN is relatively limited, although $\beta$-W$_2$N interfacial phases are found after 800°C anneals, and this appears to be a barrier to Ga outdiffusion.\(^{(49)}\)

The standard p-ohmic contact to GaN is Ni-Au, with $R_C$ values $\geq 10^2 \Omega \text{cm}^2$. Efforts to find a superior alternative have proved fruitless to date\(^{(51)}\), even though strong efforts have been made on multi-component alloyed contacts where one attempts to extract one of the lattice elements, replace it with an acceptor dopant, and simultaneously reduce the “balling-up” of the metallization during this reaction. The model system for this type of contact is AuGeNi/n-GaAs. A promising approach is to reduce the bandgap through use of p-type InGaN on the top of the GaN. To date there have been reports of achieving p-doping ($\approx 10^{17} \text{cm}^{-3}$) in compositions up to $\sim 15\%$ In.
The III-nitrides pose a problem however, in the development of low resistance ohmic contacts because of their wide band gaps. Most of the work done in the area has been focused on n-type GaN. Au and Al single metal contacts to n\textsuperscript{+}GaN and nonalloyed Au/Ti and Al/Ti were found to have contact resistances of $\sim 10^{-3}$ to $10^{-4} \Omega \text{cm}^2$.

Al-containing contacts perform best when oxidation is minimized. Lin et al.\cite{59} reported the lowest contact resistance to n\textsuperscript{+}GaN, with Ti/Al contacts after annealing at 900°C for 30 secs in a rapid thermal annealer (Rc=8x10\textsuperscript{-6} \Omega \text{cm}^2). They suggested the formation of a TiN interface as important in the formation of the low resistance contact. Most of the transition metal elements, including Ti, V and Sc react with GaN to form nitrides, gallides and metal-Ga-N ternary phases.\cite{18} Thermodynamic calculation indicate that the metals themselves are not in equilibrium with GaN under normal processing conditions, with the probability of interfacial reactions occurring.\cite{60} Both Ti and TiN have been shown to produce ohmic contacts on n-GaN,\cite{61,62} with Ti consuming GaN during reaction (a few hundred angstroms at $\sim 1000°C$ for 30 secs) to form TiN.\cite{63} Three phase equilibria for the Ti-Ga-N (and V-Ga-N and Cr-Ga-N) systems at 800°C have been reported by several groups.\cite{64-66} The annealing ambient plays a strong role, since if the N\textsubscript{2} partial pressure is greater than that in equilibrium with a metal/GaN contact during reaction, there is a driving force to incorporate nitrogen from the gas phase.\cite{18} Moreover, there is quite different behavior observed for deposited TiN/GaN contacts relative to those formed by reaction of Ti with GaN in a N\textsubscript{2} ambient. In the former case, thermionic emission appears to be the dominant conduction mechanism whereas in the latter tunnelling seems to be most important.\cite{18}

Modification of the GaN surface by high temperature annealing\cite{67} or reactive ion etching\cite{68,69} to produce preferential loss of N\textsubscript{2} can improve n-type ohmic contact resistance by increasing electron concentration in the near-surface region.
Many other metals can be employed to form bilayer Al/metal/GaN n-ohmic contacts, including Pd(69,70), Ta(71), Nd(72), Sc(18) and Hf(18). All of these form good ohmic contacts, with specific contact resistances in the $10^{-5}\Omega \text{cm}^2$ range.

A particularly attractive method for reducing $R_c$ on device structures is self-aligned implantation of $\text{Si}^+$ to heavily dope source/drain ohmic contact regions. This approach has been employed to achieve high quality contacts on heterostructure field-effect transistor structures.(73)

$W$ was found to produce low resistance ohmic contacts to $n^+\text{GaN}$ ($R_c=8\times10^{-5}\Omega \text{cm}^2$) with little interaction between the semiconductor and the metal up to 800°C.(69) $\text{WSi}_x$ on $n^+\text{GaN}$ was found to be stable to 800°C as well, with a contact resistance of $\sim 10^{-5}\Omega \text{cm}^2$. Graded contact layers to GaN have been formed with both $\text{InN}(74)$ and $\text{InGaN}$ with $\text{WSi}_x$. Ohmic contacts to $\text{InN}$ have also been investigated, with nonalloyed $\text{Ti/Pt/Au}$ producing specific contact resistance $R_c=1.8\times10^{-7}\Omega \text{cm}^2$.(74) Graded $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InN}$ contacts have also been used on $\text{GaAs/AlGaAs}$ heterojunction bipolar transistors, with $R_c$ as low as $5\times10^{-7}\Omega \text{cm}^2$.(75)

For high temperature electronics applications, or for high reliability, we would like to employ refractory metal contacts such as $W$ and $\text{WSi}_x$. Moreover, the contact resistance could be reduced if lower bandgap In-containing alloys (or InN) were used as contact layers on GaN, much as the case with $\text{InGaAs}$ on GaAs. However, the In-based nitrides are less thermally stable than GaN, and we need to establish the trade off between contact resistance and poorer temperature stability.

Recent experiments on formation of $W$, $\text{WSi}_{0.44}$ and $\text{Ti/Al}$ contacts deposited on $n^+\text{In}_{0.65}\text{Ga}_{0.35}\text{N}$, $n^+\text{InN}$ and $n^+\text{In}_{0.75}\text{Al}_{0.25}\text{N}$ have been reported.(74,75) The electrical, structural and chemical stability of these contacts were examined after anneals up to 900°C, using transmission line method (TLM) measurements, scanning electron microscopy (SEM) and Auger electron...
spectroscopy (AES). We find that InGaN allows achievement of excellent contact resistance, with stability up to ~600°C for W metallization.

The 2000 Å thick InGaN, InN and InAlN samples were grown using metal organic molecular beam epitaxy (MOMBE) on semi-insulating, (100) GaAs substrates in an Intevac Gen II system as described previously.\textsuperscript{[76,77]} The InN, In\textsubscript{0.65}Ga\textsubscript{0.35}N and In\textsubscript{0.75}Al\textsubscript{0.25}N were highly autodoped n-type (\(\sim 10^{20}\), \(\sim 10^{19}\) and \(8 \times 10^{18}\) cm\(^{-3}\), respectively) due to the presence of native defects.

The samples were rinsed in H\textsubscript{2}O:NH\textsubscript{4}OH (20:1) for 1 min just prior to deposition of the metal to remove native oxides. The metal contacts were sputter deposited to a thickness of 1000Å in the case of W and WSi\textsubscript{0.44}, and then etched in SF\textsubscript{6}/Ar in a Plasma-Therm reactive ion etcher (RIE) to create TLM patterns. For the Ti/Al contacts, 200Å of Ti and then 1000Å of Al was deposited and the TLM pattern formed by lift-off. The nitride samples were subsequently etched in Cl\textsubscript{2}/CH\textsubscript{4}/H\textsubscript{2}/Ar in an electron cyclotron resonance (ECR) etcher to produce the mesas for the TLM patterns.\textsuperscript{[78]} The samples were annealed at temperatures from 300 to 900°C for 15 sec under a nitrogen ambient in a RTA system (AG-410).

The contact resistance for W, WSi\textsubscript{x} and Ti/Al ohmic contacts to InGaN as a function of annealing temperature is shown in Figure 3. All contacts had similar contact resistance as deposited, \(\sim 2-4 \times 10^2\Omega \text{cm}^2\). Above 600°C, the Ti/Al contacts degraded rapidly, and the WSi\textsubscript{x} continued to degrade, while Re for both samples increased up to \(\sim 10^5\Omega \text{cm}^2\) at 900°C. The error in these measurements was estimated to be ±10% due mainly to geometrical contact size effects. The widths of the TLM pattern spacings varied slightly due to processing (maximum of ±5%) as determined by SEM measurements, which were taken into account when calculating the contact resistances.
SEM micrographs of W and Ti/Al contacts on InGaN as grown and annealed showed the W was still quite smooth even after 900°C anneal, while the Ti/Al had significant pitting at the lowest anneal of 500°C even though the contact resistance did not degrade until ≥600°C. AES showed that the degradation was due to outdiffusion of In and N.

The contact resistance for ohmic contacts of W, WSiₓ and Ti/Al to InN as a function of annealing temperature is shown in Figure 4. As-deposited samples had similar contact resistances to InGaN, indicating a similar conduction mechanism. WSiₓ contacts showed the most degradation at low temperature, with the resistance rising a factor of 5 after 300°C annealing and then remaining constant. Ti/Al deviated little from initial values, although there was severe pitting on samples annealed at 500°C while W resistance began to degrade at 500°C.

In Figure 5 the contact resistance is shown for W, WSiₓ and Ti/Al ohmic contacts to InAlN as a function of annealing temperature. As-deposited Ti/Al had the lowest contact resistance on this material, \( R_c = 10^{-4} \Omega \text{cm}^2 \). W had the highest initial contact resistance, \( R_c = 10^{-2} \Omega \text{cm}^2 \). The contacts showed morphological stability to 400°C (Ti/Al) to 800°C (W).

SEM micrographs of InAlN contacted with W, WSiₓ and Ti/Al as-grown and annealed at 800, 700 and 400°C, respectively, were examined. The W on InAlN remained smooth until 800°C, and then began to form hillocks, as did the WSiₓ contact at 700°C. The Ti/Al began pitting at 400°C. The pitting in the Ti/Al contacts was due to diffusion of the Al through the Ti into the sample. Hillocks appears to be formed from diffusion of In from the nitride sample into the contact layer.

In summary, W, WSiₓ and Ti/Al were found to produce low resistance ohmic contacts on \( n^+ \)InGaN and InN. W contacts proved to be the most stable, and also gave the lowest resistance to InGaN and InN, \( R_c < 10^{-7} \Omega \text{cm}^2 \) after 600°C anneal, and \( 1 \times 10^{-7} \Omega \text{cm}^2 \) after 300°C anneal.
respectively. Significant diffusion of In, N and Al, as well as Ti and W, were found after annealing. The contact resistance stability varies for each material and degraded at temperatures >400°C on InN, ≥500°C on InAlN and ≥600°C on InGaN. W contacts remained smooth at the highest anneal temperature.

(iii) p-Ohmic Contacts

One of the life-limiting factors in GaN laser diodes to date has been the p-ohmic contact. Due to the relatively poor specific contact resistance ($R_c$) achievable, the metallization will heat-up as current flows across the p-n junction, leading to metal migration down threading dislocations and eventual shorting of the junction. Removal of the dislocations, such as in epitaxial lateral overgrowth structures, will greatly extend the device lifetime. There are a number of contributing factors to the high $R_c$ values for contacts on p-GaN, including:

(i) The absence of a metal with a sufficiently high work function (the bandgap of GaN is 3.4 eV, and the electron affinity is 4.1 eV, but metal work functions are typically ≤5 eV).

(ii) The relatively low hole concentrations in p-GaN due to the deep ionization level of the Mg acceptor (~170 meV).

(iii) The tendency for the preferential loss of nitrogen from the GaN surface during processing, which may produce surface conversion to n-type conductivity.

In the search for improved contact characteristics, a wide variety of metallizations have been investigated on p-GaN besides the standard Ni/Au, including Ni, Au, Pd, Pd/Au, Pt/Au, Au/Mg/Au, Au/C/Ni, Ni/Cr/Au, and Pd/Pt/Au. Typically Ni, Pd or Pt is the metal in direct contact with the GaN, and the structure is annealed at
400-750°C. This produces contact resistances in the $10^{-1}$-$10^{-3}$Ω·cm$^2$ range. For higher temperatures severe degradation in contact morphology is observed, usually resulting from the formation of the metal gallides.

To examine thermal stability of contacts, p-type ($N_A = 10^{18}$cm$^{-3}$), Mg-doped GaN layers 1 μm thick were grown on Al$_2$O$_3$ substrates by Molecular Beam Epitaxy using solid Ga and rf plasma-activated N$_2$. Strong cathodoluminescent was observed at ~385 nm, with very little deep level emission. Undoped GaN layers ~3 μm thick were grown on Al$_2$O$_3$ by Metal Organic Chemical Vapor Deposition. These samples were implanted with 100 keV Si$^+$ ions at a dose of 5×10$^{15}$ cm$^{-2}$, and annealed with AlN caps in place to 1400°C for 10 secs. This produced a peak n-type doping concentration of ~5×10$^{20}$cm$^{-3}$. W or WSi$_{0.45}$ layers ~1000Å thick were deposited using an MRC501 sputtering system. The sample position was biased at 90 V with respect to the Ar discharge. Prior to sputtering, the native oxide was removed in a 201 H$_2$O:NH$_4$OH solution. Transmission line patterns were defined by dry etching the exposed metal with SF$_6$/Ar, and forming mesas around the contact pads using BCl$_3$/N$_2$ dry etching to confine the current flow. For comparison, on the p-GaN, Au (1000Å)/Ni (500Å) was deposited by e-beam evaporation, defined by lift-off and mesas formed by dry etching. Both n- and p-type samples were annealed for 60 secs (in some experiments this was varied for 30-300 secs) at 300-1000°C under flowing N$_2$.

From Fermi-Dirac statistics we can calculate the Fermi level position $E_F$ for p-GaN containing $10^{18}$ acceptors·cm$^{-3}$ as a function of absolute temperature $T$, from

$$
\frac{1}{N_A \left(1 + 2 \exp(-(E_a - E_F)/kT)\right)} = N_V \exp\left(-(E_F - E_V)/kT\right)
$$

where $N_A$ is the acceptor concentration, $E_a = 171$ meV for Mg in GaN and $N_V$ is the valence band density of states. Using this relation, we calculated the ionization efficiency for Mg as a
function of sample temperature, as shown in Figure 6. Since the hole concentration in the p-GaN will increase rapidly with temperature, we would expect better ohmic contact properties.

Figure 7 shows annealing temperature dependence of the I-V characteristics of the Ni/Au, W and WSi on p-GaN, with the measurements made at 25°C in all cases. Note that for the optimum anneal temperatures (700°C for Ni/Au and W, and 800°C for WSi_x), the contacts are not ohmic, but are more accurately described as leaky Schottky diodes. In the case of W and WSi, we assume that annealing above the optimum temperature produces loss of N_2 and poorer contact properties.

The contact morphology on the W and WSi metallization remained featureless to the highest temperature we investigated. This is in sharp contrast to the case of Ni/Au, as shown in Figure 8. For the latter metallization, islanding is quite severe after 700°C annealing due to reaction of the Ni with the GaN.\(^94,95\)

From the earlier discussion, we would expect the contact properties to improve at elevated temperatures because of the increased hole density and more efficient thermionic hole emission across the metal-GaN interface. Figure 9 shows the I-V characteristics for the 700°C (Ni/Au and W) or 800°C (WSi) annealed samples, as a function of the measurement temperature (25-300°C). For the Ni/Au, the contacts become ohmic at \(\geq 200°C\), while for W and WSi this occurs at 300°C. Table I shows the \(R_C\) values at 300°C are \(9.2 \times 10^{-2} \Omega \cdot cm^2\) (Ni/Au), \(6.8 \times 10^{-2} \Omega \cdot cm^2\) (W) and \(2.6 \times 10^{-2} \Omega \cdot cm^2\) (WSi). The TLM measurements showed that the substrate sheet resistance is reduced from \(1.39 \times 10^4 \Omega / \square\) at 200°C, to \(8470 \Omega / \square\) at 250°C and \(4600 \Omega / \square\) at 300°C, indicating that the increased hole concentration plays a major role in decreasing \(R_C\).

There was not a strong dependence of the room temperature I-V characteristics on annealing time. An example is shown in Figure 10 for W/p-GaN, annealed at 700°C. There is
little change in the characteristics for 30-120 secs, but the contacts become more rectifying for longer times.

As a comparison, figure 11 shows the annealing temperature dependence of $R_C$ for W contacts on Si-implanted (n-type) GaN. The specific contact resistance improves with annealing up to ~950°C, which appears to correspond to the region where the β-W$_2$N interfacial phase is formed. Cole et al.$^{49}$ reported that W and WSi contacts on GaN annealed in the range 750-850°C showed the minimum degree of metal protrusion in the interfacial regions devoid of the β-W$_2$N phase, whereas at lower annealing temperatures the horizontal spatial extent of this phase was smaller and allowed more protrusions to develop. The excellent structural stability of the W on GaN is shown in the SEM micrographs of Figure 12, where a sharp interface is retained after 750°C annealing.

In summary, one of the emerging applications for GaN is in ultra-high power electronic switches, where thermal stability of the contact metallization will be of paramount importance. Tungsten-based contacts on both n- and p-type GaN offer superior thermal stability to the standard metallization used in photonic devices, TiAl and Ni/Au respectively.

B. RAPID THERMAL PROCESSING

(1) Surface Protection

The usual environment for high-temperature annealing of III-nitrides is NH$_3$,$^{79}$ but this is inconvenient for processes such as rapid thermal annealing for implant activation, contact annealing for implant isolation. In those situations we would like to provide some form of N$_2$ overpressure to minimize loss of nitrogen from the semiconductor surface at high temperature.$^{96}$ With conventional III-V materials such as GaAs and InP this is achieved in several ways$^{97-110}$,
namely by (i) placing the sample of interest face down on a substrate of the same type\textsuperscript{101,107}, so that the onset of preferential As or P loss quickly suppresses further loss. The disadvantages of this method include the fact that some group V atoms are lost from the near surface: there is always a possibility of mechanical abrasion of the face of the sample of interest, and contamination can easily be transferred from the dummy wafer to the one of interest; and by (ii), placing the wafer in a SiC-coated graphite susceptor\textsuperscript{102,110}, which has either had its internal surfaces coated with As or P by heating a sacrificial wafer within it, or in which granulated or powdered GaAs or InP is placed in reservoirs connected to the region in which the wafer is contained. In both cases subsequent heating of the susceptor produces an As or P vapor pressure above the surface of the process wafer, suppressing loss of the group V element.

The approach described in (i) is widely used in III-V research and is known as the proximity geometry. The approach described in (ii) is widely used in industry for annealing processes for GaAs and to a lesser extent InP.

It would be convenient for GaN device processing if development of a similar process for rapid thermal processing of III-nitrides, in which an overpressure of $N_2$ is supplied to a susceptor. In this section we compare use of powdered AlN or InN as materials for use in the susceptor reservoirs, and compare the results with those obtained with simple proximity annealing.

The GaN, AlN, InN, InGaN and InAlN samples were grown using metal organic molecular beam epitaxy on semi-insulating, (100) GaAs substrates or $Al_2O_3$ c-plane substrates in an Intevac Gen II system as described previously.\textsuperscript{76,77} The group-III sources were triethylgallium, trimethylamine alane and trimethylindium, respectively, and the atomic nitrogen was derived from an electron cyclotron resonance Wavemat source operating at 200 W forward
power. The layers were single crystal with a high density \(10^{11}-10^{12} \text{ cm}^{-2}\) of stacking faults and microtwins. The GaN and AlN were resistive as-grown, and the InN was highly autodoped n-type \(^{>10^{20}}\text{cm}^{-3}\) due to the presence of native defects. InAlN and InGaN were found to contain both hexagonal and cubic forms. The In\(_{0.75}\)Al\(_{0.25}\)N and In\(_{0.5}\)Ga\(_{0.5}\)N were conducting n-type as grown \(^{\sim}10^{10} \text{cm}^{-3}\) due to residual autodoping by native defects.

The samples were annealed either (i) face down on samples of the same type, i.e. GaN when annealing GaN, InN for InN, etc., or (ii) within a SiC-coated graphite susceptor in which the reservoirs were filled with either powdered AlN or InN (average particle size \(\sim 10 \mu\text{m}\)).\(^{(11)}\)

Annealing was performed for 10 sec at peak temperatures between 650 and 1100\(^{o}\)C in flowing \(\text{N}_2\) gas. The sheet resistance was measured at room temperature on a van der Pauw Hall system with \(\text{InHg}\) alloyed contacts \(400^{o}\text{C}, 3 \text{ min}\) on the corners. An atomic force microscope (AFM), operated in tapping mode with Si tips, was used to measure the root mean square (rms) roughness of the samples. The surface morphology was examined with a scanning electron microscope (SEM). Energy dispersive x-ray spectroscopy (EDAX) was used to analyze the surface composition of some samples. Auger electron spectroscopy (AES) was used to investigate near-surface stoichiometry before and after anneal.

The rms surface roughness of binary nitrides measured by AFM after annealing face down in the proximity geometry is shown at the top of Figure 13. The InN begins to degrade above 500\(^{o}\)C, while AlN roughness at 1000\(^{o}\)C at the surface is as smooth as the as-grown material. The GaN remains smooth across the entire annealing range investigated. Similar results are shown for the ternaries at the bottom of Figure 13. The InAlN morphology degrades above 800\(^{o}\)C, and In droplets are visible on the surface by 900\(^{o}\)C. At 1000\(^{o}\)C, however, the In
droplets also evaporate, leading to an apparently better morphology as measured by AFM. The InGaN had fairly similar behavior.

A comparison of the annealing temperature dependence of nitride rms surface roughness for sample processed in the graphite susceptor with either AlN or InN powder in the reservoirs is shown in Figure 14. One would expect the InN powder to provide higher vapor pressure of N\textsubscript{2} at equivalent temperatures than AlN\textsuperscript{(129)} and this appears to be evident in the rms data for InN, where the surface roughens dramatically above 600°C with AlN powder while the roughening is less obvious with InN powder. The data in Figure 14 needs to be considered in the light of the results from the other materials. For example, the GaN and AlN rms values are consistently higher for the InN powder annealing. These results clearly indicate large-scale (~1 μm) roughness evident on the samples annealed with the InN powder. Similar results were evident for the AlN and InAlN samples, with large-scale roughness detectable by AFM on the ones annealed with the InN powder.

SEM examination of all the samples revealed the cause of this roughening. After 1000°C annealing with AlN powder there is no change in morphology from the control samples. By sharp contrast, metallic droplets are visible on samples annealed with InN powder even at 800°C. Similar droplets were observed in all materials after annealing with InN powder at ≥750°C. EDAX measurements identified these droplets as In in each case. Therefore, it is clear that the InN powder initially provides good surface protection for annealing temperatures ≥750°C through incongruent evaporation of N\textsubscript{2}. Above this temperature however, evaporation of In from the powder leads to condensation of droplets on the samples contained within the reservoir. At temperatures approaching 1100°C, these droplets evaporate from the surface of GaN or AlN, leading to an apparent surface smoothing when measured by AFM.
Some other features of the annealing are salient with respect to implant activation processes. First, if we employed 90% N$_2$;10% H$_2$ as the purge gas in the rapid thermal annealing (RTA) system instead of pure N$_2$, we noticed that the temperature at which surface dissociation was evident by either AFM or SEM was lowered by 100-200°C for each of the nitrides. A similar effect was observed if O$_2$ was present in the annealing ambient, and thus, it is critical to avoid residual O$_2$ or H$_2$ in RTA systems during annealing of the nitrides. Second, under optimized ambient conditions (pure N$_2$ purge gas, and use of either the proximity geometry or powdered AlN in the susceptor reservoirs), AES was able to detect N$_2$ loss from the surface of GaN even after 1000°C anneals, and from InAlN and InGaN after 800°C anneals. However, N$_2$ loss from AlN was detectable only after anneals at 1150°C, emphasizing the extremely good thermal stability of this material. Indeed Zolper et al. have recently reported use of sputtered AlN as an encapsulant for annealing GaN at temperatures up to 1100°C for Si$^+$ or Mg$^+$ ion implant activation. The AlN could be selectively removed with KOH solutions after the annealing process.

The loss of N$_2$ from binary nitride surfaces during annealing produced thin (<0.5 μm as determined by subsequent dry etching and remeasured) highly conducting n$^+$ regions. These were evident for annealing temperatures above 600°C in InN and at 1125°C in GaN. For example, the sheet resistance increased by 2-4 orders of magnitude in both materials. This agrees with the theoretical prediction of Maruska and Tiejen that N vacancies create a shallow donor state in binary nitrides, and the temperatures to which the materials are stable are in general agreement with the published vapor pressure and melting point data for the binary nitrides. In the ternary materials, however, the sheet resistance of the epitaxial layers increased with annealing temperature, suggesting that simple nitrogen vacancies are not the
cause of the residual n-type conductivity in these samples, since at the highest temperatures there is clear loss of nitrogen. The annealing, in this case, appears to create compensating acceptors, or else annealing of the native donors is occurring. The nature of the defects present in as-grown and annealed nitrides is currently under investigation with IR absorption and variable temperature Hall measurements.

In summary, several approaches to rapid thermal processing of binary and ternary nitrides have been investigated. In the proximity geometry AlN and GaN retain smooth stoichiometric surfaces to ≥1000°C, InAlN and InGaN to 800°Cm and InN up to 600°C. Similar thermal stabilities were obtained for face-up annealing in graphite susceptors in which AlN powder provides a N₂ overpressure. An attempt to increase this overpressure through use of InN powder was unsuccessful because of In droplet condensation on all samples at temperatures ≥750°C. This could only be rectified if one could design a two-zone rapid thermal processing chamber in which a reservoir of InN powder was maintained at ≤750°C, while the samples to be annealed were separately heated to their required temperatures.

(ii) Ultra-High Temperature Annealing

Recent interest in developing advanced electronic devices that operate at high temperature and/or high power has brought into focus many new challenges for semiconductor materials and the related processing technology. Compound semiconductors such as SiC and GaN have significant advantages for such device applications because of their wider bandgaps (higher operating temperature), larger breakdown fields (higher operating voltage), higher electron saturated drift velocity (higher operating current), and better thermal conductivity (higher power density). Some of the examples of SiC and GaN-based electronic devices are the SiC power MOSFET and the GaN junction field effect transistor (JFET). In the
development of advanced electronic devices, the technology of rapid thermal processing (RTP) plays a critical role at numerous points such as implant activation of dopant species, implantation-induced damage removal, alloying of ohmic contacts, maximization of sheet resistance in implant isolation regions, etc. High annealing temperature and short processing time have been identified as two key requirements in RTP annealing of compound semiconductors such as GaN and SiC, especially for implant activation and damage removal.\(^\text{123}\)

It has been found in high dose Si-implanted GaN that, although Si donors can be efficiently activated at 1100°C, complete removal of ion implantation-induced damage requires even higher annealing temperatures.\(^\text{124}\) A more recent study has shown that implantation-induced damage in GaN can only be significantly reduced by using annealing temperatures up to 1400°C.\(^\text{125}\)

The existing commercial RTP equipment typically relies on a series of tungsten-halogen lamps as heat sources to rapidly heat up the semiconductor wafers.\(^\text{126}\) However, this type of lamp-based RTP system suffers from many problems such as point heat source, fluctuating lamp temperature during processing and only modest temperature capacity (<1100°C). Recent interest in developing wide bandgap compound semiconductors has pushed the processing temperature requirements to much higher values (up to 1500°C). Presently, there are no specific RTP systems that can operate at such high temperatures. In the study of annealing of GaN up to 1400°C\(^\text{127}\), a custom system (based on MOCVD system) that employed RF-heating was built and utilized. Thus, there is an urgent need in compound semiconductor processing, particularly in GaN and SiC technology, to develop new RTP systems which can provide uniform heating to very high temperatures (>1500°C).

To meet such an urgent need, Micropyretics Heaters International (MHI) Inc., in collaboration with the University of Florida, has recently developed a unique high temperature
RTP unit called Zapper™. This novel RTP unit has been specifically designed to achieve very high uniform temperatures (>1500°C) and is thus especially useful for high temperature thermal processing of semiconductor materials. In this section, we first give a brief introduction about the Zapper™ unit. We then report the implant activation annealing studies of Si⁺-implanted GaN thin films (with and without an AlN encapsulation layer) using the Zapper™ unit at temperatures up to 1500°C. The electrical analysis and characterization results of such annealed samples are presented and discussed. Based on these experiments, the significant potential of the MHI Zapper™ unit in the development of advanced electronics is summarized.

Most existing RTP equipment utilized either an array of ten or more tungsten-halogen lamps, or a single arc lamp as heat sources.¹²⁶ These lamp-based RTP equipment can achieve only modest processing temperatures (<1100°C), primarily because of the point-like sources and large thermal mass of the systems. To realize higher temperature capacity, new types of heat sources have to be employed. In the past few years, MHI Inc. has developed and patented a series of novel molybdenum intermetallic composite heaters that may be used in air at temperatures up to 1900°C.¹²⁷¹²⁸ These heaters have high emissivity (up to 0.9) and allow heat up time of the order of seconds and heat fluxes up to 100 W/cm². Using proprietary fabrication technology the heaters can be made into various sizes and shapes. After extensive research on the existing RTP systems and based on the availability of such high temperature heaters, we have designed and constructed a novel furnace-based RTP unit called Zapper™. This novel RTP unit is capable of achieving much high temperatures than the lamp-based RTP equipment. Figure 15 shows some typical time-temperature fluctuation to rapidly heat up and cool down the wafer, the Zapper™ unit relies on wafer movement (in/out of furnace horizontally) to achieve rapid ramp-up and ramp-down rates. The motor-driven actuator, which controls the sample
moving in/out speed and dwell time in the furnace, features up to 10 programs in memory. Each program can do an unlimited number of steps, time delays and repetitions. The maximum moving speed and dwell time in the furnace, features up to 10 programs in memory. Each program can do an unlimited number of steps, time delays and repetitions. The maximum moving speed that can be attained is 10 in·s⁻¹. The wafer susceptor is made of quartz that is primarily transparent to the incident radiation and thus has low thermal mass. The wafer can be processed either in a vacuum or sealed ambient environment. A unique electronics system that enables the Zapper™ to perform from simple to complicated annealing treatments has also been developed. The process controller is capable of up to 20 programs with 16 segments per program. Each program recipe can give designated ramp up and ramp down rates. Communications option is also available for connecting to PLC, PC software.

A variety of undoped GaN layers ~3 μm thick were grown at ~1050°C by Metal Organic Chemical Vapor Deposition using trimethylgallium and ammonia. Growth was preceded by deposition of thin (~200Å) GaN or AlN buffers on the Al₂O₃ substrates. Capacitance-voltage measurements on the GaN showed typical n-type background carrier concentrations of ≤ 3x10¹⁶ cm⁻³. Si⁺ was implanted to a dose of 5x10¹⁵ cm⁻², 100 keV, producing a maximum Si concentration of ~6x10²⁰ cm⁻³ at a depth of ~800Å. Some of the samples were encapsulated with 1000-1500Å of AlN deposited in one of two ways. In the first, AlN was deposited by reactive sputtering of pure AlN targets in 300 mTorr of 20% N₂ Ar. The deposition temperature was 400°C. In the second method, AlN was grown by Metal Organic Molecular Beam Epitaxy (MOMBE) at 750°C using dimethylamine alane and plasma dissociated nitrogen.(77)

The samples were sealed in quartz ampoules under N₂ gas. To ensure good purity of this ambient the quartz tube (with sample inside and one end pre-doped) was subjected to an
evacuation/N₂ purge cycle for 3 repetitions before the other end of the tube was closed, producing a final N₂ pressure of ~15 psi. This negative pressure was necessary to prevent blowout of the ampoule at elevated annealing temperatures. The samples were then annealed at 1100-1500°C, for a dwell time of ~10 sec (Figure 15). The time difference for reaching the annealing temperature between 4-6 seconds. To compensate for this heating time lag inside the ampoule, the dwell time was purposely extended to ~15 seconds. Ramp rates were 80°C·s⁻¹ from 25-1000°C and 30°C·s⁻¹ from 1000-1500°C, producing an average ramp-up rate over the entire cycle of ~50°C·s⁻¹. The typical ramp-down rate was ~25°C·s⁻¹. Measurements of temperature uniformity over a typical wafer size were ±8°C at both 1400 and 1500°C. After removal of the samples from the ampoules they were examined by scanning electron microscopy (SEM), atomic force microscopy (AFM) and van der Pauw geometry Hall measurements obtained with alloyed HgIn eutectic.

SEM micrographs of unencapsulated GaN surfaces annealed at 1200°C, 1300°C, 1400°C or 1500°C showed that the 1200°C annealing does not degrade the surface, and the samples retain the same appearance as the as-grown material. After 1300°C annealing, there is a high density (~10⁸ cm⁻²) of small hexagonal pits due to incongruent evaporation from the surface. The 1400°C annealing produces complete dissociation of the GaN, and only the underlying AlN buffer survives. Annealing at 1500°C also causes loss of this buffer layer, and a smooth exposed Al₂O₃ surface is evident.

By sharp contrast to the results for GaN, both the sputtered and MOMBE AlN were found to survive annealing above 1300°C. For the sputtered material we often observed localized failure of the film, perhaps due to residual gas agglomeration. For the MOMBE films this phenomenon was absent. Also in the sputtered material the root-mean-square (RMS) surface
roughness tended to go through a maximum, due to some initial localized bubbling, followed by the film densification.

The clear result from all this data is that the implanted GaN needs to be encapsulated with AlN in order to preserve the surface quality. We have previously shown that AlN is selectively removable from GaN using KOH-based solution. Figure 16 shows the sheet carrier concentration and electron mobility in the Si⁺-implanted GaN, for both unencapsulated and AlN-encapsulated material, as a function of annealing temperature. For unencapsulated annealing we see an initial increase in electron concentration, but above 1300°C the GaN layer blows-off. By contrast, for AlN-encapsulated samples the Si⁺ implant activation percentage is higher (~90%) and peaks around 1400°C. This corresponds to a peak carrier concentration of ≥5x10²⁰ cm⁻³. For 1500°C annealing both carrier concentration and mobility decrease, and this is consistent with Si-site switching as observed in Si⁺-implanted GaAs at much lower temperatures. The results in Figure 16 are convincing evidence of the need for high annealing temperatures and the concurrent requirement for effective surface protection of the GaN.

There is clear evidence from both ion channeling and TEM measurements that temperatures above 1300°C are required to completely remove implantation damage in GaN. Since the residual damage tends to produce n-type conductivity, it is even more imperative in acceptor-implanted material to completely remove its influence. However a premium is placed on prevention of surface dissociation, because loss of nitrogen also leads to residual n-type conductivity in GaN. The combination of RTP annealing in the Zapper™ unit at 1400-1500°C and high quality AlN encapsulants produce metallic doping levels (~5x10³⁰ cm⁻³) in Si⁺-implanted GaN.
The Zapper™ unit is clearly capable of achieving much higher temperatures than conventional tungsten-halogen lamp-based RTP equipment, and displays excellent time-temperature responses. Presently the Zapper™ unit has shown significant potential for high temperature annealing of compound semiconductors and should play a major role in the development of advanced electronic devices.

(iii) Dopant Activation

The best example of how ion implantation can directly impact the performance of group III-nitride transistors is illustrated in Figure 17. The figure shows four device structures that could be employed to fabricate AlGaN/GaN high electron mobility transistors (HEMTs). To date, the majority of the AlGaN/GaN HEMT's transistors have been fabricated in a planar structure as shown in Figure 17a, where the ohmic source and drain contacts are placed directly on the wide bandgap AlGaN layer without any increased local doping to reduce the contact or access resistance.\(^{131}\) This leads to a high access resistance, reduced current capability, and a high transistor knee voltage. This in turn reduces the transistors power gain, power added efficiency, and linearity.\(^{132}\) Figure 17b and 17c show two approaches that have been taken to reduce the access resistance. One is to selectively etch away the wide bandgap material in the contact regions and then regrow highly doped GaN to improved access resistance was realized; however, the manufacturability of this approach is questionable.\(^{133}\) The recess gate approach of Figure 17c has been widely used in other mature compound semiconductors such as GaAs and InP. Although this type of structure has been demonstrated in GaN-based devices, the unavailability of controlled wet etching of GaN requires the use of a plasma recess etch.\(^{134}\) Use of a plasma etch introduces surface damage in the semiconductor in the region under Schottky gate that degrades the rectifying properties of the gate. Finally, the self-aligned ion implanted
structure of Figure 17d is used to create selective areas of highly doped regions for the source and drain contacts in a highly manufacturable fashion without any plasma etching of the gate region. To date, ion implantation has been used to realize a GaN junction field effect transistor (JFET) but has not been applied to AlGaN/GaN HEMTs.\textsuperscript{135} As will be discussed later, one of the key challenges to applying ion implantation to AlGaN/GaN HEMTs is the avoidance of surface degradation that will negatively impact the Schottky gate formation during the high temperature implant activation anneal.

