SANDIA REPORT

SAND99-0817

Unlimited Release

Printed April 1999

Wide-Bandgap Compound Semiconductors to Enable Novel Semiconductor Devices

RECEIVED
APR 26 1999
OSTI

M. H. Crawford, W. W. Chow, A. F. Wright, S. R. Lee, E. D. Jones, J. Han, and R. J. Shul

Prepared by

Sandia National Laboratories

Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (703) 605-6000
Web site: <http://www.ntis.gov/ordering.htm>

Available to the public from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SAND99-0817
Unlimited Release
Printed April 99

Wide-Bandgap Compound Semiconductors to Enable Novel Semiconductor Devices

M. H. Crawford, W. W. Chow, A. F. Wright, S. R. Lee, and E. D. Jones
Semiconductor Materials and Device Sciences Department

J. Han
Chemical Processing Science Department

R. J. Shul
Advanced Semiconductor Technology Department

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0601

Abstract

This report represents the completion of a three-year Laboratory-Directed Research and Development (LDRD) program that focused on research and development of GaN-based wide bandgap semiconductor materials (referred to as III-N materials). Our theoretical investigations include the determination of fundamental materials parameters from first-principles calculations, the study of gain properties of III-N heterostructures using a microscopic laser theory and density-functional-theory, charge-state calculations to determine the core structure and energy levels of dislocations in III-N materials. Our experimental investigations include time-resolved photoluminescence and magnetoluminescence studies of GaN epilayers and multiquantum well samples as well as x-ray diffraction studies of AlGaIn ternary alloys. In addition, we performed a number of experiments to determine how various materials processing steps affect both the optical and electrical properties of GaN-based materials. These studies include photoluminescence studies of GaN epilayers after post-growth rapid thermal annealing, ion implantation to produce n- and p-type material and electrical and optical studies of plasma-etched structures.

Key Words: Wide bandgap semiconductors, GaN, InGaIn, AlGaIn.

Acknowledgements

This work includes important technical contributions of a number of Sandians and contractors. The authors would like to acknowledge Jeff Figiel for materials growth and characterization support and Mike Banas for materials characterization. John Zolper, an original PI for the project, contributed ion implantation and annealing studies in the LDRD's first year before leaving Sandia. Finally, the authors would like to thank Jeff Nelson for providing management support throughout this project.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Contents

I.	Introduction.....	4
II.	Theoretical Investigations of III-N materials properties	5
	A. Fundamental Materials Parameters.....	5
	B. Gain calculations for III-N heterostructures.....	6
	C. Edge Dislocations and Hydrogen in GaN.....	7
III.	Experimental Investigation of Group III-N materials properties.....	8
	A. Time-resolved Photoluminescence studies.....	8
	B. Magneto-luminescence studies.....	9
	C. X-ray and photoluminescence studies of AlGaN alloys.....	10
IV.	Experimental Investigation of III-N Materials Growth and Processing.....	13
	A. MOVPE growth of III-N materials.....	13
	B. Post-growth annealing studies of GaN films.....	14
	C. Ion implantation studies of GaN films.....	15
	D. Plasma etching studies of III-N materials.....	16
V.	Conclusions.....	21
VI.	References.....	22

I. Introduction

In the past five years, the semiconductor materials community has witnessed dramatic advances in a class of semiconductors that we refer to as "III-N materials". This family of materials includes GaN, InN and AlN alloys as well as the ternary (InGa_N, AlGa_N, AlIn_N) and quaternary (AlGaIn_N) compounds that can be formed from these binary materials. One of the main reasons the III-N materials are of so much interest is the fact that they are well suited for a very wide variety of device applications. For example, these materials are currently being developed for a number of light emitting devices, such as visible and UV LEDs and laser diodes, solar blind detectors, high temperature microelectronics components and surface acoustic wave (SAW) based sensors. At the beginning of this LDRD project (October, 1995), it was clear that a major limiting factor to the development of advanced III-N devices was the general lack of information on basic materials properties. Critical parameters, such as material bandstructure, materials constants, optical and electrical properties, as well as how these properties can be changed by post-growth processing of the materials, were not well understood. Furthermore, these materials were found to have a very distinct growth evolution and microstructure as compared to more standard III-V semiconductors as well as a much higher concentration of both point and extended defects. Exactly how these structural differences might be expected to affect optical and/or electrical properties was yet another area that was not well developed.

Our goal for this LDRD project was to pursue an interdisciplinary study of the unique materials properties of the III-N materials. Our effort consisted of both a theoretical and an experimental component. As detailed below, part of our theoretical emphasis was to develop an in-depth understanding of materials bandstructure, including bowing parameters for ternary alloys. These calculations yielded critical input parameters to further calculations of optical gain in a number of relevant III-N heterostructures. Yet another area of theoretical focus was to apply ab-initio calculations to study extended defects in III-N materials. A major focus of our experimental effort was to understand the optical properties of the III-N materials, through the use of experimental techniques such as time-resolved photoluminescence and magnetoluminescence. X-ray k-mapping was also performed on a number of III-N epilayers to gain an understanding of materials evolution, strain and cracking mechanisms in these materials. Finally, a number of experimental studies were undertaken to gain insight into how these materials respond to post-growth processing. These studies include ion implantation for the purpose of enabling p- or n-type doped materials, plasma etching to enable patterned materials for various device applications, and post-growth annealing to activate dopant species and/or more generally alter the optical or electrical properties of the materials.

