Chang, Yun-Chorng. Optical Memory Effects in III-V Nitrides. (Under the direction of Robert M. Kolbas.)

Optical memory effects in III-V Nitrides have been investigated. In order to have further understanding of this effect, qualitative and then quantitative measurements were performed to investigate this memory effect. A microscopic model consistent with most of the experimental observations was developed. Finally, verification of the model was performed.

Experimental observations indicate that optical memory effects are flux-dependent effects, which require no lower power limit of the excitation source in order to produce them. Photoluminescence and cathodoluminescence studies indicate the yellow patterns are the result of increased yellow luminescence intensity from the sample. Heating up the samples can erase this memory effect.

Blue luminescence, with an energy about 2.8 eV, is important in the explanation of the memory effect since it appears in the photoluminescence spectra of all the samples that exhibit memory effects. This leads to a model with two different transitions, yellow and blue luminescence, competing with each other to explain the memory effects. The blue luminescence is caused by electron transitions from a localized oxygen level to the deep isolated and hydrogenated gallium vacancies. Transitions from shallow silicon donor levels to the gallium vacancies result in the yellow luminescence. Intense
ultraviolet light will remove hydrogen from the hydrogenated gallium vacancies and these vacancies will form complexes with neighboring oxygen atoms. These complexes will result in more yellow luminescence. Less blue luminescence and more yellow luminescence result in the yellow memory patterns observed. This model is consistent with most of the observations and several experiments strongly support this model.

Potential applications for memory effects include optical data storage and optical signal processing. Further understanding of this effect could lead to the realization of all optical memory cells and could also be used to improve the quality of III-nitrides materials.
OPTICAL MEMORY EFFECTS IN III-V NITRIDES

by

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Approved by

Robert M. Kalbar
Chairman of Advisory committee

[Signatures]
To my parents
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BIOGRAPHY

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1.1 Motivation

GaN and its related alloys (InGaN, AlGaN) have several unique physical and electrical properties that are quite different compared to conventional semiconductor materials, like GaAs and silicon. They have strong interatomic bonds and therefore are chemically and physically stable. These characteristics are required for devices working in a hostile environment. They also have a large direct bandgap and therefore are suitable for fabricating ultraviolet light emitters and detectors. They are also relatively good thermal conductors, which makes possible high power devices.

The advent of high-brightness blue light emitting diodes\(^1\) triggered extensive research on these materials and significant breakthroughs have been realized during the last ten years. High-temperature, high-power optoelectronic devices\(^2,3\) were reported. GaN-based blue laser diodes with projected lifetimes of up to 10,000 hours were also fabricated.\(^4\) The realization of short wavelength blue laser diodes will increase the data storage density on a compact disk (CD) by a factor of 5 compares to conventional GaAs laser diodes. Ultraviolet detectors grown on different substrates were reported.\(^5,6\) The transparency to the visible light of these detectors results in the creation of “Visible-
blind” and “Solar-blind” photodetectors. These ultraviolet detectors are therefore suitable for use in the sunlight without elaborate filters.

Optical data storage and memory effects in GaN materials were found by I. K. Shmagin\textsuperscript{7,8} in the Quantum Optoelectronic Group of the North Carolina State University. The potential applications for such effects include optical data storage and optical signal processing. Further understanding of this effect could lead to the realization of all optical memory cells. Metastable properties or memory effects are often indicative of the material quality. The understanding of these effects could also be used to improve the quality of the material and thus further advance research on the III-V Nitrides.

1.2 Defects in GaN

Defects in semiconductors usually take a variety of forms. Point defects are the most common defects in semiconductors. Point defects can also be divided into several categories. Isolated vacancies, interstitial atoms, or antisite atoms are all called native point defects. In GaN, both gallium or nitrogen atoms can be missing or misplaced to form these native point defects. Whenever there are missing atoms, gallium vacancies ($V_{Ga}$) and nitrogen vacancies ($V_N$) would form in GaN. However, theoretical study by Neugebauer\textsuperscript{9} indicated that nitrogen vacancies are unlikely to form in n-type GaN due to the higher formation energy compare to gallium vacancies in a system in thermodynamic equilibrium. In p-type GaN, nitrogen vacancies are the dominant intrinsic point defects. Gallium vacancies are believed to be the dominant defect and about $10^{17}$- $10^{18}$ (cm$^{-3}$)

Gallium vacancies in n-type GaN have been measured by positron annihilation
Antisites and interstitials are usually important in semiconductors like silicon and GaAs. However, researchers found that these kinds of defects are energetically less favorable in GaN, mainly because of the large mismatch in the covalent radii of gallium (1.26 Å) and nitrogen (0.75 Å).

Isolated impurity atoms, located in either substitutional or interstitial positions, would also form point defects. Several kinds of impurity atoms are common in GaN, including oxygen, silicon, carbon, hydrogen and some transition metals depending on the growth technique. Different point defects could form defect complexes with their adjacent point defects, such as donor-acceptor or impurity-vacancy pairs.

Point defects are zero-dimensional defects. Line defects, such as dislocations, are one-dimensional defects. In GaN, the dislocation density is very high compared to GaAs. It is still unknown why GaN works so well with such a high dislocation density, although the high exciton binding energy is proposed as an explanation. Defects associated with grain boundaries in a polycrystalline material are two-dimensional defects. There are also defects associated with the existence of a surface or interface.

Defects generally affect the electrical and optical properties of semiconductors. Defects could act as donors, acceptors, traps or recombination centers depending on the location of the energy level of the defects within the bandgap and the capture/emission cross-section. A donor atom usually occupies a substitutional lattice site and has one more electron than the host atom that it replaces at the site. The main binding force for an electron to a shallow donor is the long-range Coulomb force. The electronic states of these donors are derived principally from the nearby conduction band. Such donors
produce an effective-mass state with a small binding energy for electrons that is nearly fixed in the presence of changes in temperature or hydrostatic pressure. Therefore, the motions of the atoms of the host material have slight effects on the behavior of these electrons. There are no changes in the atomic positions around these shallow donors when light changes their electronic states.

Oxygen is an omnipresent impurity in the GaN material system. First-principle calculations predict that large oxygen concentrations are likely to occur in GaN because of the low formation energy of oxygen atoms on nitrogen sites (O$_\text{N}$). Therefore, O$_\text{N}$ is likely to act as one of the dominant donors in GaN, causing the unintentional n-type conductivity in as-grown samples. However, controlling n-type conductivity in GaN is commonly achieved by the incorporation of silicon. Silicon atoms can substitute for gallium atoms in the GaN lattice (Si$_\text{Ga}$) and acts as a single donor. The activation energy of silicon donors in GaN is about 27 meV, as reported in literature.

Acceptors atoms can occupy substitutional lattice sites and have one less electron than the host atoms that they replace at the sites. Carbon atoms may be unintentionally incorporated in nitrides during growth and serve as acceptors when occupying nitrogen sites. Although carbon atoms could also become donors when incorporated on gallium sites, the incorporation of carbon on a nitrogen site is energetically preferred because of a lower formation energy. However, the concentration of C$_\text{N}$ and C$_\text{Ga}$ may be comparable due to self-compensations. Substitutional C$_\text{N}$ introduces several impurity-induced levels and the most important one is located about 0.23 eV above the top of the
valence band. More information about different acceptor binding energies in GaN can be found in Ref. 17.

Traps can capture electrons or holes and the captured electrons or holes are released thermally to the nearest band. Electrons or holes captured by recombination centers have a higher probability of recombining with carriers of the opposite type than being emitted to the band from which they came. When capture or recombination occurs, the excess energy of the process will be released by the creation of a photon, or many phonons, or the excitation of free carriers. Traps and recombination centers are deep level defects. Deep level defects are quite different from shallow defects. Their electronic states are composed of contributions from both valence and conduction bands. The dominant binding force for an electron at a trap or recombination center is not the Coulomb force. The charge state of a defect is not necessarily the determining property for its capture of charge carriers. The radii of the deep-level states are near atomic size, so these states are localized. The localized character of the electronic state of a deep-level defect makes it much more sensitive to the positions of the neighboring atoms. Therefore, the interactions of the electronic and configurational changes or the electron-phonon coupling are important for these deep-level defects.

The configuration of a defect refers to its position and the positions of all the atoms in its immediate vicinity, which is usually called as a “defect center”. The configuration of a defect center can be easily described using a configuration-coordinate diagram. The major property of a configuration coordinate diagram is that electronic energies can be evaluated as if the atoms are fixed in position, with any change in
configuration permitting a reevaluation of the electronic energies by using the new positions. In Figure 1.1, the minimum conduction-band energy $E_C$ of a semiconductor represents the state in which the conduction band has a single electron, the valence band has one hole, and the carriers are far apart so they don’t interact with each other. These carriers are not localized, so $E_C$ can be represented by another parabola identical to that $E_V$, centered at the same equilibrium configuration but higher in energy. Only one electron has been excited from the ground state, so the defect D is unoccupied if the conduction band is occupied. If the excited electron occupies the defect D, then the conduction band is unoccupied. We hypothesize that the defect is electronically active when an electron occupies the center D but inactive when the electron is in the conduction band. It would appear that a defect is created since we are unaware of the presence of a defect until some change occurs. Therefore, the term “defect” means centers that are in a state in which their properties make them evident, and the remainders of the centers are called “latent defects”.

We then need to redefine the electronic energy levels in equilibrium so that they could be related to the configuration coordinate diagram. The level is defined as the energy needed to cause the defect to change from the ground state $E_V$ to the next-higher-charge state D, which is also the thermal ionization energy of the center measured from the top of the valence band. These levels are defined in equilibrium so they are closely related to the Fermi level of the material. In consequence, changing the Fermi level would also change the charge states of the defects. These levels, therefore, are required to be identified with their two relevant charge states (e.g. $E^{3-/2-}$), not a single charge. In
the case when optical excitation occurs, the electron created from the excitation is captured by the defect center. This will change the charge state of the defect center and the excess energy will be released in the form of a photon or phonons, which could account for deep level luminescence from the material.

First-principles total-energy calculations on various defects in GaN have been reported in the literature. The total energy for a given charge state \( q \) in GaN is given by:

In the equation, \( n_{\text{Ga}} \) and \( n_{\text{N}} \) are the number of gallium and nitrogen atoms. \( \mu_{\text{Ga}} \) and \( \mu_{\text{N}} \) are the chemical potentials of the corresponding atoms. \( E_f \) is the Fermi energy. \( E_f(q) \) is the formation energy of a defect in a charge state \( q \). The total-energy of a defect is based on the assumption of thermal equilibrium. Any configuration change would have time to occur. When an electron goes into the defect, the total energy of the defect would increase by the amount of the Fermi energy. The chemical potential for gallium and nitrogen are not independent, since both species are in equilibrium with GaN. Therefore, the following relation needs to be satisfied.

\[
\mu_{\text{Ga}} + \mu_{\text{N}} = \mu_{\text{Ga}N}, \mu_{\text{N}} < \mu_{\text{N}2}, \mu_{\text{Ga}} < \mu_{\text{Ga}(\text{Bulk})}
\]

where \( \mu_{\text{Ga}} \) and \( \mu_{\text{N}} \) are the chemical potentials of the corresponding atoms.

If these conditions are not satisfied, the system would be thermodynamically unstable and segregate into different components. The equation can also be expressed for the formation energy of the defect as:

\[
E_f(q) = E^{\text{tot}}(q) - n_{\text{Ga}} \cdot \mu_{\text{Ga}} - n_{\text{N}} \cdot \mu_{\text{N}} - qE_f
\]
**Figure 1.1** Configuration-coordinate diagram of a localized defect with a large lattice relaxation, in relation to the nearest band-edges $E_V$ and $E_C$.\textsuperscript{30}
Thus any variation in Fermi energy causes a change in the energy of each state that exchanges electrons. In the plot of formation energy versus Fermi energy level, Figure 1.2, the slopes of the defect formation energies characterize the charge states. This can be derived from the above equation. Therefore, any change in the slope indicates a transition from one charge-state to another.

The formation energy also indicates how easily the defect would form in the material and what is the most stable charge-state for this type of defect. The lower the formation energy, the easier the defect level would form. In n-type GaN, a gallium vacancy has lower formation energy than a nitrogen vacancy and is therefore expected to be the dominant defect. The dominant charge-state for gallium vacancies is the triply negatively one that leads to lower formation energy. The ionization levels for these vacancies are in the range of ~0.5 to 1.7 (eV) above the valence-band maximum, which shows these defects act as deep acceptors.

For other isolated point defects, like $V_{N}$, $O_{N}$ and $Si_{Ga}$, their principal charge-state is the singly positive for nearly all values of the Fermi-level. The ionization level between the singly positive and neutral charge-state lies slightly below the conduction-band edge, which shows these defects act as shallow donors in GaN.