The first work on implantation in GaN was performed by Pankove and coworkers in the earlier 1970's.\textsuperscript{136,137} They reported primarily on the photoluminescence properties of a large array of implanted impurities in GaN. The work was successful in identifying Mg as the shallowest acceptor found to date for GaN.

In 1995 Pearton et al., reported the first successful use of ion implantation to realize electrically active n- and p-type dopants in GaN.\textsuperscript{138} In that work, Si was used as the n-type dopant and Mg, with a co-implantation of P, was used to achieve p-type doping. Rapid thermal annealing (RTA) at 1100°C was employed for the activation anneal. Subsequently, implanted O was shown to also be a donor and implanted Ca an acceptor in GaN.\textsuperscript{139} While Mg demonstrated some degree of diffusion during these annealing conditions, all other impurities (Be, C, Zn, Ca, Si and O) showed no measurable diffusion.\textsuperscript{140}

Details of ion implanted isolation using either H, He or N have also been established. The damage created by H-implantation was shown to anneal out near 400°C while He and N isolation damage remained intact to ~800°C.\textsuperscript{141} From this work followed the fabrication and performance of the first ion implanted JFET fabricated in GaN.\textsuperscript{134}
To fully apply ion implantation technology to GaN-based electronics, both Schottky and ohmic contacts must be readily fabricated on the semiconductor following the implantation and activation process. For example, for an all ion implanted GaN Metal Semiconductor Field Effect Transistor (MESFET) to be achieved, a Schottky gate contact must be formed on the implanted channel regions after the activation anneal. When performing the implant activation anneal, the GaN surface can dissociate by the loss of N. Some of the work on the equilibrium pressure of N over GaN has been reviewed by Ambacher(142) and Porowski.(112) As with other compound semiconductors, two approaches have been investigated to preserve the surface during the thermal processing: 1) dielectric encapsulation or 2) local overpressure of N.

Since the activation anneal for GaN was initially done in the range of 1100°C(138,139), the formation of a Pt/Au Schottky contact on n-type GaN was studied after such a high temperature anneal with and without a AlN encapsulation layer.(114) Since AlN has a higher dissociation temperature it should act to suppress the dissociation of the GaN. One set of samples was n-type as-grown with a background donor concentration of ~5-10x10¹⁶ cm⁻³ (samples A1, A2). The second set of samples (B1, B2) was semi-insulating as-grown and was implanted with ²⁸Si (100 keV, 5x10¹³ cm⁻²) to simulate a MESFET channel implant. One sample from each set had 120 nm of AlN deposited in an Ar-plasma at 300 W using an Al-target and a 10 sccm flow of N₂. The film had an index of 2.1±0.05. All samples were annealed together in a SiC coated graphite crucible at 1100°C for 15 sec in flowing N₂. Following annealing, the AlN was removed in a selective KOH-based etch (AZ400K developer) at 60-70°C. This etch has been shown to etch AlN at rates of 60 to 10,000 Å/min, depending on the film quality, while under the same conditions no measurable etching of GaN was observed. Ti/Al ohmic contacts were deposited and defined by conventional lift-off techniques on all samples and annealed at 500°C for 15 sec.
Pt/Au Schottky contacts were deposited and defined by lift-off within a circular opening in the ohmic metal. Electrical characterization was performed on a HP4145 at room temperature on 48 \( \mu \)m diameter diodes. Samples prepared in the same way, except without any metallization, were analyzed with Auger Electron Spectrometry (AES) surface and depth profiles. The surface morphology was also characterized by atomic force microscopy (AFM) before and after annealing.

Figure 18 shows three dimensional AFM images of the surface of samples Al (uncapped) and A2 (AlN cap) after annealing at 1100°C. While both of the annealed samples displayed some increase in their root-mean-square (RMS) surface roughness (Al:4.02 nm, A2: 2.51 nm) over the as-grown sample (1.4 nm) the sample annealed without the AlN cap (A1) was markedly rougher with a dramatically different surface morphology. These differences were attributed to more N-loss in the uncapped sample as will be discussed later.

Figure 19 shows the reverse current/voltage characteristics of the Pt/Au Schottky diodes for the four samples studied. Samples Al and Bl, annealed without the AlN cap, demonstrated very leaky reverse characteristics with roughly a 3 to 4 order-of-magnitude increase in leakage current over the samples annealed with the AlN cap. In fact, sample Al approached Ohmic behavior. Samples A2 and B2, on the other hand, demonstrated very good rectification with reverse breakdown voltages in excess of 40 V where the breakdown voltage is taken at 1 \( \mu \)A/\( \mu \)m of diode perimeter current. Figure 20 shows the current/voltage characteristics for adjacent Ti/Al ohmic contacts for the two unintentionally doped samples Al and A2. In this case, the samples annealed without the AlN cap demonstrated improved ohmic behavior as compared to the samples annealed with the AlN cap. This is consistent with the Schottky characteristics and
suggests a change in the near surface stoichiometry of the GaN resulting from the uncapped anneal as discussed below.

In an attempt to quantify the change in the GaN surface resulting from annealing with and without the AlN cap, AES surface and depth profiles were performed. When comparing the Ga/N ratio for each case an increase was seen for the sample annealed without the AlN cap (Ga/N ration=2.34) as compared to the as-grown sample (Ga/N ratio=1.73). This was explained by N-loss from the GaN during the annealing process. AES depth profiles of the uncapped and annealed sample suggests that the N-loss occurred in the very near surface region (~50Å).

N-loss and the formation of N-vacancies was proposed as the key mechanism involved in changing the electrical properties of the Schottky diodes and ohmic contacts. Since N-vacancies are thought to contribute to the background n-type conductivity in GaN, an excess of N-vacancies at the surface should result in an \( n^+ \)-region (possibly a degenerate region) at the surface. This region would then contribute to tunnelling under reverse bias for the Schottky diodes and explain the increase in the reverse leakage in the uncapped samples. Similarly, a \( n^+ \)-region at the surface would improve the ohmic contact behavior as seen for the uncapped samples. The effectiveness of the AlN cap during the anneal to suppress N-loss is readily understood by the inert nature of AlN and its extreme thermal stability thereby acting as an effective diffusion barrier for N from the GaN substrate.

In summary, the viability of using reactively sputtered AlN films as an encapsulating layer for GaN during 1100°C annealing was demonstrated. The AlN cap was selectively removed in a KOH-based etch. By employing an AlN cap, Pt/Au Schottky barriers with reverse breakdown voltages in excess of 40 V were realized on samples annealed at 1100°C. Samples annealed uncapped under the same conditions have 3 to 4 orders-of-magnitude higher reverse
leakage than the capped samples while also displaying improved ohmic contact performance. These results are explained by the formation of a n⁺-layer at the surface created by N-loss and N-vacancy formation in the uncapped samples. The AlN encapsulation, on the other hand, effectively suppressed N-loss from the GaN substrate. The use of AlN capping should allow the realization of all ion implanted GaN MESFETs.

Previous work on damage accumulation during implantation had been limited to Si-implanted GaN at 77 K or room temperature. That work demonstrated that the amorphization dose for ~100 keV Si-implantation was ~2x10¹⁶ cm⁻². Recent work has addressed the damage accumulating during Ca, Ar and In implants in GaN at 77 K (Ca and Ar) and room temperature (In). Additional work has also been reported from the damage annealing characteristics for high dose Si-implantation. Figure 21 shows the change in the RBS minimum channeling yield (χₘₘ) versus dose for Ca and Ar implanted GaN at 77 K. The amorphization dose (χₘₘ=100%) is 6x10¹⁵ cm⁻² for both elements. As expected, this dose is lower than that reported for Si-implanted GaN of 2x10¹⁶ cm⁻² due to the higher mass of Ca and Ar as compared to Si. In the same study, it was determined that for a Ca-dose as low as 3x10¹⁴ cm⁻² an amorphous component to the x-ray diffraction spectra is created (see Figure 22). This suggests that local pockets of amorphous material are formed prior to the complete amorphization of the implanted region. Further study of the removal of such an amorphous material during annealing will be important to optimizing the annealing process.

The In-implantation study examined the local lattice environment after implantation and subsequent annealing using the emission channeling technique and perturbed-γ-angular-correlation. Ronning and coworkers found that the majority of the In atoms were substitutional as-implanted but within a heavily defective lattice. A gradual recovery of the
damage was seen between 600 and 900°C with about 50% of the In atoms occupying substitutional lattice sites with defect free surroundings after to 900°C anneal. Results for higher temperature annealing were not reported. It remains to be determined at what point complete lattice recovery is achieved as determined by this technique.

Additional work on Si-implantation had demonstrated significant implantation-induced damage remains in GaN ever after a 1100°C activation anneal that produces electrically active donors.\textsuperscript{149,150} This is shown the RBS spectra of Figure 23 and the Cross Sectional Transmission Electron Microscopy (XTEM) images of Figure 24. The RBS spectra shows that even after a 1100°C anneal the high channeling yield is evidence of significant damage in the crystal. This is confirmed by the XTEM images before and after annealing of Figure 24 where, despite some coarsening of the damage, no significant reduction in the damage concentration has occurred. In the following section, work on complete removal of the implantation damage by annealing up to 1500°C is presented.

As discussed in the previous section, an annealing temperature well above 1100°C is needed to remove the implantation-induced damage in GaN. However, since GaN will readily dissociate at these temperatures, special precautions must be taken. The approaches used to maintain the GaN stoichiometry at up to 1500°C were either to use an encapsulating overlayer such as the AlN described above or to perform the anneal under a high N-overpressure. Results from both approaches are presented below. Both electrical and structural data are presented to correlate the effect of the removal of implantation-induced damage to electrical activation of implanted Si donors.

To better understand the removal of implantation-induced damage, annealing experiments were performed in an MOCVD growth reactor capable for reaching 1400°C. While
the anneal was performed in flowing ammonia to help stabilize the surface against decomposition, AlN encapsulation was also studied to further suppress N-loss. The first set of samples was encapsulated with 120 nm of sputter deposited AlN. Si-implantation was performed through the AlN at an energy of 210 keV and a dose of $5 \times 10^{15} \text{cm}^{-2}$. The results of Monte Carlo TRIM calculations, shown in Figure 25a, predict that $\sim 7\%$ of the Si-ions come to rest in the AlN film with a dose of $4.6 \times 10^{15} \text{cm}^{-2}$ being placed in the GaN. The Si peak range from the GaN surface is estimated to be 80 nm. The second set of samples was unencapsulated and implanted with Si at an energy of 100 keV and dose of $5 \times 10^{15} \text{cm}^{-2}$. This also gives a range from the GaN surface of 80 nm as shown in Figure 25b. A sample from each set was annealed under one of four conditions as shown in Table II. One pair of samples was annealed in a rapid thermal annealer (RTA) inside a SiC coated graphite susceptor and processed in flowing N$_2$ since this procedure was used previously to activate implanted Si in GaN. The remaining samples were annealed in a custom built metal organic chemical vapor deposition (MOCVD) system that employed rf-heating with the samples placed on a molybdenum holder on a SiC coated graphite susceptor. The stated temperatures were measured with an Accufiber Model-10 or a Minolta Cyclota-52 pyrometer which were calibrated by the melting point of Ge at 934°C. The pressure in the MOCVD reactor was 630 mTorr with gas flows of 4 slm of N$_2$ and 3 slm of NH$_3$. The encapsulated and unencapsulated sample for a given temperature were annealed together.

Figures 26a and 26b shows the sheet electron concentration and electron Hall mobility versus the annealing conditions for the unencapsulated and AlN encapsulated samples, respectively. An unimplanted sample annealed at 1100°C for 15 sec in the RTA remained highly resistive with $n < 1 \times 10^{15} \text{cm}^{-2}$ after annealing. The mobility of this undoped film could not be reliably measured with the Hall effect due to the low carrier concentration.
First looking at the data for the unencapsulated samples (Figure 26a), the sample annealed at 1100°C for 15 sec in the RTA has a sheet electron concentration of 6.8x10^{14} \text{cm}^{-2} or 13.6\% of the implanted dose. This activation percentage is in the range reported for earlier Si-implanted GaN samples annealed in this way. After the 1100°C, 30 sec MOCVD anneal, the number of free electrons goes up to 40\% of the implanted dose before decreasing to 24\% for the 1300°C anneal. The decrease for the 1300°C sample was accompanied by a degradation of the surface of the sample as determined by observation under an electron microscope as shown in the SEM micrographs of Figure 27. This point will be revisited when discussing the C-RBS spectra later, but it is believed that the GaN layer has started to decompose during this anneal. Therefore, the reduction in the electron concentration may be due to loss of material. The Hall mobility increased with increasing thermal treatment and is suggestive of improved crystalline quality. No data is given in Figure 26a for the unencapsulated sample annealed at 1400°C since the GaN film completely sublimed or evaporated during this anneal. This was confirmed by C-RBS data for this sample that showed only the substrate Al and O peaks with a slight Ga surface peak.

Now turning to the data for the AlN encapsulated samples (Figure 26b). There is increasing sheet electron density with increasing thermal treatments for the encapsulated samples including the highest temperature anneal. The RTA sample has a lower activity than the comparable unencapsulated sample (3.6\% versus 13.6\%), however, all the other AlN encapsulated samples have higher electron concentrations than the comparable unencapsulated sample. The 1300°C sample has a sheet electron concentration of 5.2x10^{15} \text{cm}^{-2} that is 113\% of the Si dose that should have been retained in the GaN layer (4.6x10^{15} \text{cm}^{-2}). The excess electron concentration may be due to small uncertainties in the Hall measurement due to the non-ideal
contact geometry (i.e. ideal point contacts were not used). The error in the Hall measurement is estimated to be \( \sim 10\% \). The apparent excess electron concentration may also be due to indiffusion of the Si from the AlN encapsulant into the GaN substrate or to the activation of other native donor defects in the GaN layer such as N-vacancies. The sample annealed at 1400°C has a still higher free electron concentration \( (6 \times 10^{15} \text{cm}^{-2}) \) that may also be partly due to measurement errors or to activation of native defects. This sample had visible failures in the AlN layer (cracks and voids) that allowed some degree of decomposition of the GaN layer. This was confirmed by the scanning electron microscope (SEM) micrographs in Figure 28 that show regions of GaN loss. Therefore, the formation of N-vacancies in this sample is very likely and may contribute to the electron concentration. This would also contribute to the observed reduction in the electron mobility. The failure of the AlN film may be due to non-optimum deposition conditions resulting in non-stoichiometric AlN or to evolution of hydrogen from the GaN epitaxial layer that ruptures the AlN during escape. If the failure is due to non-optimum AlN properties, this can be rectified by examining the AlN deposition parameters. If hydrogen evolution is the cause of the failure an anneal \( (\sim 900°C \text{ for 5 min}) \) to drive out the hydrogen prior to AlN deposition should rectify this problem.

Figure 29 shows a compilation of the C-RBS spectra for the unencapsulated samples along with the aligned spectrum for an unimplanted sample. The as-implanted sample shows the damage peak near 100 nm with an additional peak at the surface. The surface peak may be due to preferential sputtering of the surface during Si-implantation and has been reported in earlier implantation studies\( ^{146,154} \). The sample annealed in the RTA has improved channeling and an apparent reduction in the implant damage. It should be noted, however, that the surface peak is also diminished in the RTA sample and it has previously been reported that the change in
the surface peak can account for the apparent reduction in the implantation damage peak.\footnote{154} Upon annealing at higher temperatures or longer times in the MOCVD reactor, the channeling continues to improve and approaches, but does not reach, the unimplanted aligned spectra. The 1300°C sample, however, appeared to show evidence of material loss as demonstrated by the change in position and abruptness of the substrate signal as well as the observation of surface roughing. Therefore, the reduction in the implantation damage peak in this sample may be due to sublimation or evaporation of the implanted region and not recovery of the original crystal structure. The loss of at least part of the Si-implanted region is consistent with the reduction in the free electron concentration in this sample shown in Figure 26a.

Figure 30 shows a compilation of the C-RBS spectra for the AlN encapsulated sample. The as-implanted sample has a damage peak at \(-80\) nm with no additional surface peak as seen in the unencapsulated sample. The lack of surface peak in this samples supports the hypothesis that this peak on the unencapsulated sample is due to preferential sputtering since the GaN surface of the encapsulated sample is protected from sputter loss during implantation. A significant reduction in the implantation-induced damage peak occurs after the RTA anneal with a further reduction with increasing thermal processing.

Table III summarizes the values for the minimum channeling yield \(\chi_{\text{mm}}\) of the GaN layer for the sample studied. The dechanneling for an unimplanted sample was estimated to be 2.5\% and is close to the theoretical limit.\footnote{155} For the AlN encapsulated samples the value of \(\chi_{\text{mm}}\) has had the effect of the AlN overlayer subtracted out based on spectra of unimplanted, unannealed AlN on GaN. The unencapsulated samples show a continuous reduction in \(\chi_{\text{mm}}\) with increasing annealing temperature. This reduction is at least partly due to removal of a surface damage peak as previously discussed.\footnote{154} The \(\chi_{\text{mm}}\) value at 1300°C of 6.7\% may be
anomalously low due to sublimation of the damaged region in this sample (see Figure 27). The 1400°C annealed encapsulated sample shows a significant reduction in $\chi_{\text{min}}$ from the as-implanted value of 38.6% to 12.6%. Since the RBS analysis was performed on regions of the sample with the lowest density of craters, this $\chi_{\text{min}}$ value should be characteristic of the GaN that has not decomposed during the anneal. While the reduction in $\chi_{\text{min}}$ demonstrated partial recovery of the crystal lattice, the original channeling properties were not realized. This suggests still higher temperature anneals may be required. This would be consistent with a 2/3 rule for relating the melting point ($T_{\text{mp}}$) of a semiconductor to the implantation activation temperature ($T_{\text{act}}$) since for GaN $T_{\text{mp}} \sim 2500°C$ and therefore $T_{\text{act}}$ should be $\sim 1650°C$.\(^{135}\) To reach this temperature in a controllable manner will require development of new annealing furnaces. Preferably, such a furnace should operate in a rapid thermal processing mode (i.e. with rapid heating and cooling) to minimize the thermal budget of the anneal process. This will require new equipment designs such as has been reported in the previous section. The following section presents results for annealing up to 1500°C in high N pressure that supports the need for a much higher temperature anneal to restore the crystal lattice.

High pressure, high-temperature annealing was used to study the fundamental limits of implantation induced damage removal in GaN.\(^{156}\) By employing high N-overpressures (up to 15 kbar) sample decomposition is suppressed and the damage removal can be uncompromisingly examined.\(^{157,158}\) Figure 31 shows aligned C-RBS spectra for GaN implanted with 100 keV Si at dose of $5 \times 10^{15}$ cm\(^{-2}\) and annealed under the conditions shown in the legend. Included in the legend in parenthesis is the minimum channeling yield ($\chi_{\text{min}}$) for each sample. An as implanted sample (spectra not shown) had a $\chi_{\text{min}}$ of $\sim 34\%$, therefore significant damage removal has occurred for the 1250°C ($\chi_{\text{min}}=14.28\%$) sample with continuing improvement with increased
temperature. The 1500°C sample has a channeling yield equivalent to an unimplanted sample and demonstrated no macroscopic surface decomposition. This result suggests that implantation damage can in fact be removed in GaN given a high enough annealing temperature.\(^{156}\) The next step will be to find alternative ways, besides the extremely high N-overpressure, to maintain the sample stoichiometry.

The samples of Figure 31 were also characterized by the Hall technique, by photoluminescence, and by secondary ion mass spectroscopy (SIMS). Hall data suggests 46% electric activity of the implanted Si at 1250°C with increasing activity to 88% at 1500°C. However, the SIMS data shows high levels of oxygen in the samples, therefore, the free donor concentration may also have a component due to O which is known to act as donor in GaN.\(^{139,159}\) The source of the O is unclear, however, it may have diffused out from the sapphire substrate or in from the annealing ambient. The Hall mobility of the 1250°C was \(-100\, \text{cm}^2/\text{Vs}\) and is very respectable for such a high donor level (on the order of \(10^{20}\, \text{cm}^{-3}\)). The mobility was roughly constant for the higher annealing temperatures.

The photoluminescence spectra of samples as-grown and after implantation and annealing is shown in Figure 32. The as-implanted samples (not shown) had no appreciable luminescence while the annealed samples had both near bandedge and donor/acceptor-like emission peaks. The 1500°C annealed sample has a stronger bandedge luminescence intensity than the as-grown material by a factor of three. The exact nature of this enhancement is under study, but an enhanced donor/acceptor recombination associated with the Si-doping along with removal of nonradiative centers during the annealing process was postulated.

Additional work on Zn-implantation in GaN by S. Strite and coworkers has also demonstrated the benefits of annealing the implanted samples near 1500°C at high N-pressures to
recover, and even enhance, the overall luminescence.\textsuperscript{(160)} Suski also showed that annealing unimplanted (i.e. as-grown) samples as such a high temperature and pressure can improve the luminescence efficiency of the material.\textsuperscript{(161)} At this point the details of the improvement in luminescence after such annealing is not understood by it may be due to stress relief or to defect annihilation.

While n- and p-type implantation doping of GaN was previously reported with the use of Si and O or n-type and Mg and Ca for p-type, further work was needed to optimize the implantation and annealing process.\textsuperscript{(138,139)} In particular, the limits on achievable doping levels via ion implantation are of interest. Along these lines, the dose dependence of damage formation in Si-implanted GaN at 90 keV and 77 K has been reported as discussed above.\textsuperscript{(146,154)} In that study, GaN was shown to have a Si-dose threshold for amorphization at 77 K of $\sim 2 \times 10^{16}$ cm$^{-2}$ that is much larger than the amorphization dose for GaAs ($4 \times 10^{13}$ cm$^{-2}$) but closer to the level for AlAs ($\sim 8 \times 10^{15}$ cm$^{-2}$) at this temperature. Since for other compound semiconductors the upper limit on the practical implantation dose is generally determined by the onset of amorphization and the impurity solubility level, this result suggested that very high implantation doses, and therefore high doping levels, may be possible via implantation in GaN.

The electrical properties of Si-implanted GaN up to doses of $1 \times 10^{16}$ cm$^{-2}$ were investigated to ascertain the dose dependence of electrical activation on implantation dose. Implantation of Ar, which should be a neutral impurity in GaN, was also studied to better understand the electrical nature of the implantation-induced damage.\textsuperscript{(149)}

Si-ions were implanted at 100 keV at doses from $5 \times 10^{13}$ cm$^{-2}$ to $1 \times 10^{16}$ cm$^{-2}$. Ar-ions were implanted at 140 keV and over the same dose range to place its peak range at the equivalent position as the Si. All samples were annealed at 1100$^\circ$C for 15 sec in flowing N$_2$ with the
samples in a SiC-coated graphite susceptor. This annealing sequence has previously been shown
to activate implanted dopants in GaN\textsuperscript{(138,139)}, although it was found to completely restore the
crystal lattice.\textsuperscript{(149)} Following annealing the samples were electrically characterized at room
temperature by the Hall technique with evaporated Ti/Au ohmic contacts at the corners of each
sample.

Figure 33 shows the room temperature sheet carrier concentrations versus implant dose
for the Si- and Ar-implanted samples after the 1100°C anneal. For the Si-implanted samples,
there appears to be no significant donor activation until a dose of 5\times10^{15}\text{cm}^{-2} is achieved. This is
in contrast to earlier results at a dose of 5\times10^{14}\text{cm}^{-2} where roughly 10% of the implanted Si-ions
were ionized at room temperature, corresponding to 94% of the implanted Si forming active
donors on the Ga-sublattice assuming a Si-donor ionization energy of 62 meV.\textsuperscript{(138)} The absence
of free electrons for the lower dose Si-implanted samples in this study may have been due to
compensation by background carbon in the as-grown GaN, as was postulated to exist based on
the photoluminescence spectra. For the two highest dose Si-implanted samples (5 and
10\times10^{15}\text{cm}^{-2}) 35% and 50%, respectively, of the implanted Si-ions created ionized donors at
room temperature. The possibility that implant damage alone was generating the free electrons
can be ruled out by comparing the Ar-implanted samples at the same dose with the Si-implanted
samples which had over a factor of 100 times more free electrons. If the implantation damage
were responsible for the carrier generation or for enhanced conduction by a hopping mechanism
then the Ar-implanted samples, which would have more damage than the Si-implanted samples
as a result of Ar's heavier mass, would have demonstrated at least as high a concentration of free
electrons as the Si-implanted samples. Since this is not the case, implant damage can not be the
cause of the enhanced conduction and the implanted Si must be activated as donors. The
significant activation of the implanted Si in the high-dose samples and not the lower-dose samples is explained by the need for the Si-concentration to exceed the background carbon concentration that was thought to be compensating the lower-dose Si-samples.

Recent work has shown that implanted Si is almost 100% substitutional on the Ga-site for doses up to at least $7 \times 10^{14} \text{cm}^{-2}$ and annealing at $1100^\circ \text{C}$.\(^{163}\) The lattice location was determined by a combination of ion channeling, particle-induced x-ray emission and nuclear reaction analysis. This directly ties the observed n-type conductivity to incorporation of Si donors in the GaN lattice.

In summary, although low dose samples do not show Si activation, possibly due to a background carbon level in the sample, a Si-dose of $1 \times 10^{16} \text{cm}^{-2}$ demonstrated 50% activation. The possibility that implantation damage alone is responsible for the enhanced conductivity was discounted by comparing the Si-implanted samples to Ar-implanted samples.

Er-implantation is an additional area of research related to GaN. The introduction of Er into a host III-V semiconductor is of interest as a potential source of optical emission at 1.54 μm for use in telecommunications via optical fiber links.\(^{163}\) The optical emission is a result of the Er$^{3+}$ atomic transition, in the presence of the local semiconductor field, that has the required energy level. This is the transition presently used in Er-doped fiber amplifiers (EDFA).\(^{164-166}\) If this transition can be efficiently activated within a semiconductor laser cavity, this would produce an effective source for optical fiber communications at 1.54 μm.\(^{163}\)

One of the first reports of the luminescence properties of Er-implanted GaN was by Wilson, et al.\(^{167}\), with subsequent confirmation of the results by Qin, et al.\(^{168}\) The Er was implanted along with O which has been shown to enhance the Er luminescence intensity in other semiconductors. The enhancement by O (or F) co-doping has been attributed to the impurity
atoms forming ligands with the Er atoms and converting the local bonds into a more ionic state.\textsuperscript{169-171} The Er-implanted GaN was annealed between 650 and 700°C and the luminescence spectrum shown in Figure 34 with many of the characteristic Er-emission lines was achieved under optical excitation using an Ar-ion laser at a wavelength of 457.9 nm.\textsuperscript{167} In addition, the luminescence intensity was nearly as strong at room temperature as at 77 K. This in contrast to reports of thermal quenching of the Er-emission at room temperature in narrower bandgap semiconductors. It is this suppression of the temperature dependence of the Er\textsuperscript{3+} luminescence in GaN that makes this wide bandgap host so attractive for this application.\textsuperscript{163}

The work by Qiu, et al., compared Er/O implanted GaN to similarly implanted sapphire and found only a 5% reduction in the Er-related emission between 6 and 380 K compared to an 18% reduction for the sapphire. In that study the samples were implanted at Er dose of 1 or 10x10\textsuperscript{14} cm\textsuperscript{-2} (O dose of 1x10\textsuperscript{16} cm\textsuperscript{-2}) and annealed at 900°C for 30 to 60 min in flowing NH\textsubscript{3}.\textsuperscript{168} The work confirmed the results of Wilson that Er-doped GaN maintained most of its low temperature luminescence at room temperature.\textsuperscript{167,168}

Since both of these studies used implant activation annealing temperatures of \textless 900°C, significant implantation-induced damage will still exist in the samples and degrade the luminescence efficiency. When more optimum, higher temperature annealing is applied to this technology, significant improvement in the 1.54 \mu m luminescence should result.

AlGaN layers will be employed in heterostructure transistors to realize a two dimensional electron gas (2-DEG) and to increase the transistor breakdown voltage. As discussed in the introduction, implantation can be used to reduce the transistor access resistance of the AlGaN barrier. One would anticipate that the addition of Al to the GaN matrix will increase the damage
threshold as is the case for AlGaAs as compared to GaAs, but little work has been reported in this area. Recently the first implantation doping studies have been reported for AlGaN.

For the work by Zolper, et al., the AlGaN layer used for the Si-implantation was nominally 1.0 µm thick grown on a c-plane sapphire substrate. The Al-composition was estimated to be 15% based on x-ray and photoluminescence measurements. The as-grown minimum backscattering yield measured by channeling Rutherford Backscattering was 2.0% and is comparable to a high quality GaN layer.

The AlGaN samples were implanted with Si at room temperature at an energy of 100 keV at one of two doses, 1 or 5x10¹⁵ cm⁻². The higher Si-dose has previously been shown not to amorphize GaN and produce an as-implanted channeling yield of 34% in GaN.

Samples were characterized by channeling Rutherford Backscattering (C-RBS) with a 2 meV beam with a spot size of 1 mm² at an incident angle of 155°. Aligned spectra are taken with the beam parallel to the c-axis of the GaN film. Random spectra are the average of five off-axis, off-planar orientations. Electrical characterization was done by the Hall technique at room temperature.

Figure 35 shows the sheet electron concentration and electron Hall mobility versus the annealing temperature for the Si-implanted AlGaN sample. Data for an unimplanted sample is included as a control. First of all, it is clear that the unimplanted samples have significant donors produced by the annealing process alone. This may be due to the activation of unintentional impurities, such as Si or O, in the film. O may be a particular suspect due to the tendency of O to incorporate in Al-containing material. At the highest temperature, the high dose Si-implanted sample has four times higher free electron concentration (1.7x10¹⁵ cm⁻²) than the unimplanted sample. This corresponds to 34% activation of the implanted Si.
Figure 36 shows aligned C-RBS spectra for 15% Al in AlGaN either as-grown (unimplanted), after Si-implantation at a dose of 1 or 5x10^{15} cm^{-2}, and for the higher dose samples after annealing. As was the case for GaN, the 1x10^{15} cm^{-2} sample shows limited dechannelling while the higher dose sample shows a marked damage peak. The minimum channeling yield for the high dose sample was 26.67% which is lower than that seen for GaN which showed \( \chi_{\text{min}} \) between 34 and 38% implanted under the same conditions. This means the addition of 15% aluminum to the GaN matrix increases its damage threshold as is the case for Al-additions to GaAs to form AlGaAs. The spectra for the annealed sample shows limited damage removal, again consistent with that seen for GaN at this temperature. There is evidence, however, of improvement in the near surface as seen by the reduction in the first surface peak. This peak has been suggested to be due to preferential sputtering of nitrogen from the film surface. The reduction of this peak via annealing suggests the surface stoichiometry is restored during the anneal. Further study is needed to better understand this effect.

The redistribution of implanted Si, Mg and C in Al_{0.12}Ga_{0.88}N was studied by Polyakov and coworkers. While Si and C demonstrated no measurable diffusion by SIMS after at 1140°C, 1 h anneal, Mg did show appreciable profile broadening and indiffusion under these conditions. Activation of a modest Si dose (5x10^{14} cm^{-2}) was also achieved by annealing at 1140°C with a resulting peak electron concentration of 1.2x10^{18} cm^{-2}. More work is needed on the affect of Al-composition on the implantation properties of AlGaN.

Although significant progress has been reported for ion implantation doping and annealing of GaN and AlGaN, there are still many areas for further research. For example, further work is needed to develop a manufacturable annealing process between 1300 and 1500°C at reproducible N Pressures. The role of native defects, particularly dislocation, on the activation
of implanted dopants can now be addressed with the demonstration of nearly dislocation free GaN formed by Lateral Epitaxial Overgrowth (LEO).\textsuperscript{174-176} This defect free material will make the study of p-type implantation more reproducible. Areas of interest for implant isolation include demonstration of truly thermally stable isolation, understanding the nature of hydrogen implant isolation, determination of the behavior of deeps levels such as Cr and Fe, and the effect of implant isolation on the properties of waveguide losses.

The possibilities are extensive for the application of ion implantation to group III-Nitride semiconductor devices. A few examples would be the use of selective area implantation doping to improve the contact resistance of III-N laser or FET structures or using ion implantation isolation to realize an electrically injected vertical cavity surface emitting laser or to produce LED arrays.

With continued improvements in the quality of group III-N materials, ion implantation doping and isolation can be expected to play an enabling role in the realization of many advanced device structures. As reviewed in this section, significant progress has been made in proof-of-principle demonstration. However, significant more effort is needed on the starting material and the process technology to make implantation of group III-Nitride semiconductors the same workhorse technology it is in other more mature semiconductor material systems.

C. GATE DIELECTRICS

Work in this area for power MOSFETs and gate turn-off thyristors is just commencing and some preliminary results are becoming available for AlN, AlON and Ga(Gd)O\textsubscript{x}, the latter producing excellent characteristics on GaAs and InGaAs and now being applied to GaN. Channel modulation has been demonstrated for AlN and Ga(Gd)O\textsubscript{x}, but interface, state densities
appear will above $10^{11}\text{cm}^{-2}$ at this point and much future effort is required to reduce this. Table IV shows a comparison of the properties of Ga$_2$O$_3$ (which is the major component of the dielectric) and SiO$_2$. While the latter is superior in terms of breakdown strength, Ga$_2$O$_3$ is an attractive option.

A number of GaN field effect transistors (FETs) and AlGaN/GaN heterostructure FETs have been reported, showing excellent device breakdown characteristics.\textsuperscript{(177,178)} However, the conventional low resistance n$^+$-cap layer structure for the GaAs technology cannot be applied in the nitride based material system to reduce the parasitic resistance, owing to no adequate gate recess technology being available. The III-nitrides are chemically very stable and few wet etching recipes exist. GaN may be etched by molten KOH of NaOH at $\geq 400^\circ\text{C}$, while laser enhanced HCl or KOH solutions produce etch rates of a few hundred angstroms per minute at room temperature.\textsuperscript{(179)} Virtually all of the nitride devices reported to date have employed dry etching for pattern transfer and ion bombardment induced low gate breakdown voltage were observed.\textsuperscript{(180,181)} Both of these problems may be overcome by using a MOSFET approach.

Recently, interface properties of Ga$_2$O$_3$(Gd$_2$O$_4$)/GaAs structures fabricated using \textit{in-situ} multiple-chamber molecular beam epitaxy have been investigated. The oxide films were deposited on clean, atomically ordered (100) GaAs surfaces at $\sim 550^\circ\text{C}$ by electron-beam evaporation using a Gd$_3$Ga$_5$O$_{12}$ single crystal source. A mid-gap surface state density of $2\times 10^{10}\text{cm}^{-2}\text{eV}^{-1}$ was obtained.\textsuperscript{(182)} Both n- and p-GaAs based enhancement-mode MOSFETs were also demonstrated.\textsuperscript{(183-185)}

Aluminum nitride has been proposed as a potential replacement for silicon dioxide in high temperature MIS based silicon carbide device applications. AlN is a wide bandgap semiconductor (6.2 eV) but if made undoped, its properties are most like those of an insulator. A
high relative dielectric constant (8-9) alleviates the problem of high fields in the dielectric in high voltage application. The breakdown electric field, however, is not yet fully determined. Moreover, the thermal conductivity of AlN is high, making this material a potential high temperature stable gate dielectric. One difficulty associated with this material may be its tendency to deposit as a polycrystalline layer rather than an amorphous one.