II. Theoretical Investigations of III-N materials properties

A. Fundamental Material Parameters

Many of the materials parameters needed for modeling III-Nitride laser diodes have either not yet been measured, or are poorly known due to experimental uncertainties. In an effort to fill this void, we performed first-principles calculations for AlN, GaN, InN utilizing density-functional theory combined with Sterne-Inkson-type corrections to the resulting band structures [1]. Calculated structural properties include the wurtzite and zinc-blende lattice constants, and the corresponding elastic constants needed to account for the effect of strain. Electronic properties include the effective electron and hole masses, the crystal-field splitting parameters for wurtzite, and deformation potentials (for the case of symmetry-preserving distortions in wurtzite and trigonal distortions in zinc-blende). Materials parameters for ternary alloys were obtained by composition weighting the constituent parameters, except for the case of alloy band gaps. Alloy gaps (**Figure 1** below) were estimated by calculating the band gaps of the constituents and the 50% alloys, and then fitting the results to a second-order polynomial to obtain composition-independent optical bowing parameters. Subsequent calculations showed that the bowings in AlGaIn and InGaIn alloys do have a small amount of composition dependence, but this should not be important for the laser-diode modeling.

Figure 1: Calculated bandgap of a number of III-N ternary compounds vs. alloy composition.

B. Gain calculations for III-N heterostructures

Group III-N materials and heterostructures are well suited for blue and UV laser diode development. In this LDRD, we undertook a theoretical study of the gain characteristics of various III-N heterostructures using a microscopic laser theory. The microscopic laser theory is based on the Semiconductor Bloch equations, with carrier correlations treated at the level of quantum kinetic theory in the Markovian limit. This approach gives a consistent treatment of plasma and excitonic effects, both of which are important under lasing conditions. Also, as experimental optical data suggested the importance of local fluctuations in the InGa_N/AlGa_N heterostructure, inhomogeneous broadening due to spatial variations in the quantum well thickness or composition was included in the theory by a statistical average of the homogeneously broadened spectra.

Figure 2: Gain/absorption spectra for a 4nm InGa_N/AlGa_N quantum well structure at T=300K.

As an example of some of the results from our calculations, **Figure 2** shows the computed gain/absorption spectra for a 4 nm In_{0.1}Ga_{0.9}N/ Al_{0.2}Ga_{0.8}N quantum well structure at T=300K and carrier densities of $N = 0.1, 0.5, 1.0, 2.0, 4.0$ and $6.0 \times 10^{12} \text{ cm}^{-2}$ (solid line is highest) [2]. An indium concentration variation of $\sigma = 0.01$ was assumed. The low density spectra show an exciton resonance at approximately 3.33 eV, which has been treated in our theory by Coulomb interactions included systematically in the Hamiltonian for the electron-hole system. This is a definite advance over other existing theories which employ an *ad hoc* inclusions of excitons into a free-carrier theory. At high densities, the exciton resonance vanishes and gain appears (see inset, which shows results for $N = 2, 4, 5$, and $6 \times 10^{12} \text{ cm}^{-2}$). Experimental results on lasing thresholds in

InGaN/AlGaIn laser diodes have estimated threshold current densities at approximately $8 \times 10^{12} \text{ cm}^{-2}$. Our theory predicts that this threshold carrier density would be compatible with a threshold gain of approximately 2000 cm^{-1} for an InGaIn quantum well structure with 10% In composition fluctuation. Similar calculations were performed for GaN/AlInN multi-quantum well heterostructures [3] and GaN/AlGaIn multi-quantum well heterostructures [4].

C. Edge Dislocations and Hydrogen in GaN

Dislocations are commonly found in group-III nitride epitaxial films due to their growth on a substrate (sapphire) having roughly 17% a mismatch with GaN. An unanswered question is whether these dislocations introduce defect levels into the gap. The experimental evidence is contradictory in that cathodoluminescence studies show that regions around the dislocations do not emit near the band edge, but it is nevertheless possible to fabricate highly efficient light-emitting diodes (with near-band-edge emission). In an effort to gain insight into these questions, we performed density-functional-theory, charge-state calculations to identify the dislocation core structure and to determine whether or not they introduce defect levels into the gap [5-7]. The answer to the second question is that all of the core structures studied introduce defect levels into the gap. As a result, dislocations can compensate *n*- or *p*-type dopants, depending on the specific core structure, and can therefore accumulate a significant line charge. This charge accumulation, in turn, affects the formation energy of the dislocation so that the core structure ultimately depends on the dislocation density and the background doping in the surrounding material. We modeled the charge accumulation process and were able to predict the formation energies and charge accumulation for various core structures as a function of the dislocation and dopant densities. In addition, we elucidated the dependence of these quantities on the growth conditions used to produce the material, i.e., whether growth takes place under nitrogen- or gallium-rich conditions. Growth under nitrogen-rich conditions in *n*-type material, for example, is predicted to yield edge dislocations having gallium vacancies along the dislocation core. For a donor density of 10^{17} cm^{-3} and a dislocation density of 10^{10} cm^{-2} , a line charge of 0.5 electron per 5.2 Å is predicted. Line charges for *n*-type material grown under gallium-rich conditions are in very good agreement with estimates based on analysis of Hall mobilities.