Figure 1.2 also shows the formation energy for defect complexes, like $V_{Ga-O_{N}}$ and $V_{Ga-V_{N}}$. The defect complexes of $V_{Ga-O_{N}}$ have lower formation energy which could be explained by the positively charged donor-like defects are likely to attract the negatively charged gallium vacancies by electrostatic force. The formation energy of $V_{Ga-O_{N}}$ complexes is even lower than the gallium vacancies, which suggests that the formation of
Figure 1.2 Formation energies and ionization levels for the studied defects in GaN. The dashed lines correspond to isolated point defects and the solid lines to defect complexes, respectively.\textsuperscript{19}
these complexes is very likely to happen. The dominant charge-state for these complexes is doubly negative. By theoretical calculation, Elsner et al.\textsuperscript{20} determined the absolute formation energy of the following reaction to be $\sim 1.1$ eV.

$$ (V_{Ga} - O_N)^{2-} \rightarrow V_{Ga}^{3-} + O_N^+ \quad (1.4) $$

Hydrogen atoms are also commonly seen in metal-organic chemical-vapor-deposition (MOCVD) grown GaN samples. It is expected that hydrogen atoms interact with other impurities and defects in the material. The interaction of hydrogen with the gallium vacancies is very likely in GaN. Up to four hydrogen atoms can be accommodated in the vacancy. Figure 1.3 shows the formation energy for different hydrogenated gallium vacancies.\textsuperscript{21} Hydrogenated gallium vacancies have lower formation energies than the isolated gallium vacancies. Whether these complexes actually form during growth, however, depends on the likelihood of multiple hydrogen atoms being available at the time of incorporation. The $V_{Ga}$-H\textsubscript{4} complexes are unlikely to occur in spite of their low formation energy. Hydrogen atoms can passivate gallium vacancies by forming a bound complex or compensate when unassociated hydrogen donates an electron to a vacancy acceptor level. However, complexes containing more than two hydrogen atoms are predicted to be unstable in n-type GaN.\textsuperscript{22} Therefore, the complete passivation of gallium vacancies by hydrogen atoms are precluded. The isolated gallium vacancy is a triple acceptor and occupies a triply degenerated defect level about 1 eV above the valence band in its 3- charge state. As more hydrogen atoms are introduced into the complexes, the defect levels will split due to the decrease of the symmetry, as was shown in Figure 1-4. Both $V_{Ga}$-H and $V_{Ga}$-H\textsubscript{2} complexes have levels
Figure 1.3  Formation energies as a function of Fermi energy for hydrogenated gallium vacancies in GaN. ²¹

Figure 1.4  Schematic diagram for hydrogenated Ga vacancies in GaN. The occupation of the levels is shown for charge states corresponding to full occupation. ²¹
in the bandgap only slightly lower (by 0.1 – 0.2 eV) than the isolated gallium vacancies, shown in Figure 1.4.

The binding energy between the hydrogen and the gallium vacancies reflects how much energy is gained per hydrogen atom by placing n Hydrogen atoms in the vacancy. This energy is defined as follow:

\[ nE_{\text{bind}}(V_{\text{Ga}}H_n) = -E_{\text{form}}(V_{\text{Ga}}H_n) + E_{\text{form}}(V_{\text{Ga}}) + nE_{\text{form}}(H_{\text{int}}) \]  \hspace{1cm} (1.5)

where \( E_{\text{form}}(H_{\text{int}}) \) represents the formation energy of a hydrogen atom in an interstitial configuration. The sign in the equation is chosen such that a positive value indicates a bound configuration.

The removal energy reflects how much energy is needed to remove one hydrogen atom from a complex initially containing n hydrogen atoms, leaving (n-1) hydrogen atoms behind. It is defined as follow:

\[ E_r(n \rightarrow n-1) = -E_{\text{form}}(V_{\text{Ga}}H_n) + E_{\text{form}}(V_{\text{Ga}}H_{n-1}) + E_{\text{form}}(H_{\text{int}}) \]  \hspace{1cm} (1.6)

Binding energies and removal energies for hydrogenated gallium vacancies are listed in Table 1.1. The large removal energies for hydrogenated gallium vacancies indicate hydrogen is strongly bounded to the gallium vacancies, where nitrogen dangling bonds exist.
Table 1.1 Calculated binding energies and removal

Energies for hydrogenated Ga Vacancies in GaN.\textsuperscript{21}

<table>
<thead>
<tr>
<th>( V_{\text{Ga-H}}^n )</th>
<th>( E_{\text{bind}} ) (eV)</th>
<th>( E_T ) (n( \rightarrow ) n-1) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{\text{Ga-H}} )</td>
<td>3.25</td>
<td>3.25</td>
</tr>
<tr>
<td>( V_{\text{Ga-H2}} )</td>
<td>3.13</td>
<td>3.00</td>
</tr>
<tr>
<td>( V_{\text{Ga-H3}} )</td>
<td>2.98</td>
<td>2.68</td>
</tr>
<tr>
<td>( V_{\text{Ga-H4}} )</td>
<td>2.75</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Optical transitions to these deep level defects are commonly seen in semiconductors, like yellow luminescence (YL) in GaN. The yellow luminescence in GaN is a broad luminescence band centered at around 2.2 (eV). The yellow luminescence appears from samples grown by various techniques, like molecular beam epitaxial (MBE), metal-organic chemical-vapor-deposition (MOCVD) and hydride vapor phase deposition (HVPE). Up to now, the origin of the yellow luminescence is still being debated and several models are proposed to explain this phenomenon. Ogino et al.\textsuperscript{23} and Perlin et al.\textsuperscript{24} proposed that yellow luminescence is due to transitions from a shallow donor and a deep acceptor-like level. Glaser et al.\textsuperscript{25} proposed a model of a deep donor-shallow acceptor transition. Hofmann et al.\textsuperscript{26} proposed a shallow donor-deep donor transition.

Although various models are presented to explain the origin of the yellow luminescence, additional evidence shows the yellow luminescence is a transition from shallow donor levels to deep acceptor levels. Suski et al.\textsuperscript{27} carried out high-pressure
experiments and found that the yellow luminescence exhibits pressure dependence similar to that of the bandgap. They concluded that YL results from a recombination between a shallow and a deep level located in the lower half of the bandgap.

The microscopic model of the yellow luminescence is also unclear at this point. Researchers believe gallium vacancies are important to explain the yellow luminescence. Saarinen et al. found that the concentration of gallium vacancies correlates with the intensity of the yellow luminescence using positron annihilation. The gallium vacancies are deep acceptor levels and the shallow donor levels are explained either by the silicon atoms at the substitutional gallium sites (Si_Ga) or oxygen atoms at the substitutional nitrogen site (O_N).

Besides yellow luminescence, blue luminescence (BL) is another deep level transition usually found in undoped or p-type doped GaN. Like yellow luminescence, the origin of the blue luminescence has not been clearly identified. Toth et al. suggest that oxygen and hydrogenated gallium vacancies dominates the blue luminescence in n-type GaN. Recently, Yang et al. proposed a model that the blue luminescence is a transition from the substitional O_N donor level above the conduction bandedge to the V_Ga-O_N deep level complex.

1.3 Metastable Defects in GaN

Metastable defects are usually caused by configuration changes of deep-level defects by the injection of photons or electrons. The interaction of optical photons or electrons with the material can cause an electronic excitation of localized defects, which
induces changes in the surrounding electronic charge and causes movement of the neighboring atoms. The new configuration caused by this electron-lattice interaction at the defect may not be stable and could relax back to the previous configuration promptly. The relaxation time of this process is proportional to the barrier height needed to accomplish the relaxation. The barrier can be higher for large bandgap materials, like GaN, compared to smaller bandgap materials, like GaAs. Therefore, the metastability in large bandgap materials is easier to observe because the metastable effects are usually long lived (hours, days) at room temperature. This long-lived effect is suitable for some device applications.

Figure 1.5 Stable configuration for Si-donor impurity in GaAs.\textsuperscript{30}

Photo-induced defects in III-V and II-VI semiconductors have been studied extensively.\textsuperscript{30} Effects such as persistent photoconductivity\textsuperscript{31,32,33} (PPC), optical
quenching of photoluminescence and photo-capacitance quenching are usually attributed to these metastable defects in GaAs. DX and EL2 centers are the two most common models used to explain the metastable defects in GaAs materials. The DX centers are proposed to be complexes of a donor (D) and some unknown object(s) (X), probably a vacancy. In Figure 1.5, DX centers in GaAs are illustrated. Silicon atoms are donors, which occupy either the substitutional or interstitial gallium sites. This displaced-atom model is widely accepted to explain the DX centers in GaAs.

The EL2 center is important in GaAs because it is an intrinsic defect that appears in undoped materials. It is a metastable defect and has properties similar to the DX center. Many of the observed properties of EL2 centers have been summarized together with an extensive collection of references in the previous paper. It is believed that As antisites are the origin of the EL2 centers. The misplaced gallium atom can occupy a substitutional site or an adjacent interstitial site that are of nearly the same energy. The interstitial configuration is thought to be metastable and exposure of light would excite the centers from the substitutional configuration into the metastable interstitial configuration. This would result in the observation of photo-induced recovery of photo-quenched absorption in GaAs.

Metastable effects should be easier to observe in larger bandgap materials, like GaN. Optical metastability in bulk GaN single crystals have been observed. Reconfigurable optical properties are also found in InGaN/GaN heterostructures and InGaN/GaN quantum wells grown on sapphire substrates. Similar effects were also observed in undoped GaN grown on SiC substrates. The distinguishing characteristic
of this effect is that the yellow luminescence peak intensity at 2.2 eV increases dramatically in the regions where the sample was illuminated by intense ultraviolet (UV) laser light. A yellow pattern is observed under low intensity UV light illumination for several minutes/hours depending on the sample temperature.\textsuperscript{39} Optical memory effects have also been seen in GaN epitaxial thin films that have distinct morphological features.\textsuperscript{40} UV-induced modifications in undoped GaN on sapphire grown by MOCVD were observed from 9 to 160 K by two different groups.\textsuperscript{41,42} Electrical metastability in the form of persistent photoconductivity has also been observed\textsuperscript{43,44} in silicon-doped GaN thin films.

Oxygen atoms have been reported to be a source of DX centers in Al\textsubscript{x}Ga\textsubscript{1-x}N (x > 0.27) based on the Hall effect, persistent photoconductivity and optical threshold measurements.\textsuperscript{45} First principle calculation indicated that oxygen undergoes a transition from a shallow to a deep center in wurtzite GaN under pressure, which can be called a DX center.\textsuperscript{46} However, there are still no microscopic models to explain these various metastable effects observed in GaN thin films,
1.4 Outline of the Dissertation

This dissertation is divided into two major sections: (1) Observations of the optical memory effects, and; (2) models for the memory effects.

A brief review about the defects in III-V nitrides was presented in this chapter. Chapter two provides information about the experimental tools used in this study. In Chapter three, the phenomenal observations of the memory effect are described. It contains systematic studies of the memory effect, including how to produce it, how to erase it and what is measured. A microscopic model of the origin of the memory effect is proposed in Chapter four. The associated energy level in the energy band diagram is also proposed. Several experimental results are also included to support this model. Furthermore, a summary of all the properties of the memory effect and suggestions of future research of the memory effects is included in Chapter 5.
2.1 Material Growth

Metal Organic Chemical Vapor Deposition (MOCVD) is a versatile technique for depositing thin films of semiconductor material. Recent advances in the thin film deposition of III-V nitrides have produced dramatic device results, but there remains considerable materials development to understand and control the preparation of III-V nitride material. Most of the samples used in this dissertation were grown by MOCVD by two different research laboratories.

InGaN/GaN heterostructures grown by low pressure MOCVD were obtained from Prof. R. D. Dupuis at the University of Texas at Austin. The epitaxial films were deposited on c-plane sapphire substrates in an EMCOR rotating-disk reactor using Triethylgallium (TMGa), trimethylindium (TMIn) and ammonia (NH₃) as gallium, indium and nitrogen sources, respectively. Hydrogen (H₂) and nitrogen (N₂) both serve as carrier gases. A 1.5 μm of GaN layer was grown at 1050 °C on top of a c-plane sapphire substrate. A GaN interface layer was unintentionally grown during a 5 minutes temperature ramp from 1050 °C to 750 °C and resulted in an approximately 125 nm layer
thickness. A 60 nm unintentionally doped In$_{0.14}$Ga$_{0.86}$N layer was grown following the interface layer. Detailed growth information can also be found in Ref. 47.

Undoped GaN samples grown on silicon carbide (SiC) substrates were provided by Prof. R. F. Davis of the Department of Material Science and Engineering at the North Carolina State University. The MOCVD reactor used is a resistive heated, cold walled quartz system containing a rotating (180 rpm) graphite stage. TMGa and trimethylaluminum (TMAI) carried in H$_2$ and ammonia were the reactants. Hydrogen was used as the diluent gas. A 100 nm thick AlN buffer layer was deposited on an on-axis 6H-SiC (0001) substrate at 1090 °C. A 0.3 µm GaN layer was subsequently deposited at 990 °C. The base pressure was 45 torr.