Ga$_2$O$_3$(Gd$_2$O$_3$) has recently been applied to make GaN diodes and MOSFETs. We also used a MOMBE system to grow the aluminum nitride for the alternative diode insulator. The MIS diodes using these two insulators were then fabricated and characterized with I-V and C-V measurements. The dielectric thickness and interface roughness were measured with x-ray reflectivity.$^{186,187}$

The GaN layer structure was grown on C-Al$_2$O$_3$ substrates prepared initially by HCl/HNO$_3$/H$_2$O cleaning and an in-situ H$_2$ bake at 1070°C. A GaN buffer <300Å thick was grown at 500°C using trimethylgallium and ammonia, and crystallized by ramping the temperature to 1040°C. The same precursors were again used to grow ~3 μm of undoped GaN (n <1x10$^{16}$ cm$^{-3}$) and a 2000Å Si-doped (n=2x10$^{17}$ cm$^{-3}$) active layer.$^{188}$

The diode fabrication started with ohmic contact formation by depositing In on the edge of the GaN samples by using shadow mask and heat up to 500°C. Then, the samples were transferred to growth chamber for insulator growth. For the Ga$_2$O$_3$(Ga$_2$O$_3$) growth, the sample was loaded into a solid source MBE chamber and the native oxides of GaN were thermally desorbed at a substrate temperature of 600°C. After oxide desorption, the wafer was transferred under vacuum (10$^{-10}$ torr) into a second chamber and the Ga$_2$O$_3$(Gd$_2$O$_3$) was deposited on the GaN using e-beam evaporation at a substrate temperature of 550°C.$^{189}$
For the AlN growth, a MOMBE system was used. The GaN oxides were thermally desorbed at 700°C under N\textsubscript{2} plasma, and AlN was grown with trimethylamine alane and nitrogen generated from a Wavemat ECR N\textsubscript{2} plasma at ~400°C.

After the AlN or Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) deposition, a metallization of Pt/Ti/Pt/Au (50Å/50Å/200Å/2000Å) was directly deposited on the insulator layer again through the shadow mask with different diameters to complete the diode formation.

The development of a suitable insulator for GaN MOSFET structures is a critical step. Conventional dielectrics such as SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} have generally failed on III-V materials because of high interface state densities. We believe that AlN or Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) layers offer the best opportunities for sustaining high fields at low defect densities. Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) had recently been developed as an excellent insulator on GaAs.\textsuperscript{(199)} The same approach can be extended to GaN.

As shown in Figure 37, the I-V characteristics of a Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3})/GaN diode shows a very low leakage current on both forward and reverse bias. The forward breakdown voltage (defined at 10 μA of diode current) is 6V. The charge modulation of the MOS diode was clearly demonstrated from the change from accumulation mode (positive bias) to depletion mode (negative bias) at different frequencies. The typical inversion phenomena exhibited in SiO\textsubscript{2}/Si diode is not observed, which might be due to the nature of ionic bonding of nitride-based materials which have long minority carrier lifetime.

From x-ray reflectivity measurements, the thickness of the Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) and the root-mean-square roughness of the Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3})/GaN interface were estimated to be 195Å and 3Å, respectively. The slope of the x-ray reflectivity is a function of the oxide thickness and the roughness of the Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3})/GaN interface as well as the air/ Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) interface will determine the widths of oscillation periods. With the 195Å thick Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) and the 6V
forward breakdown, the breakdown field of the oxide is >12 MV/cm. The atomic level (3Å) smoothness for the Ga$_2$O$_3$(Gd$_2$O$_3$)/GaN interface can provide a high carrier mobility for MISFET.

For the AlN/GaN material system, the diode I-V characteristics also show a very low leakage current on both forward and reverse bias. A forward breakdown of 5V was obtained, as shown in Figure 38. From C-V data the charge modulation of the MOS diode was also clearly demonstrated from accumulation mode to depletion mode at different frequencies.

The thickness of the AlN and the root-mean-square roughness of the AlN/GaN interface were determined to be 345Å and 20Å, respectively. The 20Å roughness of the AlN/GaN interface may be due to the inter-diffusion between Al and Ga, however, more detailed study is needed to confirm this. With the 345Å thick AlN and the 5V forward breakdown, the breakdown field of the oxide is around 1.4 MV/cm. The lower breakdown field may be caused by the rough AlN/GaN interface or the crystalline of AlN.

In summary, GaN MIS diodes were demonstrated using MOMBE grown AlN and MBE evaporated Ga$_2$O$_3$(Gd$_2$O$_3$) as the insulators. The breakdown fields of AlN and Ga$_2$O$_3$(Gd$_2$O$_3$) diodes are 1.4 MV/cm and 12 MV/cm, respectively. From the C-V measurement, both kinds of diodes show good charge modulation from accumulation to depletion at different frequencies. The extremely smooth Ga$_2$O$_3$(Gd$_2$O$_3$)/GaN interface was achieved and the rms of the interface roughness is 3Å which is down to the atomic range. However, the rms roughness AlN/GaN interface is around 20Å which may be caused by inter-diffusion by Al and Ga, more detailed study is needed to confirm this. For future studies, the surface cleaning (in-situ or ex-situ) wet/dry processes, including thermal oxide desorption, ozone cleaning of HF vapor, and thermal stability of the diodes are the key for the realization of the GaN based MISFET technology.
The advantages of MOSFETs relative to MESFETs are well established, but due to the absence of a suitable dielectric for compound semiconductors, GaAs-based integrated circuits use MESFETs. This means that the circuits require two supply voltages, with relatively high power consumption. In particular it is desirable to have available enhancement-mode MOSFETs to reduce circuit complexity and power consumption.

Using the Ga(Gd)O\(_x\), we have recently fabricated depletion mode GaN MOSFETs on n-type (~3x10\(^{17}\) cm\(^{-3}\)) epi layers grown on Al\(_2\)O\(_3\). Figure 39 shows I-V characteristics at 25 and 250°C. The characteristics are affected by the relatively high source/drain contact resistance, but improve at higher temperatures (Figure 40). We have tested these devices to >400°C where the characteristics continue to improve.

While Ga(Gd)O\(_x\) (where Ga is predominantly in the +3 oxidation state, Gd is the electropositive stabilizer element for stabilizing Ga in the 3+ oxidation state, and x is high enough to satisfy the requirement that Ga and Gd are essentially fully oxidized) has been the oxide that has worked on compound semiconductors to date, there are many other possible dielectrics that might have a low enough interface state density (i.e. \(<10^{11}\) cm\(^{-2}\) eV\(^{-1}\)) to successfully produce MOSFETs on GaN. Moreover, it is likely that these dielectrics could be applied to the extrinsic base region of heterojunction bipolar transistors to reduce recombination. Possible candidates other than Gd for the stabilizer element include Sc, Y, La, Nd, Dy, Ho and Er.

D. WET ETCHING

Under normal conditions, only molten salts such as KOH or NaOH at temperatures above ~250°C have been found to etch GaN at practical rates, and the difficulty of handling these
mixtures and the inability to find masks that will hold up to them has limited the application of wet etching in GaN device technology. We have found that AlN and Al-rich alloys can be wet etched in KOH at temperatures of 50-100°C. The Adesida group has recently published several reports on photochemical etching of n-GaN using 365 nm illumination of KOH solutions near room temperature, following on the work of Minsky et al. Rates of 3000Å-min⁻¹ were obtained for light intensities of 50 mW/cm², and the etch reaction was assumed to be:

\[ 2\text{GaN} + 6h^+ \rightarrow 2\text{Ga}^{3+} + \text{N}_2 + \text{H}_2 \]

The etching was generally diffusion-limited, with somewhat rough surfaces. Intrinsic and p-GaN do not etch under these conditions, and undercut encroachment occurred in some small-scale features due to light scattering and hole diffusion in the GaN itself. This process looks very promising and may be useful for several different fabrication steps in both electronic and photonic devices.

A compilation of etch results for binary and ternary nitrides is shown in Table V. These results are for non light-assisted conditions. For single crystal AlN we find that KOH-based solutions, such as AZ400K developer, produce reaction-limited etching with an activation energy of ~15.5 kCal-mol⁻¹ (Figure 41). The rates are a strong function of material quality, with higher quality AlN etching at a slower rate.

In this section, we report on an examination of the wet etching of AlN and InₓAl₁₋ₓN in KOH solutions as a function of crystal quality, etch temperature and composition. AlN sample prepared by reactive sputtering on Si substrates at ~200°C were annealed at temperatures from 400 to 1100°C and as expected, the etch rate decreased with anneal temperature, indicating improved crystal quality. We found that InAlN on Si substrates had higher wet etch rates. Both AlN and InAlN samples had an increase in etch rate with etch temperature. The etch rate for the
InAlN increased as the In composition increased from 0 to 36%, and then decreased to zero for InN. Finally, the effect of doping concentration in InAlN samples of similar In concentration (~3%) was examined and much higher etch rates were observed for the heavily doped material at solution temperatures above 60°C.

The AlN was reactively sputter deposited on a Si substrate to a thickness of ~1200Å using a N₂ discharge and a pure Al target. This type of AlN film has been shown to be an effective annealing cap for GaN at a temperature of 1100°C. The InAlN samples were grown using metalorganic molecular beam epitaxy (MOMBE) on semi-insulating, (100) GaAs substrates of p-type (1Ωcm) Si substrates in an Intevac Gea II system. The group III sources were triethylgallium, trimethylamine alane and trimethylindium, respectively, and the atomic nitrogen was derived from an ECR Wavemat source operating a 200 W forward power. The layers were single crystal with a high density (10^{11} to 10^{12} cm^{-2}) of stacking faults and microtwins. InAlN samples were found to contain both hexagonal and cubic forms. The In\_xAl\_1-xN were either conducting n-type as-grown (~10^{18} cm^{-3}) for x > 0.03 due to residual autodoping by native defects or fully depleted for x < 0.03. The compositions examined were 100, 75, 36, 29, 19, 3.1, 2.6 and 0% In.

The AlN samples were annealed in a RTA system (AG410T) face down on a GaAs substrate for 10 sec at temperatures between 500 and 1150°C in a N₂ atmosphere. For wet etching studies, all samples were masked with Apiezon wax patterns. Etch depths were obtained by Deektak stylus profilometry after the removal of mask with an approximate 5% error. Scanning electron microscopy (SEM) was used to examine the undercutting on the etched sample. AZ400K developer solution, with an active ingredient KOH, was used for the etch, and etch temperatures between 20 and 80°C.
Figure 42 shows the etch rate of the sputtered AlN as a function of etch temperature for samples as grown or annealed at 500, 700, 900, 1000 and 1100°C. The etch rates of both the as-deposited and 500°C annealed sample increase sharply as the etch temperature increases from 20 to 50°C, and then level off; the rate drops by approximately 10% with a 500°C anneal. The samples annealed at 700, 900 and 1000°C also show similar trends, with a monotonic decrease in rate for higher anneal temperatures. The crystal quality appears to increase significantly with anneal temperature as the etch rate drops accordingly. The etch rate continues to drop by ~10% with each successive anneal, to 1000°C. After 1100°C the etch rate drops and is less temperature dependent. Overall there is an ~90% reduction in etch rate from the as-deposited AlN to that annealed at 1100°C for etching at 80°C.

The activation energy for an etch solution can be determined from an Arrhenius plot, and is shown in Figure 43. The activation energies for all samples was the same within experimental error, 2.0 ±0.5 kcal mol\(^{-1}\). This is indicative of a diffusion-limited reaction. This is much lower than the activation energy of 15.45 kcal mol\(^{-1}\) reported by Mileham et al.\(^{(115)}\) for AlN grown by metalorganic molecular beam epitaxy. The quality of the material in the current experiment is much lower though, and the etch may be proceeding at such a rapid rate that the solution is becoming depleted of reactants near the materials surface.

The etch rates as a function of solution temperature for In\(_x\)Al\(_{1-x}\)N grown on either GaAs or Si, for 19% In is shown in Figure 44. At 20°C etch temperature there is no difference in etch rate. The etch rates for both materials increase with etch temperature, with the differential in etch rates also increasing with temperature. As was mentioned previously, the InAlN grown on Si has a greater concentration of crystalline defects as evident from x-ray diffraction and absorption measurements. At 80°C the etch rate for the film on the Si substrate is approximately
three times faster than for film grown on GaAs. This is another clear indication of the
dependence of wet etch rate on material quality and emphasizes why it has proven very difficult
to find etch solutions for high quality single-crystal nitrides.

Etch rates for In\textsubscript{x}Al\textsubscript{1-x}N grown on GaAs for 0 ≤ x ≤ 1 are shown in Figure 45, for etch
temperatures between 20 and 80°C. Up to 40°C the etch rates are very low and show little
dependence on In composition. The AIN etches much faster at these temperatures than any
composition of the ternary alloy InAIN. As the etch temperature increases to 60°C, the etch rates
increase, showing a peak for 36% In. This is presumably due to a tradeoff between the reduction
in average bond strength for InAIN relative to the pure binary AIN, and the fact that the chemical
sensitivity falls off at higher In concentrations. Thus the etch rates initially increase for
increasing In, but then decrease at higher concentrations because there is no chemical driving
force for etching to occur. InN did not etch in this solution at any temperature but was
occasionally lifted off during long etches because of the defective interfacial region between InN
and GaAs being attached by the KOH.

Arrhenius plots of etch rates for In\textsubscript{x}Al\textsubscript{1-x}N for 0 ≤ x ≤ 1 giving activation energies for the
etches are shown in Figure 46. There is substantial scatter in the data, but the activation energies
are all in the range 2-6 kcal mol\textsuperscript{-1}, which again is consistent with diffusion-controlled etching.
This is not desirable for device fabrication processes because the rates are then dependent on
solution agitation and the etched surface morphology are generally rougher than for reaction-
controlled solutions.

Apart from material quality or composition, another factor which often plays a role in
determining etch rates is sample conductivity. Figure 47 shows a plot of InAIN etch vs. etch rate
temperature for samples with 2.6 and 3.1% In, which were depleted (n <10\textsuperscript{16} cm\textsuperscript{-3}) and doped at
$n \approx 5 \times 10^{18} \text{cm}^{-3}$, respectively. Since the autodoping changes rapidly around this composition, but there is little change in In concentration, these samples represent a good test of any effects related to conductivity. The samples have similar etch rates at low solution temperatures. Above 60°C, however, the n-type sample etch rate increases more rapidly, approximately two times faster than the depleted sample. These results indicate that at temperatures where fast etch rates occur, the electrons in the n-type sample are part of the chemical reaction between the OH$^-$ ions and the Al in the InAlN film. They may enhance formation of these ions initially and thus the etch rate is enhanced. It will be interesting to try p-type InAlN.

Etching with KOH-based solution is completely selective for InAlN over GaN or InN. Annealing of sputtered AlN improved the crystal quality of the film, decreasing the chemical etch rate in KOH solutions. InAlN etch rates also increased with decreasing crystalline quality. Both AlN and InAlN samples had activation energies for etching in KOH ≤6 kcal mol$^{-1}$, which is typical of a diffusion-controlled etch mechanism. The etch rate for the InAlN initially increased as the In composition increased from 0 to 36%, and then decreased to zero for pure InN. The n-type InAlN etched approximately two times faster than the undoped material above 60°C, indicating that electrons play a role in the etch mechanism.

Kim et al. reported that H$_3$PO$_4$, NaOH and KOH solutions were able to remove N$_2$-deficient layers in GaN created by processes such as high temperature annealing or dry etching. The onset of etching occurred at ~160°C, with rates of ~45 Å sec$^{-1}$ at 180°C for defective GaN surface layers.

Stocker et al. found they could obtain effective crystallographic etching of wurtzite GaN in similar solutions at ~170°C. Use of glycol rather than H$_2$O as the diluent enabled them to carry out the etching at temperatures up to ~190°C. Phosphoric acid was able to etch the
and \{10\bar{1}2\} planes, molten KOH the \{10\bar{1}0\} and \{10\bar{2}1\} planes, and KOH in ethylene glycol the \{10\bar{1}0\} plane. Molten KOH has been shown previously to reveal dislocations in GaN.\(^{195,196}\)

Lee et al.\(^{197}\) found that the lowest contact resistivity for Pd/Au on p-GaN was achieved using KOH rinsing prior to metal deposition. For example, without this treatment, \(R_C\) was \(2.9 \times 10^4 \Omega \text{cm}^2\) for a p-doping level of \(3 \times 10^{16} \text{cm}^{-3}\), whereas the KOH treatment reduced this to \(7.1 \times 10^3 \Omega \text{cm}^2\). Surface analysis showed that the KOH removed native oxide, which apparently inhibits hole transport from metal-to-GaN.

E. DRY ETCHING

Due to limited wet chemical etch results for the group-III nitrides, a significant amount of effort has been devoted to the development of dry etch processing.\(^{198-202}\) Dry etch development was initially focused on mesa structures where high etch rates, anisotropic profiles, smooth sidewalls, and equi-rate etching of dissimilar materials were required. For example, commercially available LEDs and laser facets for GaN-based laser diodes were patterned using reactive ion etch (RIE). However, as interest in high power, high temperature electronics\(^{203-205}\) increased, etch requirements expanded to include smooth surface morphology, low plasma-induced damage, and selective etching of one layer over another. Dry etch development is further complicated by the inert chemical nature and strong bond energies of the group-III nitrides as compared to other compound semiconductors. GaN has a bond energy of 8.92 eV/atom, InN 7.72 eV/atom, and AlN 11.52 eV/atom as compared to GaAs which has a bond energy of 6.52 eV/atom.\(^{207}\) In this section we will review dry etch processes for the group-III nitrides.
Dry plasma etching has become the dominant patterning technique for the group-III nitrides due to the shortcomings in wet chemical etching. Plasma etching proceeds by either physical sputtering, chemical reactions, or a combination of the two often referred to as ion-assisted plasma etching. Physical sputtering is dominated by the acceleration of energetic ions formed in the plasma to the substrate surface at relatively high energies, typically > 200 eV. Due to the transfer of energy and momentum to the substrate, surface material is sputtered away. This sputter mechanism tends to yield anisotropic profiles; however, it can result in significant damage, rough surface morphology, trenching, poor selectivity, and non-stoichiometric surfaces thus minimizing device performance. Pearton and co-workers measured sputter rates for GaN, InN, AlN, and InGaN as a function of Ar\(^+\) ion energy.\(^{(208)}\) The sputter rates increased with ion energy but were quite slow, < 600 Å/min, due to the high bond energies of the group III-N bond.

Chemically dominated etch mechanisms rely on the formation of reactive species in the plasma which adsorb to the surface, form volatile etch products, and then desorb from the surface. Since ion energies are relatively low, etch rates in the vertical and lateral direction are often similar thus resulting in isotropic etch profiles and loss of critical dimensions. However, due to the low ion energies used plasma-induced damage is minimized. Alternatively, ion-assisted plasma etching relies on both chemical reactions and physical sputtering to yield anisotropic profiles at reasonably high etch rates. Provided the chemical and physical components of the etch mechanism are balanced, high resolution features with minimal damage and optimum device performance can be obtained.

**RIE Etching**

RIE utilizes both the chemical and physical components of an etch mechanism to achieve anisotropic profiles, fast etch rates, and dimensional control. RIE plasmas are typically generated at a radio frequency (rf) of 13.56 MHz between two parallel electrodes in a reactive gas (see Figure 48a). The substrate is placed on the powered electrode and ion energies, defined as they cross the plasma sheath, are typically a few hundred eV. RIE is operated at low pressure,
ranging from a few mTorr up to 200 mTorr, which promotes anisotropic etching due to increased mean free paths and reduced collisional scattering of ions.

Adesida et al. were the first to report RIE of GaN in SiCl$_4$-based plasmas.$^{(201)}$ Etch rates increased with increasing dc-bias, and were $> 500$ Å/min at -400 V. Lin et al. reported similar results for GaN in BCl$_3$ and SiCl$_4$ plasmas with etch rates of 1050 Å/min in BCl$_3$ at 150 W cathode rf-power.$^{(209)}$ Additional RIE results have been reported for HBr-,$^{(210)}$ CHF$_3$-, and CCl$_2$F$_2$-based$^{(211)}$ plasmas with etch rates typically $< 600$ Å/min. The best RIE results for the group-III nitrides have been obtained in chlorine-based plasmas under high ion energy conditions where the III-N bond breaking and the sputter desorption of etch products from the surface are most efficient. Under these conditions, plasma damage can occur and degrade both electrical and optical device performance. Lowering the ion energy or increasing the chemical activity in the plasma to minimize the damage often results in slower etch rates or less anisotropic profiles which significantly limits critical dimensions. Therefore, it is necessary to pursue alternative etch platforms which combine high quality etch characteristics with low-damage.

**High-Density Plasma Etching**

The use of high-density plasma etch systems including electron cyclotron resonance (ECR), inductively coupled plasma (ICP), and magnetron RIE (MRIE), has resulted in improved etch characteristics for the group-III nitrides as compared to RIE. This observation is attributed to plasma densities which are 2 to 4 orders of magnitude higher than 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, plasma-induced damage is more easily controlled. Figure 48b shows a schematic diagram of a typical low profile ECR etch system. High-density ECR plasmas are formed at low pressures with low plasma potentials and ion energies due to magnetic confinement of electrons in the source region. The sample is located downstream from the source to minimize exposure to the plasma and to reduce the physical component of the etch mechanism. Anisotropic etching can be achieved by superimposing an rf-bias (13.56 MHz) on the sample and operating at low pressure ($< 5$ mTorr) to minimize ion scattering and lateral etching. However, as the rf-biasing is increased the potential for damage to the surface increases.
Pearston and co-workers were the first to report ECR etching of group-III nitride films. Etch rates for GaN, InN, and AlN increased as either the ion energy (dc-bias) or ion flux (ECR source power) increased. Etch rates of 1100 Å/min for AlN and 700 Å/min for GaN at -150 V dc-bias in a Cl₂/H₂ plasma and 350 Å/min for InN in a CH₄/H₂/Ar plasma at -250 V dc-bias were reported. The etched features were anisotropic and the surface remained stoichiometric over a wide range of plasma conditions. GaN ECR etch data has been reported by several authors with etch rates as high as 1.3 µm/min.

ICP offers another high-density plasma etch platform to pattern group-III nitrides. ICP plasmas are formed in a dielectric vessel encircled by an inductive coil into which rf-power is applied (see Figure 48c). The alternating electric field between the coils induces an alternating magnetic field trapping electrons in the center of the chamber and generating a high-density plasma. Since ion energy and plasma density can be effectively decoupled, uniform density and energy distributions are transferred to the sample while keeping ion and electron energy low. Thus, ICP etching can produce low damage while maintaining fast etch rates. Anisotropy is achieved by superimposing a rf-bias on the sample. ICP etching is generally believed to have several advantages over ECR including easier scale-up for production, improved plasma uniformity over a wider area, and lower cost-of-operation. The first ICP etch results for GaN were reported in a Cl₂/H₂/Ar ICP-generated plasma with etch rates as high as ~6875 Å/min. Etch rates increased with increasing dc-bias and etch profiles were highly anisotropic with smooth etch morphologies over a wide range of plasma conditions. GaN etching has also been reported in a variety of halogen- and methane-based ICP plasmas.

MRIE is another high-density etch platform which is comparable to RIE. In MRIE, a magnetic field is used to confine electrons close to the sample and minimize electron wall loss. Under these conditions, ionization efficiencies are increased and high plasma densities and fast etch rates are achieved at much lower dc-biases (less damage) as compared to RIE. GaN etch rates of ~3500 Å/min were reported in BCl₃-based plasmas at dc-biases < -100 V. The etch was fairly smooth and anisotropic.

Additional Plasma Etch Platforms
Chemically assisted ion beam etching (CAIBE) and reactive ion beam etching (RIE) have also been used to etch group-III nitride films. Ions are generated in a high-density plasma source and accelerated by one or more grids to the substrate. In CAIBE, reactive gases are added to the plasma downstream of the acceleration grids thus enhancing the chemical component of the etch mechanism, whereas in RIE, reactive gases are introduced in the ion source. Both etch platforms rely on relatively energetic ions (200 to 2000 eV) and low chamber pressures (< 5 mTorr) to achieve anisotropic etch profiles. However, with such high ion energies, the potential for plasma-induced damage exists. Adesida and co-workers reported CAIBE etch rates for GaN as high as 2100 Å/min with 500 eV Ar\(^+\) ions and Cl\(_2\) or HCl ambients. Rates increased with beam current, reactive gas flow rate, and substrate temperature. Anisotropic profiles with smooth etch morphologies were observed. GaN etch rates of ~ 500 Å/min have been obtained in a RIBE-generated Cl\(_2\)/Ar plasma at beam voltages of 600 V. RIBE etch profiles were anisotropic with slight trenching at the base of the feature.

Low energy electron enhanced etching (LE4) of GaN has been reported by Gillis and co-workers. LE4 is an etch technique which depends on the interaction of low energy electrons (<15 eV) and reactive species at the substrate surface. The etch process results in minimal surface damage since there is negligible momentum transferred from the electrons to the substrate. GaN etch rates of ~ 500 Å/min in a H\(_2\)-based LE4 plasma and ~ 2500 Å/min in a pure Cl\(_2\) LE4 plasma have been reported. GaN has also been etched using photoassisted dry etch processes where the substrate is exposed to a reactive gas and ultraviolet laser radiation simultaneously. Vibrational and electronic excitations lead to improved bond breaking and desorption of reactant products. Leonard and Bedair reported GaN etch rates < 80 Å/min in HCl using 193 nm ArF excimer laser.

GaN etch rates are compared in Figure 49 for RIE, ECR, and ICP Cl\(_2\)/H\(_2\)/CH\(_4\)/Ar plasmas as well as a RIBE Cl\(_2\)/Ar plasma. CH\(_4\) and H\(_2\) were removed from the plasma chemistry to eliminate polymer deposition in the RIBE chamber. Etch rates increased as a function of dc-bias independent of etch technique. GaN etch rates obtained in the ICP and ECR plasmas were much faster than those obtained in RIE and RIBE. This was attributed to higher plasma densities (1 to 4 orders of magnitude higher) which resulted in more efficient breaking of the III-N bond and sputter desorption of the etch products. Slower rates observed in the RIBE may also be due to
lower operational pressures (0.3 mTorr compared to 2 mTorr for the ICP and ECR) and/or lower ion and neutral flux at the GaN surface due to the high source-to-sample separation.

**DRY ETCH PLASMA PARAMETERS: PRESSURE, ION ENERGY, AND PLASMA DENSITY**

Etch characteristics are often dependent upon plasma parameters including pressure, ion energy, and plasma density. As a function of pressure, plasma conditions including the mean free path and the collisional frequency can change resulting in changes in both ion energy and plasma density. GaN etch rates are shown as a function of pressure for an ICP-generated BCl3/Cl2 plasma in Figure 50. Etch rates increased as the pressure was increased from 1 to 2 mTorr and then decreased at higher pressures. The initial increase in etch rate suggested a reactant limited regime at low pressure, however at higher pressures the etch rates decreased due either to lower plasma densities, redeposition, or polymer formation on the substrate surface. At pressures < 10 mTorr, GaN etches were anisotropic and smooth, while at pressure <10 mTorr the etch profile was undercut and poorly defined due to a lower mean free path, collisional scattering of the ions, and increased lateral etching of the GaN.

GaN etch rates are plotted as a function of dc-bias (which correlates to ion energy) for an ICP-generated BCl3/Cl2 plasma in Figure 51. The GaN etch rates increased monotonically as the dc-bias or ion energy increased. Etch rates increased due to improved sputter desorption of etch products from the surface as well as more efficient breaking of the Ga-N bonds. Etch rates have also been observed to decrease under high ion bombardment energies due to sputter desorption of reactive species from the surface before the reactions occur. This is often referred to as an adsorption limited etch regime. In Figure 52, SEM micrographs are shown for a) -50, b) -150, and c) -300 V dc-bias. The etch profile became more anisotropic as the dc-bias increased from -50 to -150 V dc-bias due to the perpendicular path of the ions relative to the substrate surface which maintained straight wall profiles. However, as the dc-bias was increased to -300 V, a tiered etch profile with vertical striations in the sidewall was observed due to erosion of the resist mask-edge.
In Figure 53, GaN etch rates are shown as a function of ICP-source power while the dc-bias was held constant at -250 V. GaN etch rates increased as the ICP source power increased due to higher concentrations of reactive species which increased the chemical component of the etch mechanism and/or higher ion flux which increased the bond breaking and sputter desorption efficiency of the etch. Etch rates have also been observed to stabilize or decrease under high plasma flux conditions due either to saturation of reactive species at the surface or sputter desorption of reactive species from the surface before the reactions occur. The etch profile was anisotropic and smooth up to 1000 W ICP power where the feature dimensions were lost and sidewall morphology was rough due to erosion of the mask-edge under high plasma flux conditions.

In addition to etch rates, etch selectivity or the ability to etch one film at higher rates than another can be very important in device fabrication. For example, optimization of etch selectivity is critical to control threshold voltage uniformity for high electron mobility transistors (HEMTs), to accurately stop on either the emitter or collector regions for metal contacts for heterojunction bipolar transistors (HBTs), and for low resistivity n-ohmic contacts on InN layers. Several studies have recently reported etch selectivity for the group-III nitrides.[233,236,250-254] For example, Figure 54 shows GaN, InN, and AlN etch rates and etch selectivities as a function of cathode rf-power in an ICP-generated Cl₂/Ar plasma. Etch rates for all three films increased with increasing cathode rf-power or dc-bias due to improved breaking of the III-N bonds and more efficient sputter desorption of the etch products. Increasing InN etch rates were especially significant since InCl₃, the primary In etch product in a Cl-based plasma, has a relatively low etch volatility. However, under high dc-bias conditions, desorption of the InCl₃ etch products occurred prior to passivation of the etch surface.[251] The GaN:InN and GaN:AlN etch selectivities were < 8:1 and decreased as the cathode rf-power or ion energy increased. Smith and co-workers reported similar results in a Cl₂/Ar ICP plasma where GaN:AlN and GaN:AlGaN selectivities decreased as dc-bias increased.[236] At -20 V dc-bias, etch selectivities of ~ 38:1 were reported for GaN:AlN and ~ 10:1 for GaN:AlGaN.

TEMPERATURE DEPENDENT ETCHING
Temperature dependent etching of the group-III nitrides have been reported in ECR and ICP etch systems.\textsuperscript{(215,225,237)} Etch rates are often influenced by the substrate temperature which can effect the desorption rate of etch products, the gas-surface reaction kinetics, and the surface mobility of reactants. Substrate temperature can be controlled and maintained during the etch process by a variety of clamping and backside heating or cooling procedures. GaN and InN etch rates are shown in Figure 55 as a function of temperature in a Cl\textsubscript{2}/H\textsubscript{2}/Ar ICP plasma. GaN etch rates were much faster than InN due to higher volatility of the GaCl\textsubscript{3} etch products as compared to InCl\textsubscript{3} and showed little dependence on temperature. However, the InN etch rates showed a strong temperature dependence increasing at 150°C due to higher volatilities of the InCl\textsubscript{3} etch products at higher substrate temperatures.

**PLASMA CHEMISTRY**

Several different plasma chemistries have been used to etch the group-III nitrides. As established above, etch rates and profiles can be strongly affected by the volatility of the etch products formed. Table VI shows the boiling points of possible etch products for the group-III nitrides exposed to halogen- and hydrocarbon-based plasmas. For halogen-based plasmas, etch rates are often limited by the volatility of the group-III halogen etch product. For Ga- and Al-containing films, chlorine-based plasmas typically yield fast rates with anisotropic, smooth etch profiles. CH\textsubscript{4}/H\textsubscript{2}-based plasma chemistries have also yielded smooth, anisotropic profiles for Ga-containing films, however at much slower rates. Based only on a comparison of etch product volatility, slower etch rates in CH\textsubscript{4}-based plasmas is unexpected since the (CH\textsubscript{3})\textsubscript{3}Ga etch product has a much lower boiling point than GaCl\textsubscript{3}. This observation demonstrates the complexity of the etch process where redeposition, polymer formation, and gas-phase kinetics can influence the results. As shown above, etch rates for In-containing films obtained in room temperature chlorine-based plasmas tend to be slow with rough surface morphology and overcut profiles due to the low volatility of the InCl\textsubscript{3} and preferential loss of the group-V etch products. However, at elevated temperatures (>130°C), the InCl\textsubscript{3} volatility increases and the etch rates and surface morphology improve.\textsuperscript{(215,225,237,255-257)} Significantly better room temperature etch results are obtained in CH\textsubscript{4}/H\textsubscript{2}-based plasmas due to the formation of more volatile (CH\textsubscript{3})\textsubscript{3}In etch products.\textsuperscript{(213,258)}
The source of reactive plasma species and the addition of secondary gases to the plasma can vary etch rates, anisotropy, selectivity, and morphology. The fragmentation pattern and gas-phase kinetics associated with the source gas can have a significant effect on the concentration of reactive neutrals and ions generated in the plasma thus affecting the etch characteristics. Secondary gas additions and variations in gas ratios can change the chemical-physical ratio of the etch mechanism. The effect of Ar, SF6, N2, and H2 additions to Cl2- and BCl3-based ICP and ECR plasmas for GaN etching has been reported. In general, GaN etch rates were faster in Cl2-based plasmas as compared to BCl3 due to higher concentrations of reactive Cl. The addition of H2, N2, or SF6 to either Cl2- or BCl3-based plasmas changed the relative concentration of reactive Cl in the plasma which directly correlated to the GaN etch rate. For example, in Figure 56, GaN etch rates are shown as a function of %H2 concentration for ECR- and ICP-generated Cl2/H2/Ar plasmas. GaN etch rates in the ECR and ICP increased slightly as H2 was initially added to the Cl2/Ar plasma indicating a reactant limited regime. Monitoring the ECR plasma with a quadrupole mass spectrometry (QMS) showed that the Cl concentration (indicated by m/e = 35) remained relatively constant at 10% H2. As the H2 concentration was increased above 10%, the Cl concentration decreased and a peak corresponding to HCl increased. GaN etch rates decreased at H2 concentrations > 10% in both the ECR and ICP, presumably due to the consumption of reactive Cl by hydrogen. In Figure 57, H2 was added to BCl3-based ECR and ICP plasmas. In the ECR plasma, the GaN etch rate increased at 10% H2 corresponding with an increase in the reactive Cl concentration as observed by QMS. As the H2 concentration was increased further, GaN etch rates decreased, the Cl concentration decreased, and the HCl concentration increased presumably due to the consumption of reactive Cl by hydrogen. In the ICP reactor, GaN etch rates were slow and decreased as hydrogen was added to the plasma up to 80% H2 where a slight increase was observed.