Hydrogen is a common impurity in MOCVD-grown nitride films due to its presence in the metal and nitrogen precursors, and the use of H_2 as a carrier gas. While hydrogen atoms are known to play a role in the incorporation and activation of magnesium acceptors, little information is available on how they interact with native defects, dislocations, or with the crystal lattice itself. As a starting point for answering these questions, we have determined the solution sites for hydrogen in a perfect crystal (without defects) utilizing density-functional-theory, charge-state calculations. We find that H^+ in wurtzite GaN is equally stable at a bond-centered site and a nitrogen anti-bonding site. This is in contrast to H^+ in zinc-blende GaN which shows a clear preference for the nitrogen anti-bonding site. The difference in behavior is likely due to fundamental differences in the elastic properties of the two crystal structures: The wurtzite structure is more easily able to relax bond angles and accommodate the hydrogen ion in a bond-centered site. H^- is stable near a gallium anti-bonding site in zinc-blende GaN and at the center of the trigonal channel in wurtzite GaN. This trigonal

channel – extending through the entire length of the crystal in wurtzite – is not present in zinc-blende GaN, and it is therefore likely that interstitial defects may behave differently in zinc-blende and wurtzite GaN. The energy barrier for diffusion of H^+ , for example, is predicted to be 20% lower in wurtzite due to the ease of diffusion along the trigonal channel.

III. Experimental Investigation of Group III-N Materials Properties

A. Time resolved photoluminescence studies of III-N materials

One of our experimental milestones involved performing time resolved photoluminescence experiments on the III-N epilayers to evaluate radiative recombination mechanisms in these materials. These experiments were performed on all of the samples described above. Our experiments first required constructing a UV/visible time resolved spectroscopy set-up including a picosecond Ti:Sapphire laser pumping a nonlinear conversion module which enabled the spectral regions of 260-325 nm and 375-490 nm to be achieved from frequency tripling and doubling, respectively. A 15 psec resolution streak camera was integrated with a 0.5 meter spectrometer and calibrated for the temporal and spectral regions of interest. The experiments were performed both at room temperature and 10K, with laser excitation at 280 nm and powers of 0.1-3 mW. In **Figure 3**, we show representative data from our low temperature experiments. The data show the time dependent decay of photoluminescence intensity from an InGaN single quantum well sample which includes GaN barrier regions. One striking result is the

Figure 3: Photoluminescence decay of GaN and InGaN bulk epilayers at 10K.

significantly long decay of InGaN alloys ($\tau = 600$ psec) versus the GaN bulk regions ($\tau = 60$ psec). This data supports the hypothesis that local variations in the InGaN quantum well result in localized excitons with substantially increased decay rates relative to free excitons (such as in the GaN bulk regions). Similar experiments performed on a $Al_{0.15}Ga_{0.85}N$ bulk film yielded relatively long decay rates (610 psec). These results

suggest that alloy fluctuations and carrier localization may also play a role in the AlGaIn alloy system.

In the final year of the project, time-resolved photoluminescence experiments were expanded to include GaN/AlGaIn quantum well structures, which are ideal for ultraviolet LEDs. Various samples were grown with different well widths and with or without Si doping in the active region. Our studies showed that for all samples, the measured photoluminescence decay time decreased strongly with increasing sample temperature (from 10-300 K), suggesting that non-radiative recombination is dominating in these samples. Also, we found increased decay times (0.8-1.2 nsec) at 10K for wider quantum wells (2.0-3.5 nm), which we believe is due to electron-hole spatial separation resulting from internal piezoelectric fields. Note that these quantum wells have significantly longer decay times than what we measured for bulk GaN layers (60 psec) in the second year of this program.

B. Magneto-luminescence studies of III-N Materials

Another experimental investigation involved pressure dependent magneto-luminescence measurements on III-N materials to determine exciton binding energies and elucidate the nature of emission resonances. We performed low temperature photoluminescence experiments on GaN bulk films at the National High Magnet Field Laboratory in Florida, employing magnetic fields up to 30 tesla. **Figure 4** shows the resulting PL spectrum, where the upper spectrum is logarithmic intensity vs. energy.

Figure 4: Photoluminescence of GaN epilayer at T=4.2K and 30 tesla conditions.

The exciton energy shift in magnetic field can be related to the conduction-band valence-band reduced mass μ by $\Delta E = 1/2R^*\gamma^2$ where $R^* = me^4/2\hbar^2\epsilon$ is the effective rydberg energy (exciton binding energy), μ is the reduced mass, ϵ is the dielectric constant and $\gamma = \hbar\omega_c/2R^*$ is the ratio of the cyclotron energy and the effective rydberg. For GaN, $R^* = 25$ meV and for 30 tesla, the cyclotron energy is thought to be near 5 meV. The diamagnetic shift ΔE for the spectrum shown in **Figure 4** is approximately 0.2 meV which is consistent with our values for the reduced mass and exciton binding energy. It was clear from these experiments, however, that higher magnetic fields than were

accessible at the National Magnet Lab Florida facility would be necessary to make a simultaneous determination of the exciton binding energy R^* and the reduced mass μ . We therefore scheduled time on the 60 tesla pulsed magnet at the National High Magnetic Field Laboratories Los Alamos Facility. While we expected to see a shift in the photoluminescence resonance as a function of applied field, no such shift was seen. As yet, we have not understood our results and have not yet determined the exciton binding energy and reduced mass in our materials by magneto-luminescence.