2.2 Sample Preparation

For most of the measurements made in the lab, small samples with physical dimension about 1 cm by 1 cm square are used. Samples that are too big are usually cut into small pieces. To cut a large sample, the sample is scribed on the substrate side, sandwiched between two glass slides and broken with gentle pressure from a Q-tipped applicator applied to the cantilevered sample.

For photoluminescence measurement, samples are mounted on heat-conducting copper plugs with radio-TV cement (No. 10-302 from GE Electronics). Acetone is used to dissolve the cement and samples can be removed from the plug for future measurements. The copper plug is designed so it will fit into the cold finger of a liquid Dewar, which is placed inside a light house. The light house must be evacuated with a
mechanical pump during low-temperature measurements to prevent moisture from condensing on the windows and the sample. The windows of the light house are made from ultraviolet (UV)-enhanced fused silica or sapphire to insure efficient transmission of the UV excitation source and luminescence from the sample.

For transmission measurements on samples grown on unpolished substrates, polishing the backside is necessary. The usual mechanical lapping methods were used with large sized diamond grit to remove the material efficiently and with smaller grit to give a finer polish. Precautions are necessary not to mix grit sizes. The lapping pad used is a stainless steel plate and machine oils are used as lubricant.

For Secondary Electron Microscope (SEM) / Cathodoluminescence (CL) measurements, the samples were mounted on an aluminum plug with silver paste. The aluminum plug along with the samples is placed into the chamber and silver paste is used again to fix the position.
2.3 Photoluminescence Characterization

Photoluminescence is a widely used technique to study the optical properties of direct-band semiconductors. It is an efficient, fast and non-destructive measurement of the bandgap energy, alloy composition and other optical and electrical properties of semiconductors. Photoluminescence is also very sensitive to very small levels of impurities that emit light.

The light source for the photoluminescence (PL) measurement is a frequency tripled Coherent Ti: sapphire laser. A titanium-doped sapphire crystal has a gain spectrum in the spectral range from 680 to 1100 nm. This broadband spectrum is important for the generation of ultra-fast pulses in the femtosecond region. The Coherent Mira 900F Ti: sapphire laser is pumped by a Coherent Innova 415 Argon laser, which emits 14 watts of CW laser output at 514 nm. The output spectral range is optimized between 800 nm and 900 nm, which could be extended by changing the optics within the laser cavity. The repetition rate of the pulses depends on the length of the laser cavity and is 76 MHz for all Coherent made Ti: sapphire lasers. The average power output is 1.8 watts with an approximately 200 femtoseconds pulse width, which corresponds to 118 Kwatts of peak power.

Frequency doubling and tripling is carried out by using a commercially available frequency tripler made by CSK. The frequency doubling is achieved using a LBO crystal with about a 20% conversion efficiency and is tunable from 400 to 450 nm. The fundamental and frequency doubled light are sum-frequency at the third harmonic generating crystal (BBO) with a 10% overall efficiency. Both second and third harmonic...
light are available at the same time. The third harmonic output is tunable from 270 to 300 nm and is TM polarized. This UV output is suitable as the light source for wide bandgap material and is used primarily in this dissertation. The pulse width is stretched to about 250 femtoseconds after frequency tripling. The average power output at the tripled frequency is 120 mWatts, which corresponds to 6.3 Kwatts of peak power.

The pulse picker between the Ti: sapphire laser and the frequency tripler is used to reduce the repetition rate of the laser. Pulse picking greatly reduces the heat deposited on the sample by the pump beam while maintaining high peak pump power.

The output emission from the sample is collected, collimated and focused onto the slits of a 0.32 m Instrument S.A. spectrometer. The signal is analyzed using a dry-ice-cooled GaAs photomultiplier and a Keithley 617 electrometer. A personal computer controls the spectrometer and records the signal from the electrometer.
Figure 2.1 Diagram of the pulsed photoluminescence system.
2.4 Optical Absorption Measurements

Transmission measurements or absorption spectroscopy can be used to determine the optical quality of thin films. Absorption spectroscopy responds to processes that have large density of states, such as the absorption edge, and provides a measure of the bulk properties of the crystal. This technique is quick and non-destructive and is therefore a good complementary tool to the photoluminescence measurements.

The absorption measurements were carried out using a Varian Cary 5E UV-VIS-NIR dual-beam spectrometer with a scanning spectral range between 175 nm to 3.3 µm. Nitrogen purge is required for measurements of wavelengths shorter than 200 nm. Two different types of light sources are used in the instrument in order to cover the whole spectral range. A tungsten/halogen lamp can provide visible and near IR light and a deuterium lamp is the UV light source. A photomultiplier (PMT) tube is used to detect signals in the UV and visible range (200-800 nm). A lead sulfide detector is used to detect infrared light. For low-temperature measurement, an Air Product™ liquid helium cryo-system is employed. A small light house suitable for liquid nitrogen temperature (77K) measurements is also available.
2.5 SEM/CL Characterization

Cathodoluminescence (CL) differs from photoluminescence primarily because the excitation interaction volume is much deeper. The incident electron is decelerated in a series of multiple inelastic collisions after passing into the semiconductor. Some of these inelastic collisions lead to the excitation of electrons from the valence band to the conduction band, and subsequent radiative recombination, of electron-hole pairs in the semiconductor. Therefore, the CL excitation occurs from a volume, which is determined by the energy of the electron beam, as shown in Figure 2.3. The CL interaction depth was on the order of 200 nm to 300 nm, which was determined from series of CL spectra from an AlGaN/GaN structure of known thickness using the same electron-beam current.\(^{48}\)

A JEOL JSM-6400 scanning electron microscope (SEM) equipped with a model SP13064-6400 digital scan generator (DSG) is used to provide the electron beam and to characterize the sample. Digital electron microscope images are acquired by the DSG with the aid of a computer by taking control of the electron beam positioning and digitizing the video signal output of the instrument. The DSG controls the instrument’s horizontal and vertical scan coils, acquires a video signal at each pixel, and forms a digital image. Image pixel densities of up to \(2560 \times 1920\) pixels are then stored on computer as a high-resolution digital image.

The SEM is also equipped with an Oxford Instrument Mono-CL Cathodoluminescence (CL) accessory and a Hamamatsu R485 UV enhanced PMT. The signal from PMT could be collected by photon counting or could also be fed back to the scanning system as intensity for CL imaging. It is possible to obtain spectral CL scans
from 180 nm to 900 nm by using this unit. The CL imaging system allows for operation in either panchromatic or monochromatic mode. Panchromatic CL images, which produce the image based on the total CL intensity, could be obtained when the spectrometer is in panchromatic mode. Monochromatic CL images of the samples under investigation can be obtained at a selected wavelength within this wavelength range when the spectrometer is at monochromatic mode. Detailed information about this SEM/CL system can be found in Ref. 49.
Figure 2.2  Schematic Diagram of SEM/CL Spectral Analysis and Imaging System (After M. A. L. Johnson, Ref 48)

High Resolution Micrographs:
2560 X 1920 Pixels
13 msec/pixel
Figure 2.3 Schematic Representation of CL Interaction Volume Effect (After M. A. L. Johnson, Ref 48)
2.6 Heating by the Pulse Laser

Heat transport in the material can be carried out both by electrons and phonons. In a conducting material, heat transport by electrons dominates since hot electrons are free to move inside conductors. However, heat transport in an insulator requires sufficient collisions among phonons because the hot electrons are not able to move inside the material. In a semiconductor, both electrons and phonons contribute to heat transport. Since heat conduction by electrons is much quicker than by phonons, we consider the worst case and assume that electrons do not participate in the heat transport.

Conventional theories assume the physical domain for heat transport is so large that it allows hundreds of thousands phonon collisions to occur before an observation is made for the process of heat transport. Phonon collision requires a finite period of time to take place. Therefore, conventional theories dealing with heat diffusion are not very informative about the transient behavior at extremely short times. The mean free path for a phonon collision and phonon scattering is typically tenths of a micron ($10^{-7}$ m). Phonons propagate at the speed of sound, which typically is of the order of $10^4$ to $10^5$ meters per second. As a rough estimate, any response shorter than 10 picoseconds should be treated differently. In this short-pulse regime, laser energy absorbed by electron band-to-band transition is much faster than it is transferred to the lattice. Therefore, the lattice does not heat appreciably during the pulse since there is not enough time for the lattice to heat up. There is no need to track the flow of energy into the lattice to account for thermal and mechanical stresses in the ultra short-pulse regime.
To deal with the heating caused by femtosecond laser pulses from a frequency-tripled Ti: sapphire laser, heating during the pulse is not considered. Instead, the temperature response as a function of time after deposition of certain energy into the material about every 13 nanoseconds, corresponding to the 76 MHz laser repetition rate, was considered. The conventional theories about one-dimensional heat diffusion satisfy the following Poisson equation.

\[
\frac{\partial H}{\partial t} = D \frac{\partial^2 H}{\partial x^2}
\]  

(2.1)

H is the heat energy and D is the thermal diffusivity of the material. The solution for this 1-D Poisson equation is as following:

\[
H = \frac{\Delta H x}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}
\]  

(2.2)

Figure 2.4 One-dimensional heat distribution at different times, where T1<T2<T3.
In Figure 2.4, the three curves represent the one-dimensional heat distribution at different times, where T1<T2<T3. The heat would gradually diffuse out as time goes by. 

\((4Dt)^{1/2}\) represents the distance where \(H(X)\) would fall to \(1/e\) of the \(H(0)\) intensity.

In the case of three-dimensional heat diffusion, a 3-dimensional Poisson equation must be satisfied. This equation along with its solution is as following:

\[
\frac{\partial H}{\partial t} = D\left[ \frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} + \frac{\partial^2 H}{\partial z^2} \right] \tag{2.3}
\]

\[
H = \frac{\Delta H}{(\sqrt{4\pi Dt})^3} e^{-(x^2+y^2+z^2)/(4Dt)} \tag{2.4}
\]

Therefore, the temperature increased due to each deposited \(\Delta H\) at position \((x,y,z)\) at time \(t\) is given by:

\[
\Delta T = \frac{\Delta H}{\rho C_p \pi^{3/2} (4Dt)^{3/2}} e^{-x^2+y^2+z^2/(4Dt)} \tag{2.5}
\]

However, this \(\Delta T\) represents the increased temperature after \(\Delta H\) energy was deposited on a point, which does not fit our experimental conditions. The laser spot size is about 20\(\mu m\) in diameter and the energy is distributed within this area. To simulate our experiment, we first assume the spot size is a 20\(\mu m\) square spot and the laser energy is uniformly distributed within this area. The second assumption is that the temperature is the same in a small square with length of \((4D*10\text{ ps})^{1/2}\). Finally we assume the spot is
made up of thousands of these squares and each one has its own heat distribution. Hence, we need to calculate the contribution from each square after each pulse.

For example, sapphire’s thermal diffusivity is 0.117212 (cm$^2$/s) and heat capacity is 0.7524 (J/gK). The density of sapphire is 3.98 (g/cm$^3$). The laser power is assumed to be 150 (mW). The length of the square mesh is 0.02 µm and the number of mesh points is $10^6$. The value of $\Delta H$ is calculated by:

$$\Delta H = \frac{Power}{Re_{p_{rate}} \times Mesh^#} = \frac{0.15}{7.6 \times 10^7 \times 10^6} = 1.97 (fJ)$$ (2.6)

Figure 2.5 shows the transient temperature response for the first three pulses at position (0,0,0). The transient temperature increased by an amount of about 75 degrees immediately after the pulse arrives and decreases after the pulse is gone. At the moment just before the next pulse arrives, there will be still some heat remaining. By comparing the transient temperature about 10 picoseconds after each pulse, we can find that the temperature after the second pulse is higher compared to after the first pulse. The temperature is even higher after the third pulse. The heat deposited by the pulse laser will gradually build up the temperature. However, we would like to know if the temperature would reach a steady state and what this temperature is at steady state.
Figure 2.5 Transient temperature response at position (0,0,0) for the first 3 pulses.

Figure 2.6 Transient temperature response at position (0,0,0) for many pulses.
In Figure 2.6, the transient temperature as a function of time range from 10 picoseconds to one-tenth of second at position (0,0,0), which will account for millions of laser pulses. As indicated in the figure, the temperature increased to about 75 °C 10 picoseconds after the pulse arrives. At about 13 nanoseconds, the next pulse arrives and raises the temperature about 75 °C again. The computer program keeps track of the effect on the temperature from all the pulses and all the mesh elements. The temperature increases, as more pulses are input into the material but the system gradually reaches an equilibrium temperature after many pulses. This equilibrium temperature is about 190 °C. For GaN material, the coefficient of the linear thermal expansion in the a-direction is $5.59 \times 10^{-6} \text{1/°C}$. Therefore, this 190°C will result in thermal induced mismatch about 0.1%. Therefore, the result of this calculation indicates that these laser pulses are not able to produce any thermal damage to the sample.