Another example of plasma chemistry dependent etching of GaN is shown in Figure 58 for Cl2/N2/Ar and BCl3/N2/Ar ICP-generated plasmas. In the Cl2-based plasma, GaN etch rates decreased as the %N2 increased, due to less available reactive Cl. In the BCl3-based plasma GaN etch rates increased up to 40% N2 and then decreased at higher N2 concentrations. This observation has also been reported for ECR and ICP etching of GaAs, GaP, and In-containing films. Ren and co-workers first observed maximum etch rates for In-containing films in an ECR discharge at a gas ratio of 75/25 for BCl3/N2. Using optical emission spectroscopy
Ren reported maximum emission intensity for atomic and molecular Cl at 75% BCl₃ as well as a decrease in the BCl₃ intensity and the appearance of a BN emission line. The authors speculated that N₂ enhanced the dissociation of BCl₃ resulting in higher concentrations of reactive Cl and Cl ions and thus higher etch rates. Additionally, the observation of BN emission suggested that less B was available to recombine with reactive Cl. This explanation may also be applied to the peak GaN etch rates observed at 40% N₂ in the ICP BCl₃/N₂/Ar plasmas. However, OES of the BCl₃/N₂/Ar ICP discharge did not reveal higher concentrations of reactive Cl nor a BN peak emission. In Figure 59, OES spectra are shown for a) 100% BCl₃, b) 75% BCl₃ - 25% N₂, c) 25% BCl₃ - 75% N₂, and d) 100% N₂ ICP plasmas. As N₂ was added to the BCl₃ plasma, the BCl₃ emission (2710 Å) and Cl emission (5443 and 5560 Å) decreased while the BN emission (3856 Å) was not obvious.

BCl₃/Cl₂ plasmas have shown encouraging results in etching GaN films. The addition of BCl₃ to a Cl₂ plasma can improve sputter desorption due to higher mass ions and reduce surface oxidation by gettering H₂O from the chamber. In Figure 60, GaN etch rates are shown as a function of %Cl₂ in a BCl₃/Cl₂/Ar ICP plasma. As the %Cl₂ increased, GaN etch rates increased up to 80% due to higher concentrations of reactive Cl. OES was used and showed the Cl emission intensity increased and the BCl emission intensity decreased as the %Cl₂ increased. Slower GaN etch rates in a pure Cl₂ plasma were attributed to less efficient sputter desorption of etch products in the absence of BCl₃. Similar results were reported by Lee et al. The fastest GaN etch rates were observed at 10% BCl₃ where the ion current density and Cl radical density were the greatest as measured by OES and a Langmuir probe.

In general, GaN:AlN and GaN:InN etch selectivities are < 10:1 as a function of plasma chemistry for Cl₂- or BCl₃-based plasmas. GaN:AlN and GaN:InN etch selectivities were higher for Cl₂-based ICP plasmas as compared to BCl₃-based ICP plasmas due to higher concentrations of reactive Cl produced in the Cl₂-based plasmas thus resulting in faster GaN etch rates. Alternatively, InN and AlN etch rates showed much less dependence on plasma chemistry and were fairly comparable in Cl₂ and BCl₃-based plasmas. An example of etch selectivity dependence on plasma chemistry is shown in Figure 61. GaN, AlN, and InN etch rates and etch selectivities are plotted as a function of %SF₆ for an ICP Cl₂/SF₆/Ar plasma. GaN and InN etch rates decreased as SF₆ was added to the plasma due to the consumption of Cl by S and therefore lower concentrations of reactive Cl. The AlN etch rates increased with the addition of SF₆ and
reached a maximum at 20% SF$_6$. As SF$_6$ was added to the Cl$_2$ plasma, slower AlN etch rates were expected due to the formation of low volatility AlF$_3$ etch products. However, due to the high ion flux in the ICP, the sputter desorption of the AlF$_3$ may occur prior to passivation of the surface. Therefore, the GaN:AlN selectivity decreased rapidly from ~ 6:1 to < 1:1 with the addition of SF$_6$. The GaN:InN selectivity reached a maximum of 4:1 at 20% SF$_6$.

Other halogen-containing plasmas including ICl/Ar, IBr/Ar, BBr$_3$/Ar, and Bl$_3$/Ar have been used to etch GaN with promising results. Vartuli and co-workers reported GaN, InN, AlN, InN, InAlN, and InGaN etch rates and selectivities in ECR ICl/Ar and IBr/Ar plasmas. In general, etch rates increased for all films as a function of dc-bias due to improved III-N bond breaking and sputter desorption of etch products form the surface. GaN etch rates > 1.3 µm/min were obtained in the ICl/Ar plasma at a rf-power of 250 W while GaN etch rates were typically < 4000 Å/min in IBr/Ar. Cho et al. reported GaN etch rates typically < 2000 Å/min in ICP-generated Bl$_3$/Ar and BBr$_3$/Ar plasmas. ICl/Ar and IBr/Ar ECR plasmas yielded GaN:InN, GaN:AlN, GaN:InGaN, and GaN:InAlN selectivities < 6:1, however, etch selectivities > 100:1 were obtained for InN:GaN and InN:AlN in Bl$_3$/Ar plasmas. Fast etch rates obtained for InN were attributed to the high volatility of the In$_3$ etch products as compared to the Ga$_3$ and Al$_3$ etch products which can form passivation layers on the surface. Maximum selectivities of ~ 100:1 for InN:AlN and ~ 7.5 for InN:GaN were reported in the BBr$_3$/Ar plasma.

Pearton and coworkers were the first to etch group-III nitride films in an ECR-generated CH$_4$/H$_2$/Ar plasmas. Etch rates for GaN, InN, and AlN were < 400 Å/min at ~250 V dc-bias. Vartuli et al. reported ICP GaN, InN, and AlN etch rates approaching 2500 Å/min in CH$_4$/H$_2$/Ar and CH$_4$/H$_2$/N$_2$ plasmas. Etch rates increased with increasing dc-bias or ion flux and were higher in CH$_4$/H$_2$/Ar plasmas. Anisotropy and surface morphology were good over a wide range of conditions. As compared to Cl-based plasmas, etch rates were consistently slower which may make the CH$_4$/H$_2$-based processes applicable for devices where etch depths are relatively shallow and etch control is extremely important.

Vartuli and co-workers compared etch selectivities in CH$_4$/H$_2$/Ar and Cl$_2$/Ar plasmas in both RIE- and ECR-generated plasmas. For CH$_4$/H$_2$/Ar plasmas, InN:GaN and InGaN:GaN etch selectivities ranged from ~ 1:1 to 6:1 whereas etch selectivities of 1:1 or favoring GaN over the In-containing films was reported for Cl$_2$/Ar plasmas.
ETCH PROFILE AND ETCH SURFACE MORPHOLOGY

Etch profile and etch surface morphology can be critical to post-etch processing steps including the formation of metal contacts, deposition of interlevel dielectric or passivation films, or epitaxial regrowth. Figure 62 shows SEM micrographs of GaN, AlN, and InN etched in Cl₂-based plasmas. The GaN (Figure 62a) was etched at 5 mTorr chamber pressure, 500 W ICP power, 22.5 sccm Cl₂, 2.5 sccm H₂, 5 sccm Ar, 25°C temperature, and a dc-bias of -280 ± 10V. Under these conditions, the GaN etch rate was ~ 6880 Å/min with highly anisotropic, smooth sidewalls. The sapphire substrate was exposed during a 15% overetch. Pitting of the sapphire surface was attributed to defects in the substrate or growth process. The AlN (Figure 62b) and InN (Figure 62c) features were etched at 2 mTorr chamber pressure, 500 W ICP power, 25 sccm Cl₂, 5 sccm Ar, 25°C temperature, and a cathode rf-power of 250 W. Under these conditions, the AlN etch rate was ~ 980 Å/min and the InN etch rate was ~ 1300 Å/min. Anisotropic profiles were obtained over a wide range of plasma chemistries and conditions.

Sidewall morphology is especially critical in the formation of laser mesas for ridge waveguide emitters or for buried planar devices. The vertical striations observed in the GaN sidewall in Figure 62a were due to striations in the photoresist mask which were transferred into the GaN feature during the etch. The sidewall morphology and in particular the vertical striations were improved in an ICP Cl₂/BCl₃ plasma at -150 V dc-bias. In Figure 63, a SEM micrograph of GaN etched in an ICP Cl₂/BCl₃ plasma shows highly anisotropic profiles and smooth sidewall morphology. The etch conditions were at 2 mTorr chamber pressure, 500 W ICP power, 32 sccm Cl₂, 8 sccm BCl₃, 5 sccm Ar, 25°C temperature, and a dc-bias of -150 ± 10V. Ren et al. have demonstrated improved GaN sidewall morphology etched in an ECR using a SiO₂ mask. Vertical striations in the SiO₂ mask were reduced by optimizing the lithography process used to pattern the SiO₂. The SiO₂ was then patterned in a SF₆/Ar plasma in which a low temperature dielectric overcoat was used to protect the resist sidewall during the etch.

In several studies atomic force microscopy (AFM) has been used to quantify the etched surface morphology as root-mean-square (rms) roughness. Rough etch morphology often indicates a non-stoichiometric surface due to preferential removal of either the group-III or
group-V species. For example, in Figure 64, GaN and InN rms roughness is shown for as-grown samples and for samples exposed to an ECR \( \text{Cl}_2/\text{H}_2/\text{CH}_4/\text{Ar} \) plasma as a function of cathode rf-power. The rms roughness for as-grown GaN and InN was 3.21 ± 0.56 and 8.35 ± 0.50 nm, respectively. The GaN rms roughness increased as the cathode rf-power was increased reaching a maximum of ~ 85 nm at 275 W. The rms roughness for InN was greatest at 65 W cathode rf-power implying that the ion-bombardment energy is critical to balance the chemical and sputtering effect of this plasma chemistry to maintain smooth surface morphologies.

**PLASMA-INDUCED-DAMAGE**

Plasma-induced-damage often degrades the electrical and optical properties of compound semiconductor devices. Since GaN is more chemically inert than GaAs and has higher bonding energies, more aggressive etch conditions (higher ion energies and plasma flux) may be used with potentially less damage to the material. Limited data has been reported for plasma-induced damage of the group-III nitrides.\(^{268-271}\) Pearton and co-workers reported increased plasma-induced damage as a function of ion flux and ion energy for InN, InGaN, and InAlN in an ECR.\(^{268}\) The authors also reported: a) more damage in InN films as compared to InGaN, b) more damage in lower doped materials and c) more damage under high ion energy conditions due to formation of deep acceptor states which reduced the carrier mobility and increased resistivity. Post-etch annealing processes removed the damage in the InGaN while the InN damage was not entirely removed.

Ren and coworkers measured electrical characteristics for InAlN and GaN FET structures to study plasma-induced damage for ECR \( \text{BCl}_3, \text{BCl}_3/\text{N}_2, \text{and CH}_4/\text{H}_2 \) plasmas.\(^{269}\) They reported: a) doping passivation in the channel layer in the presence of hydrogen; b) high ion bombardment energies can create deep acceptor states that compensate the material; and c) preferential loss of N can produce rectifying gate characteristics. Ping and coworkers studied Schottky diodes for Ar and SiCl\(_4\) RIE plasmas.\(^{270}\) More damage was observed in pure Ar plasmas and under high dc-bias conditions. Plasma-induced damage of GaN was also evaluated in ICP and ECR Ar plasmas using photoluminescence (PL) measurements as a function of cathode rf-power and source power.\(^{271}\) The peak PL intensity decreased with increasing ion energy independent of etch technique. As a function of source power or plasma density the
results were less consistent. The PL intensity showed virtually no change at low ICP source power and then decreased as the plasma density increased. In the ECR plasma, the PL intensity increased by ~115% at low ECR source power and improved at higher ECR source powers but at a lower rate. The effect of post-etch annealing in Ar varied depending on initial film conditions, however, annealing at temperatures above 400°C resulted in a reduction in the PL intensity.

Surface stoichiometry can also be used to evaluate plasma-induced damage. Non-stoichiometric surfaces can be created by preferential loss of one of the lattice constituents. This may be attributed to higher volatility of the respective etch products, leading to enrichment of the less volatile species, or preferential sputtering of the lighter element. Auger electron spectroscopy (AES) can be used to measure surface stoichiometry. Figure 65 shows characteristic Auger spectra for (a) as-grown GaN samples and samples exposed to an ECR plasma at 850 W applied microwave power and cathode rf-powers of (b) 65 W and (c) 275 W. For the as-grown sample, the Auger spectrum showed a Ga:N ratio of 1.5 with normal amounts of adventitious carbon and native oxide on the GaN surface. Following plasma exposure, the Ga:N ratio increased as the cathode rf-power increased with some residual atomic Cl from the plasma. Under high ion energy conditions, preferential removal of the lighter N-atoms was observed resulting in Ga-rich surfaces.

CONCLUSIONS

Reliable, well-controlled patterning of the group-III nitrides can be achieved by a variety of dry etch platforms. In particular, high-density plasma ECR and ICP etch processes have yielded, smooth, highly anisotropic, etch characteristics with rates often exceeding 1.0 μm/min. These results are attributed to high ion and neutral flux which improves the III-N bond breaking efficiency and the sputter desorption of etch products formed on the surface. Halogen-based plasma chemistries, in particular Cl-, I-, and Br-based plasmas, yield high quality etch characteristics. The choice of source gas (Cl₂, BCl₃, ICl, IBr, Br₂, BBr₃, etc.) and secondary gases (H₂, N₂, SF₆, Ar, etc.) change the concentration of reactive neutrals and ions in the plasma which directly correlates to etch rate. Very smooth, anisotropic pattern transfer was obtained over a wide range of plasma etch platforms, chemistries, and conditions. Fast etch rates, high
resolution features, and low damage are obtained when the chemical and physical components of the etch mechanism are balanced.
F. IMPLANT ISOLATION

Implant isolation has been widely used in compound semiconductor devices for interdevice isolation such as in transistor circuits or to produce current channeling such as in lasers. The implantation process can compensate the semiconductor layer either by a damage or chemical mechanism. For damage compensation, the resistance typically goes through a maximum with increased post-implantation annealing temperature as the damage is annealed out and hopping conduction is reduced. At higher temperatures the defect density is further reduced below that required to compensate the material and the resistivity decreases. For chemical compensation, the post-implantation resistance again increases with annealing temperature with a reduction in hopping conduction but it then stabilizes at higher temperatures as a thermally stable compensating deep level is formed. Typically there is a minimum dose (dependent on the doping level of the sample) required for the chemically active isolation species to achieve thermally stable compensation. Thermally stable implant isolation has been reported for n- and p-type AlGaAs where an Al-O complex is thought to form and for C-doped GaAs and AlGaAs where a C-N complex is postulated. With this background, the implant isolation properties of the III-N materials are reviewed.

As shown in Figure 66, N-implantation effectively compensates both p- and n-type GaN. For both doping types the resistance first increases with annealing temperature then reaches a maximum before demonstrating a significant reduction in resistance after a 850°C anneal for n-type and a 950°C anneal for p-type GaN. This behavior is typical of implant-damage compensation. The defect levels estimated from Arrhenius plots of the resistance/temperature product are 0.83 eV for initially n-type and 0.90 eV for initially p-type GaN. These levels are still not at midgap, but are sufficiently deep to realize a sheet resistance >10^9 Ω/□.
implantation has also been reported to effectively isolate n-type GaN\(^{1(41)}\), with the material remaining compensated to over 850°C. Interestingly, H-implanted compensation of n-type GaN is reported to anneal out at ~400°C\(^{1(41)}\) with an anomalous dependence on implant energy. The reason for this is presently not known. In light of this result, however, H-implantation in GaN will require further study as H is often the ion of choice for photonic device isolation applications that require deep isolation schemes. Moreover, both the He and N isolation appear to rely solely on implantation damage without any chemical compensation effects analogous to those in the O/Al/GaAs case.\(^{272,275,276}\) However, the implantation-induced defects in GaN are more thermally stable than other III-V semiconductor materials, such as GaAs or InP, where the damage levels begin to anneal out below 700°C\(^{272}\). This may be a result of the higher bandgap of GaN or the more polar nature of the lattice causing more stable defects. Further work is still required to understand the nature of the implantation damage in GaN.

Implant isolation of the In-containing nitrides (InN, InGaN and InAlN) was first reported using F-implantation.\(^{278}\) That work showed that InN did not demonstrate significant compensation while the ternaries increased in sheet resistance by roughly an order-of-magnitude after a 500°C anneal. Data from a more extensive study of In\(_x\)Ga\(_{1-x}\)N implant isolation for varying In-composition using N- and F-implantation is summarized in Figure 67.\(^{279}\) The InGaN ternaries only realize a maximum of a 100 fold increase in sheet resistance independent of ion species after a 550°C anneal. Pure InN shows a higher increase of 3 orders-of-magnitude but still only achieves a maximum sheet resistance of 10\(^4\)Ω/□. This may be high enough for some photonic device current-guiding applications but is not sufficient for inter-device isolation in electronic circuits. The damage levels created by N-implantation are estimated from an Arrhenius plot of the resistance/temperature product to be a maximum of 390 meV below the
conduction band. The defect level is high in the energy gap, not near midgap as is ideal for implant compensation. The position of the damage level is analogous to the defect position reported for implant compensated n-type InP and InGaAs but different from the damage-associated, midgap states created in GaAs and AlGaAs.

As shown in Figure 68, In$_{0.75}$Al$_{0.25}$N, in contrast to InGaN, can be highly compensated with N- or O-implantation with over a three order-of-magnitude increase in sheet resistance after a 600-700°C anneal while F-implantation produces only one order-of-magnitude increase in sheet resistance. The compensating level in InAlN is also high in the bandgap with the deepest level estimated from Arrhenius plots as being 580 meV below the conduction band edge in high dose N-isolated material, however it is sufficiently deep to achieve highly compensated material. The enhanced compensation for N- and O-implantation, as compared to F-implantation, in InAlN suggests some chemical component to the compensation process. For N-implantation a reduction in N-vacancies, that are thought to play a role in the as-grown n-type conduction, may explain the enhance compensation. For O-implantation, the enhanced compensation may be the result of the formation of an O-Al complex as is thought to occur in O-implanted AlGaAs.

Figure 69 schematically summarizes the present knowledge of the position in the bandgap of the compensating implanted defect levels in III-N materials and compares these to those in GaAs and InP. Although the levels are not at mid-gap, as is ideal for optimum compensation as occurs in GaAs and p-type InP, with the exception of InGaN, the levels are sufficiently deep to produce high resistivity material.

Very effective isolation of AlGaN/GaN heterostructure field effect transistor (HFET) structures has been achieved using a combined P$^+/He^+$ implant process. The groups of
Asbeck and Lau at UCSD demonstrated that a dual energy (75/180 keV) P⁺ implant (doses of $5 \times 10^{11}$ and $2 \times 10^{12}$ cm⁻², respectively), followed by a 75 keV He⁺ implant ($6 \times 10^{11}$ cm⁻²) was able to produce sheet resistance of $\sim 10^{12}$ $\Omega$/sq in AlGaN/GaN structures with 1 µm thick undoped GaN buffers. The temperature dependence of the resistivity showed an activation energy of 0.71 eV, consistent with past measurements of deep states induced in GaN by implant damage.
III. ROLE OF IMPURITIES

The properties of virtually all bulk and epitaxial GaN are still strongly influenced by residual impurities such as O, Si, C and H by point and extended defects such as nitrogen vacancies and threading dislocation. The role of these entities has been reviewed previously, and in this section we will focus on H, O, C and structural defects.

A. HYDROGEN

Hydrogen is a component of most of the gases and liquids used in the growth, annealing and processing of semiconductors and a great deal of attention has been focused on the effects of hydrogen incorporation in Si, GaAs, SiC and other materials. It is fairly well established that H$_2$ (or larger aggregates) are basically electrically and optically inactive in all semiconductors, and that the diatomic species has low diffusivity once formed inside the semiconductor. By contrast, atomic hydrogen (which may exist as H$^0$, H$^+$ or H$^-$ depending on the position of the Fermi level) diffuses rapidly even at low temperatures (25-250°C) and can attach to dangling or defective bonds associated with point or line defects, and can also form neutral complexes with dopants, i.e.

$$D^+ + H^- \rightarrow (DH)^0$$

$$A^- + H^- \rightarrow (AH)^0$$

where D$^+$ and A$^-$ are ionized shallow donor and acceptor dopants, respectively. These reactions manifest themselves as increases in resistivity of the semiconductor, and an increase in carrier mobility as ionized impurity scattering is reduced. A typical signature of an unintentional hydrogen passivation process is a reduction in doping density in the near-surface region (≤1μm) due to indiffusion of atomic hydrogen from the liquid or gas in which the sample is immersed.
In GaN and related materials (AlN, InN, InGaN, InAlN, AlGaN) it has been found that hydrogen is present in relatively high concentrations in as-grown samples, especially p-type GaN, and that hydrogen is readily incorporated during many device process steps such as plasma etching, plasma-enhanced chemical vapor deposition (PECVD), solvent boiling and wet chemical etching.\(^{(304)}\)

For many years it was not possible to achieve p-type doping in GaN, due partially to the often high residual n-type background (resulting from nitrogen vacancies or Si or O impurities) and the high ionization energy level of most acceptor dopants. However even in GaN(Mg) in which the Mg concentration was easily sufficient to produce p-type conductivity, the material was generally resistive.

Amano et al.\(^{(305)}\) found that when the electron beam in a scanning electron microscope was focused on these samples, blue emission was evident, and the resistivity of the exposed area had dramatically decreased. Nakamura et al.\(^{(231,232)}\) later found low p-type conductivity in as-grown GaN(Mg). Further treatment in a low-energy electron beam irradiation facility reduced the resistivity from \(4 \times 10^4 \Omega \text{cm}\) to \(~3\Omega \text{cm}\) in the top 0.5\(\mu\) of the surface, as shown in Figure 70. A maximum hole concentration of \(7 \times 10^{18} \text{cm}^{-3}\) and a mobility of \(3\text{cm}^2/\text{V.s}\) were obtained by this method.

Subsequently, Nakamura et al.\(^{(307,308)}\) showed that low resistivity p-type GaN with uniform carrier densities throughout their entire thickness could be obtained by post-growth thermal annealing in \(N_2\) at temperatures \(\geq 700^\circ\text{C}\). Once again the resistivity was observed to drop from \(~10^6\Omega \text{cm}\) to \(2\Omega \text{cm}\). Deep level emission at \(~750\text{ nm}\) sharply decreased with annealing, while the blue (450 nm) emission was maximized at \(700^\circ\text{C}\). To elucidate the mechanism responsible for these changes, Nakamura et al.\(^{(307,308)}\) annealed p-type GaN(Mg) in either \(N_2\) or
NH₃. As shown in Figure 71, while there was no change in the resistivity with N₂ annealing, above ~500°C the GaN returned to high resistivity when NH₃ was the annealing ambient. Subsequent annealing in N₂ returned these films to their low-resistivity condition, and these changes correlated with changes in the photoluminescence spectrum from the samples (Figure 72). NH₃ decomposes above ~200°C from N₂ and H₂ (99.9% dissociation at 800°C)⁴⁰⁹, and dissociation of the hydrogen can be catalyzed by the presence of the GaN surface. Thus there is a sizable flux of atomic hydrogen available for indiffusion into the GaN film, where it can form neutral complexes with the Mg acceptors through the reactions

\[ Mg^- + H^* \rightarrow (Mg - H)^0. \]

This produces compensation of the holes from the acceptors and leads to high resistivity. The reaction can be driven in the reverse direction by either annealing or injection of minority carrier (electrons) through the low energy electron beam irradiation or by shining above bandgap light onto the sample, or by forward biasing of a p-n junction structure. One usually observes a decrease in blue emission from samples annealed above ~700°C, unless special precautions are taken, because of the onset of surface dissociation.⁴⁰⁸ Amano et al.⁴¹⁰ reported that the intensity of Zn-related blue emissions in GaN(Zn) was enhanced by electron injection, suggesting that (Zn-H)⁰ complexes also form in this material.

In as-grown GaN there are numerous potential sources of hydrogen, since the growth reaction by Metal Organic Chemical Vapor Deposition (MOCVD) proceeds as:

\[ (CH₃)₃Ga + NH₃ \rightarrow GaN + CH₄ \uparrow + H₂ \uparrow. \]

In some cases H₂ is also employed as a carrier gas for the trimethylgallium. Previous work in other semiconductor systems grown with metal–organic precursors has shown that all three of the components of the growth chemistry, i.e. Group III source, Group V source and carrier gas, can
contribute to dopant passivation. Even the dopant sources (Cp2Mg and Si2H6 are the most common for GaN) are potential supplies of hydrogen in the GaN films. There is a direct correlation of H and Mg concentrations in MOCVD GaN, suggesting that there is trapping of hydrogen at the acceptors. Further implication of hydrogen passivation as the hole reduction mechanism comes from the fact that p-GaN has been achieved by Mg-doping in Molecular Beam Epitaxy material without post-growth annealing. In this case N2 is derived from as plasma source and solid Ga is the group III source, and hence no hydrogen is present in the growth environment.

In most III-V semiconductors it is found that atomic hydrogen diffuses more rapidly in p-type material where it is likely in a positive charge state (H+), and bonds more strongly to acceptors that it does to donors. Figure 73 shows a SIMS depth profile of GaN(Mg) grown on Al2O3 by MOCVD - the as-grown material contains ~5.5x10^{19}/Mg.cm$^{-3}$, and this remains stable upon annealing at 700°C. The hole concentration in the material was ~6x10^{17} cm$^{-3}$. Note that there is ~10^{18} cm$^{-3}$ hydrogen in the as-grown sample, more than enough to compensate all the holes. Post-growth annealing at 700°C for 60 mins reduces the hydrogen concentration to 1-5x10^{17} cm$^{-3}$, which is below the hole concentration and hence the p-type conductivity returns.

An interesting point from Figure 73 is that a substantial amount of hydrogen remains in the material, probably bound at defects or internal surfaces. This residual hydrogen may give rise to effects such as current gain drift in transistors, or a dependence of apparent material resistivity on the measurement current in Hall measurements because of minority-carrier reactivation of passivated acceptors.
Figure 74 shows the hydrogen concentration in undoped, lightly Mg-doped and heavily Mg-doped GaN as a function of annealing time at 700°C under a N\textsubscript{2} ambient.\(^{328}\) The hydrogen concentration is reduced with time, but saturates at \(\sim 2 \times 10^{17}\) cm\(^{-3}\); it is not clear if this represents the background sensitivity of the SIMS apparatus, or is a real concentration. After the anneal, the heavily Mg-doped (Mg=6\times10^{19}\) cm\(^{-3}\) sample remained highly resistive. A problem with continuing to increase the Mg concentration is the onset of cracking of the GaN films, and conversion of the conductivity to n-type. The reasons for this are as yet unclear, and the presence of Mg interstitials acting as shallow donors or formation of Mg-defect complexes with donor nature are just two of the possibilities. As found by Nakamura et al. the changes in resistivity are accompanied by strong changes in the PL spectra.\(^{307,308,328}\) Figure 75 shows 5K spectra in heavily Mg-doped (Mg=6\times10^{19}\) cm\(^{-3}\) GaN before and after different annealing times at 700°C. The peak at 3.285 eV has been ascribed to a free-to-bound Mg transition, corresponding to a binding energy for Mg of 155 meV\(^{329}\), while that at 3.445 eV has been identified as a transition involving an exciton bound to Mg.\(^{330}\) Annealing for 20 min at 700°C shifts this latter peak to 3.446 eV.\(^{328,331}\) Li et al.\(^{328}\) attributed the 3.45 eV peak to a transition associated with an exciton bound to the Mg acceptor. For 60 min annealing, observation of a 3.465 eV peak was found in lightly Mg-doped GaN, consistent with a previous assignment of an exciton bound to a nitrogen vacancy.\(^{330}\) Therefore, loss of N\textsubscript{2} and compensation of the p-type doping by introduction of the shallow donor N, states appears to be another reason it is difficult to get strong p-type conductivity.

Piner et al.\(^{332}\) found that the hydrogen concentration in MOCVD In\textsubscript{x}Ga\textsubscript{1-x}N was a strong function of H\textsubscript{2} and NH\textsubscript{3} flow rates during growth, and also had a strong effect on the background C and O concentrations. Therefore, the overall compensation in the material is affected by the
hydrogen flow. Figure 76 shows H, C and O relative concentrations in InGaN grown at 730°C, as a function of NH₃ flow rate. While the H clearly originates from the ammonia and the metalorganic sources, it appears that the purified NH₃ is the source of oxygen. The reduction in carbon with NH₃ flow probably results from H scavenging reactions.⁴³³

Johnson et al.⁴³⁴ performed a series of MBE growth experiments in which GaN(Mg) was grown with either pure N₂ plasmas or mixed N₂/H₂ plasmas in order to understand the effect of hydrogen under controlled conditions. However PL examination showed only minor differences in some cases due to Mg compensation. No measurements of H concentrations were reported, and it is likely under the particular growth conditions used there was little H incorporation.

Soto⁴³⁵ reported that GaN grown by plasma-assisted MOCVD using triethylgallium and N radicals was highly resistive, and attributed to the high density of C and H (10¹⁹-10²⁰ cm⁻³) incorporated into the films. The H signal intensity was linearly related to the C signal, suggesting complexing of the C and H. Annealing at 900°C did not affect the resistivity.

Lee and Yong⁴³⁶ grew hydrogenated AlN by rf magnetron sputtering in a H₂/Ar/N₂ gas mixture. The addition of H was found to reduce the oxygen background in the material, and the activation energy for the evolution of H₂ gas from the AlN:H flow was found to be 0 eV/atom as determined by gas chromatography. A variety of N-H IR peaks were found between 2074-3532 cm⁻¹ – these bonds may hinder formation of N-O bonds.⁴³⁸ The value of 0.11 eV/atom for hydrogen evolution is consistent with hydrogen bound at N atoms.⁴³⁷

**DOPANT PASSIVATION**

We have recently seen that atomic hydrogen passivates both Mg and Zn, but a number of reports have shown passivation of Ca⁴³⁸, C⁴³⁹ and Cd.⁴⁴⁰ Theoretical considerations initially
suggested that Ca might be a shallow acceptor in GaN than Mg. Zolper et al. realized p-type doping of GaN using implantation of Ca+ alone, or a co-implantation of C+ and P+, followed by rapid thermal annealing at ¥1100°C. While the activation efficiency of Ca in both implant schemes was ~100%, temperature-dependent Hall measurements showed that the ionization level of Ca was ~168 meV, similar to that of Mg. The Ca atomic profile was thermally stable to temperatures up to 1125°C. Since Mg has a substantial memory effect in stainless steel epitaxial reactors (or in gas lines leading to quartz chamber systems), Ca may be a useful alternative p-dopant for epitaxial growth of laser diode or heterojunction bipolar transistor structures in which junction placement, and hence control of dopant profiles, is of critical importance.

In considering Ca-doped GaN for device applications it is also necessary to understand the role of hydrogen, since there is always a ready supply of atomic hydrogen available from NH3, the metalorganic group III source (typically (CH3)3Ga) or from the gaseous dopant source when using chemical vapor deposition techniques. We have also found that Ca acceptors in GaN are also readily passivated by atomic hydrogen at low temperature (250°C), but they can be reactivated by thermal annealing at ¥500°C for 1 min in lightly-doped (3x1017cm-3). As the carrier density is restored by such annealing treatments there is a true passivation and not just compensation of the Ca acceptors by the hydrogen.

Nominally undoped (n<3x1016cm-3) GaN was grown on double-side polished c-AL2O3 substrates prepared initially by HCl/HNO3/H2O cleaning and an in-situ H2 bake at 1070°C. A GaN buffer ¥300Å thick was grown at ~500°C and crystallized by ramping the temperature to 1040°C where trimethylgallium and ammonia are again used to grow the 2µm thick epitaxial layer. The materials properties have been discussed in detail earlier (326,327), but in brief the double x-ray full width at half maxima are ~300 arc.sec and the total defect density (threading...
dislocations, stacking faults) apparent in plain view transmission electron microscopy within typically 2-4x10^9 cm^-2. The as-grown films are featureless, transparent and have strong bandedge (3.47 eV) luminescence.

\(^{40}\)Ca ions were implanted at 180 keV and a dose of 5x10^{14} cm^-2. In some cases, a co-implant of P\(^+\) to the same dose at an energy of 130 keV was performed to try to enhance to substitutional fraction of Ca upon subsequent annealing in analogy to the case of Mg implantation in GaN. For the case of Ca we found there was little additional activation as a result of the co-implant. After rapid annealing at 1150°C for 15 sec under N\(_2\) in a face-to-face geometry we measured sheet carrier densities of p~1.6x10^{12} cm^-2 with a mobility at 500 K of 6cm^2/Va. Arrhenius plots of the hole density showed an ionization level of 169 meV for the Ca in GaN (Figure 77). Samples with alloyed HgIn ohmic contacts were exposed to an Electron Cyclotron Resonance (ECR) H\(_2\) or He plasma (2.45 GHz) with 850W forward power and a pressure of 10 mTorr. The exposure time was 30 min at 250°C, and the temperature was lowered to room temperature with the plasma on. The sheet carrier density and hole mobility at 300 K were obtained from Van der Pauw geometry Hall Measurements. Post-hydrogenation annealing was performed between 100-500°C for 60 sec under flowing N\(_2\) with the ohmic contacts already in place.

The initial H\(_2\) plasma exposure caused a reduction in sheet hole density of approximately an order of magnitude, as shown in Figure 78. No change in electrical properties were observed in the He-plasma treated samples, showing that pure ion bombardment effects are insignificant and the chemical interaction of hydrogen with the Ca acceptors is responsible for the conductivity changes. Post-hydrogenation annealing had no effect on the hole density up to 300°C, while the initial carrier concentration was essentially fully restored at 500°C. Assuming
the passivation mechanism is formation of neutral Ca-H complexes, then the hole mobility should increase upon hydrogenation. This is indeed the case, as shown in Figure 79. Note that the mobility decreases to its initial value with post-hydrogenation annealing. If the carrier reduction were due to introduction of compensating defects or impurities, then the hole mobility would decrease, which is not observed.

In other p-type III-V semiconductors it is generally accepted that atomic hydrogen is predominantly in a positive charge state with the donor level being around midgap. If a similar mechanism exists in GaN then the initial Coulombic attraction between ionized acceptor and hydrogen leads to formation of a neutral close pair, i.e.,

\[ Ca^+ + H^+ \leftrightarrow (Ca-H)^0. \]

The existence of the neutral complex should be verified by observation of a vibrational band\(^{(342)}\), but to obtain the sensitivity needed for such a measurement will require a relatively thick epilayer of Ca-doped GaN. Our present implanted samples do not have a sufficient Ca density-times-thickness product to be suitable for infra-red spectroscopy.

If the dissociation of the Ca-H species is a first-order process then the reactivity energy from the data in Figure 78 is ~2.2 eV\(^{(342)}\) assuming a typical attempt frequency of \(10^{14}\) s\(^{-1}\) for bond breaking processes. This is similar to the thermal stability of Mg-H complexes in GaN which we prepared in the same manner (implantation) with similar doping levels. In thicker, more heavily doped samples, the apparent thermal stability of hydrogen passivation is much higher because of the increased probability of retrapping of hydrogen at other acceptor sites.\(^{(342)}\) This is why for thick, heavily-doped \((p>10^{18} \text{cm}^{-3})\) GaN(Mg), a post-growth anneal of at least 700°C for 60 min is employed to ensure complete dehydrogenation of the Mg. True reactivation energies can only be determined in reserve-biased diode samples where the strong electric fields
present sweep the charged hydrogen out of the depletion region and minimize retrapping at the acceptors.\textsuperscript{343}

In conclusion we have found that hydrogen passivation of acceptors in GaN occurs for several different dopant impurities and that post-growth annealing will also be required to achieve full electrical activity in Ca-doped material prepared by gas-phase deposition techniques. The thermal stability of the passivation is similar for Ca-H and Mg-H complexes, with apparent reactivation energies of $\sim 2.2$ eV in lightly doped ($\sim 10^{17}$ cm$^{-3}$) material.