C. X-ray diffraction and photoluminescence studies of AlGa_xN alloys

The compositional dependence of the band gap of unstrained Al_xGa_{1-x}N alloys was measured for alloys with AlN mole fractions ranging from $x=0$ to $x=0.45$. X-ray diffraction reciprocal space mapping was used to measure the lattice-constants of a series of Al_xGa_{1-x}N single and multiple heterolayers grown on GaN/sapphire substrates. The measured lattice constants were interpreted using elasticity theory in order to determine the strain and composition of the Al_xGa_{1-x}N heterolayers. Low-temperature photoluminescence was used to measure the corresponding optical band gaps. The measured band gap versus composition data was fitted using a standard parabolic model of the band-gap bowing. Bowing in the unstrained AlGa_xN alloy system was found to be described by a bowing parameter $b=+0.69$ eV. These results were compared with calculations of the bowing parameter performed at Sandia using plane-wave pseudopotential (PWPP) theory. Measurements and calculations are in good agreement with PWPP theory predicting a bowing parameter $b=+0.53$ eV.

Additional detailed comparison of our results were made with 20 previous measurements of Al_xGa_{1-x}N band gap bowing that have now been reported in the published literature (see S. R. Lee et al., "The band gap bowing of AlGa_xN alloys", submitted to *Applied Physics Letters*, for a citation list identifying these 20 references). Approximate corrections were made to the AlGa_xN-alloy band gaps reported in the literature in order to account for variations in: (1) band-gap measurement temperature, (2) thermal-expansion-mismatch strain between epilayer and substrate, and (3) epitaxial coherency strain for those cases where thin alloy layers were grown on thick GaN. These 20 previous measurements are summarized in corrected form in **Figure 5**; reported band-gap bowing parameters vary from $b\approx-0.8$ eV to $b\approx+2.6$ eV. The applied corrections fail to unify the data; this indicates a separate major source of variability in previously reported measurements.

We therefore examined the reported details of each work seeking understanding of the observed variations. Reports were ultimately found to fall into three basic groups: Group-A works in **Figure 5** consist mostly of very early pioneering reports on Al_xGa_{1-x}N; retrospectively, it is clear from reported materials properties that the synthesized alloys were of suspect quality. Group-B works report the band gap of AlGa_xN alloys nucleated on sapphire without the benefit of low-temperature (LT) buffer layers. These LT buffers consist of ~25 nm-thick GaN, AlN, or Al_xGa_{1-x}N deposited at temperatures below ~800 °C prior to normal, high-temperature, III-nitride growth; LT buffers are now widely

known to lead to higher quality III-nitride growth on sapphire. In contrast, Group-C works report the band gap of AlGa_xN alloys grown using low-temperature buffers on sapphire.

Figure 5: Measured deviations of the band gap from linearity with x for unstrained $\text{Al}_x\text{Ga}_{1-x}\text{N}$ at 295 °K. Dashed line: theoretical bowing by Wright and Nelson [8]. Solid reference lines: $-bx(1-x)$.

As shown in **Figure 5**, most Group-B works exhibit either very strong bowing for all alloy compositions (**Fig. 6a**; $b > 1.3$ eV), or initially weak bowing with apparent discontinuous transitions to sub-gap states at higher alloy compositions (**Fig. 6b**; $b \approx 0.62$ eV). The 200 to 680 meV discontinuities seen **Figure 6b** are not consistent with the smooth, quasi-parabolic, band-gap bowing normally seen in semiconductor alloys. We submit this observation as evidence that these works probe sub-gap impurity- or defect-related states, and not the true band-gap of the alloy. These proposed sub-gap states are thought to arise from the inferior materials quality that usually results when AlGa_xN alloys are grown without LT buffers.

Comparing **Figures 6a** and **6b**, it is seen that the same set of sub-gap states seem to be active in both types of Group-B measurements. Sub-gap states 100-500 meV below full gap have been observed by several research groups using concurrent luminescence and absorption measurements; these observations are reasonably well documented in the research literature on $\text{Al}_x\text{Ga}_{1-x}\text{N}$. These previous explicit reports of sub-gap emission in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ all strongly resemble purported bowing measurements in **Figure 6**; this heretofore unrecognized similarity further supports our hypothesis that Group-B works do not probe the full gap of AlGa_xN alloys.

Figure 6: Group-B measurements of the deviation of the band gap from linearity. Characteristic trends seen for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ directly nucleated and grown at $T > 800^\circ\text{C}$ are: (a) strong quasi-continuous bowing for all x , or (b) weak bowing with discontinuous transition to deeper levels. Solid-black symbols are defined as in Fig. 5.

This leaves only Group-C works, which made use of LT buffers for the AlGaN alloy growth, as potentially valid measurements of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ band-gap bowing. We have derived a best estimate of the true bowing of unstrained $\text{Al}_x\text{Ga}_{1-x}\text{N}$ by simply averaging the bowing parameters of corrected Group-C works (present bowing results, which fall into Group-C, are included in the averaging procedure); the resulting bowing is $b = +0.62 (\pm 0.45)$ eV. As we show in **Figure 7**, present results for the band-gap bowing parameter of

Figure 7: Group-C measurements of the deviation of the band gap from linearity. Group-C experiments where $\text{Al}_x\text{Ga}_{1-x}\text{N}$ was grown on sapphire by MOCVD using LT buffers are shown.