In this calculation, worst cases parameters were chosen. For examples, all the laser energy was absorbed by the lattice and transferred into heat. However, part of the laser energy absorbed by the material will be released by band-to-band transitions in a direct semiconductor. For example, the bandgap of GaN is about 3.44 eV and the excitation photon energy is 4.51 eV. Therefore, only about 24.5 % of the excitation energy will transfer into heat, which will result in about a 47 °C temperature raised in the center of the laser spot. The other assumption for the worst case in the calculation is the selection of the substrates. Sapphire has a lower thermal conductivity (35 W/mK) than
other substrate materials (Silicon: 150 W/mK, SiC: 350 W/mK). Therefore, the heating on samples grown on these substrates will be much smaller.

In conclusion, the heating of the sample by a femtosecond pulse was discussed. During the pulse, most of the photon energy was absorbed by electrons and then transferred into the lattice after sufficient collisions among energy carriers, which usually takes about 10 picoseconds. Therefore, we only need to track the heat 10 picoseconds after each laser pulse. By using 3-dimensional Poisson equation to track the heat, computer simulations were carried out using sapphire as the material being heated. The temperature rose by the amount of 75°C 10 picoseconds after each pulse and did not relax back to the initial temperature before next pulse arrived. The heat deposited by the each pulse gradually builds up the temperature. The steady-state temperature is increased by about 190°C and will cause about a 0.1 % thermally induced mismatch for GaN. The result of this calculation indicates that the laser pulses used in this research are not able to produce any thermal damage to the sample. In this calculation, several parameters were chosen for the worst-case condition. Therefore, the actual heating by the laser pulses is expected to be less than the results of the simulation.
CHAPTER 3

QUALITATIVE AND QUANTITATIVE OBSERVATIONS OF THE OPTICAL MEMORY EFFECT

3.1 Introduction

The optical memory effect was first found in the Quantum Optoelectronic Group in the NC State University in 1996.\textsuperscript{7,8} It was discovered that intense ultraviolet laser light can produce yellow patterns that could be seen while shining low intensity ultraviolet laser light on the sample. A frequency tripled output of a pulsed Ti: sapphire laser (280 nm; 250 fs at 76 MHz) was used as the ultraviolet excitation source. Writing lines on the sample was accomplished by focusing the ultraviolet laser light to a spot size of approximately 20 µm. The average power density was approximately 30 (kW/cm\textsuperscript{2}), which is referred to the “Write” condition. Moving the spot on the sample resulted in a line pattern. In the “Read” condition, the sample was illuminated with a low power density UV laser source with an average power density of approximately 0.4 (W/cm\textsuperscript{2}), which can be accomplished by defocusing the UV source. The schematic view of the write and read conditions are presented in Fig. 3.1(a) and (b), respectively. Patterns under the “Read” condition can be observed by the human eye or captured on standard photograph film through a microscope. The observed pattern was not due to physical
damage (e.g. laser ablation) as confirmed by high power optical microscopy before or after etching the sample in HCl for several minutes. Additional information regarding the read and write conditions can be found in Ref. 7 and 8.

![Figure 3.1](image)

**Figure 3.1** Schematic views of the write and read conditions. (a) Write condition: Focused laser light with intensity of 30 kW/cm² (b) Read condition: unfocused laser light with intensity of 0.4 W/cm²

**Table 3.1** Growers’ information of the samples that exhibit memory effect.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Substrate</th>
<th>Method</th>
<th>Professor</th>
<th>Institute</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaN/GaN heterostructures</td>
<td>Sapphire</td>
<td>MOCVD</td>
<td>Prof. Dupuis</td>
<td>Univ. of Texas At Austin</td>
</tr>
<tr>
<td>InGaN/GaN MQW</td>
<td>Sapphire</td>
<td>MOCVD</td>
<td>Prof. DenBaars</td>
<td>Univ. of California At Santa-Barbara</td>
</tr>
<tr>
<td>Undoped GaN</td>
<td>SiC</td>
<td>MOCVD</td>
<td>Prof. Davis</td>
<td>NC State Univ.</td>
</tr>
<tr>
<td>Undoped GaN</td>
<td>Sapphire</td>
<td>MOCVD</td>
<td>Prof. Schetzina</td>
<td>NC State Univ.</td>
</tr>
<tr>
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<td>MOCVD</td>
<td>Prof. Schetzina</td>
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<tr>
<td>Undoped GaN</td>
<td>Sapphire</td>
<td>MOCVD</td>
<td></td>
<td>APA Optics</td>
</tr>
</tbody>
</table>
Since the initial discovery, many samples from different groups have been investigated for memory effects and some of them do exhibit memory effects. Table 3.1 lists samples that exhibit memory effect, including information about the structure, substrate, method of growth and group that grew the sample. Most of the samples that exhibit memory effect are undoped GaN grown on various substrates from different reactors. Samples grown by MBE and MOCVD were investigated. However, only the MOCVD samples exhibit memory effect. The other important trend is that samples grown from different reactors exhibit memory effects. Understanding this memory effect could be used to improve GaN films grown by MOCVD.

The other common property for all the samples is found in their photoluminescence spectra. Since multiple samples exhibit memory effects, we obtained some valuable information by comparing the photoluminescence spectra between samples that do and do not exhibit memory effect. Photoluminescence spectra from GaN samples that do not exhibit memory effect usually exhibit bandedge emission in the ultraviolet and a broadband yellow luminescence, as shown in Figure 3.2. However, Photoluminescence spectra from samples that exhibit memory effects usually exhibit strong yellow and blue luminescence along with the band-edge emission. Figure 3.3 is a good example, which shows photoluminescence spectra for an undoped GaN thin film grown on a silicon carbide substrate. Yellow luminescence could be observed on every sample and is therefore not an indicator for memory effects. However, samples that exhibit memory effects all exhibit blue luminescence at about 2.8 eV. It is believed that this blue luminescence is important for the explanation of the origin of this effect.
The photoluminescence spectra at different excitation densities can also indicate whether the sample will exhibit memory effect. Photoluminescence spectra at different pump power densities from samples that do not exhibit memory effect, shown in Figure 3.2, indicate that the ratio between the peak intensity at the bandedge emission and the yellow luminescence only changes a little. However, photoluminescence spectra at different pump power density from samples that exhibit memory effect, shown in Figure 3.3, shows that the ratio varies significantly. During the write condition, with excitation density of 30 kW/cm², the band-edge transition is strong and sharp and the intensities of the blue and yellow luminescence are also large. The band-edge emission decreases as the excitation density of the pump source decreases. However, the intensity of the yellow luminescence stays relatively constant. Competition between the band-edge and yellow luminescence transitions at different excitation densities is common and indicates that deep defect levels are involved. However, the fact that samples that exhibit memory effects all have similar photoluminescence spectra at different excitation densities provides information about the memory effects.

Most of the samples investigated are InGaN/GaN heterostructures and undoped GaN grown on SiC substrates. They have different physical structures and the memory effect properties are not entirely similar. To avoid confusion, they are discussed separately.
Figure 3.2 Room temperature photoluminescence spectra at different power densities on samples that do not exhibit memory effect. (a) High power density (b) Low power density

Figure 3.3 Room temperature photoluminescence spectra at different power densities on samples that exhibit memory effect. (a) “Write” condition [30 kW/cm²] (b) Intermediate [10 W/cm²] (c) “Read Condition” [0.4 W/cm²].
3.2 InGaN/GaN Heterostructures Grown on Sapphire Substrates

The first sample in which the memory effect was discovered was grown by Professor Dupuis from University of Texas at Austin. In order to understand the memory effect, quantitative measurements that could distinguish between the background and yellow patterns are important. However, the human eyes and photographic images were the only two methods used to report the memory effect on this sample. Qualitative properties can be described based on the observation from these two methods.

The first qualitative property observed was whether producing memory effect patterns requires a minimum laser power density or just a certain photon flux. In Figure 3.4, the laser spot size was expanded by a factor of about 50 and the laser power density was therefore reduced by about 2500 times. This laser power density is too low to be able to produce the memory effect. Figure 3.4.1 was what it looked like under the microscope at the “Read” condition at room temperature prior to exposure. In the picture, only the orange area was illuminated by low intensity laser light, which can refer to the read condition. The black lines are just scratches at the backside of the substrate. This expanded laser light was positioned at the same location and the appearance under the “Read” condition was frequently checked every few minutes. Photo Micrographs after 21 and 31 minutes are shown in Figure 3.4.2 and 3.4.3, respectively. A faint yellow pattern with a size comparable to the laser spot can be observed in Figure 3.4.2. The contrast between the pattern and background is higher when the writing time is longer. These results indicate that the memory effect appears to be a flux-dependent effect with no lower limit or a very small lower limit on the required laser power density.
Figure 3.4.1  This is the appearance of the sample before we write the memory pattern under the “READ” condition.

Figure 3.4.2  The memory pattern is the yellow spot near the center of the picture. The spot size to write this pattern is about 50 times larger than the minimum spot size.

Figure 3.4.3  After a long time of writing, the memory effect pattern is much clearer. We conclude that the memory effect is a “Flux Dependent” Effect.
Besides enlarging the laser spot size to reduce the laser power density, a 300 mW continuous wave (CW) ultraviolet output from a 305 nm Ar Ion laser was available and 240 (W/cm^2) laser power can be achieved when focus to a spot size of 20 µm in diameter. This laser light, which has a smaller power density, also produced memory effect patterns. This further proves that the memory effect is flux-dependent and can be produced by a much lower intensity ultraviolet laser source.

Producing a memory effect pattern using a low power density light requires tens of minutes of exposure to achieve the maximum possible contrast. Therefore, photoluminescence spectra can be taken during the writing process. The result is shown in Figure 3.5 and the legend of the graph indicates the exposure time in minutes. The overall photoluminescence intensity decreases as the exposure time increases. It is suggested that traps were produced during the writing process, but it is still unclear how to relate this to the yellow memory effect patterns we observed. After the yellow memory effect patterns fade away, a dark spot was observed in the same location where the memory effect patterns were before under the read condition at room temperature, as shown in Figure 3.6.1. If we fix the detection system at one wavelength (421.7 nm) and scan across the dark spot, the photoluminescence signal decreases rapidly when scanned across the boundary into the dark spot. The PL spectrum within the dark spot is similar to that after exposure to UV light for long time (T=110 minutes) and the PL spectrum outside the dark spot is similar to that at T=0 in Figure 3.5. This explains the reduction of the overall PL intensity in Figure 3.5.
The dark spot did not disappear after a long period of time (>6 months). Therefore, some permanent defects were introduced during the process instead of metastable defects. The production of this dark spot did not degrade the ability to write on the sample within the dark spot. A cross pattern across the dark spot was subsequently produced at the write condition, as shown in Figure 3.6.2. No significant changes in the efficiency of writing or in the pattern contrast were observed. These results suggest that the production of the dark spot and the yellow memory effect are from two different mechanisms.
Figure 3.5 This set of spectral curves is taken continuously under a large spot size, (~50× the minimum spot size, ~4.0 W/cm²) The overall PL intensity decreases as the expose time increases.

Figure 3.6.1 “Dark Spot” produced in taking the PL data of Figure 3.5.

Figure 3.6.2 Note that it is possible to write within the “dark spot” and observe the memory effect.
The memory effect was found to be a flux-dependent effect, but the relationship between the retention time and the writing flux was still unclear. In Figure 3-7, four parallel memory effect lines were written under the write condition. Lines from top to bottom were written back and forth 2, 4, 6 and 8 times respectively. The sample was left at room temperature and pictures were taken after various time. In the first picture, which was taken immediately after the lines were written, the contrast between the lines and the background of all four lines are similar. This indicates that the contrast would reach a maximum.

The overall contrast between the lines and the background decreases between the first picture and second picture. Part of the line that was written twice disappeared while other lines remains the same in the second picture. The decay of the contrast is much more dramatic in the third picture. Therefore, the retention time of the memory effects is proportional to the writing flux and the higher it is the longer the retention time.

All the memory effect lines disappeared after 27 hours and were not observed under the read condition. The photos in Figure 3.8 were taken two days after the lines were written at 300K and 77K at the read condition. No memory effect patterns were observed at room temperature as expected. However, line patterns can be observed under the same read condition at 77K. Some of these patterns were written at least three months before taking this picture. Therefore, the memory effects might have changed the properties of the material permanently and the contrast between the pattern and the background is too little for us to observe the difference under the read condition at 300K.
Figure 3.7 The decay of memory effect pattern with time at room temperature. The numbers by the pattern are the number of times the write beam was scanned across the sample we repeatedly wrote on the same line.
Figure 3.8 Images of the same sample at “READ” conditions at two different temperatures. Some “straight line” memory patterns are visible at 77K not at room temperature.
From previous discussion, a dark spot and the memory effects patterns both were produced after long exposure of a lower excitation density UV light. The yellow memory effect patterns fade away after one day but the dark spot exists for months. Therefore, photoluminescence taken within the dark spot previously produced can effectively exclude the influence made by the formation of the dark spot. Room temperature photoluminescence spectra were taken within the dark spot before (curve 3.9(a) and after (curve 3.9(b)) long exposure of the UV light. There is no significant difference found between these two spectra.