Abernathy et al.\textsuperscript{344} reported carbon doping of GaN using CCU in Metal Organic Molecular Beam Epitaxy, with maximum hole concentrations of $\sim 3 \times 10^{17}$ cm$^{-3}$. The total carbon concentration in these films is somewhat higher than this (1-2 orders of magnitude), but the reason for the low doping efficiency is not known at this point.\textsuperscript{345} The activation energy of acceptor ionization was reported to be $\sim 26$ meV, but this may be due to impurity band conduction.\textsuperscript{345}

Exposure of the GaN(C) samples to an Electron Cyclotron Resonance H$_2$ plasma at 250°C reduces the hole concentration by approximately a factor of three\textsuperscript{339}, with an accompanying increase in hole mobility. Annealing of the hydrogenated material restored the initial hole concentration at $\sim 450$°C. It is well established in other dopant-hydrogen complexes that the apparent thermal stability is a strong function of the doping level and sample thickness because of hydrogen retrapping effects.

Burchard et al.\textsuperscript{340} studied the formation and properties of Cd-H pairs in GaN using radioactive $^{111}$Cd and perturbed $\gamma\gamma$ angular correlation spectroscopy. The H was incorporated by 100 eV implantation, and formation of two different Cd-H complexes (different configurations) with dissociation energies of 1.1 and 1.8 eV, respectively, were found.
Table VII summarizes the information reported to date for hydrogen-acceptor complexes in GaN. To this point there have not been any direct observations of donor dopant passivation in any of the nitrides, although this is fairly typical of what has occurred previously in other semiconductor systems. For example, in Si, acceptor passivation was first reported in 1983\(^{(346)}\), and it was only in 1986 that reports of weak donor passivation were seen.\(^{(347)}\) Subsequently in 1988, the first unambiguous observations by IR spectroscopy were made\(^{(348-350)}\), but only after realizing that because of the lower binding energies for donor dopant-hydrogen complexes, the temperature at which the hydrogen was unincorporated should be lowered.\(^{(350)}\) Once the plasma injection temperature was reduced (to 120°C from the usual 200°C for p-type Si), donor passivation efficiencies over 90% were realized.\(^{(351)}\) Another feature of dopant passivation by hydrogen is that it depends on the characteristics of the plasma used for injection, i.e. the relative fluxes of \(H_2\), \(H_2^+\), \(H^0\), \(H^+\) and associated excited states, the average ion energy, and the Fermi level at the semiconductor surface.\(^{(352)}\) For example, we have seen that increasing the ion energy in a \(H_2\) plasma increases the incorporation depth of hydrogen in p-type GaAs by up to 50%\(^{(353)}\), and somewhat smaller effects have been observed in SiC.\(^{(354)}\)

DIFFUSION AND REACTIVATION MECHANISMS

Typical SIMS profiles of \(^2\text{H}\) in p-type GaN with \([\text{Mg}] \sim 2 \times 10^{19}\text{cm}^{-3}\) and hole concentration \(-1 \times 10^{17}\text{cm}^{-3}\), and in n-type GaN, with Si \(-2.5 \times 10^{18}\text{cm}^{-3}\) and electron concentration \(2 \times 10^{19}\text{cm}^{-3}\), are shown in Figure 80 and 81, respectively for samples exposed to a \(^2\text{H}\) plasma for 30 mins at 250°C. Note in the p-type material the \(^2\text{H}\) follows an indiffusion profile where \(^2\text{H}\) is trapped at Mg or defects, and there is a very high concentration shallow feature extending to \(-0.1\mu\text{m}\) from the surface. This is deeper than the usual peak due to non-equilibrium sputtering effects in
SIMS, and may result from extended $^2$H clusters or platelets. In the n-type material there is basically no measurable deuterium, suggesting that $^2$H is not readily trapped at donor dopants. However, as pointed out above, this may simply be due to non-optimized plasma conditions employed thus far.

A number of reports have shown that hydrogen can indeed pair with positively charged native donors in InN, InGaN, InAlN and AlGaN.\textsuperscript{(355-358)} Frequently undoped Al$_x$Ga$_{1-x}$N films with $x<0.4$ show electron concentration in the $10^{18}$-$10^{19}$ cm$^{-3}$ range and mobilities on the order $10$ cm$^2$V$^{-1}$s$^{-1}$.\textsuperscript{(359-364)} In addition, many groups have observed very strong tails at optical absorption near the band edge. High carrier concentrations and strong band tailing in AlGaN make it difficult to use such layers in most applications. Polyakov et al.\textsuperscript{(358)} found that hydrogen plasma exposure at $200^\circ$C for 1 h led to a substantial decrease in carrier concentration accompanied by an increase in electron mobility. The passivation efficiency appears to be higher for AlGaN than for pure GaN, and there was little change in electrical properties for the closely compensated GaN sample with initial carrier concentration of $8\times10^{14}$ cm$^{-3}$. By sharp contrast, changes in AlGaN carrier concentration still occur even when the starting concentration is low. Polyakov et al.\textsuperscript{(358)} suggested that passivation of native donors in AlGaN proceeds via pairing with negatively charged hydrogen ions\textsuperscript{(365)}, and that efficiency of passivation drops rapidly as the Fermi level crosses the hydrogen acceptor level. This would place the H$^-$ level in GaN somewhere above $E_c$-$0.2$ eV and much deeper than that in AlGaN (e.g. in Al$_{0.12}$Ga$_{0.88}$N it should be close to $E_c$-$0.5$ eV). Measurements of the temperature dependence of carrier concentration in high resistivity AlGaN samples after hydrogen treatment yield the same activation energies as before treatment (0.3 eV in Al$_{0.12}$Ga$_{0.88}$N, 0.22 eV in Al$_{0.07}$Ga$_{0.93}$N).
indicating that no deeper compensating centers have been introduced, and that the decreased
carrier concentration is a result of passivation of the existing electrically active centers.

The effect of hydrogen plasma passivation on the absorption spectra near the fundamental
absorption edge in AlGaN and AlN samples is shown in Figure 82. Prior to passivation, the
magnitude of the band tailing (manifested in deviation of the squared absorption coefficient
versus photon energy from a straight line) is substantial. This band tailing is suppressed by the
hydrogen plasma treatment. The origin of the band tails may be related to fluctuations of local
electric fields due to fluctuations of the density of charged defects. The hydrogenation treatment
reduces the concentration of these defects, reducing the near bandedge absorption. For AlN no
measurements of electrical properties could be performed because of its high resistivity. The
near bandedge absorption observed in that case could come from local fields associated with
deep levels, and suppression of such absorption could be related to the suppression of electrical
activity of these deep centers. PL measurements on these samples showed a decrease in deep
level emission and an increase in bandedge emission as a result of the hydrogenation.

The thermal stability of native donor-hydrogen complexes was measured by isochronal
annealing as shown in Figure 83. The fraction of unannealed complexes is defined as \( N_I - N_H / N_I \)
where \( N_I \) is the electron concentration before hydrogenation, \( N_H \) the electron concentration
after hydrogenation and \( N_T \) is the electron concentration after hydrogenation and subsequent
annealing at temperature \( T \). The thermal stability of the donor-hydrogen complexes increases
with AlN mole fraction, and this may play a role in the frequently observed decrease in carrier
concentration in as-grown AlGaN layers with high Al mole fractions.\(^{366,367}\)

Lower thermal stabilities were found for In-containing nitrides. Figure 84 shows the
fraction of passivated donors remaining in \( \text{In}_{0.5}\text{Al}_{0.5}\text{N} \) and \( \text{In}_{0.25}\text{Al}_{0.25}\text{Ga}_{0.5}\text{N} \) initially
hydrogenated at 250°C for 30 min, as a function of post-hydrogenation annealing temperature. Both samples displayed a decrease in carrier concentration of approximately an order of magnitude after hydrogen plasma exposure. The passivated donors begin to reactivate around 400°C and by 500°C 78% of the lost carriers were restored in InAlN and 66% in the InAlGaN. The recovery of the donor activity occurred over a broader temperature range than generally observed for other passivated dopants, and is consistent with the presence of a Gaussian distribution of activation energies. This may be due to nitrogen vacancies with different numbers of specific Group III neighbors surrounding them (i.e. two In and two Al versus one In and three Al). Assuming a Gaussian distribution of energies we obtained values of 1.4 eV for the activation energy for donor reactivation, with a full width at half maximum of ~0.3 eV.

In AlN, hydrogenation at 250°C for 30 min was able to produce a uniform concentration of H of ~10^21 cm^-3 throughout a 1μm thick sample. Since this is well above the native donor concentration, the H is presumably bound at structural defects in the material. Annealing at 800°C did not measurably affect the H profile, but after 900°C the H plasma tends to form a high density of In droplets on its surface because of preferential loss of N as NH3, whereas InGaN is more resistant to surface degradation. This is similar to the situation for InP and the related ternaries InGaAs and InAlAs.

In both Si(368-374) and GaAs(375-378) injection of minority carriers either by forward biasing of a diode structure or illumination with above bandgap light produces dissociation of neutral acceptor-hydrogen or donor-hydrogen complexes at temperatures at which they are normally thermally stable. While the details of the reactivation process are not clearly established, it is expected that for an acceptor A the reactions likely can be described by

\[
\begin{align*}
(AH)_y & \leftrightarrow A^- + H^+ \\
H^+ + e^- & \leftrightarrow H^0.
\end{align*}
\]
The neutral hydrogen most likely forms diatomic or larger clusters with other neutral or charged hydrogen species. The mechanism for acceptor activation during the e-beam irradiation process has not been studied in detail to date. To establish that minority-carrier-enhanced debonding of Mg-H complexes in GaN is responsible for this phenomenon, we examined the effect of forward biasing in hydrogenated p-n junctions. We find that the reactivation of passivated acceptors obeys second-order kinetics and that the dissociation of the Mg-H complex is greatly enhanced under minority-carrier injection conditions.

The sample was grown on c-Al2O3 by MOCVD using a rotating disk reactor. After chemical cleaning of the substrate in both acids (H2SO4) and solvents (methanol, acetone), it was baked at 1100°C under H2. A thin (≤300 Å) GaN buffer was grown at 510°C, before growth of ~1 µm undoped material. 0.5 µm of GaN(Mg) with a carrier density of p~1.5x10^17 cm^-3 after 700°C annealing and 0.3 µm GaN (Si) with a carrier density of 5x10^18 cm^-3. Some of the sample was hydrogenated by annealing under NH3 for 30 min at 500°C. This produces passivation of the Mg acceptors but has little effect on the Si donors.

Mesa p-n junction diodes were processed by patterning 500-µm-diam TiAl ohmic contacts on the n-GaN by liftoff and then performing a self-aligned dry etch with an electron cyclotron resonance BCl3/Ar plasma to exposure the p-type GaN. E-beam evaporated NiAu was patterned by liftoff to make ohmic contact to the p-type material. The carrier profiles in the p-type layer were obtained from 10 kHz capacitance-voltage measurements at room temperature. Anneals were carried out in the dark at 175°C under two different types of conditions. In the first, the diode was in the open-circuit configuration, while in the second the junction was forward biased at 9 mA to inject electrons into the p-type GaN. After each of these treatments
the samples were returned to 300K for remeasurement of the net electrically active acceptor profile in this layer.

Figure 85 shows a series of acceptor concentration profiles measured on the same p-n junction sample, after annealing at 175°C under forward bias conditions. After the NH₃ hydrogenation treatment the electrically active acceptor density decreased from 1.5x10¹⁷ to ~6-7x10¹⁶ cm⁻³. If the subsequent annealing was carried in the open-circuit configuration, there was no change in the carrier profile for periods up to 20 h at 175°C. By sharp contrast Figure 85 shows that for increasing annealing times under minority-carrier injections conditions there is a progressive reactivation of the Mg acceptors with a corresponding increase in the hole concentration. After 1 h, the majority of these acceptors have been reactivated. Clearly therefore, the injection of electrons has a dramatic influence on the stability of the MgH complexes. The Mg reactivation has a strong dependence on depth into the p-type layer, which may result from the diffusion distance of the injected electrons prior to recombination. We rule out heating of the sample during forward biasing as being a factor in the enhanced dissociation of the neutral dopant-hydrogen complexes. The samples were thermally bonded to the stainless-steel stage and the junction temperature rise is expected to be minimal (≤10°C). Moreover, from separate experiments we found that reactivation of the Mg did not begin until temperatures above ~450°C under zero-bias conditions.

Previous experiments on minority-carrier-enhanced reactivation of hydrogen passivated dopants in Si(371) and GaAs(377) have found that for long annealing times the kinetics can be described by a second order equation

\[ d[N_A - N(t)]/dt = C(N_A - N(t))^2 \]
where $N_A$ is the uniform Mg acceptor concentration in the non-hydrogenated sample. $N(t)$ is the acceptor concentration in the hydrogenated GaN after forward bias annealing for time $t$, and $C$ is a second-order annealing parameter.

In order to quantitatively analyze the reactivation kinetics of the Mg-H complexes in GaN, we measured the inactive acceptor concentrations $N_A-N(t)$ using the capacitance-voltage measurements at a depth of 0.1μm in the $p$-GaN layer. Figure 86 shows that there is a linear relationship between $[N_A-N(t)]^{-1}$ and annealing time $t$, confirming that the reactivation process can be described by a second-order equation with $C=4\times10^{-20}\text{cm}^3\text{s}^{-1}$. This value is consistent with those obtained in Si and GaAs where minority-carrier-enhanced dopant reactivation has also been reported.

The rate of reactivation of passivated acceptors is dependent on the injected minority-carrier density. Moreover, for short annealing times it was found that the dopant reactivation occurred at a faster rate than predicted by the second-order equation for very short annealing times, and that the annealing process was rate limited by the formation of stable, electrically inactive diatomic H species. At this point there have not been enough studies of the various states of hydrogen in GaN as determined by infrared spectroscopy, channeling or secondary-ion-mass spectrometry for us to conclude anything about the ultimate fate of the atomic hydrogen once it has dissociated from the Mg-H complex, but it is likely that it then reacts with other hydrogen atoms to form diatomic or larger clusters. A strong dependence of reactivation rate on injected minority-carrier density would indicate the presence of a charge state for hydrogen and therefore influence the conversion of $\text{H}^+$ into the neutral state and then into the final hydrogen complexes.
The fact that the MgH complexes are unstable against minority-carrier injection has implications for several GaN-based devices. First, in a laser structure the high level of carrier injection would rapidly dissociate any remaining Mg-H complexes and thus would be forgiving of incomplete removal of hydrogen during the post-growth annealing treatment. In a heterojunction bipolar transistor the lower level of injected minority carriers would also reactivated passivated Mg in the base layer, leading to an apparent time-dependent decrease in gain as the device was operated.

In summary, we have shown that hydrogen-passivated Mg acceptors in GaN may be reactivated at 175°C by annealing under minority-carrier injection conditions. The reactivation follows a second-order kinetics process in which the (MgH)$_0$ complexes are stable to $\geq 450^\circ$C in thin, lightly doped GaN layers. In thicker, more heavily doped layers where retrapping of hydrogen at the Mg acceptors is more prevalent, the apparent thermal stability of the passivation is higher and annealing temperatures up to 700°C may be required to achieve full activation of the Mg. Our results suggest the mechanism for Mg activation in e-beam-irradiated GaN is minority-carrier-enhanced debonding of the hydrogen.

The diffusion and trapping behavior of hydrogen in device structures is more complicated than in single-layer structures. For example, light-emitting diodes or laser diodes contain both n- and p-type GaN cladding layers with one or more InGaN active regions. The first laser reported by Nakamura et al.\cite{379} contained 26 InGaN quantum wells. In other III-V semiconductors the diffusivity of atomic hydrogen is a strong function of conductivity type and doping level since trapping by acceptors is usually more thermally stable than trapping of hydrogen by donor impurities.\cite{380,382} Moreover, hydrogen is attracted to any region of strain within multi-layer structures and has been shown to pile up at heterointerfaces in the GaAs/Si\cite{384,385},
GaAs/InP\textsuperscript{(384,385)} and GaAs/AlAs\textsuperscript{(386)} materials systems. Therefore it is of interest to investigate the reactivation of acceptors and trapping of hydrogen in double heterostructure GaN/InGaN samples, since these are the basis for optical emitters. We find that the reactivation of passivated Mg acceptors also depends on the annealing ambient, with an apparently higher stability for annealing render H\textsubscript{2} rather than N\textsubscript{2}. Hydrogen is found to redistribute to the regions of highest defect density within the structure.

The double heterostructure sample consisted of 300Å, low-temperature GaN buffer, 3.3\textmu m of n\textsuperscript{+}(Si=10\textsuperscript{18}cm\textsuperscript{-3})GaN, 0.1\textmu m undoped InGaN and 0.5\textmu m p\textsuperscript{+} GaN (p=3x10\textsuperscript{17}cm\textsuperscript{3}, Mg-doped). In the immediate vicinity of the n-GaN/Al\textsubscript{2}O\textsubscript{3} interface the defect density was high but was reduced with increasing film thickness. However after growth of the InGaN active layer the threading dislocation density increased, due to thermal decomposition of the top of the InGaN upon raising the temperature to grow the p-GaN.\textsuperscript{(387)}

XTEM of the DH-LED showed dislocations as dark lines propagating in the direction normal to the substrate. Most of the dislocations appeared to traverse the entire double heterostructure, while some appeared to bend and follow the interface for a short distance before threading out to the surface. The nature of the threading dislocations was studied by conventional XTEM using the g·b=0 criteria. The dislocation will be invisible when b lies in the reflecting plane. Some of the dislocations were invisible both in g\textsuperscript{2}=(0002) and g\textsuperscript{5}=(1101) and because b was common to both reflections, b was found to be 1/3[1120]. Assuming that the growth is the same as the translation vector of the dislocation, these defects would be pure edge type in nature. The average threading dislocation density was also found along the plane normal to the growth direction. The dislocation density was found to be ~8x10\textsuperscript{10}/cm\textsuperscript{2}. 

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The double-heterostructure sample was exposed to an electron cyclotron resonance plasma (500W of microwave power, 10 mTorr pressure) for 30 min at 200°C. The hole concentration in the p-GaN layer was reduced from $3 \times 10^{17}$ cm$^{-3}$ to $\sim 2 \times 10^{16}$ cm$^{-3}$ by this treatment, as measured by capacitance voltage (C-V) at 300K. Sections from this material were then annealed for 20 min at temperatures from 500 to 900°C under an ambient of either N$_2$ or H$_2$ in a Heatpulse 410T furnace. Figure 87 shows the percentage of passivated Mg remaining after annealing at different temperatures in these two ambients. In the case of N$_2$ ambients the Mg-H complexes show a lower apparent thermal stability (by $\sim 150^\circ$C) than with H$_2$ ambients. This has been reported previously for Si donors in InGaP and AlInP, and Be and Zn acceptors in InGaP and AlInP, respectively$^{388}$ and most likely is due to indiffusion of hydrogen from the H$_2$ ambients, causing a competition between passivation and reactivation. Therefore, an inert atmosphere is clearly preferred for the postgrowth reactivation anneal of p-GaN to avoid any ambiguity as to when the acceptors are completely active. Previous experimental results by Brandt et al.$^{389}$ and total energy calculations by Neugebauer and Van de Walle$^{291}$ suggest that considerable diffusion of hydrogen in GaN might be expected at $\leq 600^\circ$C.

Other sections of the double-heterostructure material were implanted with $^2$H$^+$ ions (50 keV, $2 \times 10^{15}$ cm$^{-2}$) through a SiN$_x$ cap in order to place the peak of the implant distribution within the $p^+$GaN layer. Some of these samples were annealed at 90°C for 20 min under N$_2$. As shown in the secondary ion mass spectrometry (SIMS) profiles of Figure 88, the $^2$H diffuses out of the $p^+$GaN layer and piles up in the defective InGaN layer, which as we saw from the TEM results, suffers from thermal degradation during growth of the $p^+$GaN. Note that there is still sufficient $^2$H in the $p^+$GaN ($\sim 10^{19}$ cm$^{-3}$) to passivate all of the acceptors present, but electrical measurements show that the p-doping level was at its maximum value of $\sim 3 \times 10^{17}$ cm$^{-3}$. These
results confirm that as in other III-V semiconductors hydrogen can exist in a number of different states, including being bound at dopant atoms or in an electrically inactive form that is quite thermally stable. We expect that after annealing above 700°C all of the Mg-H complexes have dissociated, and the electrical measurements show that they have not reformed. In other III-Vs the hydrogen in p-type material is in a bond centered position forming a strong bond with a nearby N atom, leaving the acceptor threefold coordinated.\textsuperscript{(390)} Annealing breaks this bond and allows the hydrogen to make a short-range diffusion away from the acceptor, where it probably meets up with other hydrogen atoms, forming molecules or larger clusters that are relatively immobile and electrically inactive. This seems like a plausible explanation for the results of Figures 87 and 88, where the Mg electrical activity is restored by 700°C, but hydrogen is still present in the layer at 900°C. In material hydrogenated by implantation, there is almost certainly a contribution to the apparently high thermal stability by the hydrogen being trapped at residual implant damage as is evident by the fact that the \textsuperscript{3}H profile retains a Pearson IV type distribution even after 900°C annealing. The other important point from Figure 88 is that as in other defective crystal systems, hydrogen is attracted to regions of strain, in this case the InGaN sandwiched between the adjoining GaN layers.

In conclusion, the apparent thermal stability of hydrogen-passivated Mg acceptors in p GaN is dependent on the annealing ambient, as it is in other compound semiconductors. While the acceptors are reactivated at ≤700°C for annealing under N\textsubscript{2}, hydrogen remains in the material until much higher temperatures and can accumulate in defective regions of double-heterostructure samples grown on Al\textsubscript{2}O\textsubscript{3}. It will be interesting to compare the redistribution and thermal stability of hydrogen in homoepitaxial GaN in order to assess the role of the extended defects present in the currently available heteroeptaxial material.
ROLE OF HYDROGEN DURING PROCESSING

Light-ion implantation is typically used in III-V technology to produce high resistivity material through the introduction of point defects and complexes which are electron and/or hole traps.\(^{391,392}\) The thermal stability of this effect is an important consideration for designing the device processing sequence. High resistivity material is produced by implantation of any ion, but annealing at a sufficiently high temperature will remove the trap states, and the resistivity of the material will revert to its original value. If the implanted species has a chemical deep level in the bandgap, then the material will remain resistive even at high annealing temperatures.\(^{392}\)

A number of reports have discussed implant isolation in GaN using H, He, N or O implantation.\(^{393,394}\) Binari et al.\(^{141}\) found that higher doses of implanted hydrogen were needed in comparison with He in order to isolate n\(^+\)GaN (Figure 89). This is expected on the basis of the number of stable defects created by the two different species. The H-implanted material maintained high resistivity (>10\(^9\)Ωcm) only to ~250°C, and by 400°C all samples had resistivity of only ~10\(^3\)Ωcm. In Figure 90 we compare the thermal stability of proton implant isolation in n-GaN and GaAs. The stability is surprisingly higher in GaAs, but higher stabilities for GaN can be obtained with N\(^+\), O\(^+\) or F\(^+\).\(^{394}\) The maximum incorporation depth of implanted protons in GaN is ~2μm for a typical 200kV implanter. While the deep levels in H-implanted GaN anneal out at ≤200°C, temperatures above 800°C are needed to cause most of the hydrogen to actually leave the material.\(^{395,396}\)

We find substantial differences in the thermal stability of resistivity changes depending on the initial conductivity type of hydrogen-implanted GaN and a strong Fermi-level dependence of hydrogen diffusivity. The samples were implanted with \(^2\)H\(^+\) ions under two different conditions — for diffusion experiments the samples received a single energy (150 keV) implant at
a dose of $2 \times 10^{15} \text{cm}^{-2}$, whereas for measurement of the effect on electrical properties of the layers, they were implanted with a multiple-energy (20, 50, 100, 150 keV for the p-type; 20, 50, 100, 150, 200, 250 and 300 keV for the n-type) scheme, at a dose of $2 \times 10^{14} \text{cm}^{-2}$ for each energy. The redistribution of the implanted deuterium for anneals up to 1200°C (60 sec duration) was measured by Secondary Ion Mass Spectrometry (SIMS) using a Cs$^+$ ion beam. The sheet resistance of the multiply implanted samples was obtained after different anneals using Van der Pauw geometry Hall measurements. In these samples alloyed HgIn ohmic contacts were fabricated prior to implantation.

Figure 91 shows the ratio of the sheet resistances after implantation and annealing to that before implantation, for both n- and p-type GaN. The as-implanted samples show resistances ~3-4 orders of magnitude higher than unimplanted material. This behavior is typical of ion-damaged compound semiconductors, and arises from the creation of defect states within the GaN bandgap that act as traps for both the electrons in n-type material and the holes in p-type material. From separate temperature-dependent conductivity measurements, we find that the Fermi level is at $E_F \approx -0.8 \text{eV}$ in the n-type GaN after $^3$H$^+$ implantation and at $E_F \approx +0.9 \text{eV}$ in the implanted p-type GaN. We expect that a variety of different defect levels are created by the nuclear stopping process of the implanted deuterons (which would be measurable by deep level transient spectroscopy or thermally simulated capacitance), but the temperature dependence of conductivity yields only the dominant states. As the implanted samples are annealed, quite different behavior was observed for the two conductivity types. For the n-type GaN, the resistance initially increases with annealing, reaching a maximum at ~200°C. At higher annealing temperatures the resistance decreases back to the original value. This is the same behavior typically observed in implanted compound semiconductors, and is usually ascribed to
an initial reduction of hopping conduction as annealing of some of the implant-induced defect states occurs (leading to an increase in resistance), followed by a decrease in resistance as the trap density falls below the electron concentration and electrons are returned to the conduction band. Similar behavior has been reported previously by Binari et al.\textsuperscript{114} in $^1\text{H}^+$ implanted n-GaN.

The implanted p-GaN shows an initial decrease in resistance up to ~400°C, but then the resistance again increases and remains high even at 600°C. This behavior is consistent with an initial annealing for the implant-induced deep level states, followed by the onset of hydrogen passivation of the Mg acceptors. In these bulk (electric-field-free) layers, the acceptor passivation is stable to ≥700°C. In structures with strong internal electric fields, such as reverse-biased Schottky diodes, retrapping of the charged $\text{H}^+$ back onto the negatively-charged acceptor is minimized, and reactivation of the passivated Mg occurs at lower temperature.

To confirm the above discussion, SIMS measurements were performed to determine the temperatures at which the $^2\text{H}$ is mobile in the implanted GaN. Figure 92 shows the results for the n-type GaN. There is no detectable motion of loss of $^2\text{H}$ until ~800°C, with the deuterium lost by evolution from the surface at higher temperatures. Note that the remnant $^2\text{H}$ at each temperature decorates the residual implant damage, which persists even at 1200°C. The peak of the distribution shifts from the projected range of the implant to the peak of the damage distribution, which is slightly closer to the surface as confirmed by Transport-of-Ions-In-Matter (TRIM) calculations. Since there is little affinity for hydrogen to passivate donors in GaN, then once the deep level density falls below the electron concentration, the sheet resistance of the material returns to its original value.

The results for the p-type GaN are shown in Figure 93. Diffusion of the hydrogen begins at 500°C, leading to the creation of a plateau region deeper than the original implanted $^2\text{H}$
distribution. This concentration is the same as that of the Mg accepts (interestingly not the hole density, which is a factor of ~10 lower due to the deep ionization level of the Mg, ~180 meV). The $^2$H concentration in the original implanted region continues to decrease with higher annealing temperatures, and is completely gone by 1000°C, a much lower stability than for the n-type GaN. By 700°C there is also a noticeable accumulation of deuterium at the epi-substrate interface. This is a region of strain, and it is well established in other semiconductor systems that hydrogen is attracted to, and trapped, at such places. It is clear that at annealing temperatures ≥500°C, hydrogen diffuses out of the initial implanted regions and is trapped into Mg-H pairs and the epi-substrate interface. This behavior is consistent with the electrical data of Figure 91, where the presence of acceptor passivation (and the absence of donor passivation) would explain the results. Note also that the SIMS data shows the diffusivity of $^2$H is much faster in p-GaN than in n-GaN, consistent with the predictions of Neugebauer and Van de Walle.

In summary, implanted $^2$H show substantially different thermal stability in n- and p-GaN. In the former there is no apparent chemical effect of the deuterium, with the electrical properties controlled by the implant damage-related deep level states. Upon annealing, deuterium is released from the crystal, with the residual deuterium decorating the remaining implant damage. In p-GaN, diffusion of the deuterium starts at lower temperature, leading to the formation of Mg-H complexes that control the sample resistance in the temperature range 500-700°C.

In addition to direct implantation of hydrogen, it has been found that it can be unintentionally incorporated during many processing steps, including boiling in water, dry etching, chemical vapor deposition of dielectrics and annealing in H$_2$ or NH$_3$.$^{397,398}$ For example, GaN boiled in D$_2$O at 100°C for 30 min showed incorporation of $^2$H up to ~1μm in the material.$^{397}$ It is not known how the columnar nature of the GaN growth affects the hydrogen
incorporation but comparisons with bulk crystals or homoepitaxial layers will be enlightening. Boiling in water has previously been shown to be an effective method of introducing hydrogen into Si\(^{399}\), and it generally diffuses very rapidly under these conditions because the H flux is low energy to avoid the H-H pairing reactions seen in plasma-exposed material.

KOH-based solutions readily etch AlN selectively over GaN, with etch rates that are temperature- and material quality-related.\(^{400,401}\) Exposure of undoped GaN to a solution of KOH/D\(_2\)O for 20 min leads to incorporation of \(^2\)H at a concentration of \(\sim 10^{17}\) cm\(^{-3}\) to a depth of \(\sim 0.5\mu\)m.\(^{397}\) This shows that even at quite low processing temperatures (25\(^{\circ}\)C), atomic hydrogen can be readily diffused into GaN.

Another source of hydrogen incorporation is during PECVD of dielectrics such as SiN\(_x\) and SiO\(_2\) for masking and surface passivation. It is known from GaAs work that PECVD of these dielectrics using SiN\(_x\) can cause extensive hydrogen passivation effects.\(^{402,403}\) We have previously exported that ECR-CVD of SiN\(_x\) onto GaN at a rate of 250\(\AA\) min\(^{-1}\) at 250\(^{\circ}\)C produced \(^2\)H incorporation depths of \(\sim 0.7\mu\)m using SiD\(_4\)/N\(_2\).\(^{397}\) Post-deposition annealing of the SiN\(_x\)/GaN structure at 500\(^{\circ}\)C for 20 min did not produce any further indiffusion of \(^2\)H from the SiN\(_x\), indicating that the source of the initial incorporation is the exposure of the GaN surface to the silane discharge. Seaward\(^{402}\) reported that hydrogen incorporation in GaAs during similar ECR-CVD of silicon nitride could be reduced by employing an initially fast deposition rate to encapsulate the surface as quickly as possible.

There are a variety of dry etch chemistries for GaN and related alloys, including Cl\(_2\), BCl\(_3\), SiCl\(_4\), CCl\(_2\)F\(_2\), CH\(_4\)/H\(_2\), HBr, HI, ICl and IBr.\(^{404-409}\) Additives such as Ar, N\(_2\) or H\(_2\) are often included to enhance sputter-assisted desorption of the etch products, or to balance removal of Ga and N etch products. Eddy and Molnar\(^{408}\) found that ECR CH\(_4\)/H\(_2\)/Ar discharges caused
n-GaN to become more insulating and insulating films to become conducting. However these effects may have been due to a combination of ion-induced defects (since the mobility decreased in n-GaN) and preferential loss of N from the near-surface (100Å). Annealing at 800°C for 30 sec restored most of the original electrical properties.\(^{(408)}\) If elevated sample temperatures are employed to enhance desorption of In from In-containing nitrides, then hydrogen-indiffusion can be very substantial, with incorporation depths of 0.5-2μm in 40 sec at 170°C, i.e. diffusivities of \(10^{-9}-6\times10^{-11}\text{cm}^2\text{V}^{-1}\text{s}^{-1}\).\(^{(363)}\) Similar results were found in AlN and GaN in addition to In\(_x\)Ga\(_{1-x}\)N.\(^{(33)}\) As mentioned before, it is not clear what role the extensive defect density in GaN heteroepitaxial samples plays, but it likely enhances the hydrogen diffusion substantially. The effect of H in dry etching of GaN is therefore two-fold - it may diffuse into the bulk of the sample and passivate dopants or defects, leading to an increased resistivity of the material, or it may produce preferential loss of N right at the surface, leading to a thin n\(^+\) layer ~100Å thick. In some cases if the loss of N is not too severe, annealing at 400-800°C may be able to restore the surface stoichiometry, but in In-containing nitrides the vast difference in volatility of In and N the products usually means that In droplets form and the surface cannot be restored by annealing without first removing the droplets in HCl. Room temperature etching minimizes indiffusion of hydrogen from the plasma.

**THEORY OF HYDROGEN IN NITRIDES**

Brandt et.al.\(^{(410)}\) reported a new PL line at 3.35eV after hydrogenation of p-type and unintentionally n-type GaN, suggesting the introduction of a hydrogen-related donor level. However these same workers coated created some confusion by reporting local vibrational
modes around $2200\text{cm}^{-1}$ for Mg-H complexes in GaN.$^{(411)}$ This led to a series of conflicting theoretical work that was guided by incorrect experimental data.

Okamoto et.al.$^{(412)}$ used local density approximation of the density functional theory to calculate the stable positions of Mg and Mg-H in GaN. Mg was found to occupy a Ga substitutional site, producing a shallow acceptor level. They found the bond-centered (BC) site between Mg-N was the most stable site for hydrogen by $\approx 0.1\text{eV}$ relative to an anti-bonding site (AB) near the Mg atom. The N and intervening H were found to form a strong bond with the calculated bond length (1.02Å) close to that of the NH$_3$ molecule (1.01Å), and no bond charge between Mg and H. The distance between Mg and H was 1.96Å, caused by displacement of the Mg atom from the substitutional site by 0.64Å in the out-bonding direction (away from the position of the hydrogen). It was to be energetically favorable for the H to form the Mg-H complex, rather than remain an interstitial. The calculated vibrational frequency was $\approx 3490\text{cm}^{-1}$, similar to H in NH$_3$ molecules ($3444\text{cm}^{-1}$).

Bosin et.al.$^{(413)}$ used ab-initio calculations performed within local density functional theory to understand the energetics and geometry of H and its complexes in GaN. They found H to exhibit negative-U behavior, with thermal ionization energies for H$^{-\text{m}}$ and H$^{+\text{v}}$ to be $E_{0^\text{m}}=0.8\text{eV}$ and $E_{0^\text{v}}=2.0\text{eV}$, respectively. They calculated Be$_{\text{Ga}}$ to be a relatively shallow impurity level, while C$_N$ had a deep acceptor level ($E_{v^\text{Ga}}+0.40\text{eV}$). Mg-H complexes were calculated to have vibrational modes at $\approx 3000\text{cm}^{-1}$ for AB$_v$ sites for H, and at 3600-3900\text{cm}^{-1}$ for BC site hydrogen. It was found that Be$_{\text{Ga}}$, C$_N$, Ca$_{\text{Ga}}$ and Zn$_{\text{Ga}}$ acceptors would all be susceptible to hydrogen passivation.

Estreicher and Marie$^{(414)}$ employed molecular cluster calculations to examine hydrogen in cubic GaN. They considered three possibilities for the effect of hydrogen:
(i) passivation (an electrical level moves from the gap to a band.)

(ii) activation (an electrical level moves from a band to the gap.)

(iii) level shifting (a level shifts within the gap, e.g. a shallow level becomes deep).

The latter case may be important in wide gap semiconductors because energy levels have to shift a lot to disappear from the gap. They found that H⁺ is bound to N in a BC-like position, H⁰ is at a BC site with H bound to Ga (and an activation energy for diffusion of <1eV), while H is at the AB₆ site (and an activation energy for diffusion of 1.5eV). H₂ molecules were found to be stable at the T₆ site.