$\text{Al}_x\text{Ga}_{1-x}\text{N}$ are consistent with previous Group-C works. Notably, once all existing bowing results are filtered to yield only those that seem most characteristic of the intrinsic properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$, we find reasonably good agreement among previous experiments, our recent density-functional-theory results, and our recent experimental measurements. Even with this selective filtering of the bowing data, Group-C results are not in full agreement. This remaining variability may be due in part to further variations in materials quality: early two-step growths (Refs.8 and 9 in Fig. 7), which used newly invented LT buffers, give stronger bowing than that of more recent works (all others in Fig. 7), where growths benefit from longer-term optimization efforts.

IV. Experimental Investigation of III-N Materials Growth and Processing

A. MOVPE growth of III-N materials

The majority of the III-N materials that were studied throughout this LDRD project were grown at Sandia. While we did not have specific milestones for the materials growth aspect of the project, our requirements were more generally to produce high quality III-N bulk films and heterostructures for our experimental studies. Considering the available temperature and pressure ranges, metal-organic vapor phase epitaxy (MOVPE) is recognized as the most suitable and flexible means of preparing high quality GaN epilayers and heterostructures. Built upon Sandia's extensive understanding in rotating-disk reactor configuration, we established a high-speed rotating-disk MOVPE platform capable of supporting both basic and applied research on III-N materials. A first generation III-N MOVPE system was constructed in 1996, and GaN and InGaN epilayers were demonstrated. Some of the experimental studies described in this report, including post-growth anneal studies of GaN epilayers (section IVB) and InGaN time resolved photoluminescence studies (section IIIA), were performed using material from this reactor. A major limitation of this reactor, however, was the fact that the small growth chamber only allowed for the growth of small samples (1 cm^2) and these samples showed non-uniformities in materials properties (e.g. photoluminescence) across the sample. The growth system was upgraded with a new gas manifold and a larger growth chamber in March of 1997, enabling the growth of III-N materials on 2 inch diameter sapphire substrates. Given the significantly different dimensions of the new reactor compared to the previous design, much of the growth parameters for high quality GaN epilayers had to be re-established. Before the end of FY 1997, we had demonstrated the growth of device-quality GaN epilayers, as examined by TEM, x-ray diffraction, photoluminescence, and Hall-effect measurements, through the optimization of various growth parameters such as low-temperature buffer layer thickness, partial pressures of the reactants, and growth temperatures.

In 1998 we focused our effort on the conductivity control for both p- and n-type GaN, as well as the growth of ternary AlGaN with a goal of forming AlGaN/GaN heterostructures that are suitable for photonic devices. It was quickly discovered that trimethyl-aluminum (TMAI), the most commonly used Al precursor, reacts heavily with

ammonia (NH_3) upstream of the wafer in the gas phase. The pre-reaction leads to the formation of adduct compound and inhibits the incorporation of both TMAI and TMGa. Separated injection of hydrides and metal-organic precursors was subsequently introduced, together with the selection of a reduced-pressure growth, to minimize such parasitic reactions.

These advances in reactor design coupled with extensive materials growth studies enabled us to produce n- and p-doped GaN epilayers and p-n junction structures, AlGaIn epilayers, and GaN multiquantum well structures for materials studies. In particular, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers with $x=0-0.45$ were grown for the x-ray diffraction studies discussed in section III-C, GaN epilayers, AlGaIn epilayers and GaN multiquantum well structures were provided for the time-resolved photoluminescence studies described in section III-A and doped GaN epilayers and p-n junction structures were provided for plasma etch-damage studies, detailed in section IV-D.

A. Post-growth annealing studies of GaN Films

A first year milestone for this LDRD was to evaluate the effects of post-growth annealing on the optical and electrical properties of the III-N materials. Annealing was identified as a necessary processing step for the III-N materials, as it is applied after growth to enhance the acceptor activation and significantly improve the conductivity of p-doped III-N materials. We therefore performed rapid thermal annealing (RTA) experiments on MOVPE grown GaN films in a variety of gas ambients and evaluated the effect on photoluminescence, surface morphology and electrical conductivity [9,10].

Figure 8: T=4K photoluminescence of GaN films after annealing at 1100 deg-C in (a) air, (b) N₂ and (c) unannealed. The insets show expanded views of the deep level spectra. The bandedge emission is the sharp feature near 3.5 eV

We found that RTA annealing of GaN in either Argon (Ar) or nitrogen (N₂) ambient up to 1100 °C improves both surface morphology and photoluminescence intensity. In addition, the ratio of deep-level emission to band-edge emission is improved for both cases. These results are summarized in **Figure 8**.

In addition, the 1100°C anneal was found to reduce the electrical concentration and mobility. These electrical effects were found to be consistent with a two-band conduction model for GaN, in which conduction occurs both in the conduction band and in a defect band. The annealing is expected to achieve enhanced defect band conduction, which has lower carrier mobility due to the diffusion or hopping nature of transport in the defect band. These studies were repeated on a number of MOVPE grown GaN films from different sources and some variation in the above results were seen. In particular, a decrease in the photoluminescence intensity after 1100 °C anneals was seen for some films and subsequent exposure to a hydrogen plasma could recover the intensity loss in some cases. We have determined that the effect of post growth annealing is strongly dependent on the stoichiometry, amount of in-grown hydrogen, and defect densities of the initial GaN films, as well as on the anneal temperature and gas ambient.

C. Ion Implantation Studies of GaN Films

The study of ion implantation of III-N materials was also undertaken in the first year of this project. One of the major impediments in developing III-N materials for photonic device applications is the difficulty in achieving p-type doping. We explored the ion implantation of Ca and Ca + P species to achieve p-type conductivity in GaN bulk films. Our experiments revealed that p-type conduction was possible by implanting these species and performing a post-implant anneal at temperatures of 1100°C or greater. Experimental data on the sheet resistance of ion implanted films is shown in **Figure 9**, where the transition from n-type to p-type conduction is clearly seen.