Memory effects were reported to be more dramatic when temperature is at 77K. The required excitation density is less, therefore, writing patterns can be achieved by focusing the laser light to a larger spot. Photoluminescence spectrum at low temperature was taken under the read condition when no memory patterns were written. This result is shown as curve 3.9(c). The excitation UV laser light was then focused to a spot, which was about 500µm in diameter, and slowly moved across the sample. This excitation density is high enough to write memory effects over a large area on the sample. Photoluminescence spectrum was taken again and is shown as curve 3.9(d). A broad emission peak at around 540 nm in the PL increases in the area where the memory effect patterns were written. This change can be observed at the read condition through an optical microscope where the color of the samples changes from blue to whitish. This was the first quantitatively measurable change that was observed for the memory effect.

This emission peak around 540 nm is usually called yellow luminescence in GaN. Despite the work of numerous research laboratories, the origin of this yellow
luminescence is still not clear. This memory effect might be closely related to the yellow luminescence and finding the origin of this memory effect might be as difficult as finding the explanation for the yellow luminescence. Unfortunately, the complicated structure of this sample prevented us from making any definitive conclusion about where and how the memory effect takes place. Note that there is a thin GaN layer underneath the top InGaN thin film. This GaN is grown at a lower temperature while ramping down to the InGaN growth temperature and some metastable defects are likely to occur in this region.

Investigation of memory effects on these InGaN/GaN heterostructures samples indicated that optical memory effects are flux-dependent effects, which require no lower limit or a very small lower limit on the laser power density needed produce memory effect patterns. The retention time at room temperature is longer for a higher writing flux. A dark spot, which results in the decrease of the overall photoluminescence intensity, accompanies the writing of the optical memory effect patterns. The memory effect and this dark spot are from two separate mechanisms. Further research is needed to identify the origin of the memory effect. Samples with simpler structures as described in the next section were evaluated to simplify the investigation.
Figure 3.9 Photoluminescence spectra for InGaN/GaN heterostructures before and after memory effect patterns were written on the sample at room temperature and 77K.
3.3 Undoped GaN Grown on Silicon Carbide Substrates

Undoped GaN samples were grown on 6H-SiC substrates in Professor Davis’ laboratory at North Carolina State University. These samples were designed to have simpler structures than previous samples to facilitate the study of optical memory effects. In order to understand the memory effects, quantitative measurements that could distinguish between the background and yellow patterns are important.

The first few samples grown on silicon carbide substrates that exhibited memory effects were very thin GaN thin films (~0.3 µm) with a thin AlN buffer layer between the substrate and the film. The absorption coefficient for the tripled Ti: sapphire output (~4.5 eV) is around $1.75 \times 10^5 \text{ cm}^{-1}$. About 0.5% of the excitation power can penetrate through the thin GaN film and reach the interface. Therefore, it is possible the memory effect is caused by defects that reside at the interface since the defect density should be much higher in the interface region. However, samples with different GaN layer thickness up to 2 µm GaN all exhibit memory effects. Table 3-2 lists the samples investigated from Dr. Davis’ laboratory. For a 2 µm GaN thin film, the amount of the excitation light that reaches the interface is very little ($6.3 \times 10^{-14}$%). Therefore, memory effects are not due to defects in the interface region. They must be caused by bulk or surface defects.
### Table 3.2 List of samples from Dr. Davis’ Laboratory

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Substrate</th>
<th>Buffer layer</th>
<th>Thin film</th>
<th>Memory effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO103</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.3 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>AO106</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.3 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>AO107</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.3 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>SE003</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.6 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>SE004</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.85 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>SE009</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.85 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>SE023</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>0.85 μm GaN</td>
<td>Yes</td>
</tr>
<tr>
<td>SE057</td>
<td>6H-SiC</td>
<td>0.1 μm AlN</td>
<td>2.00 μm GaN</td>
<td>Yes</td>
</tr>
</tbody>
</table>
3.3.1 Photo-induced Memory Effects

To understand the origin of the memory effect, quantitative measurements are important. The human eye is very sensitive detector and can distinguish very subtle color difference, but does not supply quantitative spectral data. No predictive models can be developed if there are no measurable quantitative measurements.

Photoluminescence measurement is a very useful tool to monitor the emission from defect levels in the material. Cathodoluminescence, like photoluminescence, is also a potential tool to monitor the memory effect. Optical transmission measurements are usually used to monitor film quality, but are not sensitive to subtle changes in the absorption characteristics. Photoluminescence measurements were taken at both at room temperature and at liquid nitrogen temperature (77K).

Photoluminescence spectrum from an undoped GaN thin film, grown on a SiC substrate, was taken under the read condition at room temperature, as shown in Figure 3.10. This spectrum shows no band-edge emission and strong emission in the blue and yellow. The excitation laser light was then focused to a tiny spot, which corresponds to the write condition, followed by translating the spot across the sample to “paint” a large area. The focusing lens was then removed and photoluminescence spectrum was taken again in the “painted” area. The peak emission around 540 nm increases dramatically after writing on the sample. This increase of the peak emission around 540 nm explains the yellow memory patterns that were observed. The entire procedure was repeated at low temperature (77K) and the results are shown in the lower portion of Figure 3.10. The
increase of the yellow luminescence is much more dramatic at 77K. The other difference is that the peak intensity around 480 nm decreases slightly. This is an indication that multiple defect levels are involved in the memory effects.

Optical chromaticity diagrams are usually used to quantify colors seen by human eyes. Each of the photoluminescence spectra shown in Figure 3.10 was converted and represented by a point in the chromaticity diagrams shown in Figure 3.11. For the chromaticity diagram at room temperature, the color changes toward a more yellow color. Although the separation between the points is small, the human eye is sensitive enough to distinguish the difference between them. For the chromaticity diagram at 77K, the original color of the sample is between blue and whitish, which is consistent with observations under the read condition through an optical microscope. After the memory patterns were written, the color becomes more yellow. The separation between points is larger because the chromaticity diagram is much more sensitive to the changing intensity of two emission peaks compared to one. Therefore, it is easier to see the patterns at low temperature.
Figure 3.10 Photoluminescence spectra for undoped GaN on SiC substrates before and after memory effect patterns were written on the sample at room temperature and 77K.
Figure 3.11 Chromaticity diagrams before and after memory effects at room temperature and 77K. Each point is converted from each spectrum in Figure 3.10.
3.3.2 Electron-beam Induced Memory Effects

Photography and photoluminescence (PL) measurement have been the principle techniques used to record and measure this metastable effect. However, electron beam and cathodoluminescence (CL) were found to be useful in writing and reading memory effect patterns on GaN. The resulting changes in the luminescence spectra are quite similar for either optical or electron beam induced patterns. In both cases, the yellow luminescence at 2.2 eV increases significantly with little change in the band-edge emission.

A JEOL JSM-6400 scanning electron microscope (SEM) equipped with a model SP13064-6400 digital scan generator (DSG) and an Oxford Instrument Mono-CL Cathodoluminescence accessory was used to characterize the samples. Cathodoluminescence from 180 nm to 900 nm can be obtained based on either the total integrated CL intensity (panchromatic) or monochromatic CL images of the sample. Detail information about this SEM/CL system can be found in Ref. 49.

First, we examined a sample with optical techniques to have an accurate comparison with the cathodoluminescence results. The appearance of the sample through an optical microscope in the read condition is shown in Fig. 3-12(a). The pattern is somewhat out of focus because of the high magnification and the off axis angle of the microscope during the experiment. Regardless, five vertical and three horizontal parallel lines can be observed. The sample was then transferred into the SEM/CL system. Panchromatic CL images and SE images were taken with a probe current of $6 \times 10^{-10}$ A
and acceleration voltage of 5 kV in the same area where the photo was taken. The Panchromatic CL image, shown in Fig. 3-12(c), clearly shows the same pattern that is observed under the optical microscope in the read condition. A secondary electron image, shown in Fig. 3-12(d), does not reveal the pattern. These images indicate that intense laser light illumination on the samples temporarily changes the material property and affects how excess carriers, generated either by laser light or electron-beam, recombine. The higher brightness from the pattern indicates more luminescence signal is collected in the patterned area.

The photoluminescence spectra on (bright) and off (dark) the written patterns are shown in Fig. 3-13(a) and 3-13(b), respectively. Note that the peak intensity at 550 nm increases while the intensity of the band-to-band transition is almost the same. The cathodoluminescence spectra on the bright and dark areas of Fig. 3-12(c) are shown as curves 3-13(c) and 3-13(d). Again, the peak intensity centered at 550 nm is higher and the band edge emission is nearly equal as in the photoluminescence spectra. The CL spectra are consistent with the CL images shown in Fig. 3-12(c).

Samples with and without optical memory effect characteristics were selected to determine if an electron beam could be used to write memory effect patterns. To produce a high-density electron beam, the magnification of the image is changed to 1600X and the probe current is increased to $6 \times 10^{-9}$ (A). Each sample was exposed to this high-intensity electron beam for about 20 minutes. The magnification of the images was subsequently changed to 500X and the probe current was turn down to $10^{-10}$ (A). Panchromatic CL images taken under this condition (write current density $= 600 \times$ read
current density) are shown in Fig. 3-14(a) and 3-14(b). Secondary electron images, Fig. 3-14(c) and 3-14(d), on the same locations were taken immediately after obtaining the CL images. Fig. 3-14(a) is the panchromatic CL image of a sample that exhibited optical memory effects. Note that the electron beam irradiated rectangular area is brighter than the rest of the sample. Hence, it is possible to generate electron-beam induced memory effects like those induced by optical means. Using the same experimental conditions, a Panchromatic CL image of a sample that did not exhibit optical memory effects is shown in Fig. 3-14(b). The exposed area is diminished in intensity leaving a faint image. This faint image observed on the sample was caused by electrostatic attraction of low vapor pressure hydrocarbons that were back streamed in the SEM vacuum system after extended exposure. The hydrocarbon buildup, while thin, attenuates the emission from the sample. This effect is quite common and can also be observed in the secondary electron images on both samples (Fig. 3-14(c) and 3-14(d)).

Monochromatic CL images of the pattern produced by the electron beam are shown in Fig. 3-15(a) for \( \lambda=365 \) nm and Fig. 3-15(b) for \( \lambda=540 \) nm. Note that there is an observable contrast in the yellow (540nm) but not at the band edge (365 nm). This is consistent with the CL spectra shown in Fig. 3-15(c). The contrast in CL spectra produced by electron-beam irradiation is very similar to change in CL spectra induced by optical irradiation. We believe that the same mechanism is responsible in both cases.
Figure 3.12 Room temperature images (320 µm × 380 µm; 100 µm reference marker) using different measurement techniques to view the memory effect pattern that is produced by intense laser light. Three horizontal and five vertical lines were optically written using the conditions shown in (b). The effect is clearly observed under optical “read” conditions (a) and panchromatic cathodoluminescence (c), but not by secondary electron imaging (d) or optical microscopy (not shown).
Figure 3.13 Comparison of room temperature photoluminescence (upper graph) and cathodoluminescence (lower graph) spectra before and after the memory effect pattern is optically produced in the “Write” condition. (a) PL - After (b) PL - Before (c) CL - After (d) CL - Before
Figure 3.14  Panchromatic cathodoluminescence images and secondary electron images, on samples that did (a) or did not (b) exhibit optically induced memory effects, after high intensity electron beam irradiation. Electron beam irradiation produces enhanced yellow emission on a sample exhibiting memory effects (a) while producing a dark image on a sample that did not exhibit optical memory effects (b). Secondary electron images of both samples reveal a dark area (buildup due to carbon) that was not observed in Figure 1(a). The size of the rectangle is approximately 60 µm × 80 µm.
Figure 3.15 Monochromatic cathodoluminescence images from a sample exhibiting memory effects after high intensity electron beam irradiation. The high contrast in the yellow but not at the band-edge is consistent with the CL spectra shown in (c).
Investigations on the undoped GaN samples grown on SiC substrates indicated that both photon and electron beam illumination will cause the luminescence properties to change. In both cases, the yellow luminescence increases after the writing process. This change can be observed through an optical microscope under low intensity UV light illumination. Cathodoluminescence images also revealed the same patterns.

### 3.4 Erasing Optical Memory Effect Patterns

The memory effect is metastable and the patterns disappear after several hours at room temperature. In order to make any useful applications using this memory effect, knowing how to erase the effect quickly is very important.