Neugebauer and Van de Walle⁴¹⁵ performed density functional calculations and found the following:

(i) isolated interstitial hydrogen has a large negative-U energy, 2.5eV, suggesting H⁰ is unstable.

(ii) the hydrogen donor level is near the conduction band and the acceptor level deep (E_y+0.9eV). For E_y<2eV, the stable state is H⁺, while above that, the stable state is H⁻. For E_y=2eV, H₂ molecules might form by association of H⁺ and H⁻.

(iii) H⁺ is at the AB₆ site, with N-H ~1Å bond length, but the BC configuration is only 0.1eV higher in energy. The activation energy for diffusion of H⁺ is 0.7eV.

(iv) H⁻ is at AB₆ site, with an activation energy for diffusion of 3.4eV.

(v) H-Mg complexes have H at the AB₆ site (Mg...N-H), with a N-H stretching frequency of 3360cm⁻¹ and a pair dissociation energy of 1.5eV.⁴¹⁶ The energetics are summarized in Figure 94.

Therefore, among theorists there is agreement on the following⁴¹⁴:

(i) H⁺ is at the AB₆ site, with a large activation energy for diffusion.
(ii) H is within ~1Å of N.

(iii) H is strongly bound to the N atom in the Mg-H pair.

There is still some disagreement on the following issues:

(i) whether H° is at the AB\textsubscript{Ca} (414,416) or BC sites.\textsuperscript{(413)}

(ii) whether H\textsuperscript{+} is at the AB\textsubscript{N} site \textsuperscript{(413,415)} or at the BC site.\textsuperscript{(414)}

(iii) Whether in the Mg-H complexes the H is at the AB\textsubscript{N} side of N\textsuperscript{389,291} with a high N-H stretching frequency, or at the BC site with a lower frequency.

Van Vechten et al.\textsuperscript{(417)} suggested that hydrogen enables p-type doping by suppression of native defects, and suggested the incorporation (and subsequent removal) of hydrogen as a method for improving doping in wide bandgap semiconductors. This was expanded upon by Neugebauer and Van de Walle\textsuperscript{(418)}, who suggested that for this method to work, hydrogen would need to be the dominant compensating center, the dissociated hydrogen must have a high diffusion coefficient and the energy needed to dissociate H-impurity complexes and remove the H would need to be lower than the formation energy of native defects.

Gotz et al.\textsuperscript{(419)} corrected their earlier work covering LVMs of Mg-H complexes in GaN, reporting a value of 3125cm\textsuperscript{-1} for Mg-H and 2321cm\textsuperscript{-1} for Mg\textsuperscript{2-}H, which were attributed to stretch modes of these complexes. Their previous work\textsuperscript{(415)}, reporting LVMs at ~2200cm\textsuperscript{-1}, presumably resulted from other defects. As-grown material was highly resistive (10\textsuperscript{10}Ωcm at 400K), while annealing at 800°C reduced this to 2Ωcm. Subsequent hydrogenation at 600°C increased the resistivity to 10\textsuperscript{5}Ωcm at 400K, due mainly to the fact this is too high a temperature to prevent substantial dissociation of the Mg-H complexes. There was a relatively poor correlation of IR signal intensity with active Mg concentration.\textsuperscript{(411)} The IR stretch frequency is
close to that of H in NH$_3$(3444 cm$^{-1}$) and similar to the value of N-H complexes in ZnSe (3195 cm$^{-1}$).\textsuperscript{(420,421)}

Schematics of the possible configurations of hydrogen-dopant complexes in GaN are shown in Figure 95. For donor dopants on either the Ga-site (e.g. Si) or the N-site (e.g. S) the hydrogen is in an anti-bonding position either attached to the dopant in the case of group IV donors or attached to the Ga neighbor in the case of a group VI donor. At this stage no reports of donor dopant passivation have been made, for the reasons outlined earlier. In acceptor dopants the hydrogen may be at a bond-centered site bonded predominantly either to the acceptor or a N-neighbor, respectively, depending on whether the acceptor is from column IV or II of the Periodic Table, or in the anti-bonding position creating a N-H bond. Current thinking favors the latter for Mg-H, as outlined above, but more work is needed to definitively establish this configuration and to see if the BC site is favored for the other acceptors.

**SUMMARY**

Hydrogen plays a particularly prominent role in p-type GaN because of its ability to passivate acceptors, requiring post-growth annealing of MOCVD material in order to electrically activate the acceptors. Donor passivation is more elusive, but probably occurs under the right conditions. The use of deuterated gases has shown that hydrogen readily enters GaN and related materials during low temperature processes such as CVD of dielectrics, plasma etching, wet etching, boiling in solvents and contact sintering (metals may act as catalysts for H$_2$ dissociation). Therefore one faces the situation that hydrogen may be unintentionally incorporated into GaN at many stages of a device fabrication process, particularly when p-type layers are uppermost in the structure (i.e. LEDs and lasers). The outdiffusion and hydrogen
retrapping behavior is more complex in multilayers (heterostructure) samples. Reactivation of passivated acceptors may be accomplished by thermal annealing or minority carrier injection to dissociate the dopant-hydrogen complexes. It will be very interesting to look at hydrogen incorporation in GaN bulk crystals with controlled doping levels (usually most of these samples are degenerately n-type, $n>10^{19}\text{cm}^{-3}$) in order to establish the role of gain and column boundaries in heteroepitaxial material in assisting hydrogen diffusion.
B. OXYGEN

(i) GaN

It has been shown experimentally that the amount of oxygen present during the growth process can have a strong influence on the background n-type conductivity\(^{159,422}\), indicating that it is a shallow donor in GaN. The source of oxygen is often the NH\(_3\) precursor used in MOCVD growth, the residual water vapor in MBE chambers or oxygen impurities leached from the quartz containment vessel often employed in N\(_2\) plasma sources. Table VIII shows typical concentrations of O (and C, H and Si, the other major residual impurities in III-nitrides) detected by Secondary Ion Mass Spectrometry (SIMS) in the binary and ternary nitrides.\(^{423}\) Under optimized conditions the O background in MOCVD material can be at the detection limit of SIMS, as shown in Figure 96. More typical results are shown in Figures 97 and 98, where the O concentration is \(\sim 10^{19}\) cm\(^{-3}\). We find that it is usually the case that high Si concentrations are also present, so that it is difficult to assign residual n-type conductivity solely to either impurity. Indeed it is possible that nitrogen vacancies, residual oxygen and residual silicon all play a role in contributing to the n-typeness of most epi (and bulk) GaN.

The work of Chung and Gershenzon\(^{159}\) found a donor state for oxygen in GaN of Ec-0.078 eV, with banding occurring at high concentrations. Zolper et al.\(^{134}\) directly implanted O\(^+\) ions into insulating GaN, and activated by annealing at 1000\(^\circ\)C. The activation efficiency of the implanted oxygen was low, \(-4\%\), but n-type material was created and an ionization level of \(-29\) meV was measured. The diffusivity was \(\leq 2.7 \times 10^{-13} \text{cm}^2\text{sec}^{-1}\) at 1125\(^\circ\)C.

Oxygen implantation into initially doped GaN produces damage-related compensation which is thermally stable to \(\leq 750\)\(^\circ\)C, and indicates that oxygen does not have a deep acceptor or donor state with high concentration in this material. InGaN which is initially n-type shows less
effective implant isolation characteristics, with a maximum of a 100 fold increase in sheet resistance independent of ion species after a 500°C anneal.

As seen in Figure 99, InAlN, in contrast to InGaN, can be highly compensated with N- or O-implantation with over a three order-of-magnitude increase in sheet resistance after a 600 to 700°C anneal while F-implantation produces only one order-of-magnitude increase in sheet resistance. The compensating level in InAlN is also high in the bandgap with the deepest level estimated at 580 meV below the conduction band edge in high dose N-isolated material, however it is sufficiently deep to achieve highly compensated material. The enhanced compensation of N- and O-implantation in InAlN may result from a reduction in N-vacancies for N-implantation or the formation of an O-Al complex for O-implantation. An O-Al complex is thought to also be responsible for thermally stable implant isolation in O-implanted AlGaAs.\(^{(275)}\)

Mattila and Nieminen\(^{(424)}\) performed an ab initio study of oxygen point defects in both GaN and AlN. \(\text{O}_N\) in GaN was determined to be a shallow donor, for basically all positions of the Fermi level. They found under Ga-rich conditions the formation energy of \(\text{O}_N^+\) was much lower than \(\text{V}_N^+\) (by about 2 eV) and also \(\text{O}_i\). This is consistent with the SIMS data discussed above, which shows large concentrations of oxygen in GaN, and also with other calculations.\(^{(429)}\) The fact that O is isoelectronic with N has been suggested as a reason for its surprising affinity for being incorporated into GaN. The formation energies for \(\text{O}_{\text{Ga}}\) were always much larger than \(\text{O}_N\) and thus these defects should not play an important role.\(^{(426)}\)

(ii) \(\text{AlN}\)

Concentrations of O up to several percent have been reported in AlN\(^{(427)}\), but high quality epi material typically contains levels in the \(10^{18}\) cm\(^{-3}\) range (Table VIII). Theoretical work has suggested that \(\text{O}_N\) is the favored state, with a relatively low formation energy. The related
ionization levels are deep in the gap for both acceptor (ON-) and donor (ON⁺) states.⁴²⁵ Experimentally it is found that AlN is almost always insulating, with a high activation energy (>2 eV).⁴²⁸ In AlGaN, isolated oxygen is predicted to have a DX-center behavior as the O moves from being a shallow donor in GaN to a deep electron trap in AlN.⁴²⁴ Little is known about O in InN.

C. CARBON

Carbon can also be a major residual impurity in MOCVD nitrides (Table VIII) – its source is typically the metalorganic gallium precursor.⁴²⁹,⁴³⁰ It is generally assumed that CN is the dominant species and thus is an acceptor, although some calculations suggest carbon is an amphoteric impurity in both GaN and AlN, with ionization levels of 0.2 eV and 0.4 eV respectively. It was also predicted that CN⁺-Ga⁺ pair formation was favorable, leading to self-compensation.⁴³¹ It is also expected that carbon can complex with defects such as Ga vacancies.⁴³²,⁴³³ Pankove and Hutchy⁴³⁶,⁴³⁷ reported strong yellow luminescence centered at 2.17 eV for C-implanted GaN, and others have also linked carbon to the yellow luminescence.⁴³⁴,⁴³⁶ Circumstantial evidence supporting this contention comes from the fact there is little yellow PL in GaN grown by halide vapor phase epitaxy which employs C-free precursors (Ga< NH₃ and HCl).⁴³⁷,⁴³⁸ Intentional carbon-doping actually produced n⁺GaN (~4x10¹⁸ cm⁻³).⁴³⁹

P-type GaN obtained by C-doping during MOMBE has been reported,¹⁸⁸ with a maximum hole concentration of ~3x10¹⁷ cm⁻³, and mobility ~100 cm²/V·sec⁻¹. There was little change in hole concentration with post-growth annealing, suggesting that little hydrogen
passivation was present. Parasitic etching by the CCl₄ precursor employed for C-doping reduced the growth rate compared to undoped material.

We find that InₓGa₁₋ₓN and InₓAl₁₋ₓN alloys grown by MOMBE are strongly n-type for x ≥0.15 (InGaN) and for x ≥0.3 (InAlN), with steadily decreasing conductivity as the In concentration is decreased. High electron concentrations have also been reported for InN grown by other methods, and are usually ascribed to the presence of N vacancies, although this seems less likely in light of trends observed in InN grown using various III/V ratios.

Furthermore, ion channeling and AES do not indicate nitrogen deficiency in these films.

Another possible explanation for the electrical behavior is the presence of unintentionally incorporated carbon. Though carbon has been shown capable of producing p-type GaN, the hole concentrations obtained have been limited to low -10¹⁷cm⁻³ even though carbon levels are measured to be 10²⁰cm⁻³ or higher. It has been found in other III-V materials that the maximum hole concentration which can be obtained using carbon is related to the difference in bond strength between the group III site and acts as a donor resulting in n-type material. Based on this simple model, it is expected that carbon will be a donor in InN and high In concentration alloys (see Figure 100). Thus at least some of the conduction observed in these ternary films may be due to carbon. Further, as the composition is reduced in In, the tendency for carbon to act as an acceptor rather than a donor increases, thus possibly explaining the reduction in electron concentration observed with increasing Ga or Al concentration. Clearly more work is needed in this area in order for the role of carbon to be fully understood.

We also implanted C into GaN and annealed at temperatures up to 1100°C, but did not obtain p-type conductivity. Based on the results to date we find that C probably displays amphoteric behavior in the nitrides, with acceptor formation under some conditions (MOMBE-
grown GaN and possible donor action in other cases (implantation in GaN; growth of In-containing alloys).
IV. DEVICES

AlGaN/GaN ELECTRONICS

MATERIALS REQUIREMENTS

a. Transistors

The potential of the wide bandgap, nitride-based, semiconductors (GaN, AlN and InN) for use in high power, high frequency transistors has been well documented. This potential is due to the advantageous materials properties summarized in Table IX along with the existence of the AlGaN/GaN heterostructure. The latter allows modulation doping to form a high mobility two dimensional electron gas (2DEG) and, equally important, the formation of piezoelectronically induced sheet carriers. The piezoelectronic effect is at least three times stronger in these materials than GaAs (see values for e31 and e33 in Table X) and contributes to the realization of high sheet electron densities (sheet electron densities up to 5x10^13 cm^-2 are predicted for an AlN/GaN interface) in AlGaN/GaN HEMTs.

To realize high performance field effect transistors the following material and doping properties must be repeatably achieved: 1) High resistivity (non compensated) buffer layers, 2) controllable n-type doping between ~1x10^17 (channel doping) to >1x10^19 (contact doping), 3) abrupt AlGaN/GaN interfaces, 4) modulation doping of AlGaN and 5) low trap densities.

In addition for bipolar devices, such as heterojunction bipolar transistors (HBTs), to be produced in the nitride semiconductors improvements in p-type doping is needed and issues related to fabricating devices with buried p-regions (e.g. how to etch down to the p-type layer without creating a n-type surface region due to etch damage) need to be addressed.

These points will be addressed in the following sections.

b. Detectors
Solid state photodetectors that are sensitive only to radiation with a wavelength less than 400 nm are desirable for detection of photons from high temperature sources without saturation occurring from lower energy photons. This interest stems from the need to monitor furnace flames or to detect missile plumes without the detector being saturated by solar radiation which is characteristically <400 nm. Al$_x$Ga$_{1-x}$N is an ideal candidate semiconductor for fabrication of such detectors since its spans bandgaps from 3.45 to 6.2 eV or wavelengths from 350 to 200 nm.

The first task for realizing Al$_x$Ga$_{1-x}$N-based photodetectors is developing suitable epitaxial processes to realize the requisite compositions. Once this is achieved, and the desirable absorption characteristics are demonstrated, defects and their role on detector leakage and response time become paramount.

III. TRANSPORT PROPERTIES

The carrier mobility and saturation velocity are the primary determinants of transistor performance. The nature of the electron saturated velocity is reviewed below followed by the electron mobility and its dependence on various scattering mechanisms.

a. Electron saturation velocity

The electron velocity dependence on applied field and low field dependence of electron mobility for GaN was first calculated by Littlejohn, et al., in 1976.$^{(463)}$ Littlejohn included electron scattering from acoustic phonons, polar optical phonons, ionized impurities and piezoelectric charge and predicted a peak in the electron drift velocity of $2 \times 10^7$ cm/s at a field of $10^5$ V/cm. The work of Littlejohn was further expanded by Gelmont, et al.$^{(464)}$, to include the effect of upper valleys in the conduction band and account for intervalley scattering using a conduction band valley separation of 1.5 eV. Gelmont predicted a peak electron velocity at 300
K of \(2.7 \times 10^7\) cm/s for an electron concentration of \(10^{17}\) cm\(^{-3}\) and a field of 150 kV/cm.\(^{(464)}\) To date, this high electron velocity has not been demonstrated in AlGaN/GaN HEMTs. The best estimate of the saturated electron velocity in present 0.15 \(\mu\)m HEMTs with an \(f_t\) for \(-65\) GHz is \(-1.5 \times 10^7\) cm/s.\(^{(465)}\) This may be due to scattering at charged dislocations or to ineffective carrier injection in the lateral HEMT structure.

The peak electron velocity of InN has also been calculated by O'Leary, et al.\(^{(466)}\), as shown in Figure 100. The calculation predicts an electron peak velocity for InN of \(4.3 \times 10^7\) cm/s at a field of 60 kV/cm or \(-2\) times the peak electron velocity of GaN.\(^{(466)}\) The saturated velocity of InN, however, was predicted to be equivalent to that of GaN or \(-2.5 \times 10^7\) cm/s. Therefore, InN-based transport layers will have increased frequency performance if ballistic transport can be achieved.

When considering the potential for ballistic transport and velocity overshoot effects in transistors it is important to know the distance over which such effects may occur. This has been calculated for InN, GaN and GaAs as shown in Figure 100 for a field twice that for the peak velocity.\(^{(467)}\) At these fields significant velocity overshoot is expected to occur with InN calculated to achieve a peak velocity of \(8 \times 10^7\) cm/s at a distance of \(-0.1\) \(\mu\)m.

\(b.\) \textbf{Mobility versus impurities/phonons}

A very thorough theoretical treatment of the effect of ionized impurity scattering, polar optical scattering, piezoelectric scattering and acoustic scattering on electron transport in GaN and AlGaN/GaN heterostructures is given by Shur, et al.\(^{(468)}\) Figure 101 shows the results of Shur for the electron mobility in bulk GaN as limited by polar optical, piezoelectric and acoustic scattering versus temperature. Polar optical scattering is seen to play a dominant role at
temperatures greater than 200 K due to the large optical phonon energy of GaN of 91.2 meV, while acoustic, and to lesser extent piezoelectric scattering, dominates at lower temperatures.

Figure 102 shows the calculated dependence of electron mobility versus temperature as limited by ionized impurity scattering for four electron and donor concentrations. It is clear that the mobility increases with electron densities which is due to increase screening of the impurities. This is particularly true for $n > N_T$ which approximates the situation in a 2DEG.

The combined effect of ionized impurity scattering, where mobility increases with temperature, and polar optical, piezoelectric and acoustic scattering, where mobility decreases with temperature, is shown in Figure 102. Both the bulk case and 2DEG case are included in Figure 103 for hexagonal and cubic GaN. At 300 K, a 2DEG mobility near 2000 cm$^2$/Vs for a AlGaN/GaN structure grown on 6H-SiC with a sheet electron density of $1.3 \times 10^{13}$ cm$^{-2}$. At 10 K the measured mobility increased to 10,250 cm$^2$/Vs.

c. Mobility versus dislocations

A model addressing the role of dislocations on electron transport perpendicular to the dislocation direction has been developed by Weimann, et al. This is a critical consideration for GaN material grown on sapphire (a 12% lattice mismatch) or SiC (a 3.5% lattice mismatch) since dislocation densities are typically between $5 \times 10^7$ to $1 \times 10^{10}$ cm$^{-2}$. They assumed the GaN grew as hexagonal columns rotated relative to each other by a small angle, (this may not be strictly true for growth on SiC but appears to be true for growth on sapphire) with dislocations propagating vertically between the columns. The dislocations were then treated as charged lines with the dependence of electron mobility calculated and measured experimentally. The increase of mobility with increased free electron concentration with a maximum near $10^{18}$ cm$^{-3}$ is due to increased screen of the charged dislocation core. This treatment suggests that transport in
vertical devices (e.g. lasers, LEDs and HBTs) will be unaffected by the dislocations due to the repulsive band bending around the dislocations and the directional dependence of the scattering.\(^{470}\)

d. NDR, Gunn effect

Devices based on negative differential resistance (NDR) such as Gunn or IMPATT are attractive diodes for high frequency oscillators. GaN is an attractive material for these devices due to its high breakdown field and high saturated electron velocity. There has been one report of the transferred-electron or NDR effect in GaN by Huang, et al.\(^{471}\) The measured current versus applied electric field between interdigitated electrodes on lightly doped \(\approx 10^{14}\) cm\(^{-3}\) GaN displayed a threshold for NDR at \(1.91 \times 10^5\) V/cm. This threshold level is much higher than that in GaAs \((3 \times 10^5\) V/cm\) or InP \((1.1 \times 10^4\) V/cm\) which is consistent with the larger bandgap and intervalley separation \(1.5\) eV\) in GaN. The threshold value is also close to that predicted theoretically by Littlejohn and by Gelmont.\(^{463,464}\)

Practical GaN NDR diodes will also require development of low resistance n- and p-type Ohmic contacts. Presently the p-type contact required for the IMPATT diode is limited by marginal p-type doping levels due to deep acceptor ionization energies and acceptor solubility limits in GaN. Further work is also needed to characterize the impact ionization rates for both holes and electrons in GaN so proper diode designs can be produced.

IV. PIEZOELECTRIC EFFECT

The strong piezoelectric coefficients of the III-Nitride semiconductors are summarized in Table X. The fact that GaN grown on sapphire and SiC forms in the noncentrosymmetric wurtzite structure, as opposed to the cubic phase, results in large piezoelectric induced charge...
across III-Nitride heterostructures due to strain at the interface.\(^{(462)}\) This effect has been known for the (111) orientation of cubic zincblende semiconductors but it is both not as large in magnitude and of opposite sign as in the III-Nitride materials.\(^{(472-474)}\) The fact that the polarization field is in the opposite direction for the III-Nitrides as compared to other III-V's is due to the greater ionicity of the nitrides. This causes the dipole moment arising from the rigid displacement of the atomic core to increase in importance relative to the strain-induced changes in the charge distribution along the bond direction and within the atomic cores.\(^{(472,473)}\)

Figure 104 shows the calculated and experimental results for the piezoelectrically induced sheet charge in an AlGaN/GaN heterostructure versus Al-composition in the AlGaN.\(^{(472)}\) The dashed curve in Figure 104 assumes a Schottky barrier at the AlGaN surface while the solid curve is for an unpinned Fermi level at the AlGaN surface. While it is clear that the nature of the surface plays an important role in the absolute sheet carrier concentration, the presence of the piezoelectrically induced charge is clear and on the order of \(2.5 \times 10^{13} \times X_{\text{Al}} \) electrons/cm\(^2\).\(^{(472)}\)

The piezoelectric effect can also be employed to accumulate free holes when the nature of the strain is compressive as opposed to tensile in the case of AlGaN on GaN.\(^{(472,476)}\) This is illustrated in Figure 105 where a buried AlGaN layer is included below an AlGaN/GaN heterostructure. As seen in the figure, a second buried channel is induced at the first AlGaN/GaN interface and the concentration of induced electrons in the upper channel is reduced to account for the charge balance across the buried AlGaN layer. The reduction in the induced electron concentration at the upper AlGaN/GaN interface was confirmed by CV profiling for structures with and without the buried AlGaN layer.\(^{(476)}\) This same mechanism may be useful to enhance the 2-dimensional hole gas in the base of HBT's or at p-type contacts to increase the effective p-type doping level at interfaces of these materials.
V. PROPERTIES OF AlGaN/GaN TRANSISTORS

a. DC performance

AlGaN/GaN transistor development has followed the materials improvements driven by photonic devices such as LEDs and laser diodes. Table XI outlines the key historical results for this technology.

As seen in Table XII, the first reports of GaN based transistors were by M.A. Khan, et. al. with the demonstration of a GaN MESFET and an AlGaN/GaN HEMT. Both transistors had gate lengths of 4 μm with the MESFET having a $g_m$ of 23 mS/mm and $I_{DS(max)}$ of -180 mA/mm (@ $V_{GS} = 0$ V, $V_{DS} = 20$ V). The AlGaN/GaN HEMT achieved a $g_m$ of 28 mS/mm at 300 K (46 mS/mm at 77 K) and $I_{DS(max)}$ of ~50 mA/mm (@$V_{GS} = 0.5$ V, $V_{DS} = 25$ V). The HEMT structure had a 2 DEG mobility of 563 cm$^2$/Vs at 300 K and 1517 cm$^2$/Vs at 77 K. The first microwave results were published by Binari, et. al., for a GaN MESFET with a demonstrated $f_t$ of 8 GHz and a $f_{max}$ of 17 GHz for a gate length of 0.7 μm.

Since the early results, significant improvements have been made in material quality and device processing. AlGaN/GaN 2DEG mobilities up to 2019 cm$^2$/Vs have been reported for growth on 6H-SiC substrates and ~1600 cm$^2$/Vs for growth on sapphire substrates. The saturation current has been pushed to 1.6 A/mm and the transconductance has reached 340 mS/mm.

b. microwave small and large signal performance

Improvements in the small signal microwave performance of AlGaN/GaN HEMTs has tracked the DC improvements. The present state-of-the-art for unity current cut-off frequency ($f_t$) is 75 GHz; and for the maximum frequency of oscillation ($f_{max}$) is 140 GHz by L. Eastman.
and coworkers at Cornell University.\textsuperscript{542} Large signal power results for HEMT on SiC substrates include total power of 4 W (2 mm wide gate) at 10 GHz with 10 dB of gain with a power density of 6.8 W/mm (4.1 W/mm at 16 GHz) measured on smaller devices.\textsuperscript{502} At 18 GHz a power density of 3.1 W/mm has been achieved on a sapphire substrate.\textsuperscript{519} Total power results have also been pushed up with 7.6 W achieved at 4 GHz for HEMTs grown on sapphire and flip-chip mounted on AlN carriers.\textsuperscript{543} These large signal results, however, are still not up to the level one would predict from the DC characteristics and the small signal performance of up to \sim 10 W/mm at 10 GHz. In some cases, the performance short fall is evident in current and gain compression at high applied voltages.\textsuperscript{544-547} This compression is due to traps in the bandgap, possibly at the surface, in the AlGaN barrier, or in the GaN buffer. Presently, the origin of the traps is still being studied, however, a similar phenomena was observed in the early GaAs device work and later overcome. In the GaAs case, the traps were due to surface states but this may not be the same in the AlGaN/GaN system.

c. Elevated Temperature Performance

The group III-Nitride semiconductors have been considered an ideal candidate for high temperature electronic devices due to their large bandgap and resulting low thermal carrier generation rate.\textsuperscript{548} For this potential to be realized, defect levels in the bandgap must be reduced since they will enhance undesirable dark and shunt currents. This can be seen in the temperature dependence of conduction reported by M.A. Khan, et.al.\textsuperscript{540}, where a AlGaN/GaN HEMT demonstrated a large shunt current apparently resulting from defect assisted conduction in the GaN buffer layer already at 200°C. Subsequently a GaN MESFET with an improved semi-insulating buffer was shown by Binari, et.al., to maintain reasonable pinch-off
characteristics at 400°C. When taken to 500°C, the MESFET gate electrode began to interact with the GaN surface and irreversibly degrade the transistor operation. A AlGaN/GaN HEMT has been further pushed to operate at 750°C by achieving a 1.0 eV activation energy for conduction in the buffer layer and employing a thermally stable Pt-Au gate contact. More work is needed to optimize such elevated temperature operation and device packaging will also need to be considered.

e. Future direction for GaN electronics

The progress in field effect AlGaN/GaN transistors has been impressive but they may not meet the linearity requirements of some future electromagnetic systems, particularly for the military applications where ultra wide bandwidth and linearity are desired. Therefore, III-Nitride based heterostructure bipolar transistors (HBTs) are now being studied since, in GaAs and InP, HBTs have demonstrated improved linearity over the FET counterpart. The first AlGaN/GaN HBTs have been reported, however, the current gain was only 3-10. The initial results were limited by a high base resistance. Key issues remain to be resolved for group III-nitride HBTs. First among these is how to overcome the high ionization energy of p(Mg)-GaN that causes a high base resistance. A potential solution includes invoking the piezoelectric field to induce free holes and thereby reduce the base resistance. A second concern is achieving sufficiently long minority carrier lifetimes in the base to realize good current gain.

VI. MINORITY CARRIER LIFETIME

Minority carrier lifetime is a critical parameter in the frequency response and detectivity of detectors, the gain of bipolar transistors, and the conductivity modulation of thyristors.
Lifetime is also a critical measure of material quality as it relates to traps and recombination centers. Several reports exist for measurement of recombination lifetimes in GaN with dislocation densities $> 1 \times 10^7 \text{cm}^{-2}$. While the lifetime will depend on sample doping and surface quality (i.e. the surface recombination velocity), there are three reports on the minority hole diffusion length in n-type GaN giving values of 0.1 to 0.3 $\mu\text{m}$ for n-type layers in the range of $1$-$10 \times 10^{17} \text{cm}^{-3}$ and dislocation densities in the $\sim 10^9 \text{cm}^{-2}$\textsuperscript{547,551,552}. This corresponds to a minority hole lifetime on the order of 2 to 7 ns. These values can be expected to improve as the dislocation density and point defect concentration is reduced.

XI. IMPACT OF REDUCED DISLOCATION VIA LEO

To this point the discussion has dealt with GaN material grown on SiC or sapphire that has dislocation densities of $> 1 \times 10^7 \text{cm}^{-2}$, however the use of lateral epitaxial overgrowth (LEO) had lead to GaN material with threading dislocation densities below the detectable limit of TEM ($< 1 \times 10^4 \text{cm}^{-2}$).\textsuperscript{553-555} The effectiveness of the LEO technique to limit threading dislocation propagation into the overgrown regions is clearly seen in TEM micrographs (see ref 81 for example). This approach has been applied to blue laser diodes to extend the room temperature lifetime out to $> 3000$ hours of CW operation.\textsuperscript{6} An explicit understanding of the reason for the laser diode lifetime improvement has not been put forward, but it may be due to a reduction in contact metal spiking down dislocations, reduced optical scattering at dislocations thereby reducing the lasing threshold, or improved doping efficiency (particularly p-type) in the absence of dislocation also reducing the lasing threshold. More work is needed to understand the laser operation in the LEO material.
LEO material is also being developed for transistor applications to improve carrier mobility and device reliability. The first electrical data for low dislocation material compared directly to "conventional" high dislocation material was reported by Kozodoy, et al.\(^{556}\), for p/n junction diodes. Small area diodes (2x20 \(\mu\text{m}^2\)) were fabricated in adjacent regions of overgrown low dislocation GaN and GaN grown over the mask opening. In this way variations between wafers could be eliminated and the two material regions could be more closely compared. Figure 106 shows the reverse current voltage characteristics of the two diodes with the diode in the LEO material having ~4 orders-of-magnitude less leakage current than the conventional material. Initial results for HEMTs on the LEO material show a large reduction in gate leakage but still have trap induced current compression. Therefore, the defects alone are not the cause of the traps, although they most likely do degrade the electron mobility. Work is underway to characterize the mobility in the LEO material either by growing large overgrowth regions for Hall measurement or implementing a micro-Hall pattern.\(^{557}\) The reduced leakage should translate to improved transistor breakdown characteristics and mobility enhancement will result lower on resistance and thereby better power performance.

XII. SUMMARY OF ELECTRONICS ISSUES

Progress in GaN-based electronics has been remarkably rapid due to several factors. One of these is that the experience gained in GaAs/AlGaAs HEMTs has been quickly applied to the GaN/AlGaN system. At one time it was thought that MBE and related techniques would be the best choice for growth of electronic device structures, and this may still be the case if GaN substrates become available. However for heteroepitaxial growth there is still a need to grow thick buffer or ELO structures, which are best done with MOCVD. The rapid advances in
material purity, ohmic contact quality and gate contact stability have fueled the progress in HFETs in the GaN/AlGaN system. Much work remains to be done on vertical device structures such as thyristors and HBTs, where minority carrier lifetime, interface quality and doping control are important factors. As with GaAs electronics, much of the impetus for nitride electronics is coming from defense applications and there is as yet no commercialization of these devices.
B. Ultra-high Power Switches

There is a strong interest in developing wide bandgap power devices for use in the electric power utility industry. With the onset of deregulation in the industry, there will be increasing numbers of transactions on the power grid in the US, with different companies buying and selling power. The main applications are in the primary distribution system (100-2000 kVA) and in subsidiary transmission systems (1-50MVA). A major problem in the current grid is momentary voltage sags, which affect motor drives, computers and digital controls. Therefore, a system for eliminating power sags and switching transients would dramatically improve power quality. For example it is estimated that a 2-second outage at a large computer center can cost $600,000 or more, and an outage of less than one cycle, or a voltage sag of 25% for two cycles, can cause a microprocessor to malfunction. In particular, computerized technologies have led to strong consumer demands for less expensive electricity, premium quality power and uninterruptible power.

The basic power electronics hierarchy would include the use of widegap devices such as Gate Turn-Off Thyristors (GTOs), MOS-Controlled Thyristors (MCT) or Insulated Gate Bipolar Transistors (IGBTs) combined with appropriate packaging and thermal management techniques to make subsystems (such as switches, rectifiers or adjustable speed devices) which then comprise a system such as Flexible AC Transmissions (FACTS). A schematic of a typical layout for such a system is shown in Figure 107. Common power electronics systems, which are inserted between the incoming power and the electrical load include uninterruptible power supplies, advanced motors, adjustable speed drives and motor controls, switching power supplies, solid-state circuit breakers and power conditioning equipment. About 50% of the electricity in the US is consumed by motors. Motor repairs cost ~$5B each year and could be
dramatically reduced by high power electronic devices that permit smoother switching and control. Moreover, control electronics could dramatically improve motor efficiency. Other end uses include lighting, computers, heating and air-conditioning.

The FACTS concept employed in electricity transmission aims for the following:

- Precisely regulate power flow on particular lines.
- Better system stability by instantly counteracting transients.
- Load transmission lines closer to their thermal limits (increase capacity) using:
  Thyristor controlled series capacitor (changes line impedance).
  Static condenser (STATCOM based on GTO thyristors (provides voltage support on lines by generating or absorbing reactive power without need for large external reactors or capacitor banks and mitigates disturbances.
  United Power Flow Controller (comprehensively controls power flow, reduces line impedance, shifts phase angle, provides voltage support).

On the distribution side there is a need to precisely manage power quality and flow for variable loads. The components include the dynamic static compensator (DSTATCOM), which protects the line from a “dirty” load (and generally involves Si IGBTs), the dynamic voltage restorer, which protects a sensitive load from line disturbances (and also employs Si IGBTs) and solid-state breaker/transfer switches, which prevent black-outs (and employ semiconductor-controlled rectifiers and GTOs).

Thus the technology drivers for high power semiconductor devices from the utility viewpoint are:
FACTS (Flexible AC Transmission System) Devices that allow power grids to be tuned for maximum performance like low-power integrated circuits, increasing asset utilization.

- Distribution system components that enable precise subcycle regulation of voltage and power flow, including solid-state transfer switch (SSTS), solid-state circuit breaker (SSCB), dynamic voltage restorer (DVR), distribution static compensator (D-STATCOM), advanced transformer, fault current limiter.

- Power electronics interconnection technologies (ac/dc inverters, frequency changers) that enable wider application of low- and no-emission systems for energy generation and storage including fuel cells, wind power, photovoltaics, batteries and superconducting magnetic energy storage.

- Advanced motor speed controllers that reduce or eliminate the significant power disturbances produced by existing adjustable speed drive.

- Power management technologies for electric vehicles that reduce pollution and dependence on imported oil.

Other high-power electronics applications include hybrid drivetrain (electric) vehicles, next generation ("all-electric") battleships and the "more-electric" airplane for both military and commercial deployment.

Some desirable attributes of next generation, widegap power electronics include the ability to withstand currents in excess of 5 kA and voltages in excess of 50 kV, provide rapid switching, maintain good thermal stability while operating at temperatures above 250°C, have small size and light-weight, and be able to function without bulky heat-dissipating systems.

The primary limits of Si-based power electronics are:
(i) Maximum voltage ratings <7 kV
   - Multiple devices must be placed in series for high-voltage systems.