Figure 9: Sheet resistance versus annealing temperature for Ca and P implanted GaN films

Temperature dependent Hall measurements were performed and revealed an estimated acceptor activation energy of 169 meV. This is the first report of an acceptor species in GaN, other than Mg, with an ionization energy less than 180 meV [11-13].

D. Plasma Etching Studies of III-N materials

Anisotropic, smooth etching of the group-III nitrides has been reported at relatively high rates in high-density plasma etch systems. However, such etch results are often obtained under high dc-bias and/or high plasma flux conditions where plasma induced damage can be significant. Despite the fact that the group-III nitrides have higher bonding energies than more conventional III-V compounds, plasma-induced etch damage is still a concern. Attempts to minimize such damage by reducing the ion energy or increasing the chemical activity in the plasma often result in a loss of etch rate or anisotropy which significantly limits critical dimensions and reduces the utility of the process for device applications requiring vertical etch profiles. It is therefore necessary to develop plasma etch processes which couple anisotropy for critical dimension and sidewall profile control and high etch rates with low-damage for optimum device performance.

Plasma-induced-damage can include defects or dislocations in the lattice, formation of dangling bonds on the surface, implanted etch ions, or deposition of material on the sample. Attempts to minimize the damage by reducing the ion energy below the damage threshold for compound semiconductors (<40 eV) or by increasing the chemical component of the etch often results in more isotropic profiles, significantly limits minimum dimensions, and reduces the etch rate. Since GaN is more chemically inert than GaAs and has higher bonding energies, higher ion energies may be used during the etch process with potentially less damage to the material.

One of the our milestones for this LDRD was to examine plasma etch induced damage in the III-N materials, and specifically how plasma etching under different conditions affects both the optical and electrical properties of the materials. Both ICP (inductively-coupled plasma) and ECR (electron cyclotron resonance) plasma-induced-damage of GaN was evaluated. The optical studies involved using photoluminescence (PL) measurements as a function of rf-cathode-power and source power. In **Figure 10**, the % change in the peak PL intensity versus rf-cathode-power is plotted for both ECR and ICP etching. GaN samples were exposed to ICP- and ECR-generated Ar plasmas for 1 minute under identical plasma conditions while the rf-cathode-power was increased. For the ICP case, at relatively low rf-cathode-powers (1 and 50 W) the PL intensity only slightly degraded, but as the rf-cathode-power was increased up to 250 W increasing degradation in PL intensity was seen. Depth profiling of similar films at a rf-cathode-power of 1 W (~ 10 V dc-bias) revealed no detectable removal of GaN whereas at 250 W etch (~ 300 V dc-bias) ~ 770 Å of GaN was lost during a 1 minute exposure. Distinctly different results were obtained for etching in the ECR plasma system. Etching with very low rf-cathode-power (1 W) resulted in $>80\%$ increase in the PL intensity and virtually no sputter loss of GaN. Etching at higher rf-cathode-powers also improved the PL intensity, but to a lesser degree as the rf-cathode-power was increased. The highest rf-cathode-power (150 W) etch resulted in a very slight decrease in PL intensity and a GaN sputter rate of ~ 820 Å/min. While the exact nature of surface oxides and surface states in

GaN are not well understood, the data show that the PL efficiency can be strongly affected by exposure to an Ar plasma and is highly sensitive to the plasma conditions.

Figure 10: Percent change in bandedge photoluminescence intensity as a function of applied RF power for both ECR and ICP etching.

Plasma etch damage in GaN was further evaluated by electrical (via Ohmic contact formation), morphological (via atomic force microscopy) and chemical (via Auger surface spectroscopy) techniques. For GaN, the ion bombardment present during plasma etching can selectively remove N-atoms and convert the surface to n-type with the formation of N-vacancy donors. Various plasmas were investigated, and it was found that physical sputtering in an Ar-plasma caused the most preferential N-removal as determined by the Ga/N ratio measured via Auger Spectroscopy and hence formed the best Ohmic contacts. The addition of any chemical component to the etch (e.g. Cl, H, or N) caused less preferential N-loss.

We have recently reported the effect of plasma-induced-damage on n- and p-type GaN by monitoring changes in the sheet resistance (R_s) and specific contact resistance (r_c) of thin conducting layers under a variety of ICP plasma conditions simulating those used during device etching [14]. Sheet resistance and specific contact resistance determined from the circular transmission line model (TLM) are used to evaluate plasma-induced-damage. The GaN films etched in this study were grown by either metal organic chemical vapor deposition (MOCVD) or RF-molecular beam epitaxy (MBE). Both n- and p-GaN were evaluated for plasma-induced damage in an ICP reactor. Ohmic contacts for circular TLM patterns were formed by metal evaporation and liftoff using standard photolithography techniques. In order to evaluate changes in sheet resistance (ΔR_s), GaN samples were first metallized and then exposed to an Ar plasma. Sheet resistance was measured at the same position before and after the plasma exposure. Therefore the effect of the doping nonuniformity across the wafer was minimized. To

evaluate the specific contact resistance (r_c) as a function of the plasma conditions, the samples were initially patterned with photoresist, exposed to the Ar plasma, and then metallized over areas exposed to the plasma. Measurements were taken at minimum of 4 positions on each sample. It is important to realize that the use of a pure Ar plasma creates a worse case scenario for plasma-induced damage due to the lack of chemical interactions. With the introduction of reactive gases to the plasma for a given plasma power and density, the damage will be reduced when compared to a sputter mechanism since damaged material is typically being removed at a higher rate, leaving a shallower damage depth. Samples were exposed to ICP-generated Ar plasmas for 30 seconds.