Heating up the sample and providing thermal energy to the lattice could change the configuration of the localized defects, which is usually related to the metastability of a material. Therefore, a sample that exhibits memory effects was mounted on a copper stage that could be heated by a cartridge heater. Memory effect patterns were written on the sample under the write condition and can be clearly seen under the read condition. The sample was then heated up to about 110 °C and the patterns quickly disappeared under the same read condition. It was also found that the retention time is dependent on the temperature. The retention time is a few seconds at 110 °C, and increases dramatically at room temperature. At 35 °C, the patterns would not disappear after several minutes. Heating up the sample to 110 °C was found to be a reliable way to erase the memory effects.
Memory effects can be written and read by ultraviolet laser light. Although memory effects can be erased by heat, this is not a quick process and would limit the application and speed of a practical storage device. Optical memory cells could be realized if the memory effect could also be erased optically.

Ultraviolet light is found to be able to write the memory effect patterns. Since deep level defects are involved, photons with less energy are the most promising candidates to optically erase the patterns. Laser light with different wavelength is available in the lab. The fundamental light of the output of the Ti: sapphire laser is at 820 nm and the second harmonic light is at 410 nm. The Argon Ion laser used to pump the Ti: sapphire laser is at 513 nm. A diode laser that with emission wavelength at 980 nm is also available. None of these laser wavelengths were found effective in optically erasing the memory effect patterns.
3.5 Other Observations Related to the Memory Effect

Most of the observations in previous sections are from samples that exhibit memory effects. Observations from other samples can also help to explain this effect. For example, persistent photoconductivity (PPC) is considered to be a metastable effect. Do PPC and optical memory effects have the same origin? Do samples grown by molecular-beam epitaxy (MBE) have optical memory effects? Is there any difference in the optical transmission spectrum before and after the memory effect is written? These observations can also provide valuable information about optical memory effects.

3.5.1 Persistent Photoconductivity and Optical Memory Effects

Persistent photoconductivity is the most common metastable property observed in GaN. Beadie et al. reported that persistent photoconductivity would disappear at a temperature of about 130 °C, which is similar to the temperature at which the memory effect disappears. We suspected that both of these metastable effects might have the same origin.

Dr. Beadie from Naval Research Laboratory sent us 4 samples that he used in his publication. One of them didn’t exhibit PPC and the other 3 exhibit PPC. However, none of these samples exhibit any optical memory effects. The sample list and the result are shown in Table 3.3. Based on these results persistent photoconductivity and the optical memory effects appear to be arising from two different mechanisms.
Table 3-3 List of MOCVD grown samples from Naval Research Laboratory

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nucleation Layer</th>
<th>Target growth</th>
<th>Hall data</th>
<th>PPC?</th>
<th>Memory effect?</th>
</tr>
</thead>
</table>
| A      | a plane AlN 20nm | 2.7 µm layer uniformly doped | N = 1.9  
μ = 400 | No   | No            |
| C      | a plane AlN 20nm | 0.25 µm doped layer on 3µm HR GaN | N = 1.7  
μ = 410 | Yes  | No            |
| D      | a plane AlN 20nm | 2.7 µm layer uniformly doped | N = 1.3  
μ = 70 | Yes  | No            |
| E      | a plane AlN 20nm | 0.2 µm doped layer on 3µm HR GaN | N = 0.4  
μ = 70 | Yes  | No            |

3.5.2 Controlled Oxygen Doping of GaN Grown by MBE and Optical Memory Effects

Molecular-beam epitaxy (MBE) is another popular growth technique for GaN materials. GaN samples grown by MBE contain less of certain impurities compared to samples grown by MOCVD. By collaborating with Dr. Myers from West Virginia University, we are able to evaluate several MBE grown GaN films with sample description shown in Table 3.4. Detailed growth information about the samples can be found in ref. 51. Samples with different oxygen concentration were accomplished by precise control of an ultrahigh vacuum leak valve and monitoring using a residual gas analyzer.

Oxygen partial pressure, oxygen concentration measured by SIMS and carrier density measured by Hall measurement are listed in Table 3.4 for several samples. However, none of these samples exhibit memory effects. Hence, the presence or absence of oxygen alone does not correlate with the optical memory effect. Some other or
additional impurities must be involved. Carbon, hydrogen and silicon atoms are candidates for participating in the memory effects.

**Table 3-4** List of GaN samples from Dr. Myers with different oxygen concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen pressure (Torr)</th>
<th>Oxygen concentration (cm$^{-3}$)</th>
<th>Hall data N (cm$^{-3}$)</th>
<th>Memory effect?</th>
</tr>
</thead>
<tbody>
<tr>
<td>00103</td>
<td>2×10$^{-10}$</td>
<td>~1×10$^{16}$</td>
<td>1.2×10$^{16}$</td>
<td>No</td>
</tr>
<tr>
<td>00124</td>
<td>1×10$^{-9}$</td>
<td>~5×10$^{16}$</td>
<td>2.8×10$^{16}$</td>
<td>No</td>
</tr>
<tr>
<td>00105</td>
<td>4×10$^{-12}$</td>
<td>&lt;5×10$^{14}$</td>
<td>~5×10$^{14}$</td>
<td>No</td>
</tr>
<tr>
<td>0078</td>
<td>7×10$^{-10}$</td>
<td>~2×10$^{17}$</td>
<td>2×10$^{17}$</td>
<td>No</td>
</tr>
</tbody>
</table>

**3.5.3 Optical Transmission Measurements**

Optical transmission is also a useful tool to investigate the quality of semiconductor materials. An undoped GaN sample grown on an unpolished SiC substrate was used in this investigation. First, the backside of this sample was polished using diamond paste in order to avoid the light scattering on the unpolished side of the sample. A transmission spectrum was acquired at room temperature. Memory effect patterns were written on the area under investigation and a transmission spectrum was acquired again. The results were shown in Fig. 3-16. A transmission spectrum for a bare SiC substrate was also taken at room temperature. There is no observable change between the transmission spectra before and after the memory effects were written. The SiC substrates would absorb light with wavelength shorter than 413 nm, which corresponds to its bandgap energy. Therefore, optical memory effects do not cause any
observable changes in transmission spectra of the samples. Since optical transmission measurements are not very sensitive to low density defects in the material, it is reasonable that no difference was observed before and after memory effects were written on the sample.

Figure 3.16 Room temperature transmission data before and after memory effects on an undoped GaN grown on SiC substrates
3.6 Summary

In this chapter, qualitative and quantitative observations of optical memory effects were discussed. Samples that exhibit memory effects were grown by metalorganic chemical vapor deposition (MOCVD) by different research groups. Memory effects could be found on samples grown on different types of substrates. However, GaN samples with controlled oxygen doping grown by Molecular-beam epitaxy (MBE) did not exhibit memory effects.

Photoluminescence spectra from samples that exhibit memory effects usually exhibit both strong yellow and blue luminescence. The variation of the ratio of the intensity of the band-edge emission versus yellow luminescence at different optical excitation densities from samples that exhibit memory effects is much higher than those that do not exhibit memory effects. Optical memory effects were found to be flux-dependent effects, which require no lower limit or a very small lower limit of laser power density in order to produce the patterns. At room temperature, the retention time of the effect is longer as the writing flux is higher.

Measurable difference can be observed both in photoluminescence and cathodoluminescence spectra before and after the memory effect patterns were written at room temperature. The emission intensity of yellow luminescence is higher after the patterns were written. Optical memory effects are more dramatic at 77K. At this low temperature (77K), the peak intensity of the blue luminescence decreases after the memory effect patterns were written. Optical memory effects can also be observed in
cathodoluminescence (CL) images. An electron beam was also found to produce similar effects on samples that exhibit optical memory effects. The intensity of yellow luminescence in the cathodoluminescence spectra also increases after the patterns were produced. The contrast in CL spectra produced by electron-beam irradiation is very similar to that produced by optical irradiation.

Heating the samples to about 110 °C can quickly erase the memory effect patterns. The retention time of the memory effect decreases dramatically from 35°C to 110 °C. Removal of the memory effect optically was not achieved after testing several different wavelength of laser light. No measurable difference was found by the optical transmission measurements on samples that exhibit memory effects.

Persistent photoconductivity (PPC) is the other metastable property that is commonly observed in GaN. However, PPC and optical memory effects appear to be arising from two different mechanisms. MBE grown GaN samples with different oxygen concentration were also investigated. The presence or absence of oxygen alone does not correlate with the optical memory effect. Optical transmission measurements on the sample that exhibited memory effects were also investigated and no measurable changes were observed after optical memory effects were written.
CHAPTER 4

OPTICAL MEMORY EFFECT MODEL

4.1 Model for the Memory Effect

The phenomena of optical memory effects were discussed in chapter 3. The goal of this chapter is to provide appropriate models for these memory effects from both a band-diagram and microscopic point of view. This will be done by proposing a few potential models and then eliminating those models that are not consistent with the data. Several different experiments and samples are used to select and refine the model. The end result of this process is a model that is based on luminescence from two transitions \((\text{Si} \rightarrow V_{\text{Ga}}, \text{yellow}; \text{O} \rightarrow V_{\text{Ga}}, \text{blue})\) and the movement of hydrogen on and off gallium vacancies \([V_{\text{Ga}}, (V_{\text{Ga}}H)_2, (V_{\text{Ga}}H_2)^{1-}]\).

The increased intensity of the yellow luminescence from samples that exhibit memory effects was considered to be the cause of the memory effects. Three different models that can explain an increase in yellow luminescence are shown in Figure 4.1. An increase in the number of yellow luminescence emitters in the sample can result in higher yellow luminescence intensity, as shown in Model I in Figure 4.1.1. Another possibility is that the rate of recombination through a fixed number of yellow luminescence centers...
increases, as shown in Model II in Figure 4.1.2. Model III assumes that the increase of
the yellow luminescence is caused by a decrease in the rate of luminescence through
other competing deep defects levels. This will result in more carriers recombining
through the yellow luminescence centers and higher yellow luminescence intensity, as
shown in Figure 4.1.3.

All three models can explain the increase of the yellow luminescence. With
additional data, we can eliminate two of the models. For example, annealing the sample
at relative low temperature (~100°C) compared to the growth temperature (~1000°C)
erases the patterns. If the first model was correct, then the low temperature annealing
would likely eliminate all the yellow luminescence, which does not happen. The second
model, based on the change in the recombination processes, would be quite unusual given
that the experimental conditions are the same before and after the patterns are written.
The apparent change in radiative lifetime is usually due to competitive processes, not
changes in the kinetics (rates) of the process in question. The first two models both
assume that only one deep defect is responsible for the memory effect. However, several
deep level defects in GaN have been identified in the literature and multiple levels are
likely to be involved in the process.

From the findings in chapter 3, samples that exhibit memory effects all exhibit
both blue luminescence (2.8 eV) and yellow luminescence (2.2 eV). Low temperature
photoluminescence spectra before and after the memory effects, shown in Figure 3.10,
indicate the blue luminescence centered at about 480nm decreases and the yellow
luminescence increases. This evidence strongly supports the third model proposed in Figure 4.1.3.

A more detailed version of the third model is shown in Figure 4.2. The yellow luminescence is caused by transitions from a shallow silicon donor level to deep acceptor levels, which originates from isolated and hydrogenated gallium vacancies. The energy levels for the isolated and hydrogenated gallium vacancies were found to be at about 1.1 eV above the valence band. Both $V\text{Ga}\cdot\text{H}$ and $V\text{Ga}\cdot\text{H}_2$ complexes have levels in the bandgap only slightly lower (by 0.1 – 0.2 eV) than isolated gallium vacancies, as shown in Figure 1.4.

The blue luminescence originates from transitions from the substitutional oxygen donor ($O_N$) level, which is at 0.25 eV above the conduction band, to isolated and hydrogenated gallium vacancies. The relationship between blue luminescence and oxygen have been reported in literature by several different groups.

Up to four hydrogen atoms can bind to a gallium vacancy to form complexes. However, researchers have found that complexes containing more than two hydrogen atoms are unstable in n-type GaN. Isolated gallium vacancies and hydrogenated gallium vacancies with up to 2 hydrogen atoms can be found in the n-type GaN. Some of these gallium vacancies will have substitutional oxygen atoms in the neighboring nitrogen sites. Some of these gallium vacancies would form defect complexes with oxygen and some will not due to the passivation by hydrogen atoms. The recombination between the substitutional oxygen donor ($O_N$) levels and the hydrogenated gallium vacancies will be efficient and result in the blue luminescence from the GaN.
Figure 4.1.1 Model I - The yellow memory effect is caused by an increase in the number of yellow luminescence centers.

Figure 4.1.2 Model II - The yellow memory effect is caused by an increase in the recombination rate of the yellow luminescence centers, while the number of the centers stays the same.