(ii) Insufficient current-carrying capacity
   - Multiple devices must be placed in parallel for typical power grid applications.

(iii) Conductivity in one direction only
   - Identical pairs of devices must be installed in anti-parallel for switchable circuits.

(iv) Inadequate thermal management
   - Heat damage is a primary cause of failure and expense.

(v) High initial cost
   - Applications are limited to the highest-value settings.

(vi) Large and heavy components
   - Costs are high for installation and servicing, and equipment is unsuitable for many customers.

For these reasons, there is a strong development effort on widegap power devices, predominantly SiC, with lesser efforts in GaN and diamond, which should have benefits that Si-based or electromechanical power electronics cannot attain. The higher stand-off voltages should eliminate the need for series stacking of devices and the associated packaging difficulties. In addition, these widegap devices should have higher switching frequency in pulse-width-modulated rectifiers and inverters.

The current state-of-the-art in Si power devices includes 6" diameter light-triggered thyristors rated at 8 kV, 3.5 kA average current\(^{(562,563)}\), GTO thyristors rated at 6 kV and 2 kA in
practical applications\textsuperscript{(563)} and press-pack reverse-conducting IGBTs rated at 2.5 kV and 1 kA\textsuperscript{(564)}. Light triggering is often needed in stacked devices to ensure all of them turn-on at the same time. This might be used to advantage in power grid applications in another way, namely that control signals could be carried on the extensive optical fiber network that accompanies the power grid, and could be used to trigger GaN-based devices. Moreover, Er-doped GaN emitters could be used to send status signals back through the same network.

The absence of Si devices capable of application to 13.8 kV distribution lines (a common primary distribution mode) opens a major opportunity for widegap electronics. However, cost will be an issue, with values of $200-2000 per kVA necessary to have an impact. It is virtually certain that SiC switches will become commercially available within 3-5 years, and begin to be applied to the 13.8 kV lines. MOS Turn-Off-Thyristors involving a SiC GTO and SiC MOSFET are a promising approach.\textsuperscript{(565)} An inverter module can be constructed from an MTO and in SiC power diode.

Bandic et al.\textsuperscript{(566)} predict that a 5 kV stand-off voltage can be supported by a 20 \textmu m Al\textsubscript{0.2}Ga\textsubscript{0.8}N layer doped at \textasciitilde10\textsuperscript{16} cm\textsuperscript{3}. One of the questions marks about the GaN/AlGaN system is whether because there are direct gap materials and have extremely short minority-carrier lifetimes, that thyristors will not be possible due to an inability to build up sufficient charge in thick drift layers. At Al concentrations >0.5, the AlGaN is indirect, but little information is available on lifetimes in the material. As a first step to building these devices, Ren et al.\textsuperscript{(503)} recently demonstrated a GaN/AlGaN HBT capable of operation at \textasciitilde300\degree C.

Packaging and thermal management will be a key part of future power devices. For current Si IGBTs, there are two basic package types – the first is a standard attached die, wire bond package utilizing soft-solder and wire-bonds as contacts, while the second is the presspack,
which employs dry-pressed contacts for both electrical and thermal paths.\textsuperscript{(567,568)} In the classical package, the IGBTs and control diodes are soldered onto ceramic substrates, such as AlN, which provide electrical insulation, and this in turn is mounted to a heat sink (typically Cu). Thick Al wires (500 μm) are used for electrical connections, while silicone gel fills the package.\textsuperscript{(567)} In the newer presspack style, the IGBT and diode are clamped between Cu electrodes, buffered by materials such as molybdenum or composites\textsuperscript{(568)} whose purpose is to account for the thermal expansion coefficient differences between Si and Cu. The package is again filled with gel for electrical insulation and corrosion resistance.
C. Laser Diodes

The achievement of continuous wave GaN-InGaN laser diodes has tremendous technological significance. For commercially acceptable laser lifetimes (typically ≥10,000 hrs), there is immediate application in the compact disk data storage market. The recording and reading of data on these disks is currently performed with near-infrared (~780 nm) laser diodes. The switch to the much shorter wavelength (~400 nm) GaN-based laser diodes will allow higher recording densities (by ~ \( \frac{780}{400} \)^2 or almost a factor of 4). There is also a large potential market in projection displays, where laser diodes with the three primary colors (red, green and blue) would replace the existing liquid crystal modulation system. The laser-based system would have advantages in terms of greater design simplicity, lower cost and broader color coverage. The key development is the need to develop reliable green InGaN laser diodes. The high output power of GaN-based lasers and fast off/on times should also have advantages for improved printer technology, with higher resolution than existing systems based on infra-red lasers. In underwater military systems, GaN lasers may have application for covert communications because of a transmission passband in water between 450-550 nm.

While a number of groups have now reported room-temperature lasers in the InGaN/GaN/AlGaN heterostructure system under pulsed\(^{569-580}\) and CW operation\(^{581-589}\), the field has been completely dominated by Nakamura et al.\(^{569-574,576,577,581-589}\) The growth is performed by MOCVD, generally at atmospheric pressure. Initial structures were grown on c-plane (0001) sapphire, with a low temperature (550°C) GaN buffer, a thick n^+GaN lower contact region, an n^+InGaN strain-relief layer, an n^+AlGaN cladding layer, a light-guiding region of GaN, then a multi-quantum well region consisting of Si-doped In\(_{0.15}\)Ga\(_{0.85}\)N wells separated by Si-doped In\(_{0.05}\)Ga\(_{0.95}\)N barriers. The p-side of the device consisted of sequential layers of
p-AlGaN, p+GaN light-guiding, p-Al0.09Ga0.92N cladding and p+GaN contact. A ridge geometry was fabricated by dry etching in most cases (material removed down to the p-Al0.09Ga0.92N layer), followed by dry etching, cleaving or polishing to form a mirror facet. These facets are coated (with TiO2/SiO2 in the Nichia case) to reduce laser threshold, while Ni/Au (p-type) and Ti/Al (n-type) were employed for ohmic metallization. The typical Nichia structure is shown in Figure 108.

For this type of structure, threshold current densities are typically \( \geq 4 \text{kA-cm}^{-2} \) with an operating voltage of \( \geq 5\text{V} \) at the threshold current. The emission mechanism is still the subject of intense study, but may be related to localization of excitons at compositional fluctuations (leading to potential minima in the band structure) in the InGaN wells.\(^{590-592}\) These devices display relatively short lifetimes under CW operation, typically tens to hundreds of hours. The failure mechanism is most commonly short-circuiting of the p-n junction, a result of p-contact metallization punch-through. It is not surprising that in this high defect density material that the metal can migrate down threading dislocations or voids under high drive-current conditions. The threshold carrier density of the laser diodes on sapphire are typically \( \sim 10^{20}\text{cm}^{-3} \), well above the theoretical values \( \sim 10^{19}\text{cm}^{-3} \).\(^{593-595}\)

A major breakthrough in laser diode lifetime occurred with two changes to the growth. The first was replacement of the AlGaN cladding layers with AlGaN/GaN strained-layer superlattices, combined with modulation doping. These changes had the effect of reducing formation of cracks that often occurred in the AlGaN, and also to reduce the diode operating voltage.\(^{596}\) The second was the use of epitaxial lateral overgrowth (ELOG).\(^{553,568,596}\) In this technique GaN is selectively grown on an SiO2 masked GaN/Al2O3 structure. After \( \sim 10\mu\text{m} \) of GaN is deposited over the SiO2 stripes, it coalesces to produce a flat surface.\(^{597}\) For a
sufficiently wide stripe width, the dislocation density becomes negligible, compared to \( \geq 10^9 \text{cm}^{-2} \) in the window regions. A typical laser diode structure grown by the ELOG method is shown in Figure 109. The laser itself is fabricated slightly off-center from the mask regions, due to gaps that occur there due to imperfect coalescence of the GaN. These devices have lower threshold current density (\( \leq 4 \text{ kA-cm}^{-2} \)) and operating voltage (4-6 V), and much longer (10,000 hours) room-temperature lifetimes.\(^{(588,589)}\) The reduction in threading dislocation density dramatically changes the lifetime, since the p-metal no longer has a direct path for shorting out the junction during operation. The carrier density at threshold is also reduced to \( \sim 3 \times 10^{19} \text{cm}^{-3} \), not far above the expected values. Output power \( >400 \text{ mW} \), and lifetime \( >160 \text{ hours} \) at 30 mW constant output power has been reported.\(^{(589)}\)

Subsequent work from Nichia has focussed on growth of the laser diodes on quasi-GaN substrates.\(^{(588,589)}\) The thick (100-200 \( \mu \text{m} \)) GaN is grown on ELOG structures by either MOCVD or hydride VPE. The sapphire substrate is then removed by polishing, to leave a free-standing GaN substrate. The mirror facet can then be formed by cleaving. The GaN substrate has better thermal conductivity than sapphire.

The mixed group V-nitrides, such as GaAsN, InAsN, AlAsN, GaPN, InPN, AlPN, GaInAsN, GaAlAsN and so on, are of interest for infra-red laser and detector applications.\(^{(598-606)}\) The addition of N into InGaAs\(^{(607)}\) and InAsP\(^{(599)}\) improves the temperature characteristics of long wavelength lasers, both quantum well diode structures and vertical cavity surface-emitting diodes.\(^{(606)}\) The use of GaInNAs allows for growth on GaAs substrates\(^{(603)}\), and produces a large conduction bond discontinuity (\( \sim 0.5 \text{ eV} \)). This leads to better electron confinement at high operation temperatures. Moreover, the large bowing properties of the bandgap as nitrogen is added to both GaAs and InP means that it may be possible to produce a zero bandgap at
relatively low ($\leq 10\%$) concentrations.\textsuperscript{(609)} These features indicate the possibility of fabricating strain-compensated, quantum-well structures with lasing wavelength $>1.55$ $\mu$m. A potential problem is a shift from type I heterostructure band line-up to type II behavior as the nitrogen concentration increases.\textsuperscript{(608)} There is of course, a large miscibility gap for the arsenides and phosphides with the nitrides, so that continuous alloy compositions over the entire range are not possible.
D. Light-Emitting Diodes

GaN-based LEDs operating in the green to violet range of the visible spectrum are commercially available. The total market for these devices worldwide is over $200M per year, divided between Nichia, Cree, Toyota Gosei and Hewlett-Packard. The blue Nichia diodes emitting at 470 nm have luminous intensities of 2 cd with radiant flux 3 mW and spectral half-width 30 nm, while the green diodes emitting at 525 nm have intensity 6 cd, radiant flux 2 mW and spectral half-width 40 nm. Single quantum well devices emitting in the yellow and even red (and hence requiring large In contents in the InGaN active region) are also soon to be available.

Currently the AlInGaP system is employed for yellow, red and orange LEDs, with efficiency superior to unfiltered incandescent lamps.\(^{13}\) Typical visible LEDs now have efficiencies above 10 lumens-W\(^{-1}\), extremely good lifetimes (>5 years), rapid response times. This makes them the light source of choice for applications ranging from full-color outdoor displays and signs, interior automotive lighting, exterior running lights on trucks and traffic lights. The energy savings and cost efficiency of LEDs relative to tungsten-filament incandescent lamps has been the main impetus behind their success.

The availability of the primary colors raises the possibility of white light sources. There are two basic options – the first is color conversion through use of a phosphor or organic dye inside the package to convert the blue light from a GaN LED into white light. The second method would be color mixing through integration of red, blue and green LEDs in the same package. Nichia produced white light LED products based on combining a blue GaN LED with a yttrium aluminum garnet (YAG) fluorescent layer. The efficiency of this approach is less than that of the color-mixing technique since the phosphor efficiency is less than 100%, but it has substantial savings in terms of cost. There is also a program underway to develop this
technology for fluorescent tubes for lighting applications, because of the much longer lifetime and reduced energy consumption relative to incandescent and conventional fluorescent lamps. A similar approach is being taken by Siemens.\(^\text{(609)}\)

The GaN-based LEDs evolved from simple p-n junction devices comprising only GaN to single quantum well InGaN structures. The GaN p-n junction LED emission wavelengths were in the range 370-390 nm, together with deep level emission at \(-550\) nm.\(^\text{(610,611,613)}\) By employing InGaN/AlGaN double heterostructures, the output power was increased due to improved carrier confinement and the width of the spectral peak was roughly half that of the homostructure GaN LEDs.\(^\text{(612-613)}\) A limitation of these double heterostructure devices was the limited wavelength range due to rapidly degrading InGaN material quality at high In contents (high misfit dislocation density and thermal mismatch between the InGaN active region and the AlGaN cladding layers). Moreover the InGaN had to be Zn-doped to produce efficient blue and green emission. These drawbacks can be overcome by use of a single InGaN quantum well, whose thickness is below the critical value for dislocation introduction. This has been the standard structure for high-brightness LEDs, with colors ranging from blue to red.\(^\text{(616,619)}\)

Extensive investigations of the emission characteristics of the blue/green InGaN single quantum well have been carried out.\(^\text{(584,620)}\) The electroluminescence is found to originate from carrier recombination at deep localized states, which are equivalent to three-dimensionally confined quantum dots. This explains the blue shift of the emission wavelength with current density in the green LEDs, as these states are filled. The InGaN layers show spatial inhomogeneity of the bandgap, due to compositional fluctuations. Phase separation in InGaN has been reported by a number of groups\(^\text{(621-627)}\), even at relatively low InN mole fractions (<0.2).
The potential minima have been examined by monochromatic cathodoluminescence mapping, and found to vary from 60-300 nm in lateral size.
E. UV Photodetectors

The AlGaN system, spanning bandgaps of 3.4-6.2 eV, is ideal for fabrication of solar-blind UV detectors. Smaller gap materials also are sensitive to visible and infra-red radiation. The applications for the nitride devices include missile plume detection, flame sensing, ozone monitors, laser detectors and pollution monitoring. By varying the Al content, the responsivity cut-off wavelength can be varied from 365-170 nm. Since the quantum efficiencies are high due to the direct gap of the Ga-rich alloys, there is the ability to form heterojunctions and high temperature operation is possible, Al$_x$Ga$_{1-x}$N appears to be ideally suited to UV detector fabrication.$^{(628-646)}$ SiC p-n junction photodiodes are also operable at high temperatures, but they lack the other advantages of AlGaN devices. However one drawback with AlGaN is the presence of deep states that store charge.

Figure 110 shows a schematic representation of different types of AlGaN photodetectors.$^{(629)}$ N-type material is generally used because of its higher carrier mobility. The standard photoconductor geometries often suffer from high dark currents, dc drift and slow response time$^{(641)}$, and faster response can be achieved with p-n junction or Schottky diodes, which separate the generated charge more rapidly. The use of heterojunction photodiodes allows one to add an additional short wavelength cut-off.$^{(641,643)}$ Typical p-n and p-i-n junction UV photodiode responsivities are $\sim$0-1 A-W$^{-1}$, which correspond to external quantum efficiencies (i.e. collected e-h pairs per incident photon) of roughly 35%.$^{(645)}$ While Schottky photodiodes have better responsivity (0-18 A-W$^{-1}$)$^{(636)}$, there is the disadvantage because of light absorption by the metal contact. It is difficult to realize avalanche photodiodes in GaN due to the high breakdown field needed.
SUMMARY

GaN and related alloys are one of the few instances where device applications have appeared before there was a complete understanding of the growth and defect issues. The rapid development and commercialization of blue and green LEDs, and the achievement of long-lifetime laser diodes has been followed by realization of UV photodetectors and numerous different electronic devices. The applications for GaN-based devices include displays and data storage, solar-blind UV detectors, new sensor technologies, wireless communications, solid-state lighting and high power microwave generation for radar. In our viewpoint several factors have played a key role in realizing these devices, such as better control over the residual oxygen concentration in the MOCVD growth process (especially by use of improved purity precursors, NH₃, and (CH₃)₃Ga) and use of optimized buffer layers as a template for active layer growth; the development of low defect density epitaxy, using the ELO or quasi GaN-substrate approaches; ability to grow high In-content InGaN; better stoichiometry control to avoid high n-type doping backgrounds in epitaxial material; improved processing methods in the areas of ohmic and rectifying contacts, dry etching, facet coating, cleaving and implant activation and isolation, and finally in device design. As a better understanding of the defect and impurity issues in these materials evolves, we expect continued rapid development in the areas of LEDs (where a broader range of emission wavelengths will be available through use of higher In content InGaN active layers), laser diodes, microwave and digital electronic devices, UV detectors and high voltage unipolar and bipolar devices.
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FIGURE CAPTIONS

Figure 1. Schematic of an ultra high breakdown voltage GaN power MOSFET.

Figure 2. Compilation of published results for Schottky barrier heights on GaN (after refs. 18, 28 and 68).

Figure 3. Contact resistance for W, WSi_{0.44} and Ti/Al ohmic contacts to InGaN as a function of annealing temperature.

Figure 4. Contact resistance for ohmic contacts of W, WSi_{x} and Ti/Al to InN as a function of annealing temperature.

Figure 5. Contact resistance for W, WSi_{x} and Ti/Al ohmic contacts to InAlN as a function of annealing temperature.

Figure 6. Ionization efficiency of Mg acceptors in GaN and Fermi level position for GaN containing 10^{18} \text{cm}^{-3} \text{Mg acceptors}, as a function of temperature.

Figure 7. Annealing temperature dependence of I-V characteristics of WSi, W and Ni/Au contacts on p-GaN (60 sec anneal times).
Figure 8. SEM micrographs of Ni/Au contacts on p-GaN after 60 sec anneals at either 400°C (top left) or 700°C (top right), or W contacts after similar annealing at 400°C (bottom left) or 900°C (bottom right).

Figure 9. Measurement temperature dependence of I-V characteristics of Ni/Au, W or WSi_x contacts on p-GaN.

Figure 10. Annealing time dependence at 700°C of I-V characteristics from W contacts on p-GaN.

Figure 11. Annealing temperature dependence of R_c for W contacts on Si-implanted GaN.

Figure 12. SEM micrographs of W contacts on Si-implanted GaN after annealing at 750°C.

Figure 13. Root-mean-square surface roughness normalized to the as-grown value, as a function of anneal temperature for AlN, GaN and InN (top) and InAlN and InGaN (bottom) annealed in the proximity geometry.

Figure 14. Root-mean-square surface roughness of nitrides normalized to the as-grown value, as a function of anneal temperature using either AlN powder (top) or InN powder (bottom) in the susceptor reservoirs.

Figure 15. Time-temperature profiles for RTP annealing of GaN at 1500°C.
Figure 16. Sheet carrier density and electron mobility in capped and uncapped Si-implanted GaN, as a function of annealing temperature.

Figure 17. Comparison of GaN-based HFET structures: (a) planar, (b) recessed gate, (c) regrown $n^+$ ohmic regions and (d) self-aligned, implanted. Implantation is the most practical means to achieve the selective area doping required to reduce the transistor access resistance.

Figure 18. Atomic force microscope images of GaN after an 1100°C, 15 sec anneal either (a) uncapped or (b) capped with reactively sputtered AlN. The AlN film was removed in a selective KOH-based etch (AZ400K developer) at 60-70°C. On both images, the vertical scale is 50 nm per division and the horizontal scale is 2 μm per division.

Figure 19. Reverse current/voltage characteristics for Pt/Au Schottky contacts on GaN annealed at 1100°C, 15 sec either uncapped (samples A1, B1) or capped with AlN (samples A2, B2). Figure (a) is for unintentionally doped GaN with an as-grown donor concentration of $5-10 \times 10^{16}$ cm$^{-3}$ and (b) is for initially semi-insulating GaN implanted with $^{28}$Si (100 keV, $5 \times 10^{13}$ cm$^{-2}$) to simulate a MESFET channel implant.
Figure 20. Current/voltage characteristics for Ti/Al ohmic contacts on GaN after an 1100°C, 15 sec anneal either (a) uncapped or (b) capped with reactively sputtered AlN. The as-grown GaN was n-type with a background concentration of $5\times10^{16}\text{cm}^{-3}$. Note the change in scale for the current axis between the two plots.

Figure 21. Change in the RBS minimum channeling yield ($\chi_{\text{min}}$) versus implant dose for 180 keV Ca and Ar implanted GaN at 77 K.

Figure 22. X-ray diffraction spectrum and its fitting results for GaN implanted with Ca (180 keV, $3\times10^{14}\text{cm}^{-2}$). The inset table shows the fitting results: the position (2θ) and the FWHM of each peak. Peak A, expanded GaN (0002); Peak B, amorphous component; Peak C, undamaged GaN (0002) after implantation; and Peak D the cubic GaN (111) peak.

Figure 23. Channeling Rutherford Backscattering (C-RBS) spectra for as-grown (random and aligned, unimplanted) and Si-implanted (90 keV, $6\times10^{15}\text{cm}^{-2}$) GaN (as-implanted and after a 1100°C, 30 sec anneal). The implants were performed at room temperature.

Figure 24. Cross-sectional Transmission Electron Micrograph (XTEM) of Si-implanted GaN (90 keV, $6\times10^{15}\text{cm}^{-2}$): a) as-implanted and b) after a 1100°C, 30 sec anneal. The implants were performed at room temperature.
Figure 25. Calculated Si-implantation profiles using TRIM92 code a) 210 keV, 5x10^{15} \text{cm}^{-2} Si in AlN/GaN and b) 100 keV, 5x10^{15} \text{cm}^{-2} Si in GaN.

Figure 26. Sheet electron concentration and electron Hall mobility versus annealing treatment for a) unencapsulated and b) AlN encapsulated Si-implanted GaN.

Figure 27. SEM micrograph of a) 1100°C and b) 1300°C annealed unencapsulated sample showing degradation of the surface after the 1300°C anneal.

Figure 28. SEM micrographs of Si-implanted and annealed [a) 1100°C, b) 1300°C and c) 1400°C] AlN-encapsulated GaN. The anneals were performed in flow N_2/NH_3. Craters have started to form on the 1300°C sample and enlarged on the 1400°C sample in regions where the AlN encapsulant failed.

Figure 29. Channeling Rutherford Backscattering (C-RBS) spectra for Si-implanted (100 keV, 5x10^{15} \text{cm}^{-2}) GaN either as-implanted or annealed as shown in the legend.

Figure 30. Channeling Rutherford Backscattering (C-RBS) spectra for Si-implanted (210 keV, 5x10^{15} \text{cm}^{-2}), GaN encapsulated with 120nm of AlN either as-implanted or annealed as shown in the legend.
Figure 31. Aligned C-RBS spectra for Si-implanted (100 keV, 5x10^{15} \text{cm}^{-2}) GaN annealed for 15 min under the conditions show. In parenthesis is the minimum channeling yield ($\chi_{\text{min}}$) for each sample.

Figure 32. The photoluminescence spectra of samples as-grown and after implantation (Si: 100 keV, 5x10^{15} \text{cm}^{-2}) and annealing as listed in the legend.

Figure 33. Sheet electron density versus implantation dose of each ion for Si- and Ar-implanted GaN annealed at 1100°C for 15 sec. The top line represents 100% activation of the implanted dose assuming full ionization.

Figure 34. Photoluminescence spectra from Er-implanted GaN co-implanted with O and annealed at 700°C.

Figure 35. Sheet electron concentration for unimplanted and Si-implanted (100 keV) AlGaN (15% AlN) at the doses shown versus annealing temperature.

Figure 36. Channeling Rutherford Backscattering (C-RBS) spectra for as-grown, unimplanted, Si-implanted (100 keV, 1 or 5x10^{15} \text{cm}^{-2}), and implanted (100 keV, 5x10^{15} \text{cm}^{-2}) annealed at AlGaN.

Figure 37. Comparison of the I-V characteristics of Schottky gate and Ga_{2}O_{3}(Gd_{2}O_{3})/GaN diode.
Figure 38. Comparison of the I-V characteristics of a Schottky gate and AlN/GaN diode.

Figure 39. GaN D-MOSFET I-V characteristics measured at different temperatures.

Figure 40. Temperature dependence of contact properties for Ti/WSi_x/Ti/Au on n-GaN.

Figure 41. Arrhenius plot of etch rate of three different AlN samples in AZ400K developer solution. The higher the AlN quality, as measured by XRD, the slower the etch rate.

Figure 42. Etch rate of AlN as a function of etch temperature for samples as-deposited or annealed at 500, 700, 900, 1000 and 1100°C.

Figure 43. Arrhenius plots of etch rates for as-deposited or annealed AlN as a function of reciprocal etch temperature.

Figure 44. Etch rates as a function of etch temperature for In_{x}Al_{1-x}N grown on GaAs and Si for 19% In.

Figure 45. Etch rate for In_{x}Al_{1-x}N for 0 \leq x \leq 1 at solution temperatures between 20 and 80°C.
Figure 46. Arrhenius plots of etch rates for In$_x$Al$_{1-x}$N for $0 \leq x \leq 1$ as function of reciprocal etch temperature, giving activation energy for etch.

Figure 47. Etch rate for n-type (3.1% In) and depleted InAlN (2.6% In) as a function of solution temperature.

Figure 48. Schematic diagram of a) RIE, b) ECR, and c) ICP etch platforms.

Figure 49. GaN etch rates in RIE, ECR, ICP, and RIBE Cl$_2$-based plasmas as a function of dc-bias.

Figure 50. GaN etch rates as a function of pressure in an ICP-generated BCl$_3$/Cl$_2$/Ar plasma at 32 sccm Cl$_2$, 8 sccm BCl$_3$, 5 sccm Ar, 500 W ICP source power, dc-bias -250 V, and 10°C electrode temperature.

Figure 51. GaN etch rates as a function of dc-bias in an ICP-generated BCl$_3$/Cl$_2$/Ar plasma at 32 sccm Cl$_2$, 8 sccm BCl$_3$, 5 sccm Ar, 500 W ICP source power, 2 mTorr pressure, and 10°C electrode temperature.

Figure 52. SEM micrographs for GaN etched at a) -50, b) -150, and c) -300 V dc-bias. ICP etch conditions were 32 sccm Cl$_2$, 8 sccm BCl$_3$, 5 sccm Ar, 500 W ICP source power, 2 mTorr pressure, and 10°C electrode temperature.

Figure 53. GaN etch rates as a function of ICP source power in an ICP-generated BCl$_3$/Cl$_2$/Ar plasma at 32 sccm Cl$_2$, 8 sccm BCl$_3$, 5 sccm Ar, -250 V dc-bias, 2 mTorr pressure, and 10°C electrode temperature.
Figure 54. GaN, InN, and AlN a) etch rates and b) GaN:AlN and GaN:InN etch selectivities as a function of dc-bias in a Cl₂/Ar ICP plasma. Plasma conditions were: 25 sccm Cl₂, 5 sccm Ar, 2 mTorr chamber pressure, 500 W ICP-source power, and 25°C cathode temperature.

Figure 55. GaN and InN etch rates as a function of temperature for an ICP-generated Cl₂/H₂/Ar plasma. ICP etch conditions were 22.5 sccm Cl₂, 2.5 sccm H₂, 5 sccm Ar, 500 W ICP source power, -250 V dc-bias, and 2 mTorr pressure.

Figure 56. GaN etch rates in an ICP and ECR Cl₂/H₂/Ar plasma as a function of %H₂.

Figure 57. GaN etch rates in an ICP and ECR BCl₃/H₂/Ar plasma as a function of %H₂.

Figure 58. GaN etch rates as a function of %N₂ for ICP-generated Cl₂- and BCl₃-based plasmas.

Figure 59. Optical emission spectra (OES) for an ICP-generated BCl₃/N₂ plasma.

Figure 60. GaN etch rates in an ICP BCl₃/Cl₂ plasma as a function of %Cl₂.

Figure 61. GaN, InN, and AlN a) etch rates and b) GaN:AlN and GaN:InN etch selectivities as a function of %SF₆ in a Cl₂/SF₆/Ar ICP plasma.

Figure 62. SEM micrographs of a) GaN, b) AlN, and c) InN etched in Cl₂-based ICP plasmas.

Figure 63. SEM micrographs of GaN etched in a BCl₃/Cl₂-based ICP plasmas.

Figure 64. AFM micrographs for (a) GaN and InN as-grown, (b) GaN and InN etched at a rf-cathode-power of 65W, and (c) GaN and InN etched at a rf-cathode-power of 275 W in an ECR-generated Cl₂/H₂/CH₄/Ar plasma. The Z-scale is 100 nm/division.
Figure 65. AES surface scans of GaN (a) before exposure to the plasma, (b) at 65 W, and (c) 275 W rf-cathode-power, 1 mTorr, 170°C, and 850 W microwave power in an ECR-generated Cl₂/H₂ discharge.

Figure 66. Sheet resistance versus annealing temperature for N-implanted initially n- and p-type GaN. The N was implanted at multiple energies to give an approximately uniform ion concentration of 4x10¹⁸ cm⁻³ across ~500 nm.

Figure 67. Maximum sheet resistance versus percent In for InGaN either as-grown or implanted with F or N and annealed at the temperature for maximum compensation for each composition (ion concentration ~5x10¹⁹ cm⁻³).

Figure 68. Sheet resistance versus annealing temperature for O-, N- or F-implanted In₀.7₅Al₀.₂₅N (ion concentration ~ 5x10¹⁸ cm⁻³).

Figure 69. Schematic representation of the position in the energy gap of compensating defect levels from implant isolation in GaAs, InP, In₀.₄₇Ga₀.₅₃N, In₀.₇₅Al₀.₂₅N and GaN.

Figure 70. Resistivity change of GaN(Mg) layer after low energy electron beam irradiation, as a function of depth from the surface (after ref. 306).

Figure 71. Resistivity of GaN(Mg) layers as a function of annealing temperature in either NH₃ or NH₂ ambients (after ref. 308).
Figure 72. PL spectra of GaN(Mg) layers after sequential (a) N\textsubscript{2} ambient annealing at 800°C (b) subsequent NH\textsubscript{3} ambient annealing at 800°C (c) subsequent N\textsubscript{2} ambient annealing at 800°C (after ref. 308).

Figure 73. SIMS depth profile of MOCVD grown GaN(Mg) before and after 700°C, 60 min anneal in N\textsubscript{2}.

Figure 74. Hydrogen concentration in undoped or Mg-doped GaN as a function of annealing time at 700°C in a N\textsubscript{2} ambient (after ref. 328).

Figure 75. Low temperature (5K) PL spectra from heavily Mg-doped (Mg=6x10\textsuperscript{19}cm\textsuperscript{-3}) GaN as a function of annealing time at 700°C in a N\textsubscript{2} ambient (after ref. 328).

Figure 76. H, C and O relative concentrations as a function of NH\textsubscript{3} flow in MOCVD InGaN (after ref. 372).

Figure 77. Annealing plot of sheet hole density in Ca-implanted GaN. The activation energy is 169±12 meV.

Figure 78. Sheet hole density at 300K in hydrogenated GaN(Ca) as a function of subsequent annealing temperature.
Figure 79. Hole mobility at 300K in hydrogenated GaN(Ca) as a function of subsequent annealing temperature.

Figure 80. SIMS profiles of $^2$H and Mg in GaN(Mg) exposed to a $^2$H plasma for 30 mins at 250°C.

Figure 81. SIMS profiles of $^2$H and Si in GaN(Si) exposed to a $^2$H plasma for 30 mins at 250°C.

Figure 82. Dependence of absorption coefficient squared on photon energy before and after hydrogenation of AlGaN samples of various Al contents.

Figure 83. Dependence of the fraction of unannealed native donor-hydrogen complexes in AlGaN.

Figure 84. Fraction of passivated donors remaining in InAlN or InGaN after deuteration at 250°C and subsequent annealing at different temperatures.

Figure 85. Carrier concentration profiles in hydrogenated GaN(Mg) after annealing for various times at 175°C under forward bias conditions.

Figure 86. Plot of inverse net active Mg concentration determined from Figure 63 at a depth of 0.1μm from the junction, as a function of forward bias annealing time.
Figure 87. Fraction of passivated Mg acceptors remaining in hydrogenated p-type GaN after annealing for 20 min at various temperatures in either N₂ or H₂ ambients.

Figure 88. SIMS profiles of $^{3}$H in an implanted (50 keV, $2\times10^{15}$ cm$^{-2}$ through a SiN₅ cap) double-heterostructure sample, before and after annealing at 900°C for 20 min.

Figure 89. As-implanted GaN resistivity for He- and H-implanted material, as a function of implant volume concentration (after ref. 141).

Figure 90. Thermal stability of proton implant isolation in n-GaN or GaAs.

Figure 91. Ratio of sample sheet resistance after implantation, $R$, to the control value ($R_0$) for p-type GaN implanted with multiple-energy $^{3}$H⁺ ions, and subsequently annealed at different temperature.

Figure 92. Profiles of $^{3}$H⁺ implanted n-type GaN, subsequently annealed at different temperatures.

Figure 93. SIM profiles of $^{3}$H⁺ implanted p-type GaN, subsequently annealed at different temperatures.

Figure 94. Formation energy of H⁺, H⁻ and H° as a function of Fermi level position. Results are shown from Mg-H complexes and H₂ molecules (after ref. 416).
Figure 95. Schematic representations of H-dopant complexes in GaN. The H occupies either an anti-bonding (AB) or bond-centered (BC) site.

Figure 96. SIMS profiles of high quality Si-doped MOCVD GaN.

Figure 97. SIMS profiles of typical undoped MOCVD GaN grown at low pressure.

Figure 98. SIMS profiles of typical undoped MOCVD GaN grown at atmospheric pressure.

Figure 99. Maximum reported carrier concentration for materials with various group III-carbon and group V-carbon bond strengths, as a function of the difference between the two bonds.

Figure 100. Velocity curves for InN, and GaN and GaAs (after ref. 466).

Figure 101. Contributions to electron mobility in GaN from polar optical, piezoelectric and acoustic scattering, as a function of temperature (after ref. 453).

Figure 102. Effect of ionized impurity scattering on electron mobility in GaN for total ionized impurity concentration of $7.5 \times 10^{16}$ cm$^{-3}$, and carrier densities of (1) $5 \times 10^{17}$ cm$^{-3}$, (2) $2 \times 10^{17}$ cm$^{-3}$, (3) $7.5 \times 10^{16}$ cm$^{-3}$, (4) $2 \times 10^{16}$ cm$^{-3}$ (after ref. 468).
Figure 103. Electron mobilities in cubic (dashed lines) and hexagonal (solid lines) GaN (after ref. 468).

Figure 104. Sheet electron density versus Al mole fraction in nominally undoped Al$_x$Ga$_{1-x}$N/GaN HFET epitaxial layer. Points are from Hall measurements. The dashed line is the calculated variation assuming a Schottky barrier at the AlGaN surface while the solid curve is calculated assuming an unpinned Fermi level at the AlGaN surface (after ref. 468).

Figure 105. Illustration of the effect of a buried AlGaN layer on the piezoelectronically induced electron concentration at the upper AlGaN/GaN interface. (a) Schematic diagram of a doped Al$_{0.15}$Ga$_{0.85}$N/GaN HFET with a buried Al$_{0.15}$Ga$_{0.85}$N layer. (b) Conduction band energy diagram for the structure in (a) with the dotted line representing the Fermi level. (c) Schematic of piezoelectronically induced charge ($\sigma_{pz}$) and free-carrier charge ($\sigma_{2deq}$) (after ref. 472).

Figure 106. I-V characteristics from p-n junctions on defective or low dislocation GaN (after ref. 556).

Figure 107. Schematic of power flow control system utilizing power electronics.

Figure 108. Schematic of GaN/InGaN/AlGaN laser diodes grown on Al$_2$O$_3$ (after ref. 569).
Figure 109. Schematic of GaN/InGaN/AlGaN laser diodes grown on ELOG substrates (after ref. 587).

Figure 110. Schematic of different types of AlGaN photodetectors (after ref. 629).
Table I. Temperature-dependent contact data for p-GaN.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Measurement temperature (°C)</th>
<th>Specific contact resistance (Ω-cm²)</th>
<th>Contact resistivity (Ω-mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Au</td>
<td>200</td>
<td>0.125</td>
<td>415.7</td>
</tr>
<tr>
<td>Ni/Au</td>
<td>250</td>
<td>0.121</td>
<td>319.5</td>
</tr>
<tr>
<td>Ni/Au</td>
<td>300</td>
<td>0.092</td>
<td>205.9</td>
</tr>
<tr>
<td>W</td>
<td>300</td>
<td>0.682</td>
<td>758.4</td>
</tr>
<tr>
<td>WSi</td>
<td>300</td>
<td>0.026</td>
<td>1728.3</td>
</tr>
</tbody>
</table>
Table II. Summary of annealing conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Anneal Temperature (°C)/time(s)</th>
<th>Reactor</th>
<th>Ambient</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, 8</td>
<td>1100/15</td>
<td>RTA</td>
<td>N₂</td>
</tr>
<tr>
<td>3, 7</td>
<td>1100/30</td>
<td>MOCVD</td>
<td>N₂/NH₃</td>
</tr>
<tr>
<td>2, 6</td>
<td>1300/30</td>
<td>MOCVD</td>
<td>N₂/NH₃</td>
</tr>
<tr>
<td>1, 5</td>
<td>1400/30</td>
<td>MOCVD</td>
<td>N₂/NH₃</td>
</tr>
</tbody>
</table>
Table III. Summary of C-RBS results for Si-implanted AlN-encapsulated and unencapsulated GaN annealed under the conditions shown. All 30 sec anneals were done in an MOCVD reactor under flowing N₂/ NH₃ and the 15 sec anneals were done in a RTA under flowing N₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal (temperature/time) (°C)</th>
<th>( \chi_{\text{min}} ) for GaN (%)</th>
<th>GaN thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN as-grown</td>
<td>none</td>
<td>2.5</td>
<td>1.12</td>
</tr>
<tr>
<td>AlN/GaN as-implanted</td>
<td>None</td>
<td>38.6</td>
<td>1.36</td>
</tr>
<tr>
<td>1</td>
<td>1400, 30</td>
<td>17.2</td>
<td>1.23</td>
</tr>
<tr>
<td>3</td>
<td>1100, 30</td>
<td>20.2</td>
<td>1.23</td>
</tr>
<tr>
<td>4</td>
<td>1100, 15</td>
<td>23.6</td>
<td>1.29</td>
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<tr>
<td>GaN as-implanted</td>
<td>None</td>
<td>34.1</td>
<td>0.90</td>
</tr>
<tr>
<td>5</td>
<td>1400, 30</td>
<td>a)</td>
<td>----</td>
</tr>
<tr>
<td>6</td>
<td>1300, 30</td>
<td>6.7</td>
<td>0.90</td>
</tr>
<tr>
<td>7</td>
<td>1100, 30</td>
<td>17.2</td>
<td>0.98</td>
</tr>
<tr>
<td>8</td>
<td>1100, 15</td>
<td>20.8</td>
<td>0.94</td>
</tr>
</tbody>
</table>

a) The GaN layer completely evaporated during the anneal.
Table IV. Comparison of Ga$_2$O$_3$ and SiO$_2$.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ga$_2$O$_3$</th>
<th>SiO$_2$</th>
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</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>1850</td>
<td>1600</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>10.2-14.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Energy Gap (eV)</td>
<td>4.4</td>
<td>9</td>
</tr>
<tr>
<td>Dielectric Strength (V/cm)</td>
<td>3.5x10$^6$</td>
<td>10$^7$</td>
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</tbody>
</table>
Table V. Compilation of etching results in acid and base solutions, performed at room temperature (25°C) unless otherwise noted.

<table>
<thead>
<tr>
<th>Solution</th>
<th>GaN</th>
<th>InN</th>
<th>AlN</th>
<th>InAlN</th>
<th>InGaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric Acid (75°C)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>Succinic acid (75°C)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxalic acid (75°C)</td>
<td>0</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Nitric acid (75°C)</td>
<td>0</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Phosphoric acid (75°C)</td>
<td>0</td>
<td>0</td>
<td>Oxide removed</td>
<td>Oxide removed</td>
<td>0</td>
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<tr>
<td>Hydrofluoric acid</td>
<td>0</td>
<td>Lifts off</td>
<td>0</td>
<td>0</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Hydriodic acid</td>
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<td>0</td>
<td>0</td>
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<td>Potassium iodide</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>2% Bromine-methanol</td>
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<td>0</td>
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<td>n-Methyl-2-pyrrolidone</td>
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<td>0</td>
<td>0</td>
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<td>Sodium hydroxide</td>
<td>0</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Az400K Photoresist developer (75°C)</td>
<td>0</td>
<td>Lifts off</td>
<td>~60-10,000 Amin⁻¹</td>
<td>Composition dependent</td>
<td>0</td>
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<tr>
<td>Hydriodic acid/hydrogen peroxide</td>
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<tr>
<td>Hydrochloric acid/hydrogen peroxide</td>
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<td>0</td>
<td>0</td>
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<td>Potassium triphosphite (75°C)</td>
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<td>0</td>
<td>0</td>
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<td>Nitric acid/potassium triphosphite (75°C)</td>
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<td>Lifts off</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Hydrochloric acid/potassium triphosphite (75°C)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>Boric acid (75°C)</td>
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<td>0</td>
<td>0</td>
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<td>Nitric/boric acid (75°C)</td>
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<td>Lifts off</td>
<td>0</td>
<td>0</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Nitric/boric/hydrogen peroxide</td>
<td>0</td>
<td>Lifts off</td>
<td>0</td>
<td>0</td>
<td>Removes oxide</td>
</tr>
<tr>
<td>HCl/H₂O₂/HNO₃</td>
<td>0</td>
<td>Lifts off</td>
<td>0</td>
<td>0</td>
<td>Lifts off</td>
</tr>
<tr>
<td>Potassium tetaborate (75°C)</td>
<td>0</td>
<td>Oxide removal</td>
<td>Oxide removal</td>
<td>Oxide removal</td>
<td>Oxide removal</td>
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<td>Sodium tetaborate (75°C)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>Sodium tetaborate/hydrogen peroxide</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Potassium triphosphite (75°C)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>Potassium triphosphite/hydrogen peroxide</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>
Table VI. Boiling points for possible etch products of group-III nitride films etched in halogen- or CH\textsubscript{3}/H\textsubscript{2}-based plasmas.

<table>
<thead>
<tr>
<th>Etch Products</th>
<th>Boiling Points (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl\textsubscript{3}</td>
<td>183</td>
</tr>
<tr>
<td>AlF\textsubscript{3}</td>
<td>na</td>
</tr>
<tr>
<td>AlI\textsubscript{3}</td>
<td>360</td>
</tr>
<tr>
<td>AlBr\textsubscript{3}</td>
<td>263</td>
</tr>
<tr>
<td>(CH\textsubscript{3})\textsubscript{3}Al</td>
<td>126</td>
</tr>
<tr>
<td>GaCl\textsubscript{3}</td>
<td>201</td>
</tr>
<tr>
<td>GaF\textsubscript{3}</td>
<td>1000</td>
</tr>
<tr>
<td>GaI\textsubscript{3}</td>
<td>sublimes 345</td>
</tr>
<tr>
<td>GaBr\textsubscript{3}</td>
<td>279</td>
</tr>
<tr>
<td>(CH\textsubscript{3})\textsubscript{3}Ga</td>
<td>55.7</td>
</tr>
<tr>
<td>InCl\textsubscript{3}</td>
<td>600</td>
</tr>
<tr>
<td>InF\textsubscript{3}</td>
<td>&gt;1200</td>
</tr>
<tr>
<td>InI\textsubscript{3}</td>
<td>na</td>
</tr>
<tr>
<td>InBr\textsubscript{3}</td>
<td>sublimes</td>
</tr>
<tr>
<td>(CH\textsubscript{3})\textsubscript{3}In</td>
<td>134</td>
</tr>
<tr>
<td>NCl\textsubscript{3}</td>
<td>&lt;71</td>
</tr>
<tr>
<td>NF\textsubscript{3}</td>
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</tr>
<tr>
<td>NBr\textsubscript{3}</td>
<td>na</td>
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<td>N\textsubscript{3}</td>
<td>explodes</td>
</tr>
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<td>-33</td>
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<td>N\textsubscript{2}</td>
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<tr>
<td>(CH\textsubscript{3})\textsubscript{3}N</td>
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</table>
Table VII.  *p*-dopants found to be passivated by atomic hydrogen in GaN.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>residual hydrogen in growth ambient leads to high resistivity in as-grown GaN(Mg)</td>
<td>305-307,328</td>
</tr>
<tr>
<td>Zn</td>
<td>electron injection increases Zn-related emissions in GaN(Zn)</td>
<td>310</td>
</tr>
<tr>
<td>C</td>
<td>H$_2$ plasma exposure decreases hole density by a factor of 3 – thermally reversible</td>
<td>339</td>
</tr>
<tr>
<td>Ca</td>
<td>H$_2$ plasma exposure decreases hole density by a factor of 10 – thermally reversible</td>
<td>338</td>
</tr>
<tr>
<td>Cd</td>
<td>formation of Cd-H complexes seen by PAC - dissociate at &lt;350°C</td>
<td>338</td>
</tr>
</tbody>
</table>
Table VIII. Impurity densities in III-nitrides (cm$^3$)

<table>
<thead>
<tr>
<th>Nitride</th>
<th>Growth</th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>MOCVD (Source A)</td>
<td>5x17</td>
<td>1x17</td>
<td>1x18</td>
<td>5x16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4x18</td>
<td>7x16</td>
<td>2x18</td>
<td>2x17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4x18</td>
<td>3x17</td>
<td>4x18</td>
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<tr>
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<td>2x17</td>
<td>5x18</td>
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<tr>
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<td>-</td>
</tr>
<tr>
<td></td>
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<td>8x17</td>
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<td>4x18</td>
<td>2.5x19</td>
<td>7x17</td>
</tr>
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<td>GaN</td>
<td>MOCVD (Source B)</td>
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<td>2x17</td>
<td>1.5x17</td>
</tr>
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<td>1x17</td>
<td>3x16</td>
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<tr>
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<td>3x18</td>
<td>2.5x17</td>
<td>9x17</td>
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<td>2x18</td>
<td>5x16</td>
<td>2x17</td>
<td>-</td>
</tr>
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<td>GaN</td>
<td>MOCVD (Source C)</td>
<td>4x18</td>
<td>1.5x18</td>
<td>8x18</td>
<td>8x17</td>
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<td></td>
<td>2x19</td>
<td>3x17</td>
<td>5x18</td>
<td>2x17</td>
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<tr>
<td>GaN</td>
<td>MOCVD (Source D)</td>
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<td>3x17</td>
<td>5x16</td>
<td>-</td>
</tr>
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<td>GaN</td>
<td>MOCVD (Source E)</td>
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<td>3x15</td>
<td>2x16</td>
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<td>MOCVD (Source F)</td>
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<td>1x18</td>
<td>5x19</td>
<td>1x19</td>
</tr>
<tr>
<td>AlN</td>
<td>CVD</td>
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<td>5x18</td>
<td>8x18</td>
<td>-</td>
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<tr>
<td>AlN</td>
<td>CVD</td>
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<td>1.5x18</td>
<td>8x18</td>
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<td>2x18</td>
<td>5x18</td>
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<tr>
<td>AlGaN</td>
<td>MOCVD</td>
<td>7x18</td>
<td>8x18</td>
<td>2x19</td>
<td>7x17</td>
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<tr>
<td>AlInN</td>
<td>MOMBE</td>
<td>5x18</td>
<td>3x18</td>
<td>2x19</td>
<td>1x20</td>
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<tr>
<td>InN</td>
<td>MOMBE</td>
<td>8x20</td>
<td>7x19</td>
<td>1x21</td>
<td>2x19</td>
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**Table IX. Nitride Parameters (after B.E. Foutz; see http://iiiv.tn.cornell.edu/www/foutz/nitride.html).**

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Units</th>
<th>GaN</th>
<th>AlN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/cm</td>
<td>6.15 (447)</td>
<td>3.23 (447)</td>
<td>6.81 (447)</td>
</tr>
<tr>
<td>Transverse Constant (C&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>dyn/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.42x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
<td>4.42x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
<td>4.42x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
</tr>
<tr>
<td>Longitudinal Constant (C&lt;sub&gt;l&lt;/sub&gt;)</td>
<td>dyn/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2.65x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
<td>2.65x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
<td>2.65x10&lt;sup&gt;11&lt;/sup&gt; (447)</td>
</tr>
<tr>
<td>Transverse Sound Velocity</td>
<td>cm/s</td>
<td>2.68x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>3.70x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2.55x10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Longitudinal Sound Velocity</td>
<td>cm/s</td>
<td>6.56x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>9.06x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>6.24x10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Static Dielectric Constant</td>
<td></td>
<td>8.9 (448)</td>
<td>8.5 (447)</td>
<td>13.3 (448)</td>
</tr>
<tr>
<td>High Frequency Dielectric Constant</td>
<td></td>
<td>5.35 (448,461)</td>
<td>4.77 (447)</td>
<td>8.4 (448)</td>
</tr>
<tr>
<td>Energy Gap (G Valley)</td>
<td>eV</td>
<td>3.39 (458)</td>
<td>6.2 (459)</td>
<td>1.89 (460)</td>
</tr>
<tr>
<td>Electron Effective Mass (G Valley)</td>
<td>m&lt;sub&gt;e&lt;/sub&gt;</td>
<td>0.20 (448)</td>
<td>0.48 (447)</td>
<td>0.11 (448)</td>
</tr>
<tr>
<td>Deformation Potential</td>
<td>eV</td>
<td>8.2 (447)</td>
<td>9.5 (447)</td>
<td>7.1 (447)</td>
</tr>
<tr>
<td>Polar Optical Phonon Energy</td>
<td>meV</td>
<td>91.2 (447)</td>
<td>99.2 (447)</td>
<td>89.0 (447)</td>
</tr>
<tr>
<td>Piezoelectric Constant e&lt;sub&gt;14&lt;/sub&gt;</td>
<td>C/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.375 (447)</td>
<td>0.92</td>
<td>0.375 (447)</td>
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<tr>
<td>Piezoelectric Constant e&lt;sub&gt;15&lt;/sub&gt;</td>
<td>C/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>-</td>
<td>-0.58 (449)</td>
<td>-</td>
</tr>
<tr>
<td>Piezoelectric Constant e&lt;sub&gt;31&lt;/sub&gt;</td>
<td>C/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>-</td>
<td>-0.48 (449)</td>
<td>-</td>
</tr>
<tr>
<td>Piezoelectric Constant e&lt;sub&gt;33&lt;/sub&gt;</td>
<td>C/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.55 (449)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Intervalley Coupling Coefficient</td>
<td>eV</td>
<td>91.2</td>
<td>99.2</td>
<td>89.0</td>
</tr>
<tr>
<td>Intervalley Deformation Potential</td>
<td>eV/cm</td>
<td>1x10&lt;sup&gt;9&lt;/sup&gt;</td>
<td>1x10&lt;sup&gt;9&lt;/sup&gt;</td>
<td>1x10&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td>Lattice Constant, a</td>
<td>Å</td>
<td>3.189 (454)</td>
<td>3.11 (454)</td>
<td>3.54 (454)</td>
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<tr>
<td>Lattice Constant, c</td>
<td>Å</td>
<td>5.185 (454)</td>
<td>4.98 (454)</td>
<td>5.70 (454)</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt;/Vs</td>
<td>1000 bulk 2000 (2D-gas) (455)</td>
<td>135 (456)</td>
<td>3200 Bulk (455)</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt;/Vs</td>
<td>30 (454)</td>
<td>14 (454)</td>
<td>-</td>
</tr>
<tr>
<td>Hole Lifetime</td>
<td>ns</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hole Diffusion Length (300K)</td>
<td>m</td>
<td>-0.8x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Non-Parabolicity Constant</td>
<td>(eV)&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.189</td>
<td>-</td>
<td>0.419</td>
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<tr>
<td>Saturation velocity</td>
<td>cm/s</td>
<td>2.5x10&lt;sup&gt;7&lt;/sup&gt; (455)</td>
<td>1.4x10&lt;sup&gt;7&lt;/sup&gt; (456)</td>
<td>2.5x10&lt;sup&gt;7&lt;/sup&gt; (466)</td>
</tr>
<tr>
<td>Peak velocity</td>
<td>cm/s</td>
<td>3.1x10&lt;sup&gt;7&lt;/sup&gt; (455)</td>
<td>1.7x10&lt;sup&gt;7&lt;/sup&gt; (456)</td>
<td>4.3x10&lt;sup&gt;7&lt;/sup&gt; (466)</td>
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<tr>
<td>Peak velocity field</td>
<td>kV/cm</td>
<td>150 (455)</td>
<td>450 (456)</td>
<td>67 (466)</td>
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<tr>
<td>Breakdown field</td>
<td>V/cm</td>
<td>&gt;5x10&lt;sup&gt;5&lt;/sup&gt; (454)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Light hole mass</td>
<td>m&lt;sub&gt;e&lt;/sub&gt;</td>
<td>0.259 (454)</td>
<td>0.471 (454)</td>
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<tr>
<td>Thermal Conductivity</td>
<td>W/cmK</td>
<td>1.5 (454)</td>
<td>2 (454)</td>
<td>-</td>
</tr>
<tr>
<td>Melting Temp</td>
<td>°C</td>
<td>&gt;1700 (454)</td>
<td>3000 (454)</td>
<td>1100 (454)</td>
</tr>
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</table>
Table X. Summary of key material parameters for AlGaAs/GaAs, 4H-SiC, and AlGaN/GaN transistors (after ref. 444-446)

<table>
<thead>
<tr>
<th>Metric</th>
<th>AlGaAs/GaAs</th>
<th>4H SiC</th>
<th>AlGaN/GaN</th>
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</thead>
<tbody>
<tr>
<td>Maximum sheet electron density (cm$^{-2}$)</td>
<td>2-3x10$^{12}$</td>
<td>na</td>
<td>1-5x10$^{13}$</td>
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<tr>
<td>Breakdown field (V/cm) (x10$^5$)</td>
<td>4</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>2 Dimensional Electron Mobility (cm$^2$/V s)</td>
<td>8500</td>
<td>na</td>
<td>2000</td>
</tr>
<tr>
<td>Saturated electron velocity (x10$^7$ cm/s)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm K)</td>
<td>0.53</td>
<td>4.9$^a$</td>
<td>1.3$^b$</td>
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<tr>
<td>Piezoelectric coefficient (C/m$^2$)</td>
<td>$e_{31}$ 0.093</td>
<td></td>
<td>-0.36</td>
</tr>
<tr>
<td></td>
<td>$e_{33}$ -0.185</td>
<td>0.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a. This is for undoped SiC. Doped or semi-insulating SiC has a thermal conductivity of 3.3 W/cmK.
b. This is for highly dislocated GaN. Theory predicts 1.7 W/cmK for low dislocation material (G.A. Slack, J. Phys. Chem. Solid. 34, 321 (1973)).
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Authors</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969</td>
<td>GaN by hydride vapor phase epitaxy</td>
<td>Maruska and Tietjen</td>
<td>16</td>
</tr>
<tr>
<td>1971</td>
<td>MIS LEDs</td>
<td>Pankove, et. al.</td>
<td>433</td>
</tr>
<tr>
<td></td>
<td>GaN by MOCVD</td>
<td>Manasevit, et. al.</td>
<td>477</td>
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<tr>
<td>1974</td>
<td>GaN by MBE</td>
<td>Akasaki, et. al.</td>
<td>479</td>
</tr>
<tr>
<td>1983</td>
<td>AlN intermediate layer by MBE</td>
<td>Yoshida, et. al.</td>
<td>480</td>
</tr>
<tr>
<td>1986</td>
<td>Specular films using AlN buffer</td>
<td>Amano, et. al.</td>
<td>305</td>
</tr>
<tr>
<td>1989</td>
<td>p-type Mg-doped GaN by LEEBI and GaN p-n junction LED</td>
<td>Amano, et. al.</td>
<td>305</td>
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<tr>
<td>1991</td>
<td>GaN buffer layer by MOCVD</td>
<td>Nakamura</td>
<td>481</td>
</tr>
<tr>
<td>1992</td>
<td>Mg activation by thermal annealing</td>
<td>Nakamura, et. al.</td>
<td>482</td>
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<tr>
<td></td>
<td>AlGaN/GaN 2 Dimensional Electron Gas</td>
<td>M.A. Khan, et. al.</td>
<td>483</td>
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<tr>
<td>1993</td>
<td>GaN MESFET</td>
<td>M.A. Khan, et. al.</td>
<td>52</td>
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<td></td>
<td>AlGaN/GaN HEMT</td>
<td>M.A. Khan, et. al.</td>
<td>484</td>
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<tr>
<td></td>
<td>Theoretical prediction of piezoelectric effect in AlGaN/GaN</td>
<td>A. Bykhovski, et. al.</td>
<td>485</td>
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<tr>
<td>1994</td>
<td>InGaN/AlGaN DH blue LEDs (1 cd)</td>
<td>Nakamura, et. al.</td>
<td>486</td>
</tr>
<tr>
<td></td>
<td>Microwave GaN MESFET</td>
<td>S.C. Binari, et. al.</td>
<td>487</td>
</tr>
<tr>
<td></td>
<td>Microwave HEMT, MISFET</td>
<td>S.C. Binari, et. al.; M.A. Khan, et. al.</td>
<td>488</td>
</tr>
<tr>
<td></td>
<td>GaN/SiC HBT</td>
<td>J. Pankove, et. al.</td>
<td>489</td>
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<tr>
<td>1995</td>
<td>AlGaN/GaN HEMT by MBE</td>
<td>A. Ozgur, et. al.</td>
<td>490</td>
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<tr>
<td>1996</td>
<td>Doped channel AlGaN/GaN HEMT</td>
<td>M.A. Khan, et. al.</td>
<td>491</td>
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<td></td>
<td>Ion-implanted GaN JFET</td>
<td>J.C. Zolper, et. al.</td>
<td>492</td>
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<td></td>
<td>340 V V&lt;sub&gt;d&lt;/sub&gt; AlGaN/GaN HEMT</td>
<td>Y.F. Wu, et. al.</td>
<td>493,494</td>
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<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; blue laser diode</td>
<td>Nakamura, et. al.</td>
<td>495</td>
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<td>1997</td>
<td>Quantification of Piezoelectric effect</td>
<td>P.M. Asbeck, et. al.</td>
<td>496</td>
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<td></td>
<td>AlGaN/GaN HEMT on SiC</td>
<td>S.C. Binari, et. al.; A.T. Ping, et. al.</td>
<td>497</td>
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<tr>
<td></td>
<td>1.4 W @ 4 GHz</td>
<td>R. Gaska, et. al.</td>
<td>498</td>
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<tr>
<td></td>
<td>0.85 W @ 10 GHz</td>
<td>B.I. Thibeault, et. al.</td>
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<tr>
<td></td>
<td>3.1 W/mm at 18 GHz</td>
<td>S. Sheppard, et. al.</td>
<td></td>
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<tr>
<td></td>
<td>3.3 W @ 10 GHz</td>
<td>G.J. Sullivan, et. al.</td>
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<td></td>
<td>p/n junction in LEO GaN HEMT</td>
<td>P. Kozody, et. al.</td>
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<tr>
<td></td>
<td>HEMT in LEO GaN</td>
<td>U. Mishra, et. al.</td>
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<tr>
<td></td>
<td>6.8 W/mm (4 W) @ 10 GHz HEMT on SiC</td>
<td>S. Sheppard, et. al.</td>
<td></td>
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<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Hooge factor for HEMT on SiC</td>
<td>M.E. Levinstein, et. al.</td>
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<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; AlGaN/GaN HBT</td>
<td>L.S. McCarthy, et. al.</td>
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<td></td>
<td>213</td>
<td>Ren, et. al.</td>
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Table XII. AlGaN/GaN HFET device results in reverse chronological order (after B.E. Foutz, http://www.foutz.com and ref. 506-541).

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<th>Gate</th>
<th>Length</th>
<th>$I_{SD}$</th>
<th>$f_T$</th>
<th>$f_{max}$</th>
<th>$I_{d}$</th>
<th>RF Power</th>
<th>$g_{max}$</th>
<th>Reference</th>
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<tr>
<td>micron</td>
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<td>GHz</td>
<td>GHz</td>
<td>A/mm</td>
<td>W/mm at GHz</td>
<td>mS/mm</td>
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<td>0.15</td>
<td>65</td>
<td>80</td>
<td>1.300</td>
<td>1.8 at 4</td>
<td>300</td>
<td>Unpublished</td>
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<tr>
<td>3</td>
<td>0.800</td>
<td>140</td>
<td>509</td>
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<td></td>
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<td></td>
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<tr>
<td>0.45</td>
<td>28</td>
<td>114</td>
<td>0.680</td>
<td>6.8 at 10</td>
<td>200</td>
<td>502</td>
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<td>0.7</td>
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<td>15</td>
<td>42</td>
<td>1.100</td>
<td>2.82 at 10</td>
<td>270</td>
<td>499,510</td>
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<td>26</td>
<td>51</td>
<td>0.85</td>
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<td>511</td>
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<td>1.4</td>
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<td>0.15</td>
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<td>28</td>
<td>40</td>
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<td>41</td>
<td>1.400</td>
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<td>1</td>
<td>3</td>
<td>15</td>
<td>24</td>
<td>1.220</td>
<td>205</td>
<td>516</td>
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<td>44</td>
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<td>517</td>
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<tr>
<td>0.9</td>
<td>2</td>
<td>15</td>
<td>35</td>
<td>1.000</td>
<td>255</td>
<td>517</td>
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<tr>
<td>0.25</td>
<td>2</td>
<td>45</td>
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<td>1.020</td>
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<td>518</td>
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<td>52</td>
<td>82</td>
<td>1.130</td>
<td>3.3 at 18</td>
<td>240</td>
<td>519</td>
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<td>0.2</td>
<td>1.6</td>
<td>50</td>
<td>92</td>
<td>0.806</td>
<td>1.7 at 10</td>
<td>240</td>
<td>520</td>
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<tr>
<td>0.12</td>
<td>46.9</td>
<td>103</td>
<td>0.550</td>
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<td>120</td>
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<td>1.000</td>
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<td>523</td>
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<td>4</td>
<td>6</td>
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<td>130</td>
<td>523</td>
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<td>2</td>
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$\text{Ga}_2\text{O}_3 / \text{Gd}_2\text{O}_3$

p-Well Contact Source Contact Gate Contact Drain Contact

Sapphire Substrate

10$\mu$m GaN n$^-$-Layer
InN

Contact Resistance (ohm-cm$^2$)

Anneal Temperature (°C)
Mg in GaN
$E_A - E_V = 171$ meV
The figure shows current-voltage (I-V) characteristics of Au/Ni/p-GaN, W/p-GaN, and WSi/p-GaN at various temperatures. The graphs indicate that the electrical behavior changes with temperature, showing a semiconductor-like diode behavior with an asymmetrical current flow. The as-deposited samples at 400 °C to 800 °C show different resistance and conductivity levels, with 800 °C showing the highest resistance. The WSi/p-GaN sample at 800 °C shows the most significant change in current at a given voltage, indicating potential improvements in contact resistance or increased doping at this temperature.
W/Si-implanted GaN
30 second anneals
Sheet Carrier Concentration (cm$^{-2}$)

Annealing Temperature (°C)

Carrier Mobility (cm$^2$/Vs)
Ohmic Metal

Schottky Gate

AlGaN

GaN

(a) planar

(b) regrown contacts

Ohmic Metal

Schottky Gate

AlGaN

regrown n-type GaN

GaN

(c) recessed

(d) implanted, self-aligned
(a) RMS = 4.02 nm
(b) RMS = 2.51 nm
Peak 2θ FWHM
A 34.28° 0.0712°
B 34.38° 0.1931°
C 34.51° 0.0706°
D 34.38° 0.0635°

GaN (0002)

experimental
fitted spectrum

new peak

Intensity (arb. units)

33.8 34.0 34.2 34.4 34.6 34.8 35.0

Diffraction angle 2θ (degree)
6x10^{15} \text{ cm}^{-2}$ as implanted

- Random energy (MeV)
Si concentration (cm$^{-3}$)

depth (Å)
(a)
- as grown, aligned
- as implanted, aligned
- 1100 °C, RTA
- 1100 °C, MOCVD
- 1300 °C, MOCVD
1200
1000
~
1100°C, RTA
B
1300°C, MOCVD

counts

1100°C, MOCVD

1400°C, MOCVD

as implanted, aligned

depth (µm)

1.6 1.2 0.8 0.4 0
channel number

counts
Room Temperature

250
Spec. Contact Resistivity (ohm-cm$^2$)  Transfer Resistance (ohm-mm)

Chuck Temperature (C)

n-GaTl/WSiTi/Au
Annealed at 450 C

Chuck Temperature (C)

GaTl/WSiTi/Au
Annealed at 450 C
Etch Rate (Å/min)

AIN: AZ400K

$E_a = 15.45 \pm 0.44$ Kcal/mol

$1000 / T (K)$
The graph shows the etch rate (Å/min) as a function of etch temperature (°C) for different AlN samples.

- **As deposited**
- **500 °C**
- **700 °C**
- **900 °C**
- **1000 °C**
- **1100 °C**

The etch rate increases with increasing etch temperature for all samples, with the highest etch rate observed for the sample etched at 1100 °C.
InAlN

Etch Rate (A/min) vs. Etch Temperature (°C)

- ● depleted
- ■ n=5x10^{18} cm^{-3}
ICP power: 500 W
DC bias: -250V
Cl\textsubscript{2}: 32 sccm
BCl\textsubscript{3}: 8 sccm
Ar: 5 sccm
Etch rate (Å/min) vs. dc-Bias (-V) graph.

- ICP Power: 500 W
- Pressure: 2 mTorr
- Cl₂: 32 sccm
- BCl₃: 8 sccm
- Ar: 5 sccm
dc bias: -250V
Pressure: 2 mTorr
Cl\textsubscript{2}: 32 sccm
BCl\textsubscript{3}: 8 sccm
Ar: 5 sccm
(a) Etch Rate (Å/min) vs. Cathode rf-Power (W)

(b) Selectivity vs. Cathode rf-Power (W)
ICP power: 500 W
de-bias: -250 V
Pressure: 2 mTorr
Cl₂: 22.5 sccm
H₂: 2.5 sccm
Ar: 5 sccm
%Cl₂ Concentration in BCl₃/Cl₂ vs. Etch Rate (Å/min)

- Etch Rate (Å/min)
- %Cl₂ Concentration in BCl₃/Cl₂
a) Etch Rate (Å/min) vs. %SF$_6$ Concentration in Cl$_2$/SF$_6$ Plasma

- □ - AlN
- △ - InN
- ○ - GaN

b) Selectivity vs. %SF$_6$ Concentration in Cl$_2$/SF$_6$ Plasma

- ■ - GaN : AlN
- ▲ - GaN : InN
$\rho_s (\Omega \cdot \square)$

- as-grown
- F-isolation
- N-isolation

percent In

$10^8$

$10^7$

$10^6$

$10^5$

$10^4$

$10^3$

$10^2$

$10^1$

$10^0$
n p-GaAs  p n-GaAs  n p-InP

\[ E_C \]

\[ E_g/2 \]

\[ E_V \]

\[ E_0 = 1.42 \text{ eV} \]

\[ 1.35 \text{ eV} \]

\[ <2.5 \text{ eV} \]

\[ >2.5 \text{ eV} \]

\[ 2.38 \text{ eV} \]
The graph shows the resistivity (Ω·m) as a function of temperature (°C) for different ambient conditions. The resistivity is plotted on a logarithmic scale.

Key:
- □ NH₃ Ambient
- ● N₂ Ambient

The resistivity remains relatively constant at lower temperatures and increases sharply at higher temperatures, indicating a phase transition in the material.
Undoped GaN(A)
Lightly Mg doped GaN(B)
Heavily Mg doped GaN(C)
Photon Energy (eV) vs. Intensity (a.u.)

- 3.455 eV
- 3.285 eV
- 3.446 eV

- 60 min anneal
- 20 min anneal
- Unannealed
The diagrams show the relationship between ammonia flow rate (slm) and impurity concentration (a.u.) for different impurities:

(a) Hydrogen
(b) Carbon
(c) Oxygen

The graphs indicate that as the ammonia flow rate increases, the concentration of Hydrogen and Oxygen increases, while the concentration of Carbon decreases.

Ammonia Flow Rate (slm)
before hydrogenation

after hydrogenation

GaN (Ca)
H$_2$ plasma 0.5h 250°C
60 sec anneals
GaN (Ca) H₂ plasma 0.5h 250°C
60 sec anneals

mobility (cm²/V·s)

annealing temperature (°C)

- ■ before hydrogenation
- ▲ after hydrogenation
ATOM DENSITY (cm\(^{-3}\))

SECPNDARY ION COUNTS

DEPTH (cm)

10^5 10^6 10^7 10^8 10^9 10^10

10^1 10^2 10^3 10^4 10^5 10^6
FRACTION OF PASSIVATED DONORS

InGaN-InAIGaN

ANNEALING TEMPERATURE (°C)

FRACTION OF PASSIVATED DONORS
PERCENTAGE OF PASSIVATED Mg REMAINING (%)
$^2\text{H}$ in n-GaN
50keV, $2 \times 10^{15}$cm$^{-2}$
SECONDARY ION INTENSITY (cts/sec)

$^{2}\text{H}$ in p-GaN
50keV, 2x10$^{15}$cm$^{-2}$

No anneal
500$^\circ$C
600$^\circ$C
700$^\circ$C
800$^\circ$C & 900$^\circ$C
1000, 1100 and 1200$^\circ$C anneals

ATOM DENSITY (cm$^{-3}$)

DEPTH (nm)
ATOM DENSITY (cm$^3$)

SECONDARY ION INTENSITY (cts/sec)

COMMERCIAL GaN SI-DOPED

DEPTH (nm)
MAXIMUM REPORTED CARRIER CONCENTRATION (cm⁻³)

Graph showing data points and concentrations.
Electric Field (kV/cm)

Drift Velocity (10^5 cm/s)

- InN
- GaN
The diagram shows the relationship between the Al mole fraction and the carrier density ($n_s$) in different types of AlGaN films. The graph is labeled as follows:

- Dashed line: Schottky barrier
- Solid line: unpinned AlGaN
- Squares: MOCVD-grown
- Triangles: MBE-grown

The Al mole fraction is plotted on the x-axis, ranging from 0 to 0.4, and the carrier density ($n_s$) is plotted on the y-axis, ranging from 0.0E+00 to 2.0E+13.
Transmission

Distribution

Flexible AC Transmission/Custom Power System (FACTS) Devices
Mult-Quantum-Well Structure (MQW)

- p-electrode
- p-GaN
- p-Al_{0.08}Ga_{0.92}N
- p-GaN
- In_{x}Ga_{(1-x)}N
- n-GaN
- n-Al_{0.08}Ga_{0.92}N
- n-In_{0.05}Ga_{0.95}N
- GaN buffer layer
- (0001) sapphire substrate
p-electrode

p-GaN

p-Al_{0.14}Ga_{0.86}N/GaN MD-SLS

SiO₂

n-GaN

n-Al_{0.14}Ga_{0.86}N/GaN MD-SLS

In_{0.02}Ga_{0.98}N/In_{0.15}Ga_{0.85}N MQW

n-In_{0.1}Ga_{0.9}N

(0001) sapphire substrate