As dc-bias increased, the change in sheet resistance for both n- and p-GaN increased monotonically. This implied that as the ion bombardment energy associated with dc-bias increased so did the plasma-induced damage mechanism. Compared to n-GaN, the p-GaN samples showed a much more significant increase in sheet resistance with increasing dc-bias, 95% change at -350 V dc-bias. The much stronger effect of plasma-induced damage on p-GaN was attributed to the preferential loss of lighter nitrogen atoms under energetic ion bombardment, which created n-type N-vacancies and compensated the p-GaN. In addition, thinner p-GaN layers ($\sim 0.3 \mu\text{m}$ as compared to $\sim 1.2 \mu\text{m}$ for n-GaN) and lower hole concentrations ($\sim 3 \times 10^{17} \text{ cm}^{-3}$ as compared to $8 \times 10^{17} \text{ cm}^{-3}$ electron concentration in n-GaN) made the conductivity of p-GaN film more sensitive to the plasma-induced damages at the surface. However, the plasma-induced damage did not produce a lower sheet resistance for n-GaN despite higher electron concentrations at the surface due to n-type N-vacancies generated by the plasma. The ΔR_{sh} increased up to $\sim 20\%$ at -350 V DC bias. This may be attributed to either a thinner n-GaN layer caused by Ar ion sputtering, lower electron mobility in the damaged n-GaN layer, or trapping of electrons by the plasma-induced defects. An example of the change in n-GaN sheet resistance as a function of dc-bias is shown in **Figure 11**.

Figure 11: Change in sheet resistance for MOCVD n-GaN as a function of dc-bias in an ICP Ar plasma.

Sheet resistance was also studied as a function of plasma flux for n- and p-GaN. The sheet resistance showed less than a 10% change independent of plasma flux. We believe the slight change was attributed to the low dc-bias (-100V) used during the plasma exposure. Thus under low physical dominated plasma conditions, low dc-bias, the damage is low. Similar trends were observed for contact resistance studies where plasma-induced damage was much more sensitive to dc-bias as compared to plasma flux and p-GaN was more highly damaged as compared to n-GaN.

We have also studied plasma-induced sidewall damage effects on reverse-bias electrical characteristics of GaN pn-junction diodes using ICP BCl_3/Cl_2 plasmas. As shown in the schematic in **Figure 12**, Ni/Pt/Au was deposited and alloyed to form the p-metal contact as well as act as the mask for the mesa etch. The mesa was then etched in the ICP under different ion bombardment energies and plasma flux conditions. The n-metal (Ti/Al/Pt/Au) was then deposited and reverse leakage bias currents were measured. As shown in **Figure 13**, the GaN etch rate increased as the dc-bias or ion bombardment energy increased while the reverse leakage bias current at -30 V remained relatively constant up to -350 V. At 350 V dc-bias the mask began to erode thus causing significant roughness of the sidewall morphology and increased damage. Additionally, at high ion energies, ion scattering increased and generated more sidewall damage and higher reverse leakage currents. As a function of plasma flux, the GaN etch rate increased by more than a factor of 4 as the ICP source energy increased from 150 W to 1000 W. Under these conditions, the reverse bias leakage current showed little effect below 250 W, but increased by more than 3 orders of magnitude up to 750 W. Additionally the sidewall morphology became significantly rougher under high plasma flux conditions due to mask-edge erosion. Under chemically dominated plasma conditions (high ion and neutral flux conditions), ion scattering was relatively high causing significant sidewall damage and higher reverse leakage currents.

Figure 12: Schematic diagram of GaN p-n junction diode structure used to evaluate sidewall plasma-induced damage in an ICP BCl_3/Cl_2 plasma.

Figure 13: GaN etch rate and reverse leakage current as a function of dc-bias in an ICP BCl_3/Cl_2 plasma.

The optimization of the etch process based on these results will be critical when etching down to p-type regions since surface type conversion will dramatically degrade p-type Ohmic contact formation. Overall, GaN surfaces are considerably more sensitive to process-induced changes than is widely recognized.

V. Conclusions

Through a combination of theoretical and experimental studies, this LDRD project has enabled substantial contributions to current understanding of III-N materials properties. Fundamental III-N materials properties, such as lattice constants, effective masses, deformation potentials and bandgaps of alloys were determined from first-principles calculations. A microscopic laser theory was utilized to model the gain characteristics of InGaN multi-quantum well and GaN multi-quantum well laser structures. Our theory predicts that the threshold carrier density that has been reported experimentally for InGaN multi-quantum well lasers would be compatible with a threshold gain of approximately 2000 cm^{-1} when a 10% In composition fluctuation in the well is assumed. Density-functional theory, charge-state calculations were performed to study dislocations in III-N materials, and these studies led to the determination that dislocations can compensate *n*- or *p*-type dopants, depending on the specific core structure, and can therefore accumulate a significant line charge. This characteristic is expected to significantly impact the transport properties of III-N materials.

The optical properties of III-N materials were studied by a number of spectroscopic techniques, including time-resolved photoluminescence. These studies demonstrated the potential effect of carrier localization and piezo-electric fields on the photoluminescence decay time. X-ray diffraction reciprocal space mapping was used to measure the lattice-constants of a series of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epilayers grown on GaN/sapphire substrates and low-temperature photoluminescence was used to measure the corresponding optical band gaps. The measured band gap versus composition data was fit using a standard parabolic model of the band-gap bowing and these results were compared with calculations of the bowing parameter performed at Sandia using plane-wave pseudopotential (PWPP) theory. Measurements and calculations are in good agreement with PWPP theory predicting a bowing parameter $b=+0.53$ eV.

Several experiments were performed to evaluate the effect of post-growth materials processing on the optical and electrical properties of III-N materials. High temperature (1100 deg-C) rapid thermal annealing in particular environments (e.g. N_2) was found to improve the relative band-edge photoluminescence intensity and the surface morphology of GaN epilayers. A study of Ca and Ca+P ion implantation of GaN films was carried out and led to the first report of an acceptor species in GaN, other than Mg, with an ionization energy less than 180 meV. Plasma etching studies demonstrated that the photoluminescence efficiency of GaN films can be strongly affected by exposure to an Ar plasma, yielding either increased or decreased photoluminescence intensity, depending on the plasma etching conditions. Studies of leakage currents in plasma etched GaN p-i-n diodes were performed to evaluate plasma-induced sidewall damage effects. No significant increases in reverse-bias leakage currents were seen for mesa structures etched with an ICP dc bias below 250 W.

VI. References

- [1] A. F. Wright, *Elastic properties of zincblende and wurtzite AlN, GaN and InN*, J. Appl. Phys. **82**, pp. 2833-2839 (1997).
- [2] W. W. Chow, A. F. Wright, A. Girndt, F. Jahnke and S. W. Koch, *Microscopic theory of gain for an InGaN/AlGaIn quantum-well laser*, Appl. Phys. Lett. **71**, pp. 2608-2610 (1997).
- [3] W. W. Chow, A. F. Wright and J. S. Nelson, *Theoretical study of room temperature optical gain in GaN strained quantum wells*, Appl. Phys. Lett. **68**, pp. 296-298 (1996).
- [4] W. W. Chow, M. Hagerott Crawford, A. Girndt and S. W. Koch, *Threshold conditions for a ultraviolet wavelength GaN quantum well laser*, IEEE J. Selected Topics in Quantum Electron. **4**, 314-319 (1998).
- [5] A. F. Wright and Ulrike Grossner, *The effect of doping and growth stoichiometry on the core structure of a threading edge dislocation in GaN*, Appl. Phys. Lett. **73**, pp. 2751-2753 (1998).
- [6] A. F. Wright and J. Furthmüller, *Theoretical Investigation of edge dislocations in AlN*, Appl. Phys. Lett. **72**, 3467 (1998).
- [7] A. F. Wright, *Theoretical Investigation of Extended Defects in Group-III Nitrides*, Mat. Res. Soc. Symp. Proc. **482**, 795 (1998).
- [8] A. F. Wright and J. S. Nelson, *Consistent structural properties for AlN, GaN and InN*, Phys. Rev. B. **51**, pp. 7866-7869 (1995).
- [9] J. C. Zolper, M. H. Crawford, A. J. Howard, J. Ramer and S. D. Hersee, *Morphology and photoluminescence improvements from high temperature rapid thermal annealing of GaN*, Appl. Phys. Lett. **68**, pp. 200-202 (1996).
- [10] J. C. Zolper, M. H. Crawford, S. J. Pearton, C. R. Abernathy, C. B. Vartuli, C. Yuan and R. A. Stall, *Ion implantation and rapid thermal processing of III-V nitrides*, Journal of Electronic Materials **25**, pp. 839-844, (1996).
- [11] J. C. Zolper, *Ion-implantation in Group-III nitride semiconductors: a tool for doping and defect studies*, Journal of Crystal Growth **178**, pp. 157-167 (1997).
- [12] J. C. Zolper and R. J. Shul, *Implantation and dry-etching of group-III nitride semiconductors*, MRS Bulletin, **22**, pp. 36-42, (1997).
- [13] J. C. Zolper, R. G. Wilson, S. J. Pearton and R. A. Stall, *Ca and O ion-implantation doping of GaN*, Appl. Phys. Lett. **68**, pp. 1945-1947 (1996).

- [14] R. J. Shul, G. A. Vawter, C. G. Willison, M. M. Bridges, J. W. Lee, S. J. Pearton and C. R. Abernathy, *Comparison of plasma etch techniques for III-V nitrides*, Solid-state Electronics **42**, pp. 2259-2267 (1998).

DISTRIBUTION:

1	MS9018	Central Technical Files, 8940-2
2	MS0899	Technical Library, 4916
1	MS0619	Review & Approval Desk, 00111 for DOE/OSTI

1	MS0188	LDRD Office
1	MS0601	W. W. Chow, 1113
10	MS0601	M. H. Crawford, 1113
1	MS0601	E. D. Jones, 1113
1	MS0601	S. R. Lee, 1113
1	MS0601	J. S. Nelson, 1113
1	MS0601	J. Han, 1126
1	MS0601	J. Y. Tsao, 1126
1	MS0603	R. J. Shul, 1713
1	MS0603	T. E. Zipperian, 1713
1	MS1415	A. F. Wright, 1113
1	MS1427	S. T. Picraux, 1100