Figure 4.1.3 Model III - The yellow memory effect is caused by the decrease of the number of the other competing recombination centers which result in more recombination through the yellow luminescence emitters.
Figure 4.2.1 Transition model for the sample before memory effects. Yellow luminescence is caused by Si donor level to isolated and hydrogenated Ga vacancies. Blue luminescence is caused by transitions between oxygen and isolated and hydrogenated Ga vacancies.

Figure 4.2.2 Transition model for the sample after memory effects. Some hydrogenated Ga vacancies lose hydrogen and form complex with the some oxygen. Therefore, blue luminescence decreases and yellow luminescence increases.
Hydrogenated gallium vacancies are stable in the undoped GaN due to the large energy needed to remove hydrogen (~3 eV). However, ultraviolet photon excitation and/or a high-energy electron beam can provide enough energy for the removal of the hydrogen from the hydrogenated gallium vacancies. By removal we mean the displacement of the hydrogen atoms from its bond with gallium vacancies to a nearby interstitial site. Once hydrogen atoms are removed from the complexes, they will become isolated gallium vacancies and more negatively charged compare to the previous hydrogenated gallium vacancies. When an oxygen atom occupies the neighboring nitrogen site, the isolated gallium vacancy can form a defect complex with it. This will result in more gallium vacancy-oxygen defect complexes in the material.

Gallium vacancies-oxygen complexes ($V_{Ga}$-$O_N$) will induced a deep acceptor level at 1.1 eV above the valence band. Therefore, the transition between the conduction band and this acceptor level can also contribute to the yellow luminescence. Therefore, the intensity of yellow luminescence will increase due to the formation of the $V_{Ga}$-$O_N$ complexes. At the same time, the amount of the substitutional oxygen (O$_N$) decreases and therefore decreases the intensity of the blue luminescence. The net effect can be explained as the yellow memory effect patterns observed under the read condition.

After the memory effects were written, the configuration gradually returns to its initial condition. The microscopic explanation of this relaxation is that the $V_{Ga}$-$O_N$ complexes will break apart and the memory effect pattern will disappear after the defect relaxes to its original configuration.
4.2 Experimental Support for the Proposed Model

The proposed model in the previous section was based on information of deep level defects in the literature. Experimental support of the model is very important. Several experiments were done and the results were consistent with the proposed model. Hence, we can divide these experiments into three major categories: (1) thermal activation energy, (2) impurities, and (3) doping levels.

4.2.1 Thermal Activation Energy

At room temperature, the photoluminescence within patterns was investigated by taking spectra at the read condition before and after writing a pattern on the samples. The result was shown in Figure 3.10. The peak intensity at 550 nm increased significantly after writing. The enhanced yellow PL peak was consistent with visual observations. After writing, the yellow peak intensity decreases slowly with time. At room temperature, the peak intensity returned to its initial value and the yellow memory patterns disappeared after several hours. This decay of the yellow luminescence was only observed in samples that do not exhibit optical memory effects. In chapter 3, heating up the sample to 110 °C was found to erase the memory effects and the retention time was shorter when the temperature was higher. Therefore, monitoring the decay of the yellow peak intensity at various temperatures can provide key kinetic information of this metastable defect and help to develop a good model.
Five different temperatures were chosen and the decay of the yellow peak intensity was recorded as a function of time, as shown in Figure 4.3.1. Temperatures lower than 35°C were not chosen because the decay rate was too slow. At temperature higher than 60°C, the decay rate is too high for taking accurate measurements. Many decay processes are exponential decay that can be best analyzed by using a logarithmic scale plot, as shown in Figure 4.3.2. However, fitting the data into a simple exponential equation did not provide a good fit. A stretched exponential function was necessary to analyze the data, which is commonly used to study persistent photoconductivity.\textsuperscript{43,44}
Figure 4.3.1 Decay of the photoluminescence peak intensity at 550 nm after the patterns were created at various temperatures (a) 35°C (b) 45°C (c) 50°C (d) 55°C

Figure 4.3.2 Modified plot of the decay of the photoluminescence peak intensity at 550 nm under the same condition as Figure 4.3.2 in a log scale plot.
The central feature of the stretched exponential function is that the time constant is not a single value. Non-identical values of physical parameters at different locations in the material results in a distribution of the time constant, which can be apply to the following equation:

\[
I(t) = \int_{0}^{\infty} f(\tau) \exp\left[-\frac{t}{\tau}\right]
\]

(4-1)

where \( f(\tau) \) is a distribution of the contributing time constants. The above stretched exponential function can be expressed as:

\[
I_{\text{mem}}(t) = I_{\text{NO}} + (I_{0} - I_{\text{NO}}) \times \exp[-(t / \tau)]^{\beta}
\]

(4-2)

where \( I_{\text{NO}} \) is the PL intensity when there is no memory effect, \( I_{0} \) is the initial yellow peak intensity, \( \tau \) is the time scale of the process, and \( \beta \) is the deviation from a single exponential decay.

A comparison between the simple exponential and the stretched exponential can provide information about the stretched exponential. Figure 4.4.1 and 4.4.2 are results from a stretch exponential function with log scales and linear scales, respectively. The stretched exponential function used is described as follow:

\[
F(X) = 1 - 0.99 \exp[-X^{\beta}]
\]

(4-3)

Three values of \( \beta \) with values of 1, 0.8 and 0.5 were selected. Compared to the simple exponential function (\( \beta=1 \)), the stretched exponential changes more rapidly at shorter times and more slowly at longer time. The word “stretched” comes from the stretch of the function at longer times. More detailed information about the stretched exponential can be found in Ref. 30 and 52.
Figure 4.4.1 Comparison of a simple exponential and a stretch exponential with different $\beta$ value in a log-log scale. (a) $\beta=1$ (a) $\beta=0.8$ (a) $\beta=0.5$

Figure 4.4.2 Comparison of a simple exponential and a stretch exponential with different $\beta$ value in linear scales. (a) $\beta=1$ (a) $\beta=0.8$ (a) $\beta=0.5$
The summary of the stretched exponential analysis of the data in Figure 4.3.1 is presented in Table 4.1 and Figure 4.5. The correlation for each fitting is very close to one, which indicates that using stretched exponential functions results in good fits. The result that $\beta$ is similar throughout the temperature range investigated suggests that the mechanism of the decay is similar as well. The time constant clearly decreases as the temperature increases, which is consistent with the observation of the memory effects.

The temperature dependence of $\tau$ can be described as follow:

$$
\tau = \tau_0 \exp\left(\frac{-\Delta E}{kT}\right)
$$

where $\Delta E$ is the thermal activation energy, $\tau_0$ represents the time constant at 0 degree K. The experimental data for $\tau$ at different temperatures can be fitted by a least square fit and is shown in Figure 4-6. The slope of the fitted curve represents the thermal activation energy $\Delta E$ and the $\ln(\tau_0)$ is the intercept at the y axis. The result of $\Delta E$ is 1.34 and $\ln(\tau_0)$ is $-40.475$. Note that when the temperature exceeds 90 °C, the fitted value of $\tau$ is less than 1 second, which means the pattern would disappear before a PL spectrum can be acquired. This agrees with our observation at elevated temperatures.

This thermal activation energy, which is about 1.34 eV, is close to the calculated formation energy of the following reaction, which is about 1.1eV.\(^{20}\)

$$
(V_{Ga} - O_N)^{2-} \rightarrow V_{Ga}^{3-} + O_N^+
$$

(4-5)

In the proposed model, the memory effects will restore when the defect complexes $V_{Ga}$-$O_N$ are broken apart. Therefore, the model is consistent with the results of this experiment.
**TABLE 4.1** Stretched exponential analysis used to fit the decay of the yellow luminescence.

<table>
<thead>
<tr>
<th>TEMP. (°C)</th>
<th>β</th>
<th>τ (SECONDS)</th>
<th>CORRELATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.60587</td>
<td>1824.753</td>
<td>0.991480</td>
</tr>
<tr>
<td>45</td>
<td>0.66372</td>
<td>382.189</td>
<td>0.994652</td>
</tr>
<tr>
<td>50</td>
<td>0.76306</td>
<td>90.349</td>
<td>0.995469</td>
</tr>
<tr>
<td>55</td>
<td>0.61504</td>
<td>69.527</td>
<td>0.971633</td>
</tr>
<tr>
<td>60</td>
<td>0.75029</td>
<td>49.904</td>
<td>0.979249</td>
</tr>
</tbody>
</table>

**Figure 4.5** Results from the stretched exponential analysis used to fit the decay of the yellow luminescence.
Figure 4.6 Experimental data points (square blocks) and fitted curve (solid line) according to a stretch exponential equation.
4.2.2 The Role of Impurities

In the proposed model, both oxygen and gallium vacancies play important roles. There must be enough hydrogenated gallium vacancies with oxygen at the neighboring nitrogen sites in order for the model to work. Therefore, the oxygen concentration must be sufficiently high in samples that exhibit memory effects.

There are two ways to test the role of oxygen. First, we could ion implant oxygen atoms into GaN thin films that do not exhibit memory effects and look for memory effects from the sample after ion implantation and annealing. However, Zolper et al.\textsuperscript{53} reported a very low activation efficiency for implanted oxygen to be ionized. They also proposed that the implanted oxygen is lighter than nitrogen and is unable to substitute for the nitrogen. Therefore, a significant portion of the implanted oxygen remains in interstitial positions. The other problem is related to the high dose of oxygen that is required and the lattice damage that can occur. Ion implantation of oxygen would create a lot of new problems and is not the preferred choice to test the role of oxygen.

Second, we could evaluate two samples grown from the same reactor, one that exhibits memory effects and one that does not. Secondary Ion Mass Spectroscopy (SIMS) measurements were performed on each of the samples to monitor the oxygen concentration. The results are shown in Figure 4.7. The oxygen concentration difference between the samples does not differ much in the bulk region. However, the one that exhibits memory effects does have a slightly higher oxygen concentration in the film and a much higher oxygen concentration at the front and back surface. This result leads one to believe that the memory effect is a surface effect.
The result from SIMS measurement supports that oxygen atoms play important roles in the explanation of the memory effects.

**Figure 4.7** Secondary Ion Mass Spectroscopy (SIMS) measurement for oxygen on samples that exhibit and does not exhibit memory effects.
4.2.3 Effects of Doping

From chapter 1, we saw that the formation energy of each defect level is a function of the Fermi level of the material. A particular defect level is more likely to occur than another if it has a lower formation energy. Therefore, the likelihood of creating a defect can increase or decrease significantly if the Fermi level shifts.

One way to change the Fermi level is by doping the sample with donor or acceptor atoms. Silicon atoms are the most common intentional donor impurity in GaN. Table 4.2 lists three silicon-doped GaN samples grown on silicon carbide substrates. No memory effects were observed on samples with a silicon concentration in excess of 4.5×10^{18} \text{ cm}^{-3}.

Room temperature photoluminescence spectra at the read condition for each Si-doped sample are shown in Figure 4.8. The intensity of yellow luminescence clearly increases as the silicon concentration increases. At the same time, blue luminescence decreases as the silicon concentration increases. This further supports the proposition that blue luminescence is important for the explanation of memory effects. This result also supports the proposed model, which included two different transitions (yellow and blue).
TABLE 4.2 Relation between Silicon-doping concentration and memory effects.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silicon concentration (cm$^{-3}$)</th>
<th>Memory effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE031</td>
<td>1.3×10$^{18}$</td>
<td>Yes</td>
</tr>
<tr>
<td>SE032</td>
<td>4.5×10$^{18}$</td>
<td>No</td>
</tr>
<tr>
<td>SE033</td>
<td>&gt; 4.5×10$^{18}$</td>
<td>No</td>
</tr>
</tbody>
</table>

Figure 4.8 Room temperature photoluminescence spectra for various Si-doped GaN samples taken at the read condition.
The theoretical calculation of the Fermi level is based on equations as follow:

\[ n_0 = N_C F_{1/2}(\eta) \quad p_0 = N_V F_{1/2}(-\eta - \varepsilon_g) \quad (4-6) \]

\[ \varepsilon = \frac{E - E_C}{k_BT}, \eta = -\frac{(E_C - E_f)}{k_BT}, \varepsilon_g = \frac{(E_C - E_V)}{k_BT} \quad (4-7) \]

\[ N_C = 2\left(\frac{2\pi m^*_{n} k_B T}{h^2}\right)^{3/2} = 2.5 \times 10^{19} \left(\frac{T}{300}\right)^{3/2} \left(\frac{m^*_{n}}{m_0}\right)^{3/2} \quad (4-8) \]

\[ N_V = 2\left(\frac{2\pi m^*_{p} k_B T}{h^2}\right)^{3/2} = 2.5 \times 10^{19} \left(\frac{T}{300}\right)^{3/2} \left(\frac{m^*_{p}}{m_0}\right)^{3/2} \quad (4-9) \]

\[ F_{1/2}(\eta) = \left(\frac{2}{\sqrt{\pi}}\right) \int_0^\infty \frac{e^{1/2}}{[1 + e^{(\varepsilon-\eta)}]} \quad (4-10) \]

\[ N^+_d = \frac{N_d}{1 + 2e^{(E_f-E_d)/kT}} \quad N^-_a = \frac{N_a}{1 + 4e^{(E_a-E_f)/kT}} \quad (4-11) \]

\[ \Rightarrow p_0 + N^+_d = n_0 + N^-_a \quad (4-12) \]

The parameters used in this calculation are summarized in Table 4.3. The result of the calculation is shown in Figure 4-9, in which the Fermi level versus silicon doping density is plotted at various temperatures. Notice that the Fermi level is at mid-gap when the doping concentration is about \(10^{-10} \text{ (cm}^3\text{)}\), which is unusually small compared to other semiconductors. This is because GaN has a large bandgap. Therefore, a few donors inside the material can change the Fermi level dramatically. The other thing to notice is the resulting Fermi level at certain doping concentration is higher when the temperature decreases.
TABLE 4.3 Material properties of GaN for the Fermi level calculation\textsuperscript{54}

\begin{tabular}{|c|c|c|}
\hline
m\textsubscript{n} & 0.20 & E\textsubscript{so} & 0.008 (eV) \\
\hline
m\textsubscript{hh} & 1.40 & E\textsubscript{cr} & 0.04 (eV) \\
\hline
m\textsubscript{lh} & 0.30 & E\textsubscript{d} (Si\textsubscript{Ga}) & 0.027 (eV) \\
\hline
m\textsubscript{so} & 0.60 & E\textsubscript{d} (C\textsubscript{N}) & 0.230 (eV) \\
\hline
\end{tabular}

Figure 4.9 Fermi-level calculations at different Silicon doping concentration at various temperatures.
Silicon atoms are efficient shallow donors with a binding energy of about 27 meV. Carbon atoms are shallow acceptors located at about 0.23 eV above the valence band when located on nitrogen sites. Both of these two impurities can change Fermi level of the material. If we assume that silicon and carbon are the dominant donors and acceptors in these samples, the relation between the Fermi level and the concentration difference of silicon and carbon is shown in Figure 4.10. Formation energies and ionization levels for the various defects in GaN versus Fermi level are also shown in Figure 4.10\(^{17}\). Notice that at about \(E_f = 3.25\) eV, the formation energies of \(O_N\) and \(V_{Ga-O_N}\) are equal. Above that, \(O_N\) will have higher formation energy than \(V_{Ga-O_N}\) complexes. In other words, \(V_{Ga-O_N}\) complexes are more favorable than \(O_N\) in the material at \(E_f > 3.25\) eV. Therefore, if an \(O_N\) has a neighboring \(V_{Ga}\) available, these two point defects will form a defect complex promptly. For \(E_f > 3.25\) eV, intense ultraviolet laser light will have little impact on the formation of the \(V_{Ga-O_N}\) complexes since fewer free \(O_N\) are available.

In a sample with high silicon doping (~\(4.5 \times 10^{18}\) cm\(^{-3}\), Figure 4.11.1) and lower concentration of acceptors (\(Nd-Na>0\)), we would expect the Fermi level to be quite high in the bandgap and the memory effect suppressed. In a sample with lower silicon doping (~\(1.3 \times 10^{18}\) cm\(^{-3}\), Figure 4.11.2) and an acceptor impurity concentration greater than the silicon (\(Nd-Na<0\)), we would expect the Fermi level to be quite low in the bandgap and the memory effect could be observed. This reasoning is consistent with the data from SIMS measurements shown in Figure 4.11 (assuming that the concentration are measured by SIMS is proportional to the electrically active silicon and carbon).
Figure 4.10 Formation energies and ionization levels for the various defects in GaN.\textsuperscript{19} The blue line indicates the relation between the Fermi level and Nd-Na, which is the concentration difference between donors and acceptors.
Figure 4.11.1  SIMs measurement on SE032 (without memory effect)

Figure 4.11.2  SIMs measurement on SE031 (with memory effect)
4.2.4 Other Observations that Are Consistent with the Proposed Model

According to the proposed model, shown in Figure 4.2, both yellow luminescence and blue luminescence are transitions from higher energy defect states to isolated and hydrogenated gallium vacancies. Therefore, the FWHM of yellow and blue luminescence should be comparable and should be around 300 meV. This agrees with observations from the low temperature photoluminescence spectra shown in Figure 3.10.

In chapter 3, controlled oxygen doping of GaN thin films grown by plasma assisted molecular-beam epitaxy (MBE) were investigated. No memory effects were found in any of the samples. Therefore, other impurities must be included in the model. In the proposed model, the availability of hydrogenated gallium vacancies is also important for the sample to show memory effects and the amount of hydrogen available in samples grown by MBE is very limited. This fact also supports the proposed model.

According to the model, the removal of hydrogen atoms (i.e. displacement to an interstitial site) from hydrogenated gallium vacancies induces the memory effects. Therefore, as long as the excitation energy is high enough to remove the hydrogen from the complexes, which requires about 3 eV, the number of the defects complexes created will be proportional to the excitation flux. This agrees with the observation of the memory effects. This high hydrogen removal energy of the hydrogenated gallium vacancies also agrees with the fact that only photon energy higher than 4.0 eV (305 nm) can produce the memory effect and photon with less energy (3.0 eV, 412.5 nm) cannot. The removal of the memory effect is related to the dissociation of \( V_{\text{Ga-O}} \) complexes.
according to the proposed model. Therefore, the retention time of this effect should also be proportional to the writing flux, which also agrees with the observations in chapter 3.
5.1 Summary of Observations

In chapter 3, qualitative and quantitative observations of optical memory effects were reported. Samples grown by different groups and reactors were investigated. Optical memory effects were only observed in samples grown by metalorganic chemical vapor deposition (MO-CVD). Several samples grown by Molecular-beam epitaxy (MBE) were also investigated and did not exhibit memory effects. Memory effects could be found on samples grown on different types of substrates, including sapphire, 6H-SiC and silicon. For samples grown on SiC substrates, memory effects were observed on thin films with thickness range from 0.3 µm to 2.0 µm. This observation suggests that this memory effect does not originate from the substrate interface region.

Blue luminescence (2.8 eV) plays an important role for the memory effect since photoluminescence spectra from samples that exhibit memory effects exhibit both strong yellow and blue luminescence. The other signature for the memory effect is a variation of the ratio of the intensity of the band-edge emission versus yellow luminescence at different excitation densities. The variation is much higher from samples that exhibit memory effects than those that do not exhibit memory effects. Optical memory effects were found to be flux-dependent effects, which require no lower limit or a very small
lower limit of laser power density in order to produce the patterns. At room temperature, the retention time of the effect is longer as the writing flux is higher.

Measurable differences are important for selecting a good model for the memory effects. The emission intensity of the yellow luminescence is higher after the patterns were written. This can be used to explain the yellow memory patterns that were observed. Optical memory effects are more dramatic at 77K. At this low temperature (77K), the peak intensity of blue luminescence decreases after the memory effect patterns were written. Memory effect patterns produced optically can be observed in cathodoluminescence (CL) images. Electron beam was also found to be able to produce similar effects on samples that exhibit memory effects. The intensity of yellow luminescence in the cathodoluminescence spectra also increases after the patterns were produced. The contrast in CL spectra produced by electron-beam irradiation is very similar to that produced by optical irradiation. No measurable difference was found by the optical transmission measurements on samples that exhibit memory effects.

Heating the samples to about 110 °C can quickly erase the memory effect patterns, which is important for applications in practical devices. The retention time of the memory effect decreases dramatically from 35°C to 110 °C. Knowing how to erase optical memory effects optically is crucial for the realization of all-optical memory cells. However, it was not achieved after testing several different wavelengths of laser light [412.5 nm (2nd harmonic of Ti: sapphire), 515 nm (Ar Ion Laser), 825 nm (Ti: sapphire) and 980 nm (Diode laser)].
Samples that exhibit persistent photoconductivity (PPC) were also investigated. The results indicated that PPC and optical memory effects appear to be from two different mechanisms. Molecular-beam epitaxy (MBE) grown samples with different oxygen concentration were also investigated. The presence or absence of oxygen alone does not correlate with the optical memory effects.

**5.2 Summary of the Proposed Model**

A detailed model of the memory effect was presented in chapter 4. Yellow luminescence from samples that exhibit memory effects is caused by transitions from a shallow silicon donor level to deep acceptor levels. These deep acceptor levels originate from isolated and hydrogenated gallium vacancies, which are located at about 1.1 eV above the valence band. Blue luminescence originates from transitions from the substitutional oxygen donor (O\textsubscript{N}) level, which is at 0.25 eV above the conduction band, to isolated and hydrogenated gallium vacancies. Some of these isolated gallium vacancies and hydrogenated gallium vacancies with up to 2 hydrogen atoms will have substitutional oxygen atoms in the neighboring nitrogen sites.

Hydrogenated gallium vacancies are stable in the undoped GaN due to the large energy needed to remove hydrogen (~3 eV). However, ultraviolet photon excitation and/or a high-energy electron beam can provide enough energy for the removal of the hydrogen from the hydrogenated gallium vacancies. Once hydrogen atoms are removed from the complexes, they will become isolated gallium vacancies and more negatively charged compared to the previous hydrogenated gallium vacancies. When an oxygen
atom occupies the neighboring nitrogen site, the isolated gallium vacancy can form a defect complex with it. This will result in more gallium vacancy-oxygen defect complexes in the material, which induce a deep acceptor level at 1.1 eV above the valence band. Therefore, the transition between the conduction band and this acceptor level can also contribute to the yellow luminescence. Hence, the intensity of yellow luminescence will increase due to the formation of the V_{Ga-O_N} complexes. At the same time, the amount of the substitutional oxygen (O_N) will decreases and therefore decreases the intensity of the blue luminescence. The net effect can be explained as the yellow memory effect patterns observed under the read condition.

After the memory effects were written, the configuration will gradually returns to its initial condition. The microscopic explanation of this relaxation is that the V_{Ga-O_N} complexes will break apart and the memory effect pattern will disappear after the defect relaxes to its original configuration.

This proposed model is consistent with most of the observations of the memory effect. Yellow luminescence increases and blue luminescence decreases after the memory effect patterns were written is reported in chapter 3. The thermal activation energy of the erasing process, which is extracted from stretched exponential analysis of the decay of the yellow luminescence at various temperatures, is about 1.3 eV. This number agrees with the energy need to break the V_{Ga-O_N} complexes from theoretical calculation. Secondary Ion Mass Spectroscopy (SIMS) measurements indicate that the oxygen concentration is higher in the sample that exhibits memory effects, which could be used to confirm the importance of the oxygen atoms for the memory effect. Doping
with donors and acceptors can change the fermi level of the sample, and change the favorable configuration of defects at the same time. Combining the results from fermi-level calculations and first-principle calculation of the defect formation energy, $V_{\text{Ga-O}}$ complexes are much more favorable in the case when $E_f > 3.25$ eV. This material should not exhibit memory effect, which is consistent with the observation.

The proposed model was (1) developed through extensive experimental observations; (2) based on theoretical and experimental energy levels of known impurities and defects, and; (3) refined by additional experiments. We believe this is the best model to explain optical memory effects based the experimental results available this time.

**5.3 Future Plans**

Most of the experimental observations from the memory effects agree with the proposed model. However, there may be other models that also support most of the observed results. Several recommendations are discussed here in order to further understand these memory effects.

In the proposed model, oxygen atoms play an important role. Careful control of the oxygen concentration using MOCVD growth techniques could clarify the role of oxygen in the material. Several samples grown by MBE with various oxygen concentrations do not exhibit optical memory effects. It is also recommended that more samples grown by MBE be evaluated since not all the samples grown by MOCVD exhibit this effect. If MBE grown samples indeed do not exhibit memory effects,
impurity atoms incorporated with the MOCVD growth may be the cause of the memory effect. Carefully incorporating different kinds of impurity atoms into the materials by MBE can also help to refine the model. Obtaining more samples with different growth conditions can also help. By doing SIMS measurements on these samples and comparing the difference between samples that exhibit and do not exhibit memory effects, we could further verify the role of oxygen in the explanation of the memory effects.

The intensity change of yellow and blue luminescence is the cause of optical memory effects. Time-resolved photoluminescence measurements on the samples can provide information about any changes in transition mechanisms. Photoluminescence Excitation (PLE) measurement, which can give us the response of transitions at different excitation wavelength, can also help to define a more suitable model.

Besides optical measurements, electric measurements, like Capacitance-Voltage (CV), Current-Voltage (IV) and Hall measurements, could also provide valuable information about the model and expand potential device application of the memory effect if it indeed changes in these electrical properties are discovered.

Finally, erasing the memory effect optically will result in the realization of all-optical memory devices. Therefore, a continuing search for suitable light source that can erase the patterns optically is very important.
REFERENCES:


