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ELECTRICAL CHARACTERIZATION OF DEFECTS IN n-GaN

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor in Philosophy in the Graduate
School of The Ohio State University

By
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********

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ABSTRACT

GaN is a wide gap semiconductor that has already been shown to be highly suitable for light emitting diodes and lasers in the UV-blue-visible spectrum and that shows great promise for microelectronic devices. However, the efficiency of these devices can be very dependent on the electrically active defects present in the material. These defects can generate deep levels within the otherwise forbidden bandgap that can act as carrier traps as well as recombination-generation centers. The aim of this work has been to characterize these deep levels throughout the bandgap of n-GaN grown by metal organic chemical vapor deposition (MOCVD) using deep level transient and optical spectroscopies.

The deep level spectrum of MOCVD-grown n-GaN presents traps at $E_c - E_t = 0.58, 0.61, 1.35, 2.64-2.80, 3.04$ and $3.22$ eV, with concentrations varying from $10^{13}$ to $10^{16}$ cm$^{-3}$. In general, changes in the concentrations of all these deep levels are not followed by equivalent changes in the TD density, suggesting a point defect origin for all these levels. Indeed, the 0.58 and 1.35 eV are found to be directly related to point defects or complexes of point defects, since they are highly passivated by hydrogen incorporation but no changes are found in the electrical activity of the threading dislocation (TD)-related regions. Moreover, one or both of these deep levels behaves as a recombination-generation center, indicating that point defects likely play a role in current leakage in n-...
GaN devices. The 2.64-2.80 eV band of states behaves both as an electron and hole traps. Moreover, its behavior under hydrogenation indicates that it is most likely related to \(V_{Ga^3-}(V_{Ga-H})^2\) and \((V_{Ga-H_2})^-\) complexes. This band of states shows the carrier capture kinetics of an ideal extended defect, and thus is most likely found decorating the TDs. Hence, it may be responsible for current leakage and carrier trapping properties conventionally assigned to these extended defects. Finally, the 3.22 eV level has been found to be related to extrinsic \(Mg_{Ga}\) point defects that arise as a result of diffusion of residual Mg found in the growth reactor, element that is commonly used as a p-type dopant.
TO MY PARENTS

FOR TEACHING ME TO APPRECIATE KNOWLEDGE
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CHAPTER 1

INTRODUCTION

1.1 Motivation for the study of GaN

Over the past few years the role of III-V nitrides in optoelectronic applications [1] has become very important. The primary reason has been the large tunable bandgap associated with the Al-Ga-In-N system, which spans the entire visible-blue-UV spectrum (Figure 1(a)). Indeed, InN has a bandgap of ~1.9 eV (red emission) while GaN has a ~3.4 eV bandgap (blue emission), and with ternary Ga_xIn_{1-x}N compounds any emission in the visible spectrum can be obtained. While arsenides and phosphides produced increasingly brighter LEDs in the red-yellow spectrum over the 70s to the 90s, the nitrides took over the green-blue range in the mid-late 90s (Figure 1(b)), and III-nitride LEDs are currently commercially available. The other main advantage of nitrides over other wide gap materials arises from their stronger chemical bond which yields a large resistance to degradation from large electric currents and intense light illumination, which are usually found in the active region of an LED and specially of a laser.
Figure 1.1: a) Bandgap energy-lattice constant diagram for wide bandgap materials. Sapphire (not shown) has a lattice constant of ~2.77 Å (courtesy of J. Schetzina). b) Evolution of visible LEDs. An incandescent tungsten filament emits ~20 lumens/watt. After 1994 the nitrides took over the green-to-blue range. The upper and lower bars in 1997 correspond to laboratory and production performance, respectively (after [1]).
However, it took several decades for the nitrides to evolve to a state where they could be applied to commercial LEDs. While GaN metal-insulator LEDs were first demonstrated in 1971 by Pankove et al. [2], issues like growing smooth films (growth modes could not be controlled), controlling the n-type conductivity as well as producing p-type conductivity, and choice of substrates were obstacles that blocked the nitride development in favor of other wide bandgap semiconductors. It was not until 1986 that Akasaki and Amano [3] grew the first smooth surfaces of GaN films and controlled the n-type doping (using SiH₄), providing a significant improvement in both the electrical and luminescent properties of these films. In 1989, Akasaki and Amano were able to use Mg as an acceptor (after reactivating them) producing a film with enough hole concentration to allow the first p-n junction blue LED [4]. Finally in 1992, Nakamura showed superior hole concentration by thermal annealing after growth. All these developments led to the brighter LEDs by Akasahi, Amano and others in 1992, which culminated in plans for mass production of a bright blue LED by Nichia Chemical Industries in Japan. Green InGaN LEDs can already be found in traffic lights, and combined with blue InGaN and red AlGaAs LEDs are already used in large flat panel displays (e.g. used by Spice Girls in their concerts).

However, some issues regarding structural defects in nitrides have not been solved yet. As seen in Figure 1.1(a) there is a lack of suitable substrates for GaN growth (see Section 1.2). Thus, substrates with large lattice-mismatch, such as SiC (3 %) and sapphire (15 %), have to be used. This allows for the large threading dislocation (TD) densities that are still found in commercial GaN/sapphire LEDs (Figure 1.2) [5]. Indeed, TD
densities of the order of $\sim 10^{10}$ cm$^{-2}$ have been observed by transmission electron microscopy (TEM) in the active region of GaN LED's commercialized by Nichia [6], the leading GaN LED and Laser company. This contrasts with the small TD densities ($<10^4$ cm$^{-2}$) that III-V arsenide and phosphide-based optoelectronics can withstand before rapid device degradation. Even though such high TD densities are currently found in commercial GaN LEDs, optical emissions from this material are remarkably high. Such large optical emissions have been attributed to a combination of the small minority carrier diffusion length ($\sim 50$ nm) [5] together with the favorable TD geometry found in GaN, which minimize dislocation-related degradation. Under these conditions, minority carriers can recombine with majority carriers prior to undergoing non-radiative recombination.
events at a dislocation, producing reasonable optical emissions. However, TDs are still an important source for device degradation [5]; indeed GaN lasers with long lifetimes (~10,000 hours) have only been demonstrated so far in low TD density GaN grown by lateral epitaxial overgrowth (LEO) (see Section 1.2). Hence, there is a large push for developing GaN substrates for homoepitaxy since LEO is limited in its application to small growth areas.

While the application of III-nitrides to optoelectronic has experienced a substantial development, nitride microelectronics have seen a much slower evolution. Indeed, III-nitrides are highly attractive for high power and high temperature microelectronic devices. Among the most interesting properties of GaN are the high breakdown field ($2.7 \times 10^6$ V/cm), the high saturation velocity ($2.7 \times 10^7$ cm/s) and the excellent chemical stability [7]. In addition, GaN can be grown on SiC (~3 % lattice mismatch); since SiC has a very large thermal conductivity (~4x10^7 W/cm-K) GaN/SiC devices have a thermal impedance close to that of SiC, which makes this tandem very attractive for high temperature applications. All these properties taken together indicate that III-nitrides have great potential for high power microelectronic applications operating at high temperature [7]. However, the development of this area is at an earlier stage than optoelectronics, and several issues need to still be addressed in order to allow the full development of GaN-based microelectronic devices. These include the large detrimental effect observed in FET characteristics due to trapped carriers (Figure 1.3). Indeed, while it is currently believed that such electrically active defects play a very important role,
Figure 1.3: Ids-Vds characteristics from a GaN JFET grown on sapphire. The curves were measured after 5 m illumination (solid lines), and in the dark (dashed lines). Note that Ids collapses at Vds ~ 25 V due to a partially depleted channel by electrons trapped in the GaN buffer layer below the channel (after [7]).

little or nothing is known regarding deep levels associated with such processes, and what physical defects are responsible for these levels.

In summary, deep levels are now looked at as potential limiting factors. Indeed, as device performance requirements become more demanding it is likely they will reveal themselves as an important issue that will need to be addressed. In particular the transition from LEDs to lasers will likely be affected by the impact of traps on device performance. Indeed, as it was mentioned above, efficient nitride lasers can only be grown on LEO material where lower TD densities are found, but it is desirable that they
can be grown on much larger areas. In addition, as electronic devices are being developed, traps are already known to be detrimental in general, and will likely play an important role as new devices arise.

1.2 Background on defects in GaN and motivation for this research

The development of GaN-based devices has been limited by several factors. Perhaps the most obvious of these is the lack of a lattice-matched GaN substrate to support homoepitaxy. Indeed, the growth of single GaN crystals sufficiently large to serve as economical substrates for GaN device fabrication has not been achieved yet, and limits the practicality of this choice of substrate. This is due to the thermodynamic properties of this material, such as the extremely high melting temperature (~2800 K) and very high decomposition pressures at melting, which eliminate traditional growth techniques such as Czochralski or Bridgman growth from a melt. This lack of lattice-matched substrates has led to the use of other substrates such as sapphire and SiC. However, in addition to the difference in thermal expansion coefficient, the ~15 % lattice-mismatch between GaN and sapphire (Figure 1.1(a)), which is commonly used as the substrate, leads to large strain during growth and cooling processes and is responsible for high defect density.

The large lattice-mismatch between GaN and sapphire is believed to be responsible for the high TD densities observed in GaN epitaxial layers. Misfit dislocations and lateral island growth form concurrently during the initial nucleation of GaN on sapphire [8]. At a later stage of the growth the GaN islands coalesce leading to additional generation of TDs [8], which add up to the initial misfit dislocations producing
a highly defective material. The high TD density is believed to be partially responsible for the limitations observed in the performance of GaN devices. As an example, a combination of cathodoluminescence (CL) and atomic force microscope (AFM) studies on GaN buffer layers has demonstrated that GaN regions associated with TDs have reduced bandgap emission intensity, implying that high TD density is likely responsible for non-radiative recombination (in essence, carrier recombination at a trap) [9]. Moreover, in some cases, carrier mobilities in heteroepitaxial n-GaN grown on sapphire have been shown to follow a model where Coulomb scattering by negatively charged extended defects found perpendicular to the current path is the predominant scattering process [10]. This effect can be the result of either the TD acting as a trap itself, or because the TD can enhance the formation of point defects and other related complexes that may act themselves as carrier traps.

A clearer indication of the role of TDs in carrier transport is shown for GaN grown by LEO. In this technique, planar GaN layers (which contain high TD density) are partially masked and then regrown upon. The GaN grown vertically over the mask opening retains the high TD density (>10^8 - 10^9 cm^-2) of the underlying GaN layer whereas the material grown laterally over the mask (away from the unmasked region) has a drastically reduced TD density (~10^6 cm^-2) [11]. P-n junctions grown on the low TD density region show reverse-bias leakage currents that are reduced by over three orders of magnitude compared to the high TD density region (Figure 1.4) [11].

The study of the role of point defects in nitrides and their potential for trap generation is at an even earlier stage. Theoretical studies have shown that different
Figure 1.4: Reverse-bias leakage current for several GaN p-n diodes grown on LEO GaN and on the window region (dislocated GaN) (after [11]).

vacancies and interstitials may be responsible for levels found within the bandgap of GaN and therefore require experimental verification (Figure 1.5) [12]. For example, \( V_{Ga} \) defects have been predicted to generate a deep level at \(~1\) eV above the valence band [13]. Such \( V_{Ga} \) defects are more likely to form in n-type material, and their formation energy is reduced when they complex with other donor impurities such as Si or O [14]. By means of positron annihilation measurements \( V_{Ga} \) defects have been associated with the yellow PL band [15]. This deep level PL emission is observed only in n-type material, which correlates with the lower formation energy calculated for \( V_{Ga} \) defects in n-GaN [14]. Oxygen in a N substitutional site (O\(_N\)) has also been shown to correlate with the
Figure 1.5: Schematic of the levels introduced by point defects in GaN based on theoretical calculations. Different levels arising from the same point defect correspond to different occupation states. V\textsubscript{N} and Ga\textsubscript{i} are donors, V\textsubscript{Ga} is an acceptor, and N\textsubscript{i}, Ga\textsubscript{N} and N\textsubscript{Ga} are amphoteric. Both interstitials and antisites have high formation energies and are therefore unlikely to occur in any significant concentration in GaN (after [12]).

Even though it is likely that point defects play an important role in deep level generation in GaN it is not clear at this point for which levels they are responsible. For example, by means of electron irradiation, V\textsubscript{N} are created in GaN and have been reported to generate a shallow donor at $E_c$-0.07 eV [18], as obtained from temperature-dependent Hall measurements. Electron irradiation of GaN has also been shown to create O\textsubscript{N} which...
are directly related to a deep level PL emission at \(-0.88\) eV [19]. Deep level PL emissions at \(-0.85\) and \(-0.93\) eV have also been reported and by means of magnetic resonance spectroscopy have been assigned to Ga\(_1\)-complexes which were created as a result of electron irradiation [20]. The problem with some of these results is that even though the relation of such point defects to the PL emissions is proved, the actual deep levels involved in the PL emission, including position within the bandgap and concentration, are not known. It is here where techniques such as deep level optical spectroscopy (DLOS) and deep level transient spectroscopy (DLTS) can play an important role.

Thus, the aim of this work is to characterize and quantify the electrically active defects responsible for the electron and hole traps found within the bandgap of n-GaN grown by MOCVD, allowing the determination of the deep level spectrum of this material, which will serve as a basis for future work on III-N alloys and LEO-grown nitrides. The electrical properties of the traps related to such defects will be studied in detail and the electrical and optical signatures of each level will be investigated. Correlation to growth conditions, structural properties and chemical composition will help the identification of the physical sources for these defects, allowing the identification of the chemical species and structural origin of these defects. In particular, the role of TDs and point defects in deep levels formation, and their possible impact on device properties via generation of recombination-generation centers will be addressed. These studies will be complemented by the investigation of the behavior of these defects with post-growth hydrogen incorporation as well as electron irradiation which will further help reveal their physical origin.
1.3 Outline of this Dissertation

This investigation begins in Chapter 2 with a discussion of the physics behind the two main experimental techniques used for this work, which involve the study of changes in junction capacitance due to variations of the concentration of trapped carriers in this region: deep level transient spectroscopy (DLTS) and deep level optical spectroscopy (DLOS). Since the major experimental contribution of this investigation is the design of a DLOS setup, this technique is discussed in some detail. Thus, Chapter 3 shows the application of this technique to a II-VI wide bandgap material, ZnSe/InGaAs, which was used as a test structure for the analysis and understanding of the results obtained by DLOS. In addition, this piece of work produced very interesting results that are discussed in this chapter. Next, Chapter 4 shows a general overview of the additional supporting experimental techniques used to complement the defect spectroscopy focus of this work. Chapter 5 starts the discussion on traps in n-GaN by establishing the impact of the type of junction on the deep level spectrum, and by establishing a correlation between the results observed here and those reported in literature. Trap passivation via hydrogen incorporation is next studied in Chapter 6, and also serves as an aid in the identification of the physical sources of the deep levels. In Chapter 7 the origin of the hole traps in n-GaN is investigated in further detail by means of electron irradiation, and helps identify the role of point defects in deep level formation. Since significant amounts of residual Mg can be present in the MOCVD chamber during n-GaN growth, a study of the role of Mg
incorporation during growth and its impact on defect formation is also presented in Chapter 7 helping in the identification of acceptor states in n-GaN. Chapter 8 then addresses the impact that both TDs dislocations and point defects have on deep level formation, and how some of these levels behave as recombination-generation centers. These results also bring light into the role that given traps play, and how these could explain some of the properties traditionally assigned to the TDs in n-GaN. Finally, Chapter 9 presents the conclusions of this investigation and recommendations for future work.
1.4 References


CHAPTER 2

DEPLETION REGION CAPACITANCE AND RELATED SPECTROSCOPIC TECHNIQUES

In the depletion region thermal and optical emission of carriers causes a transient in the junction capacitance of a p-n or Schottky diode, which provides a highly sensitive way for the determination of the properties of deep levels found in that region. Studying deep levels by depletion region techniques are of great interest because [1]:

1. Measurements of the depletion region capacitance are sensitive to charge transients from deep states found only within such region.

2. The high resolution of a capacitance measurement allows the determination of the trap concentration with a sensitivity of up to five orders of magnitude smaller than the background doping concentration.

3. Thermal or optical emissions can be isolated from other processes due to the lack of carrier capture processes within the depletion region.

4. Depth distribution of traps can be obtained by controlling the bias during carrier filling and/or emission from traps.
Two spectroscopic techniques based on changes in the depletion region capacitance will be discussed here: deep level transient spectroscopy (DLTS) and deep level optical spectroscopy (DLOS), which are respectively based on thermal and optical emissions of carriers from deep levels to either the conduction or the valence band. DLOS allows the study of deep levels found throughout the entire bandgap except the ~0.5 eV region close to the majority carrier band, whereas DLTS can be used to complement the DLOS measurements in the band gap region found close to either the conduction or valence band. However, while DLTS is a well known technique and commercially available, DLOS has been applied little in the past to material characterization and will be discussed here in greater detail.

2.1 Electron and hole traps

The electron occupancy $n_t$ of a carrier trap in a semiconductor is in general given by the rate equation [1]

$$\frac{dn_t}{dt} = a(N_t - n_t) - bn_t \tag{2.1}$$

where $N_t$ is the trap density of states, and $a$ and $b$ are given by $a = c_n + c_p = $ electron gain rate, $b = e_n + c_p = $ electron loss rate; $c_n$, $c_p$, and $e_n$, $e_p$, are the capture and emission rates of electrons and holes. The emission rate includes both the thermally and optically
stimulated contributions $e^h$ and $e^o$. It can be shown that when the trap is initially occupied
when $[1]$

$$n_t(t) = \frac{a}{a+b} N_t + \frac{b}{a+b} N_t e^{-(a+b)t}, n_t(0) = N_t$$  \hspace{1cm} (2.2)$$

and when it is initially empty

$$n_t(t) = \frac{a}{a+b} N_t (1 - e^{-(a+b)t}), n_t(0) = 0$$  \hspace{1cm} (2.3)$$

Thus, the steady state electron occupancy is given by

$$n_t(\infty) = \frac{a}{a+b} N_t$$  \hspace{1cm} (2.4)$$

When electron and hole traps are found in n-type and p-type material respectively, they
are called majority carrier traps. Otherwise they are called minority carrier traps.
Depending on which case we are studying, different processes will prevail. For example,
in an electron trap in p-type material, where $n\sim 0$, one may neglect electron capture, i.e.
$c_n\sim 0$. Since the dominant processes will be both hole capture and electron emission, it can
be seen that by means of Equation (2.4) in steady state: $a = e_p, b = e_n + c_p$ and $c_p > e_n$, and
$p_t = N_t, n_t = 0$ are obtained.
It is interesting to note that in the cases of minority carrier traps, $E_t$ is usually close to the minority carrier band, and the equilibrium occupancy is determined by the interaction of the trap with both bands. Thus, their occupancy cannot be perturbed by just changing the majority carrier concentration. Both the majority and minority carrier concentrations need be controlled, thus making minority carrier traps more difficult to be experimentally characterized.

2.1.1 Impact of trap concentration on the junction capacitance

Assuming a large depletion depth, the capacitance transient due to the change in the electron trap occupancy in the depletion region of a $p^-n$ or $n$-Schottky junction for a single trap is given by [1]

$$\frac{1}{C} \frac{dC}{dt} = -\frac{1}{2N_d} \frac{dn_t}{dt}$$  \hspace{1cm} (2.5)

and by integration of (2.5) for $N_t<<N_d$

$$\frac{\Delta C(0)}{C} \equiv -\frac{N_t}{2N_d} (n_t(0) - n_t(\infty))$$  \hspace{1cm} (2.6)

For optical emission processes only, neglecting thermal emission and capture, and assuming $n_t(0)=N_t$ and steady state conditions, Equations (2.2) and (2.4) give $n_t(\infty)$, which leads to
In the case of a emission from a majority carrier trap, \( n_i(\infty) = 0 \), and by means of Equations (2.2) and (2.6)

\[
\frac{\Delta C(0)}{C} \equiv \frac{N_t}{2N_d} \frac{\varepsilon_n^0}{e_n^0 + e_p^0}
\]  

Thus, by determining the change in junction capacitance during a thermal or optical process, and knowing the dopant concentration in the region, one can obtain the total concentration for a given deep level.

2.2 Deep level transient spectroscopy (DLTS)

DLTS allows the observation of deep levels within the bandgap. However, since this technique relies on thermal emission of carriers only those levels found within \( \sim 1 \) eV from the bands can be probed due to practical equipment and contact limitations with temperature and observation time. The concentration, activation energy and capture cross section can be accurately obtained for the deep levels and help determine the electrical signature of a trap [1]. In addition, the depth distribution within the semiconductor of defects responsible for the deep levels can be obtained by DLTS. The behavior of the DLTS signal can also allow for the discrimination between deep levels generated by
extended versus point defects. We will now briefly describe the general principles in majority-carrier DLTS, where the thermal emission from majority carrier traps is observed. By definition, majority carrier traps are found in the upper and lower half of the bandgap in n-type and p-type semiconductors, respectively. Note that minority carriers can also be studied by means of minority carrier injection DLTS but will not be discussed here [1].

During the majority carrier DLTS experiment a bias applied on the test diode is pulsed between a bias near zero and some reverse bias \( V_r \) with a repetition time \( t_r \) (Figure 2.1(a)). The zero bias condition is held for a time \( t_f \) during which traps are filled with majority carriers. During the reverse bias pulse the trapped carriers are emitted at a rate \( e_n \) producing an exponential transient in the junction capacitance (Figure 2.1(b)). The essence of DLTS is to feed the capacitance transient to a "rate window" which provides a maximum output when the time constant \( \tau = e_n^{-1} \) equals a preset time constant \( \tau_{\text{ref}} \).

As an example let us consider a material with two different traps. These traps will be characterized by a trap signature in the form of a linear plot of \( \ln(\tau) \) vs. \( T^{-1} \) (where \( \tau = e_n^{-1} \)). As the temperature of the diode is increased the emission rate of carriers increases and a peak is obtained in the rate window output when \( \tau \) passes through \( \tau_{\text{ref}} \) for each trap (Figure 2.1(d)). For a given \( \tau_{\text{ref}} \) the peak temperature \( T_{pk} \) is characteristic of each trap and the peak height gives the trap concentration \( N_t \) (Figure 2.1(a)). By repeating the scan using different values for \( \tau_{\text{ref}} \) sets of values of \( e_n \) and \( T_{pk} \) are obtained from which Arrhenius plots of \( \ln(e_n^{-1}T^2) \) vs. \( T^{-1} \) can be generated, and \( E_{\text{act}} \) and \( \sigma_n \) (assumed to be temperature independent, see discussion in 2.3.1) determined for each trap from the slope and y-
Figure 2.1: Schematic with the principles of a DLTS experiment (after [21]).
intercept, respectively (Figure 2.1(b)). Moreover, the measurement can be repeated and averaged for several cycles since time constants ($\tau_{\text{ref}}$) of the order of 1-10 ms can be used, producing a very high signal-to-noise ratio.

2.3 Steady state photocapacitance and deep level optical spectroscopy (DLOS)

Steady state photocapacitance spectroscopy can be used to study optical thresholds and concentrations of deep levels in semiconductors and semi-insulators with bandgaps up to $\sim 10$ eV, limited by light sources and optics. During the experiment, monochromatized light is used as the excitation source and is focused on the junction. Electrons or holes are then promoted from deep levels in the band gap to the conduction band (CB) or valence band (VB), respectively, which creates a capacitance transient that is recorded as a function of the incident light energy. As it was previously discussed, assuming thermal processes to be negligible (i.e. thermal emission rates much smaller than optical emission rates) the steady state photocapacitance of a one-sided junction or Schottky junction can be expressed as [1]

\[
\frac{\Delta C_{ss}}{C} = \frac{N_f}{2N_d} \frac{\sigma_n}{\sigma_n + \sigma_p}
\]

(2.9)

where $N_f$ is the filled deep level concentration, $N_d$ is the dopant concentration, $C$ is the quasi-equilibrium junction capacitance, $\Delta C_{ss}$ is the total change (steady state) in...
capacitance resulting from illumination, and $\sigma_n$ and $\sigma_p$ are the electron and hole optical cross sections, respectively. Provided the junction capacitance is allowed to reach its quasi-equilibrium value in the dark (or by applying a filling voltage pulse), deep levels below the Fermi level in the depletion region of an n-type sample will be filled with electrons prior to illumination. Under a photon flux such that $h\nu < E_g/2$, only electrons from deep levels found in the upper half of the bandgap can be excited into the conduction band, and since in this case $\sigma_p = 0$, the change in steady state photocapacitance produces a direct quantification of $N_t$ for such deep levels using Equation (2.9). However, for illumination with $h\nu > E_g/2$ both electrons and holes can be promoted from a deep level to the conduction and valence bands, respectively. In this case both $\sigma_n$ and $\sigma_p$ have to be accounted for in Equation (2.9) and then the steady state photocapacitance only yields a lower limit for the concentration of those deep levels. Provided $\Delta C_s/C$ increases with excitation energy, all optical thresholds observed in the steady state photocapacitance will yield energy levels with reference to the conduction band for an n-type sample. On the contrary, a decrease in the steady state photocapacitance for $h\nu > E_g/2$ would indicate an emission of holes to the valence band, and the optical threshold (energy level) associated with this feature would then be referenced to the valence band. The concentration of each observed deep level is given by its associated step in the steady state photocapacitance spectrum. See Chapter 3 for applications of this technique.

However, steady state photocapacitance lacks the sensitivity of deep level transient spectroscopy (DLTS), since the measurement is not repetitive and averaged, and $N_t$ can only be obtained with precision for majority carrier traps. Moreover, this technique
provides no information on the spectral shape of the optical cross section that is ultimately the optical fingerprint of the trap. These shortcomings are avoided by performing deep level optical spectroscopy.

In general, for an optical excitation by a photon flux $\Phi(h\nu)$, the optical emission rate of carriers from a given deep level can be written as

$$e_{n,p}^o(h\nu) = \Phi(h\nu)\sigma_{n,p}^o(h\nu)$$

(2.10)

where $\sigma_{n,p}^o(h\nu)$ is the optical cross section for electrons or holes, and $\Phi(h\nu)$ is the photon flux ($\#$photons/area-time). The optical emission rate depends not only on the trap properties (like the thermal emission rate, $e_{n,p}^{th}$, does), but also on the photon flux, and ultimately on the incident photon energy. Thus, what really characterizes the trap is $\sigma^o(h\nu)$. However, measuring the absolute value of the optical cross section is a difficult task, and traps are usually just characterized by the spectral distribution of $\sigma^o(h\nu)$.

The optical cross section provides us with information on ionization energies, electron-phonon interactions and temperature dependence of deep levels [2]. In order to measure $\sigma^o(h\nu)$, a technique with a high sensitivity from repetitive internal averaging, like DLTS, is needed. In DLTS the concept of rate windows has been successfully applied. However, since the optical emission rate is a function of $h\nu$ that same approach cannot be used in an optical spectroscopy equivalent to DLTS. Deep level optical spectroscopy (DLOS) was first proposed in detail by Chantre et al. in 1981 [2]. This technique has
proven to be a powerful tool, with the same sensitivity as DLTS, which can be used to probe deep levels within the entire bandgap in nitrides.

The main feature of DLOS is the study of the capacitance transient at $t\to 0$, i.e. the opposite limit to steady state photocapacitance. Assuming the temperature to be low enough, or the deep levels to be far enough from either the conduction or the valence band, one can neglect thermal emission of carriers. If the deep levels are filled at $t=0$, i.e. $n_i(0)=N_i$, it can be shown that the electron trap concentration $n_i(t)$ becomes [2]

$$\left.\frac{dn_i(t)}{dt}\right|_{t=0} = -\sigma_a^e \Phi N_i$$

and when all deep levels are empty prior to illumination, i.e. $n_i(0)=0$, then

$$\left.\frac{dn_i(t)}{dt}\right|_{t=0} = \sigma_p^e \Phi N_i$$

Moreover, the change in trap concentration due to illumination produces a variation in the junction capacitance which can be expressed as

$$\left.\frac{1}{C} \frac{dC(t)}{dt}\right|_{t=0} \equiv -\frac{1}{2N_d} \left.\frac{dn_i(t)}{dt}\right|_{t=0}$$
Thus, combining Eqs. (2.11) or (2.12) and (2.13) the photoionization spectrum for the electron and hole optical cross sections can be obtained from the change in the photocapacitance transient derivative at $t=0$ as a function of incident light energy. As an example, Figure 2.2 shows $\sigma_p^0(h\nu)$ for a hole trap found at $\sim0.8\ eV$ from the valence band in n-GaN, which is believed to be caused by $V_{Ga}$ and $V_{Ga-H_n}$, and partially responsible for the yellow PL emission (discussed later in Chapters 5 and 6).

Figure 2.2: Hole optical cross section of a trap found at $E_v+0.9\ eV$ in n-GaN believed to be related to $V_{Ga}$. Optical DLOS was used to perform this measurement with a pump beam at 2.80 eV.
The adequate initial conditions to perform the DLOS measurement can be achieved through electrical, thermal or optical excitation (Figure 2.3) [2]. In electrical DLOS a majority carrier pulse is applied on either a p-n junction or Schottky barriers and ensures that traps are initially filled. Using a p-n junction minority carriers can also be injected ensuring the traps are initially empty, and allows the determination of the optical cross section for minority carrier traps. In thermal DLOS, temperature is chosen such that the state is initially filled with electrons or holes. In n-type materials, for example, a temperature high enough is chosen such that states in the upper half of the band gap are emptied. This way $\sigma_p^0(h\nu)$ can be obtained for those states, and $\sigma_n^0(h\nu)$ for the deep states in the lower half band gap. In optical DLOS, optical excitation is used to fill the traps, with an energy $h\nu_{ext}$ such that $\sigma_n^0(h\nu_{ext}) \gg \sigma_p^0(h\nu_{ext})$ or vice versa, which is the case for states far from the middle of the band gap. The three different processes are summarized in Figure 2.3.
Figure 2.3: Different modes for DLOS operation which allow the determination of the optical cross section of deep levels (after [22]).
2.3.1 Determination of trap energies: DLTS vs. DLOS

In this section we first approach the differences in the determination of energy levels of defects by means of DLOS and DLTS. Later on, the deep level emissions measured by photoluminescence (PL) are also addressed, but as it will be evident, comparing PL emissions to results from DLOS and DLTS is not straightforward and it may require designing particular sets of samples and experiments.

Generally, in the energy band diagrams deep states are assigned an energy level \(E_t\) which with respect to the conduction or valence band edges \(E_c\) or \(E_v\) defines the energy required to excite an electron or hole from the state. This approach is valid for an optical measurement, such as DLOS, where the temperature \(T\) is kept constant. However, in DLTS the change in temperature causes a change in the bandgap during the measurement, and as the bandgap varies one or both of the energy separations being measured \((E_c-E_t)\) or \((E_t-E_v)\) also change. To account for this change we need a more detailed understanding of the energy band diagram and the meaning of energy level.

The energy level of a defect is defined as the change in chemical potential required for the formation of a free carrier and an ionized defect, while the chemical potential is defined as the increase in Gibbs free energy per carrier-ionized defect pair at constant temperature and pressure [1]. Thus, it follows that the energy band diagram represents the Gibbs free energies for the pair, and that the thermal emission of carriers from the deep level \(e_n\) at temperature \(T\) can be expressed as [1]
where $\sigma_n(T)$ is the capture cross section, and $\Delta G(T)$ is the energy between the band edge and the state at temperature $T$ and is given by

$$\Delta G(T) = E_e(T) - E_i(T)$$

(2.15)

Since the change in Gibbs free energy is thermodynamically given by

$$\Delta G(T) = \Delta H - T \Delta S$$

(2.16)

where $\Delta H$ and $\Delta S$ are the change in enthalpy and entropy, respectively, Equation (2.16) can be expressed as

$$e_n(T) \propto \sigma_n(T) \cdot T^2 \cdot e^{\frac{\Delta H}{kT}} \cdot e^{\frac{\Delta S}{k}}$$

(2.17)

The change of entropy of the system $\Delta S$ is the result of the change in lattice vibrations on emission of the carrier from the deep level as well as the change in the electronic configuration of the defect. Assuming the capture cross section to be $T$ independent (in general done in DLTS experiments) we see that an Arrhenius plot of $e_n/T^2$ vs. $T^{-1}$ has a
slope proportional to $\Delta H$. Thus, when performing a DLTS measurement, where $T$ is varied, the change in enthalpy $\Delta H$ rather than the Gibbs free energy for the ionization of the deep level (given by Equation (2.17)) is obtained. In contrast, $\Delta G$ is directly obtained from the threshold photon energy in an optical experiment provided it is isothermal (like DLOS). Therefore, DTLS does not in general give the energy position of the deep level and it is necessary to measure values of both $e_n(T)$ and $\sigma_n(T)$ at the desired $T$ to obtain $\Delta G(T)$ from Equation (2.16). Thus, the magnitude obtained from a DLTS measurement is just the thermal activation energy of the level, which can differ from the real energy level by as much as 15% for deep levels with constant capture cross sections. When the capture cross section is $T$ dependent, the difference increases and the thermal activation energy can be as much as three times larger than the energy level [1]. Indeed, at OSU we have shown that the energy level induced by the $V_{Ga}$ in n-GaN is found $\sim E_v + 0.92$ eV, whereas DLTS gives a thermal activation energy of $\sim E_v + 0.87$ eV (<10% smaller than the energy level) indicating that the capture cross section of this level over the DLTS temperature scan (300-400 K) is weakly dependant on $T$.

Physically the difference between the energies obtained by isothermal optical measurement (like DLOS) and the thermally scanned measurement (like DLTS) can be explained by the variation with $T$ of the entropy of the system ($\Delta S$) due to the variation in carrier occupancy of the deep level. Since the carriers are bound to the defect they influence the defect-lattice coupling changing the vibrational entropy. The differences between optical and thermal experiments are usually observed only for deep states. They are not found in shallow hydrogenic donor states where the trapped carrier is only weakly
bound to the impurity by a Coulomb attraction, and the impurity is still bound to the lattice by the usual number of covalent electrons. Thus, when the trapped electron is excited to the conduction band (becoming a free carrier) there is no change in the bonding configuration of the donor which implies $\Delta S = 0$, and $\Delta G = \Delta H = E_c - E_t$.

Summarizing, the energy level is directly obtained from DLOS whereas DLTS only provides the thermal activation energy of the defect. Generally, when performing DLTS, it is assumed that $E_c - E_t = \Delta H$, which implies that the Gibbs free energy and thermal activation energy are assumed equal (only true at $T=0$ K), whereas the capture cross section is also extrapolated to $T=0$ K. In order to obtain the energy level, $e_n(t)$ and $\sigma_n(T)$ (if necessary) have to be measured and accounted for in Equation (2.14). This is a difficult task which can only be realistically done if the thermal capacitance transient has contributions from only one deep level. A possible way to verify whether a DLTS and DLOS energies are the same would be to calculate the deep level concentration (available by both techniques) and make sure they are consistent. In any case, it must be noted that the thermal activation energy and capture cross section (at $T=0$K) still provide a unique electrical signature for a given defect in a semiconductor.

Next, we approach photoluminescence spectroscopy (PL) applied to the determination of energy levels. PL is an isothermal optical technique (provided it is used under low pump beam intensity conditions) and therefore lacks the complexity of analysis involved in thermally scanned techniques. However, PL adds an additional variable since in general a deep level PL emission can be the result of a transition of an electron from $E_c$ to the deep level, between two deep levels, or between a deep level and the valence band.
This is the result of the optical pumping conditions that do not allow in general to control the initial deep level concentration. There are certain approaches that give indications on the nature of the transition. For example, for a transition between $E_c$ and a deep level, when the intensity of the pump beam is increased a blue shift should be observed in the PL deep level emission due to the filling of the bottom of the conduction band which causes electrons found with higher energies in the conduction band to be dominantly captured by the defect (a transition from the conduction band to the deep level). Under such conditions and for low pump beam intensities the energy of the deep level PL emission should be equal to $E_c-E_i$, and to that obtained by DLOS. Indeed, we have reported before at OSU how a deep level found at $E_c-E_i=1.46$ eV by DLOS in n-ZnSe was also observed at $E_c-E_i=1.45$ eV by cathodoluminescence (see Chapter 3) [3]. However, in general the type of transition that is responsible for a deep level PL emission is not known, and comparing the PL energies to those obtained by DLOS is incorrect. Other approaches have to be pursued, such as studying a set of samples with different intensities of a given PL emission, and comparing them to the concentrations of the levels observed by DLOS looking for consistent behaviors. This is actually the approach used by Calleja et al. [4] who were able to assign the yellow PL emission ($\sim 2.2$ eV) in n-GaN to a deep level found at $\sim E_v+1$ eV (or at $\sim E_c-2.4$ eV) observed by DLOS.

In summary, a direct comparison of deep level energies obtained from DLTS, PL and DLOS is incorrect since one has to account for the differences in the physical processes behind the measurements. Regarding PL, unless measurements are done in parallel to DLOS or DLTS on the same samples, it is not possible to correlate deep level
PL emissions to those obtained from DLOS and DLTS on different samples. When it comes to comparing DLTS and DLOS energies, DLOS always gives the actual energy level, whereas DLTS provides the thermal activation energy. However, certain simple precautions can be taken to allow a comparison of the two in a given set of samples: first, comparing the concentration of the levels, which should be similar for the same level; second, similar depth-profile behaviors of the deep levels should be obtained by either technique; third, DLTS measurements should be performed under a fill pulse bias close to the reverse bias and on samples with low doping concentration to avoid the effect that a large electric field in the depletion region has on the thermal activation energy. Ideally, the real energy level should be obtained by DLTS as stated before, but this requires a quite ideal capacitance transient behavior as well as more involved experimental procedures.

2.3.2 Experimental setup of DLOS

In this section the design of a DLOS setup is briefly described. The aim of this work was to design a fully automated experiment which would allow the performance of DLOS measurements with illumination energies of ~0.5-6.0 eV at different sample temperatures. This allows for materials with bandgaps up to 12 eV to be probed.

The setup consists of four main sections: the light source and related optics, the sample chamber, the electronics, and the software (Figure 2.4). A 450 W Xe lamp was chosen as the light source because of its large and smooth UV emission, whereas a 600 W
Figure 2.4: Schematic of the DLOS setup.
quartz-halogen lamp was used for illumination purposes in the IR-VIS region. The light from the lamp is collimated and then focused on a ¼ m high-resolution monochromator. The monochromator uses an automated grating turret which mounts four gratings at once, allowing large automated spectral scans (0.2 to ~2.5 μm). Long-pass filters mounted on an automated filter wheel were used at the output of the monochromator to cut all higher orders. This prevents the generation of false signals due to band to band absorption from the sample. Finally the light is focused on the sample, where light fluxes of the order of \(~10^{15}-10^{16}\) cm\(^{-2}\)s\(^{-1}\) were obtained. Light fluxes were measured by means of a thermopile detector which has a flat spectral response in the region of interest, and is factory-calibrated. All lenses and windows used in this setup had to be UV-grade fused silica to allow large transmission in the UV.

The sample chamber allows thermal scanning between 80 and 400 K and external illumination at the same time. A fast computer-controlled shutter placed on top of the sample chamber allowed the control of the illumination. The photocapacitance measurement was performed using either a Boonton meter at a sampling frequency of 1 MHz or a lock-in amplifier which allowed sampling frequencies lower than 1 MHz. The output voltage was then recorded with two oscilloscopes set at different time scales which allows both fast and slow capacitance transients to be recorded with great precision. The oscilloscopes were triggered from the shutter in order to obtain precise signal timing. Finally, the output from the oscilloscopes was digitally recorded in a computer via a GPIB card. All software was written in LabView and allowed the control of all the components. This is of great importance since some of the DLOS experiments can run for
12 hours. Additional software was developed to study the data, allowing the
determination of trap emission rates, concentrations and optical cross sections by means
of theoretical fitting of the digitalized photocapacitance transients.

All software used for analysis was designed and developed in house using
LabView as the platform. This software allowed the analysis of both steady state and
transient behavior of the photocapacitance transients recorded during the DLOS
experiments and used the mathematical formalism presented previously in this chapter.


2.4 References


CHAPTER 3

DLOS TEST CASE: APPLICATION TO ZnSe/In_{x}Ga_{1-x}As HETEROSTRUCTURES

3.1 Introduction

This chapter presents a detailed study of the deep level spectrum of ZnSe/InGaAs heterostructures. This work allowed us to test both the experimental DLOS setup and the physics and analysis tools that will be later employed to study GaN. ZnSe was chosen for this test study since it is a wide gap semiconductor (E_{g}~2.8 eV) and thus provides the right framework for analysis of traps far from the conduction and valence bands. In addition, substantial information on the electronic properties of ZnSe was available in the literature, providing a good background for testing the validity of our results. Thus, the details on the analysis of the experimental photocapacitance data will only be discussed in this chapter, and will be applied for GaN (Chapters 5 to 9) following the same approach.

3.2 Background on ZnSe

ZnSe and related II-VI semiconductors have received substantial attention for optoelectronic applications in the green-ultraviolet regime of the electromagnetic...
spectrum by virtue of their wide and adjustable bandgaps [1-5]. Typically, ZnSe-based devices are grown on GaAs substrates since the lattice mismatch between ZnSe and GaAs is small (0.27 %), and since GaAs is a readily available substrate material. However, in spite of the relatively good lattice match, the II-VI/III-V interface has been shown to generate performance-degrading defects whose concentrations are highly dependent upon the detailed properties of the II-VI/III-V interface at the monolayer scale [6-14]. There has been substantial work to reveal and solve the complex defect generation issues characteristic of II-VI/III-V interfaces, and a reasonable level of understanding has been achieved. The stoichiometry of the initial ZnSe nucleation layer, as well as the GaAs surface treatment prior to growth also have a strong impact on the structural quality of ZnSe/GaAs, although there is some controversy in this regard [7-11]. For example, Heun et al [10,11] have reported that Se rich vs. Zn rich growth of the initial ZnSe layer reduces the concentration of stacking faults by up to four orders of magnitude, whereas Kuo et al [7-9] have reported that initial Zn treatment of the GaAs surface decreased the concentration of such extended defects by an equivalent amount.

Such sensitivity of interfacial properties and structural defects on nucleation conditions may also be expected to manifest as complex electronic properties. Indeed cathodoluminescence spectroscopy (CLS) has been used extensively to reveal the existence and origin of deep electronic states localized at the ZnSe/GaAs interface as a function of Zn:Se beam pressure ratio (BPR) during nucleation of thin ZnSe epitaxial layers [12-14] These studies indicated a strong dependence of the concentration and spectrum of deep states on BPR in regions close to the interface. Other unrelated work
has focused more on the presence and properties of deep levels within the ZnSe bulk, although these studies were not correlated with the details of the formation of the ZnSe/GaAs interface [15-20]. Such studies of bulk deep levels have primarily utilized conventional DLTS which can probe deep level information from electronic levels having activation energies of less than ~ 0.9 eV from either band edge. For bulk ZnSe, this translates into the middle ~ 1.0 eV of the bandgap being unprobed. However it is this very region that is likely to be most problematic from the viewpoint of recombination since midgap states will have the highest probability for electron-hole recombination.

Over the past number of years, photocapacitance measurements [21] have been applied to wide bandgap systems ranging from ZnSe and GaN to oxides [22-25]. There have been very few reports on the application of such measurements to ZnSe layers [26-29] and none, to our knowledge, that have systematically attempted to correlate the complete deep level spectrum within the ZnSe bulk with interface formation conditions that are already known to dramatically affect the deep level spectrum of interface-localized states and generation of extended defects. Hence this chapter focuses on the study of the bulk deep level spectra within molecular beam epitaxy (MBE) -grown nominally undoped $n$-ZnSe by means of DLOS as a function of interface formation conditions.
3.3 Experiment and analysis procedure

3.3.1 Growth and measurement conditions

The growth of the samples used for this study were performed by A. Franciosi and coworkers at Trieste, Italy. The ZnSe/GaAs heterostructures were grown by solid source MBE in a system with interconnected chambers used for the III-V and II-VI growths. Two μm thick ZnSe layers were grown at 290 °C on GaAs(001) substrates having a 0.5 μm thick As-terminated GaAs(001) buffer layer. For lattice-matching experiments a 1 μm thick As-terminated In_{0.05}Ga_{0.95}As(001) layer was grown following the GaAs buffer layer, prior to ZnSe growth [30]. Although a 4 % In concentration would give lattice matching in bulk alloys, any micron-thick buffer layer is only partially relaxed. We thus used an In_{x}Ga_{1-x}As buffer layer with an In concentration of 4.8 % in order to compensate for the partial character of strain relaxation within the 1 μm thick buffer layer [30]. For simplicity the notation In_{0.05}Ga_{0.95}As will be used throughout the rest of this chapter. For different growth runs, the Zn:Se BPR was varied from 0.1 to 1 and 10 during the initial 2 nm growth of the ZnSe layer producing a composition-controlled interface layer (CIL) which provided a set of ZnSe layers initiated by Se-rich, stoichiometric, or Zn-rich nucleation conditions, respectively [31]. The ZnSe BPR was determined from an ion gauge positioned at the sample location and the Se- or Zn-rich character of the CIL interface was calibrated using in-situ x-ray photoemission spectroscopy [31]. The rest of the ZnSe layer was grown with BPR=1 in all cases.
The ZnSe epitaxial layers were intentionally undoped to increase sensitivity in DLOS measurements. C-V dopant profiling revealed the background doping to be $n$-type, with $n = 2.9 \times 10^{15}$ cm$^{-3}$. Prior to contact deposition, the ZnSe native oxide was removed by chemical etch (1.0 g Na$_2$S$_2$O$_3$ and 0.6 g NaOH in 75 ml of H$_2$O) at 90 °C for 4 min [32]. Semitransparent Schottky front contacts were deposited by evaporation of 80 Å thick Au films after ZnSe native oxide removal. The contact area was 3.33 mm$^2$. A 0.2 mm$^2$, 1200 Å thick Au contact was deposited inside the semi-transparent contact area at a point tangent to its perimeter for electrical contact purposes. In was used as a back contact to $n$-GaAs. I-V and C-V measurements were performed to ensure device quality for DLOS measurements.

Photocapacitance measurements were performed using 450 W Xe and 100 W Quartz-Halogen lamps as light sources using the monochromator-based setup discussed in Chapter 2. Photon fluxes were maintained within the range of $2-7 \times 10^{15}$ sec$^{-1}$ cm$^{-2}$ (calibrated by a thermopile) with an energy resolution of 0.02 eV. The sample temperature was maintained at 100 K to minimize thermal emission from deep states so that to first order only optical emission/capture processes were active. All DLOS measurements were done at zero bias, yielding a depletion depth of $\sim 0.8$ μm from the Au/ZnSe Schottky interface. Prior to photon excitation, the samples were allowed to relax in the dark for 10 sec at 0 V bias until the capacitance reached the quasi-equilibrium value. The DLOS experiments were performed by measuring the photocapacitance transients as a function of optical excitation energy from 1.0 to 2.86 eV. The photocapacitance transients were digitally recorded as a function of incident photon...
energy within time windows of 10 msec to 10 sec after the onset of illumination. The steady state photocapacitance, \( \Delta C_{ss} = C(\infty) - C(0) \), was used to obtain the initial trapping spectrum and for calculating trap densities. The complete transients were used to obtain trap energy levels with greater precision. The analysis details are described in the next sections.

3.3.2 Steady state photocapacitance measurements and analysis

Figure 3.1 shows a typical steady state photocapacitance spectrum obtained for the ZnSe/In_{0.05}Ga_{0.95}As/GaAs BPR=1 sample which will be used to first demonstrate how the different characteristics of the deep levels are extracted from photocapacitance measurements. The concentration of each observed deep level is given by its associated step in the steady state photocapacitance spectrum as shown in this figure and can be obtained following the procedure established in Chapter 2. This procedure will be followed in the analysis of the deep level concentrations presented in Section 3.3.

3.3.3 Transient photocapacitance analysis

While the steady state photocapacitance spectrum provides information on the concentration of the deep levels and a reasonable estimate of their position in the bandgap, the energy levels (i.e. optical threshold energies) can more accurately be obtained via analysis of the photocapacitance transients themselves. Since this is not
Figure 3.1: (a) Steady state photocapacitance spectrum obtained at T=100K for ZnSe on In$_{0.05}$Ga$_{0.95}$As/GaAs with initial BPR=1 showing, on a logarithmic scale, how both optical threshold energies and concentrations are obtained for the observed deep levels. The ZnSe near band-edge emission can be observed at ~2.74 eV. (b) Same spectrum plotted in a linear scale showing more clearly the 1.90 eV level.
commonly used [22], we present in this section an example of such analysis for a typical set of photocapacitance transient data from the ZnSe/In_{0.05}Ga_{0.95}As/GaAs BPR=1 sample.

From the derivation presented in Chapter 2 the photocapacitance transient evaluated at the onset of illumination (t=0) can be expressed as [33]

$$\frac{1}{C} \left. \frac{dC}{dt} \right|_{t=0} = \frac{N_t}{2N_d} \phi (\sigma_n + \sigma_p)$$

(3.1)

where $\phi$ is the photon flux, $N_t$ is the filled deep level concentration, $N_d$ is the dopant concentration, $C$ is the quasi-equilibrium junction capacitance, and $\sigma_n$ and $\sigma_p$ are the electron and hole optical cross sections, respectively. Thus, assuming $\sigma_n$ to be dominant, the onset for the optical cross section can be obtained by evaluating the derivative of the photocapacitance transient as a function of incident energy. Each level will generally produce a photocapacitance transient that is dominant over a particular time window according to its characteristic emission rate. This fact can be exploited to obtain more accurate optical thresholds by avoiding screening effects from other levels, which can affect more usual steady state photocapacitance measurements. To demonstrate this approach Figure 3.2 shows photocapacitance transients obtained for three different photon excitation energies (1.3, 1.7 and 2.1 eV). These incident photon energies were chosen to ensure that the contributions to the photocapacitance transient from each of the deep levels detected in the steady state photocapacitance (Figure 3.1) could be clearly observed. When a 1.3 eV photon energy is used only the 1.15 eV level should be observed. However, due to the small concentration of this level in this sample (see
Figure 3.2: (a) Photocapacitance transient for three different incident photon energies from the ZnSe layer grown on In$_{0.05}$Ga$_{0.95}$As/GaAs with initial BPR=1. (b) The inset shows how the transient at $\nu=1.7$ eV saturates only within the first few msec after illumination due to the 1.46 eV level contribution.
Section 3.3, the photocapacitance transient is difficult to resolve for this BPR=1 sample (later we will show that this level is very dependent on lattice-matching) (Figure 3.2(a)). At an incident photon energy of 1.7 eV (Figs. 3.2(a) and (b)) the transient saturates within a time window of ~2 ms due to the excitation of the 1.46 eV level. Finally, under 2.1 eV illumination energy the transient shows the contribution from the 1.46 eV level at short times and a new slowly growing addition within a much larger time window (~5000 ms). This new contribution to the photocapacitance transient is now from the 1.90 eV level. Note that all levels with optical threshold energies less than the incident photon energy will be excited.

Following Equation (3.1), Figure 3.3 shows the derivative of each transient as a function of photon energy at the beginning of the time windows over which the deep levels were observed, from which the optical threshold energies were obtained. For a time window of 0 to 1 ms a sharp onset can then be observed at 1.46 ± 0.02 eV (Figure 3.3(a)), correlating well with that obtained from the steady state photocapacitance spectrum. For a longer time window, from 20 to 200 ms, another onset at 1.90 ± 0.05 eV can be seen in Figure 3.3(b). Equivalent results regarding the 1.46 and 1.90 eV levels were obtained for all samples by this technique, as will be discussed in the remaining sections.
Figure 3.3: Photocapacitance transient derivatives obtained at $t=0$ as a function of incident photon energy from a linear regression fitting to the photocapacitance transients within different time windows for the ZnSe layer grown on In$_{0.05}$Ga$_{0.95}$As/GaAs with BPR=1. Time windows of 0 to 10 msec and 20 to 200 msec were used for (a) and (b) respectively. The inset in (b) shows a magnified view of the photocapacitance transient derivative where the 1.90 eV onset can be more clearly seen.
3.4 Results and discussion

3.4.1 The effect of the initial ZnSe nucleation

We now focus on the effect of the BPR during nucleation and initial growth of the ZnSe layer. For this purpose we investigated three ZnSe samples grown with initial BPR's of 10, 1 and 0.1 on In_{0.05}Ga_{0.95}As/GaAs. Note that all photocapacitance spectra shown in this chapter were plotted for $2N_d\Delta C/C$ in order to account for changes found in the background doping concentration from sample to sample. As shown in Figure 3.4, the BPR has a large impact on the magnitude of the photocapacitance spectrum. The same deep levels at $E_c-E_t = 1.15, 1.46$ and 1.90 eV were found for all three BPR's. However, the sample grown under Se-rich conditions (BPR=0.1) showed a steady state photocapacitance spectrum with a smaller magnitude than both the stoichiometric (BPR=1) and Zn-rich (BPR=10) grown samples. The concentrations of the three levels for the three BPR's are shown in Table 3.1 and were extracted from the steady state photocapacitance as explained in Section 3.2.2. The 1.15 eV level concentration showed no dependence on BPR since the small variation observed in Table 3.1 is within our experimental error. The 1.90 eV level concentration was also unaffected by the BPR as seen in Table 3.1.

Although the 1.15 eV level does not show a clear dependence on BPR, it correlates well with a CLS emission at $\sim$1.14 eV reported by Raisanen et al [12,13] that has been associated with a Se vacancy. However, for that study the BPR was varied.
Figure 3.4: (a) Steady state photocapacitance spectra of ZnSe grown on In_{0.05}Ga_{0.95}As with initial BPR=10 (dotted line), 1 (solid line) and 0.1 (dashed-dotted line) measured at 100 K. (b) Magnified view of the same spectra for illumination energies of 1 to 2.4 eV, where the 1.15, 1.46 and 1.90 eV levels can be more clearly observed. Note that in the sample grown with BPR=0.1, the 1.90 eV optical threshold energy is clear since the 1.46 eV level has a smaller contribution to the steady state photocapacitance due to its smaller concentration for that BPR condition. For all BPR’s the 1.90 eV optical threshold energy was more accurately obtained following the procedure shown in Fig. 3.3.
Ec-Et = 1.15 eV
± 0.05 eV)
Ec-Et = 1.46 eV
± 0.02 eV)
Ec-Et = 1.90 eV
± 0.05 eV)

<table>
<thead>
<tr>
<th>System</th>
<th>Ec-Et = 1.15 eV</th>
<th>Ec-Et = 1.46 eV</th>
<th>Ec-Et = 1.90 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe/ZnSe BPR=0.1/In0.05Ga0.95As/GaAs</td>
<td>4x10^{12}</td>
<td>8x10^{12}</td>
<td>3x10^{13}</td>
</tr>
<tr>
<td>ZnSe/In0.05Ga0.95As/GaAs</td>
<td>7x10^{12}</td>
<td>5x10^{13}</td>
<td>3x10^{13}</td>
</tr>
<tr>
<td>ZnSe/ZnSe BPR=10/In0.05Ga0.95As/GaAs</td>
<td>3x10^{12}</td>
<td>6x10^{13}</td>
<td>4x10^{13}</td>
</tr>
</tbody>
</table>

Table 3.1: Concentration (cm^{-3}) of deep levels present in ZnSe grown on In_{0.05}Ga_{0.95}As/GaAs with initial BPR's of 0.1 (Se rich), 1 and 10 (Zn rich).

throughout the entire ZnSe layer, whereas we are actually probing a 2 µm thick stoichiometric ZnSe layer grown on a 2 nm thick non-stoichiometric layer. Thus, although we do not see the direct effect of BPR on the 1.15 eV level, this level may still be related to such a point defect. A similar reasoning can be used with the 1.90 eV level whose concentration shows no trend with BPR, but correlates well with a CLS emission at ~1.9 eV previously reported in thermally annealed ZnSe [14]. This emission was associated to a Zn vacancy or outdiffused Ga_{Zn} substitutional defects. Annealing of the DLOS samples may clarify this point and a report in this regard may follow in the future if relevant results are obtained.

In contrast to the 1.15 and 1.90 eV level, the 1.46 eV level [28,29,34] showed a strong dependence on initial BPR within the ZnSe bulk (Figure 3.4). As seen in Table 3.1, the trap concentration for the 1.46 eV level decreased by a factor of ~8 for a Se-rich vs. Zn-rich nucleation conditions. This behavior clearly indicates a systematic relation

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between the initial BPR and the observed deep level emission. The BPR is also known to affect the stacking fault density and possibly the density of Se and Zn vacancies. It is therefore possible that the variation in the concentration of the 1.46 eV level with Se concentration might be related to defect complexes involving Se vacancies. This explanation contrasts that one used above for the 1.15 eV level, suggesting that the origin of the 1.46 eV level is of a more involved nature than that of the 1.15 eV. However, its behavior also correlates well with TEM studies performed by Heun et al [11] on samples grown in the same MBE system, where it was reported that Se-rich growth of the ZnSe CIL reduces the presence of Shockley stacking fault pairs by three to four orders of magnitude and Frank stacking faults by a factor of 5 to 10. It also is interesting to note that the 1.46 eV level is very difficult to control since both BPR and lattice matching of the II-VI/III-V interface (see Section 3.3.2) have a strong effect on its concentration. Since this level is present in the largest concentration for both the BPR=10 and 1 samples we now discuss its properties in greater detail.

In general, for a single deep level contributing to the photocapacitance transient, the change in capacitance can be written as [33]

\[ \Delta C(t) = \Delta C_{ss} \left(1 - e^{-t/e_n}\right) \]  

(3.2)

where \( \Delta C_{ss} \) is the steady state photocapacitance and \( e_n \) is the emission rate. Fitting of this expression to the photocapacitance transient for the ZnSe/In_{0.05}Ga_{0.95}As/GaAs BPR=1 sample within a window of 0 to 10 msec, where the 1.46 eV level contribution to the

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transient is dominant (see Figure 3.2), results in Figure 3.5 where $e_n$ is shown for the 1.46 eV level as a function of incident photon energy. Since for this range the photon energy is $h\nu>E_g/2$, the obtained $e_n$ with a value of $\sim 10^3$ sec$^{-1}$ is actually an effective emission rate to the conduction band, and does not necessarily yield the electron optical cross section $\sigma_n$. Equivalent plots to that shown in Figure 3.5 could not be obtained for the 1.15 and 1.90 eV levels since their contributions to the photocapacitance transient are less distinct than that from the 1.46 eV level because of their lower concentrations and optical cross sections (see following discussion).

In order to compare the emission rate of the 1.46 eV level to those of the other levels observed, we first performed a fitting of the photocapacitance transient from the ZnSe/In$_{0.05}$Ga$_{0.95}$As/GaAs BPR=1 sample to Equation (3.2) for a photon energy range of 1.90 to 2.10 eV within a time window of 20 to 8500 msec. Under these conditions the contribution from the 1.9 eV level to the transient is dominant (but is still not screened by a level found at 2.25 eV that will be introduced in Section 3.3.3). This analysis produced an $e_n\sim 0.6$ sec$^{-1}$ for the 1.90 eV level. Similar values for the emission rate of the 1.90 eV level were obtained for all samples.

Since the 1.15 eV level was present in a very small concentration in all ZnSe layers grown on In$_{0.05}$Ga$_{0.95}$As/GaAs, fitting the photocapacitance transient for this level could not be performed. However, for ZnSe grown directly on GaAs which is discussed in greater detail in the next section, the concentration of the 1.15 eV level increased dramatically, allowing for accurate analysis of the photocapacitance as shown in Figure 3.6(a). The $t=0$ derivative of the transient is shown in Figure 3.6(b), where the 1.15 ± 0.05
Figure 3.5: Emission rate of the 1.46 eV level obtained by fitting the photocapacitance transients from the ZnSe layer grown on In_{0.05}Ga_{0.95}As/GaAs with initial BPR=1 within a 0 to 10 msec window. A photon flux of \( \sim 7 \times 10^{15} \) cm\(^{-2}\) sec\(^{-1}\) was used. Similar results were obtained for all of the other samples.
Figure 3.6: (a) Photocapacitance transient for a 1.3 eV incident photon energy from the ZnSe layer grown on GaAs with initial BPR=1. The transient shows a large contribution from the 1.15 eV level. (b) Analysis of the photocapacitance transients from the ZnSe/GaAs BPR=1 sample following the same procedure as that used for Fig. 3, using a time window of 2 to 20 msec. An onset at 1.15 ± 0.05 eV can be observed. The 1.46 eV onset corresponds to a hole emission from the 1.46 eV level to the valence band as shown in Figure 3.7.
eV onset can now be clearly observed so that a calculation of the approximate emission rate for the 1.15 eV level within the ZnSe/GaAs BPR=1 sample is possible. By fitting Equation (3.2) to the photocapacitance transient between 0 and 300 ms for a 1.20 to 1.35 eV incident photon energy range so that only the 1.15 eV level is excited, an \( e_n \sim 60 \text{ s}^{-1} \) was obtained for the 1.15 eV level.

Both the emission rates of the 1.15 and 1.90 eV levels (\( \sim 60 \) and \( \sim 0.6 \text{ s}^{-1} \), respectively) are well below that of the 1.46 eV level of \( \sim 10^3 \text{ s}^{-1} \). Thus, the 1.46 eV level has the largest optical cross section, which in addition to its near midgap position indicates that this level may be a dominant recombination-generation center in ZnSe [25].

The previous discussion is reinforced by the fact that for both the ZnSe/GaAs and ZnSe/In\(_{0.05}\)Ga\(_{0.95}\)As/GaAs samples grown with BPR=1 and 10, the photocapacitance transient indicates a strong interaction of the 1.46 eV level with both the conduction and the valence bands. Indeed, the photocapacitance transient data in Figure 3.7 shows for \( h\nu > 1.46 \text{ eV} \) a contribution from electron emission within a time window of \( \sim 0 \) to 10 ms and a contribution from hole emission within the \( \sim 10 \) to 300 ms time window. As discussed in Section 3.2.2, since the samples are \( n \)-type, the region of positive slope in the transient is an indication of the electron emission to the conduction band whereas the region of negative slope indicates hole emission to the valence band. This behavior also explains why in Figure 3.6(b) the photocapacitance transient derivative becomes negative for \( h\nu > 1.46 \text{ eV} \). Thus, we can conclude that the 1.46 eV level should be the dominant recombination-generation center in the ZnSe layer since it has the largest optical cross section and it shows a strong interaction with both bands.
Figure 3.7: (a) Photocapacitance transient from the ZnSe layer grown with initial BPR=10 on In_{0.05}Ga_{0.95}As/GaA for an illumination energy of 1.6 eV. The negative slope within the 10 to 200 msec window indicates hole emission to the valence band from the 1.46 eV level. (b) Magnified view of the photocapacitance transient near t=0. The positive slope within the 0 to 2 msec window indicates the dominant electron emission to the conduction band.
To demonstrate that the 1.46 eV emission is not associated with the GaAs or In$_{0.05}$Ga$_{0.95}$As buffer layers, which have a 1.5 and 1.42 eV bandgaps at 100 K, respectively, we present a number of observations which rule out this possibility. First, DLOS measures changes in capacitance arising from the depletion region. Even with a Debye uncertainty of ~0.05 μm for ZnSe at 100 K, the 2 μm thick ZnSe layer ensures that at least ~1.2 μm of undepleted ZnSe is between the ~0.8 μm wide depletion region and the III-V substrate. Second, photocurrent measurements obtained on the same samples at several forward and reverse bias voltages revealed no features below the ZnSe band to band emission. Selected results at zero bias are shown as an example in Figure 3.8. Third, the GaAs band to band emission would not display any dependence on BPR and lattice matching (see Section 3.3.2) as is observed in the steady state spectrum of Figs.3.4 and 3.9. Finally, the 1.46 eV feature was found to be independent of temperature, in contrast to the behavior of the GaAs and In$_{0.05}$Ga$_{0.95}$As bandgaps [29].
Figure 3.8: Photocurrent spectrum from the ZnSe layer grown on In$_{0.05}$Ga$_{0.95}$As/GaAs with BPR=1 under a 0V bias. Only the ZnSe band-edge features are observed, indicating that we are not probing the GaAs substrate.
3.4.2 The effect of lattice matching

Although the lattice mismatch between ZnSe and GaAs is only 0.27 %, the thickness (2 μm) of the ZnSe layers required for the DLOS studies is well beyond the Mathews-Blakeslee critical thickness of ~0.15 μm. Hence it was both necessary and of interest to test what impact, if any, a lattice-matched buffer layer would have on the ZnSe trap spectrum. In this section we compare the DLOS results for BPR=1 ZnSe layers grown on GaAs and In_{0.05}Ga_{0.95}As/GaAs respectively, in order to evaluate the influence of lattice-mismatch and possible resulting defects on the bulk deep level spectrum.

Stoichiometric ZnSe (BPR=1) layers on either GaAs or In_{0.05}Ga_{0.95}As/GaAs substrates display an identical set of deep levels, with optical thresholds at 1.15, 1.46 and 1.90 eV from the conduction band as shown in Figure 3.9. However, a large change in the magnitude of the steady state photocapacitance spectrum is observed when a lattice-matched interface is used. By extracting the concentration of each level as explained in Section 3.2.2, it can be seen in Table 3.1 that the concentrations of the 1.15 and 1.46 eV levels are substantially reduced while the 1.90 eV level concentration is unaffected as a result of including the In_{0.05}Ga_{0.95}As lattice-matched interlayer.

From Table 3.1, the 1.15 eV level concentration decreased by a factor of ~17 and the 1.46 eV level concentration was reduced by a factor of ~5 when the ZnSe layer was grown on In_{0.05}Ga_{0.95}As/GaAs. As discussed in Section 3.3.1, the 1.15 eV level may be related to Se vacancies while the 1.46 eV level shows a more complex behavior. The fact
Figure 3.9: (a) Steady state photocapacitance spectra for ZnSe grown on GaAs (solid line) and on In$_{0.05}$Ga$_{0.95}$As/GaAs (dash-dotted line) both with initial BPR=1 measured at 100 K. (b) Magnified view of the spectra for illumination energies of 1 and 2.4 eV showing levels at 1.15, 1.46 and 1.90 eV from the conduction band. The 1.90 eV optical threshold energy was more accurately obtained following the procedure shown in Fig. 3.3.
Table 3.2: Concentration (cm$^{-3}$) of deep levels present in ZnSe grown on GaAs and on In$_{0.05}$Ga$_{0.95}$As/GaAs with initial BPR=1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>$E_c-E_v=1.15$ eV (±0.05 eV)</th>
<th>$E_c-E_v=1.46$ eV (±0.02 eV)</th>
<th>$E_c-E_v=1.90$ eV (±0.05 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe/GaAs</td>
<td>$1\times10^{14}$</td>
<td>$2\times10^{14}$</td>
<td>$2\times10^{13}$</td>
</tr>
<tr>
<td>ZnSe/In$<em>{0.05}$Ga$</em>{0.95}$As</td>
<td>$7\times10^{12}$</td>
<td>$5\times10^{13}$</td>
<td>$3\times10^{13}$</td>
</tr>
</tbody>
</table>

that their concentration decreases so substantially by including a lattice-matched buffer layer suggests that strain relaxation in thick ZnSe layers may play a role in the enhancement of point defect generation within this layer. The degree of lattice matching is known to affect the misfit dislocation density, the threading dislocation density and possibly the point defect formation energy. Thus, the decrease of the concentration of the 1.15 and 1.46 eV levels with lattice mismatch may be related to defect complexes nucleated at dislocation cores. This explanation is supported by the work of Heun et al [11], who found no significant changes in the concentration of stacking faults in the ZnSe layer when the In$_{0.05}$Ga$_{0.95}$As interlayer was used.

3.4.3 Depth resolved photocapacitance

In order to study the spatial distribution of the deep levels within the ZnSe layer to address the question posed above concerning the physical origin, depth resolved photocapacitance measurements were performed. The reverse bias voltage applied on the
Au/ZnSe contact was varied from 0 to $-1.5$ and $-3$ V, yielding a change in the depletion region width of $\sim 0.8$, $\sim 1.1$ and $\sim 1.3$ $\mu$m, respectively. Trap filling was provided by a 0V bias applied to the contacts during 10 sec prior to illumination. Since the change in the junction capacitance arises from uncovering additional deep levels in the depletion region, this measurement provides a depth profile of the distribution of the deep levels within the ZnSe layer. Figure 3.10(a) shows the steady state photocapacitance spectra for the ZnSe/In$_{0.05}$Ga$_{0.95}$As/GaAs BPR=1 sample for 0, $-1.5$ and $-3$ V reverse bias voltages. A new emission at $E_c-E_T=2.25 \pm 0.05$ eV becomes apparent as the depletion edge moves closer to the ZnSe/In$_{0.05}$Ga$_{0.95}$As interface. This level was similarly observed with increasing reverse bias for all other samples grown both with different initial BPR’s and without the In$_{0.05}$Ga$_{0.95}$As interlayer, and has a concentration highly dependent on depth, changing by a factor of $\sim 2$ for a change in the depletion region width of $\sim 0.5$ $\mu$m.

Following the procedure established in Section 3.2.3 to extract the optical threshold energy by analysis of the photocapacitance transient derivative, the 2.25 eV level was observed within a time window of 100 to 300 ms (Figure 3.10(b)). An emission rate of $\sim 0.5$ s$^{-1}$ was obtained by fitting Equation (3.2) to the entire photocapacitance transients from the ZnSe/In$_{0.05}$Ga$_{0.95}$As/GaAs BPR=1 sample at a reverse bias voltage of $-3$V using a time window of 100 to 8500 ms, a range over which the contribution from the 2.25 eV level to the transients is most important.
Figure 3.10: (a) Steady state photocapacitance spectra for 0 V (dotted line), −1.5 V (dashed-dotted line) and −3 V (solid line) reverse bias voltages for the ZnSe layer grown on In$_{0.05}$Ga$_{0.95}$As with initial BPR=1. A new level is now observed at 2.25 eV from the conduction band with increasing depletion width. (b) Photocapacitance transient derivative as a function of incident photon energy obtained from the photocapacitance transients under a reverse bias of −3 V, calculated equivalently to those shown in Fig. 3.3, from the ZnSe layer grown on In$_{0.05}$Ga$_{0.95}$As with initial BPR=1. A time window of 80 to 300 ms was used. The inset shows a magnified view of the photocapacitance transient derivative.
In contrast, the traps at 1.15, 1.46 and 1.90 eV did not display a depth dependent concentration. Note that the fact that the 1.46 eV level concentration did not change with depth supports the earlier assertion that this level is not due to the GaAs bandedge emission.

Because of its energy position in the steady state photocapacitance spectrum, the 2.25 eV level has a concentration difficult to quantify although the increase with increasing depletion width is clear from Figure 3.10(a). At high incident photon energies the contribution from this level to the photocapacitance spectrum merges with the ZnSe bandgap. Thus, attributing a step in the spectrum to this level cannot be done very precisely. However, we estimate the concentration of the 2.25 eV level to be at least \( \sim 10^{14} \) cm\(^{-3} \) at a 0V reverse bias voltage. Note that this value did not show a dependence, within experimental error, on either lattice matching or BPR.

The \( E_c-2.25 \) eV level is actually positioned at 0.53 eV above the valence band, and thus may be related to the 0.51 eV hole trap reported by Hu et al [16] in nitrogen-doped ZnSe. In that work, a similar increase in the concentration of the 0.51 eV level was observed as the ZnSe/GaAs interface was approached. However, because the concentration of this level displayed a strong dependence on doping, this level was explained to result from nitrogen. The fact that we are observing the same level in our MBE-grown n-type ZnSe suggests instead a native physical source that could act to enhance nitrogen nucleation in nitrogen-doped ZnSe films [20]. Finally, the fact that we
can observe this trap within the lower half of the bandgap in n-type material demonstrates the capability of photocapacitance-based DLOS in spanning the entire bandgap and accessing minority and majority carrier trap information within the same sample.

3.5 Conclusions

We have used n-ZnSe grown by MBE as a test semiconductor to verify the validity of our DLOS experimental setup and analysis. This study has allowed the determination of the deep level position within the entire ZnSe bandgap, as well as the determination of their concentration and electronic properties. Moreover, by means of correlation to growth conditions we have been able to discuss potential physical origins for the electronic states. Analysis of both the steady state and transient photocapacitance reveals deep levels at $E_c - E_t = 1.15, 1.46, 1.90$ and $2.25$ eV with concentrations in the $10^{12}$ to $10^{14}$ cm$^{-3}$ range. We have shown that the concentrations of the $1.15$ and $1.46$ eV levels strongly depend on lattice-matching of the ZnSe/GaAs interface, decreasing when an In$_{0.05}$Ga$_{0.95}$As buffer layer is used prior to the ZnSe layer deposition. Such a decrease indicates that the $1.15$ and $1.46$ eV levels might be related to defect complexes nucleated at dislocation cores. Moreover, the concentration of the $1.46$ eV level shows a strong dependence on the BPR of the CIL, decreasing by a factor of $\sim 8$ for Se rich growths (BPR=0.1). The fact that the $1.46$ eV level concentration in the bulk ZnSe (BPR=1) has such a dependence on the BPR of the CIL indicates that the nature of the $1.46$ eV level requires a more involved explanation. On the other hand, the $2.25$ eV level showed no
dependence on BPR or lattice-matching but instead showed a clear depth dependence within each ZnSe layer, with its concentration increasing as the ZnSe/III-VI interface is reached. Detailed study of the photocapacitance transients revealed emission rates for the 1.15, 1.90 and 2.25 eV levels that are a factor of 17-1700 times smaller than that of the 1.46 eV level of $\sim10^3$ s$^{-1}$. Thus, because of its large optical cross section and its near midgap position the 1.46 eV level is likely the dominant recombination-generation center in our $n$-ZnSe samples [25], and should play a major role in ZnSe-based devices. The concentrations of the 1.46 and 1.15 eV levels can be reduced by a factor of $\sim5$ and $\sim17$, respectively, by including a lattice-matched In$_{0.05}$Ga$_{0.95}$As interlayer prior to the growth of the ZnSe layer. In addition, the concentration of the 1.46 eV level can be further reduced (by a factor of $\sim8$) when a ZnSe CIL grown with a Zn:Se BPR=0.1 (Se-rich) is used. Thus, growth of the ZnSe layers under such conditions should lead to higher quality epitaxial layers, which in turn should have a positive impact on the efficiencies of ZnSe-based devices.

Once the validity of DLOS has been demonstrated on this wide-gap semiconductor, we are now in the position to apply the same experimental and data analysis approach to $n$-GaN, which is the main goal of this research.
3.6 References

CHAPTER 4

DEVICE FABRICATION, EXPERIMENTAL CONDITIONS AND SUPPORTING CHARACTERIZATION TECHNIQUES

4.1 Test device growth and fabrication

The $p^+n$ and Schottky samples used in this study were grown in a two-flow horizontal metal-organic chemical vapor deposition (MOCVD) reactor on $c$-plane sapphire substrates at the University of California, Santa Barbara, under a collaboration with Dr. J.S. Speck. The buffer structure consisted of an unintentionally doped ($n=3 \times 10^{16}$ cm$^{-3}$) 0.5 $\mu$m-thick layer which was followed by a 0.5 $\mu$m-thick Si-doped ($n=3 \times 10^{18}$ cm$^{-3}$) GaN layer and a 1$\mu$m-thick Si-doped ($n=8 \times 10^{18}$ cm$^{-3}$) GaN layer [1]. The probed layer is 1.2 $\mu$m-thick grown unintentionally doped ($n=3 \times 10^{16}$ cm$^{-3}$) in order to increase the DLOS and DLTS sensitivity. For the $p^+n$ structures, this layer is followed by 0.16 $\mu$m-thick Mg-doped ($p=0.8-1 \times 10^{18}$ cm$^{-3}$) GaN. The diodes were mesa-etched with an area of 0.23 mm$^2$. Semitransparent 80 Å-thick front contacts were fabricated by metal deposition of Ni and Pd/Au for the Schottky and $p^+n$ samples, respectively. Back contact to the 1 $\mu$m-thick Si-doped layer was obtained with a ~1 $\mu$m-thick Ti/Al/Ni/Au metal deposition. The $p^+n$ and
Schottky diodes showed a reverse leakage current at $-1 \text{ V}$ of $\sim 4 \times 10^{-10}$ and $\sim 2 \times 10^{-9} \text{ A/cm}^2$ and a turn-on voltage of $\sim 2.2$ and $\sim 0.4 \text{ V}$, respectively, at 300 K. An schematic of the device layer structure is presented in Figure 4.1.

![Schematic of device layer structure](image)

Figure 4.1. P-n test sample schematic.

### 4.2 Hydrogenation of test devices

Hydrogenation was only performed on Schottky devices in order to avoid the large passivation effect that H would have on the p$^+$-cap layer of a p$^+$-n device (see discussion in Chapter 6). It was performed using an RF-plasma reactor operating at 13.56 MHz with an RF power of 30 mW. The completed GaN Schottky diodes were first coated with a H-permeable 200 Å-thick SiN$_x$ cap to protect the surface from damage during H-plasma exposure [2]. All samples were then exposed to a H-plasma for 30 minutes and kept at a temperature of 200 °C. After hydrogenation, no changes were found in the I-V
characteristics of the Schottky diodes. Moreover, C-V profiling showed no change in the carrier concentration in n-GaN, indicating no compensation or passivation of donors, consistent with previous reports for hydrogenated n-GaN [3,4,5].

4.3 DLOS and DLTS experimental conditions

The DLOS experiments were performed by digitally recording the photocapacitance transients for 250 s illumination time at each photon energy [6]. During illumination the samples were kept at a constant reverse bias of −1 V. Prior to illumination the traps were filled with electrons with a 0 V bias pulse for 10 s, followed by a 30 s delay in order to minimize any possible thermal transient contributions to the photocapacitance from deep levels found at \( E_c - E_t \leq 0.8 \) eV. To probe for possible levels shallower than those which can be detected by DLOS, DLTS experiments were performed with rate windows from 200 to 4 s\(^{-1}\), under a quiescent reverse bias of −1 V. Majority carrier trap filling was ensured by a 10 ms-long pulse under a fill pulse voltage \((V_p)\) of −0.2 V for both the p\(^+\)-n and Schottky diodes. Depth resolved DLTS measurements of the majority carrier traps were achieved by changing \(V_p\) from −0.2 to 1, 1.5, and 2 V in the p\(^+\)-n diodes. Positive \(V_p\) also provided minority carrier injection in the p\(^+\)-n sample, allowing the observation of hole traps in the n-side of the junction.

4.4 Supporting material characterization techniques

While the combination of DLTS and DLOS are the main experimental characterization tools used here to study the electrically active defects in n-GaN (see
Chapter 2), several other complementary techniques are needed to aid in the identification of potential physical sources for the detected deep levels. They include transmission electron microscopy, electron irradiation, secondary ion mass spectroscopy, capacitance-voltage profiling, scanning electron microscopy and electron beam induced current microscopy. These techniques have supplied supplementary information on the structural, chemical and electrical properties of these defects, and will be discussed in this chapter.

4.4.1 Structural Characterization

4.4.1.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is used to image dislocations in a material. It employs an incident electron beam with an energy of ~200 keV that is focused on a sample. Dislocations will cause a local distortion in the Bragg planes diffracting a small part of the incident beam. An aperture placed in the TEM allows the diffracted or direct beam to be blocked, thereby producing a dark or light image at the dislocations [7]. These images are referred to as bright field or dark field dislocation images, respectively. Since the TEM images are obtained in transmission mode, the sample must be electron-transparent, which requires a maximum sample thickness of ~1 μm achieved by means of mechanical polishing and ion milling. TEM sample preparation is thereby a destructive characterization technique. Analysis of plan-view TEM images (see Figure 4.2) allows
Figure 4.2: Typical bright-field plan view (a) and cross-sectional (b) TEM images of an MOCVD-grown GaN film on a sapphire substrate. Note the large density of TDs, typically observed in such films ((b) after [2]).
the determination of the TD density in semiconductors that present densities of $\sim 10^7 \text{ cm}^{-2}$ or higher. When the TD density is smaller, other techniques, such as electron beam induced current microscopy (see below), have to be used.

TEM analysis of the samples used for this study were performed at the University of California, Santa Barbara, on a JEOL 2000 Fx microscope operated at 200 kV. The specimens for these studies were prepared by wedge polishing followed by Ar$^+$ ion milling. Figure 4.2 shows typical cross-sectional and plan view images of a GaN film [8].

**4.4.1.2 Electron irradiation: controlled point defect introduction**

Electron irradiation is used to induce point defects in the samples, and combined with DLTS and DLOS can allow the identification of the physical origin of traps and recombination-generation centers. In contrast to microscopy techniques such as TEM and EBIC, where the defects already present are analyzed, here we intentionally introduce known types of defects and then look for changes in electronic defects in order to establish a precise correlation. During this experiment, a high energy electron beam is used to induce controlled structural damage in the semiconductor lattice. Since the electron beam has to reach the bulk of the semiconductor film, a thin front metallic contact should be used so as to allow maximum penetration of the electrons.

Electron irradiation has already been observed before to generate $V_N$ defects in GaN that are responsible for a shallow level at $E_c-0.07$ eV [9]. We focus here on the impact that this irradiation can have on the deep level spectrum via generation of point
defects, including $V_N$ and possibly $V_{Ga}$. Indeed, as it will be discussed in Chapter 7, we have strong experimental evidence that indicates that $V_{Ga}$ are also created and are responsible for different changes in the deep level spectrum.

The electron irradiation of the films used for this study were performed at Wright State University, Ohio, in a collaboration with Dr. D.C. Look. Electron fluences of $5 \times 10^{15}$ and $10^{16}$ cm$^{-2}$ with a 1 MeV energy were generated by a Van de Graaf accelerator at a beam current of 10 $\mu$A/cm$^2$. As discussed in Chapter 7, under these conditions, increases in the point defect concentration in the film of approximately $10^{14}$ cm$^{-3}$ were observed.

4.4.2 Chemical Characterization

4.4.2.1 Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy (SIMS) is commonly used to determine the concentration of impurities, including dopants, as a function of depth in a semiconductor film. During this measurement an ion gun is used to sputter material away from the semiconductor (creating a crater), while simultaneously an ion mass spectrometer analyses the spectrum of ions removed from the material during the sputtering process. Typically, ion beam energies of 10-20 keV are used. The sensitivity of this technique depends on several factors. First of all, only a small percentage of the removed material is actually ionized ($\sim 1\%$), and it is only these ions that are detected by the mass spectrometer. Thus, in order to increase the concentration of ions, different ion beam sources are used. Electropositive elements are more efficiently removed by $O_2^+$, whereas
Figure 4.3: Example of a SIMS analysis of a GaN film. The abrupt change in the Mg concentration at ~0.2 µm corresponds to a p⁺-n interface. The large increase in the Si concentration at ~1.0 µm corresponds to an n-n⁺ interface. The layer structure is discussed in detail in Chapter 5.
Cs\(^+\) is more efficient for sputtering of electronegative elements. Other factors, such as the host matrix and the level of background impurities in the SIMS chamber also play an important role in limiting its sensitivity. In order to obtain the total concentration of a given element in the matrix, a calibrated sample of the same host material and with the same types of impurities has to be used. In addition, the etching rate of a given ion source for each type of matrix has to be known before hand in order to allow an accurate determination of the depth-dependence of the impurities concentrations. Figure 4.3 shows a typical SIMS analysis of the Mg, C and Si present in the samples studied here.

4.4.3 Electrical Characterization

4.4.3.1 Capacitance-Voltage Profiling

Capacitance-voltage (C-V) measurements allow the determination of the net carrier concentration (N) as well as its depth profile in semiconductors. This is achieved by recording the change in the junction capacitance as a function of applied reverse bias on a Schottky or an abrupt p-n junction \([10]\). During this measurement the capacitance is measured with a 1 MHz signal of 15 mV rms superimposed to the reverse bias (\(V_r\)). A Boonton 72-4B capacitance bridge meter together with a Techtronics AFG 310 signal generator were used for these measurements. Once the C-V curve of the junction is determined, the carrier concentration can be obtained from analysis of the derivative of the C-V curve by means of \([10]\)
where $A$ is the junction area and $\varepsilon$ is the dielectric constant of the material, and can also be expressed as a function of depth by means of

$$C = \varepsilon \frac{A}{W_d}$$

(4.2)

where $W_d$ is the depletion edge depth. The spatial resolution of the C-V profiling measurement is limited by the Debye length, $L_D$, given by

$$L_D = \left( \frac{kT\varepsilon}{Nq^2} \right)^{1/2}$$

(4.3)

where $k$ and $T$ are Boltzmann's constant and the sample temperature, respectively. For the experiments in this study samples with doping levels in the $3-6 \times 10^{16}$ cm$^{-3}$ range were used, producing a Debye length of $\sim 0.02$ μm.

4.4.3.2 Electron Beam Induced Current Microscopy

Electron beam induced current (EBIC) is an experimental technique that provides information on the electrical activity of the defects found in the depletion region of a
Schottky or p-n junction [11]. A scanning electron microscope (SEM) is used as an excitation source providing micro-scale resolution [12]. The electron beam generates electron-hole pairs in the sample at different depths (Figure 4.4). The electrons and holes found close to the junction can get collected generating a drift current. However, electron-hole pairs may encounter a recombination-generation center prior to drifting, and can recombine non-radiatively at this defect, producing a decrease in the current collected at this point. If the SEM beam is scanned across the sample and the collected current is plotted as a gray-scale image, regions associated with recombination-generation centers will show up as dark spots [13] (Figure 4.5). This technique can be used both in plan-view and cross-sectional modes. The former allows the study of threading dislocations and can provide the threading dislocation density (non-destructively, in contrast to TEM). Other properties of the material directly related to the presence of electrically active defects, such as the minority carrier diffusion length, can also be studied. Cross-sectional mode analysis provides information of the location of the junction within the device.

The schematic for an EBIC experiment is shown in Figure 4.6. The sample is mounted inside an SEM chamber with the electron beam focused on its surface. The signal is in the form of collected current. Thus, electrical contact to both sides of the junction in the material is required. Moreover, since the electron beam has to reach the junction, a thin front contact has to be used in the plan-view mode. Typically, front metal contacts 80 Å-thick were used here. For these experiments, a Philips XL-3-FEG SEM located at the Center for Electron Optics at the Ohio State University was used. The collection electronics consisted of a series of current amplifiers. For most EBIC
experiments accelerating voltages of 7 kV and beam currents of ~ 2 nA were used, with spot sizes of ~ 7 nm, producing an average penetration depth of ~ 0.3 μm. All samples used for this research had their junctions located close to the front surface (or right below it, as in the case of Schottky diodes). Thus, a small accelerating voltage was used since this allows regions close to the front surface to be probed. Typically, the total collected current from an EBIC image was ~ $10^{-6}$-$10^{-7}$ A.
Figure 4.4: Plot of the excitation volume generated by the SEM electron beam. For a typical beam energy of ~2-10 keV, the Auger electrons emerge from a depth of ~5-20 Å, whereas the x-rays emerge from ~0.1-10 m (from Reference [5]).
Figure 4.5: Example of an EBIC image from a n-GaN film grown on sapphire. The black spots correspond to the TD regions, and indicate that a non-radiative recombination center is present in these regions. See Chapter 8 for further details.
Figure 4.6: Schematic of an EBIC system. The amplified current signal is fed into an SEM input so as to get a mapping of current generation as a function of position in the sample.
4.5 References


CHAPTER 5

DEEP LEVELS IN n-TYPE SCHOTTKY AND p⁺-n GaN DIODES

5.1 Introduction

Once the theoretical background and the different experimental techniques have been determined (Chapters 2 through 4), we focus for the rest of this work on the application of those tools to the analysis of the electrically active defects in n-GaN. First of all, we need to establish a baseline that will serve as a starting point to understand the GaN bulk deep level spectrum, and upon which the rest of this dissertation will be built.

As it was discussed in Chapter 2, in order to analyze the deep level spectrum by means of DLOS and DLTS an abrupt p-n or a Schottky junction has to be used. However, the actual choice of junction could have an impact on the deep level spectrum because of the differences in interface chemistry found between the two, which could be responsible for different carrier traps. Thus, we first need to verify the role, if any, that the type of junction plays in the DLOS and DLTS deep level spectra. In addition, while p⁺-n junctions are the choice for the junction configuration for devices such as LED’s and lasers, Schottky junctions are required for field effect transistors. Thus, this study is also of interest from a technological point of view. Indeed, the performance of devices based
on either type of junction can be limited by deep levels found within the GaN bandgap, which have the capability to act as traps and/or recombination-generation centers that reduce device speed, gain and efficiency. Though several reports on deep levels are available on n-GaN Schottky diodes [1,2,3,4,5,6,7], to date and to the best of our knowledge no studies have been performed on p⁺-n GaN junctions. In this chapter we compare the deep level spectra and properties in unintentionally doped n-GaN using Schottky and p⁺-n device configurations. Both DLOS [8] and DLTS under majority and minority carrier injection are used in p⁺-n and Schottky diodes order to quantify the deep level properties throughout the entire bandgap. The results from the combination of the two techniques together with SIMS analysis on the same set of samples are used to develop correlations with possible physical sources for the deep levels. Details of the layer structure, metal contacts and diode size can be found in Chapter 4.

5.2 Results and discussion

5.2.1 DLOS

Figure 5.1(a) shows the steady state photocapcitance spectra of the p⁺-n (dashed line) and Schottky (solid line) samples at T=300 K. The same set of deep levels are observed for each, at $E_c-E_f=1.35$, 2.64 and 3.22 eV. The concentrations of the 1.35 and 2.64 eV levels were $1.7 \times 10^{15}$ and $2.32 \times 10^{16}$ cm⁻³ for the p⁺-n sample, and $7.2 \times 10^{15}$ and $2.39 \times 10^{16}$ cm⁻³ for the Schottky sample, respectively, all measured under a constant photon flux of $\sim 7 \times 10^{15}$ cm⁻² s⁻¹. Note that due to the overlap of the 3.22 eV and the near
Figure 5.1: (a) Steady state photocapacitance spectra from the $p^+-n$ (dash-dotted line) and Schottky (solid line) samples measured at 300 K. Under a smaller vertical scale the 1.35 eV threshold can easily be observed at 1.35 ± 0.06 eV. The feature observed at ~2.8 eV is related to a trap and is discussed in detail in Chapter 6. (b) Photocapacitance transient derivative obtained from a linear regression fitting to the photocapacitance transients within a time window of 0 to 1 s (top curve) and 5 to 10 s (bottom curve) for the $p^+-n$ sample. Data are offset for clarity. Two sharp onsets can be observed at 2.64 ± 0.02 and 3.22 ± 0.02 eV. Similar results were obtained for the Schottky sample.
band-edge emissions the concentration of the 3.22 eV level cannot be determined precisely. Its concentration is at least $2.43 \times 10^{16}$ and $3.08 \times 10^{16}$ cm$^{-3}$ for the Schottky and p$^+$-n sample, respectively. Analysis of the derivative of the photocapacitance transient allows us to determine the optical threshold of the deep levels with greater precision [9]. As an example Figure 5.1(b) shows the derivative of the photocapacitance transient for the p$^+$-n sample in the 5 to 10 s time window plotted as a function of incident photon energy, showing a very sharp increase at $2.64 \pm 0.02$ eV. Equivalent analysis with a 0 to 1 s time window also shows a sharp onset at $3.22 \pm 0.02$ eV (Figure 5.1(b)). Because of the small signal at low incident photon energies the 1.35 eV level is better observed in the steady state photocapacitance spectra at $1.35 \pm 0.06$ eV. From the fitting of the photocapacitance transients, an effective optical emission rate for the deep levels can be calculated [9]. Since both emission of electrons and holes from a single deep level can occur at $h\nu>E_g/2$, this calculation provides a lower bound for the total electron optical emission rate for levels in the lower half of the n-GaN bandgap. Under a photon flux of $\sim 7 \times 10^{15}$ cm$^{-2}$s$^{-1}$, emission rates of $\sim 0.20$, 0.37 and 40 s$^{-1}$ were obtained for the 1.35, 2.64 and 3.22 eV levels, respectively.

Because of its position in the bandgap the 3.22 eV level is most likely related to residual acceptors in MOCVD-grown GaN. The ionization energy of this level is $\sim 220$ meV, close to those measured by photoluminescence for acceptor levels at $\sim 230$ meV [10] and $\sim 290$ meV [11] assigned to C and Mg, respectively. Earlier studies have reported detection of a level at $E_c - 3.25$ eV that was correlated to residual acceptors other than Mg in n-GaN Schottky diodes [1]. SIMS analysis shows a clearly observable residual Mg and
C content in the n-side of the p⁺-n junction and in the near surface region of the n-
Schottky sample (Figure 5.2), which supports the possibility that either Mg or C is the
source for the 3.22 eV level [12]. This point will be clarified in Chapter 7 when we
present the results for n-GaN grown in a Mg-free MOCVD reactor.

The 1.35 eV level [1,2] may be an efficient recombination-generation center in n-
GaN due to its deep position in the GaN bandgap. As observed in Figure 5.1(a) its
concentration decreases by a factor of ~3.7 for the p⁺-n sample compared to the Schottky
structure. While we cannot yet assign a source for this level, it is noteworthy to mention
that such a change follows the decrease of carbon concentration from ~1×10¹⁸ to ~3×10¹⁷
cm⁻³ between the Schottky and p⁺-n samples at V_p=0 V (Figure 5.2), whereas the O
concentration is similar in the probed regions for both samples. However, this decrease is
likely due to the thermal anneal cycle that this sample was exposed to in order to
reactivate the Mg acceptors in the p⁺-cap layer. The fact that this level may partially
annealed out suggests that it is point defect – related, consistent with the correlation
presented in Chapter 8.

As shown in Figure 5.1(a) the concentration of the 2.64 eV level did not vary
significantly between samples. The \( E_c-E_F=2.64 \) eV level is in the energy range of those
previously detected in MOCVD-grown n-GaN Schottky diodes at 0.85 to 1 eV above the
valence band [3,4], and similar to calculated deep levels produced by \( V_{Ga-O} \) and \( V_{Ga-}
 donor complexes [13]. These levels were shown to be directly related to the yellow PL
band, decreasing in concentration with reduced yellow PL emission intensity [3,4].
Figure 5.2: SIMS analysis data from the p\textsuperscript{+}-n (a) and Schottky samples (b). The Si concentration is constant within the shown range but is not shown here for clarity. The vertical dashed lines show the approximate location of the depletion region edge at the indicated voltage. For the p\textsuperscript{+}-n sample these positions were calculated using the p\textsuperscript{+}-side target thickness (1600 Å). The detection limits for C, O, and Mg are 2×10\textsuperscript{17}, 1×10\textsuperscript{17}, and 5×10\textsuperscript{15} cm\textsuperscript{-3}, respectively.
5.2.2 DLTS

5.2.2.1 Majority carrier injection

To complement the DLOS measurements, conventional thermally-stimulated DLTS measurements were performed on the same p⁺-n and Schottky samples to provide deep level information close to the conduction and valence band edges. Figure 5.3(a) shows a single dominant DLTS peak for the Schottky sample when a fill pulse of -0.2 V is used, with an activation energy of $E_c-E_f=0.62$ eV (Figure 5.3(b)) and a concentration of $\sim 4.1 \times 10^{14}$ cm⁻³. In contrast, under the same fill pulse bias the p⁺-n junction did not show any detectable levels (Figure 5.3(a)). However, as $V_p$ is increased toward a forward bias a similar DLTS feature appears with an activation energy of $E_c-E_f=0.58$ eV and a concentration of $\sim 2.7 \times 10^{14}$ cm⁻³ at $V_p=2$ V. The similar Arrhenius behavior of the 0.58 and 0.62 eV levels shown in Figure 5.3(b) indicates that they are the same level, with a capture cross section of $\sim 1-5 \times 10^{-15}$ cm². To avoid future confusions we will refer to this level as the 0.58 eV level throughout the rest of this dissertation, regardless of whether it was observed in a Schottky or in a p-n junction.

However, note that for a given rate window (50 s⁻¹ in Figure 5.3) the DLTS peak associated with the 0.58-0.62 eV level shows a small shift to higher temperatures from the Schottky to the p⁺-n diode, which in turn produces the 0.04 eV shift in activation energy shown in Figure 5.3(b). Such a shift can be explained in terms of the difference in
Figure 5.3: (a) DLTS spectra from the Schottky and p^-n samples for a rate window of 50 s^-1. (b) Arrhenius plot for the different deep levels observed by DLTS. The circles and squares correspond to deep levels observed in the p^-n and Schottky samples, respectively.
the magnitude of the electric field present in the depletion region in both samples. Indeed, Figure 5.4 shows a turn-on voltage of \( \sim 0.4 \) V and \( \sim 2.2 \) V for the Schottky and \( p^-n \) diodes, respectively, which implies that a larger junction barrier is present in the \( p^-n \) diode. This indicates that the electric field is much larger in the \( p^-n \) sample. Under these conditions emission from the 0.58-0.62 eV level is enhanced by the larger field in the \( p^-n \) diode, producing a decrease in the measured activation energy \([14]\).

The behavior of the 0.58-0.62 eV level closely matches the E2 level reported elsewhere in n-GaN Schottky diodes \([5]\). The E2 level concentration has been observed \([7]\) to depend on the \( \text{Cp}_2\text{Mg} \) flow rate during growth of the n-GaN layer, increasing under higher flow conditions. As shown in Figure 5.3, the 0.58 eV level emission is highly dependent on fill pulse bias, increasing in magnitude by at least a factor of 15 from \(-0.2\) to 2 V, which corresponds to a shift in the depletion region width of \( \sim 0.2 \) \( \mu \)m towards the \( p^- \)-side of the junction. Such a large increase in concentration tracks the residual Mg concentration profile in the n-side of the junction observed by SIMS (Figure 5.5). The Mg concentration at \( V_p=-0.2 \) V is \( \sim 4 \times 10^{16} \) cm\(^{-3} \) whereas at \( V_p=2 \) V is \( \sim 10^{18} \) cm\(^{-3} \). Note that since the depletion region width is \( \sim 30 \) times larger on the n-side of the \( p^- \)-n junction and the injected current is \( \leq 1 \) nA under the measurement conditions, the source of the 0.58 eV level is almost certainly in the n-GaN layer. The fact that we can observe the 0.58-0.62 eV level in the Schottky sample is likely due to its \( \sim 0.13 \) \( \mu \)m transition distance (\( \lambda \)). Indeed, all defects responsible for the 0.58-0.62 eV level found in the region \( w_d(V_p=-0.2V)-\lambda \), where \( w_d(V_p=-0.2V)\sim 0.14 \) \( \mu \)m is the depletion region width (see Figure 5.2), will contribute to the DLTS signal and thus allow the detection of the large Mg content.
Figure 5.4: I-V curves measured at 300K for the n-Schottky and p\textsuperscript{+}-n GaN diodes. As expected, a much larger built-in voltage is observed for the p\textsuperscript{+}-n diode.
Figure 5.5: DLTS spectrum obtained from the $p^+$-n GaN diode for a rate window of 50 sec$^{-1}$ as a function of fill pulse bias voltages.
close to the sample surface. Note that the Mg nature of this trap is also consistent with that of a donor level found at $E_c-E_r\sim 0.4-0.5$ eV which has been ascribed to the blue band emission in GaN [15].

5.2.2.2 Minority carrier injection

Under minority carrier injection conditions ($V_p>0$ V) another prominent DLTS feature appears in the p$^+$-n sample at $E_r-E_v=0.87$ eV (Figure 5.6). The concentration of this trap is $\sim 7 \times 10^{14}$ cm$^{-3}$ under a $V_p=2$ V, and the capture cross section is $\sim 6 \times 10^{-14}$ cm$^2$. The low injected current under these conditions taken together with the much larger depletion region width on the n-side of the p$^+$-n junction support the assertion that this feature is a minority carrier level hole trap found in the n-GaN layer. This level could not be observed in the Schottky sample under forward fill voltage conditions, as would be expected for a Schottky junction where minority carrier injection is not possible. The $E_r-E_v=0.87$ eV level is most likely the same level observed in the DLOS spectra in Figure 5.1 at $E_c-E_r=2.64$ eV, which is found at $E_r-E_v=0.80$ eV assuming $E_g=3.44$ eV, and is likely related to the yellow photoluminescence band [4]. Although the $E_r-E_v=0.87$ eV feature shows a smaller concentration than the $E_c-E_r=2.64$ eV, the minority injection fill pulse in the DLTS measurement does not ensure complete filling of the level producing a lower bound estimate for its concentration. It is interesting to note that the thermal activation and optical threshold energies from this level are in fair agreement with each other.
Figure 5.6: Minority carrier DLTS spectra from the p⁺-n GaN diode at Vp=2 V for different rate windows.
5.3 Conclusions

In summary, the combination of DLOS and DLTS measurements allowed the observation of a rich deep level spectrum throughout the entire bandgap in n-GaN and the determination of their electrical signatures. Correlation to SIMS analysis provides some insight into possible physical sources for some of the levels. The comparison of \( p^+ \)-n and n-Schottky diodes shows similar deep levels at \( E_c-E_t \approx 0.58-0.62, 1.35, 2.57-2.64, \) and 3.22 eV with concentrations of \( \sim 10^{14}-10^{16} \) cm\(^{-3}\). The 0.58-0.62 eV level is observed only when the probed region approaches the \( p^+ \)-side of the \( p^+ \)-n junction, tracking the large increase in residual Mg concentration. In addition, the 2.64 eV level (also observed at \( E_v+0.87 \) eV), which is likely related to the yellow band \([3,4]\), has been both thermally and optically characterized providing a comprehensive electrical signature for this trap.
5.4 References


CHAPTER 6

HYDROGEN PASSIVATION OF DEEP LEVELS IN n-GaN

6.1 Introduction

Hydrogen is known to have an important and verified impact on almost every semiconductor material. In the case of GaN, H incorporation during growth and processing [1] results in strong electrical passivation of Mg acceptors in p-GaN, and hence acceptor-H complexes have been studied in some detail [2,3,4,5]. In contrast, the impact of H incorporation on deep electronic levels in n-GaN and their physical sources is not yet understood. The electronic properties of deep levels and how they are influenced by process variables are expected to be significant issues as GaN devices continue to evolve. To date, little or no quantifiable data on deep level-H interactions in GaN have been reported. However, early studies have demonstrated that H-deep level interactions can have a strong influence on bulk traps as reported using both PL [2,5,6] and electrical conductance measurements [7]. Hence, in this chapter we have evaluated the direct impact of post-growth H incorporation on the deep level spectra of n-Schottky GaN diodes. Schottky n-GaN diodes are of interest for FET's and it is thus important to investigate the effect of hydrogenation on deep levels which may act as traps and/or
recombination-generation (R-G) centers. Moreover, the details of the interaction of H with specific levels can provide an effective tool to assess the physical origin of such deep levels.

The samples used for this study were the same Schottky devices studied in Chapter 5, and were analyzed under equal DLOS and DLTS conditions (Chapter 4) [8]. Details on the diode layer structure and hydrogenation conditions can be found in Chapter 4 [9]. Note that hydrogenation had no effect on the I-V characteristics of the Schottky diodes. Moreover, C-V profiling showed no change in the carrier concentration in n-GaN, indicating no compensation or passivation of donors, consistent with previous reports for hydrogenated n-GaN [3,5,10].

6.2 Results and discussion

Figures 6.1 and 6.2 show that hydrogenation has a dramatic and non-uniform effect on deep levels within n-GaN detected by DLTS and DLOS, differentially passivating some of the traps. First, two deep levels at $E_c-E_t = 0.58$ eV [8,11] and 1.35 eV [8] show a strong decrease in their concentration, by a factor of $\geq 30$ and $\sim 14$, respectively (Figure 6.1 and 6.2). Second, the $E_c-E_t = 2.64$ eV [8] threshold (Figure 6.2) is shifted to 2.74 eV, while the 2.80 eV [8] threshold is unaffected and the overall trap concentration of the band of states at 2.64-2.80 and 2.74-2.80 eV remains constant (Table 6.1). Finally, the 3.22 eV [8] trap concentration is unaffected by H incorporation. We now discuss the
Figure 6.1: Effect of hydrogenation on the DLTS spectra of n-GaN. The $E_e-E_r=0.62$ eV level concentration decreases by at least a factor of 30. Spectra shown for a rate window of 200 s$^{-1}$. The inset shows the Arrhenius behavior of this trap prior to hydrogenation.
Figure 6.2: a) Steady state photocapacitance spectra from n-GaN prior (solid line) and after hydrogenation (dash-dotted line) measured at T=300 K. The concentration of a trap is proportional to the step it creates in the spectrum. b) Magnified view of the photocapacitance spectra where the strong effect of hydrogenation on the concentration of the 1.35 eV trap together with the 2.64 to 2.74 eV shift can be observed.
Table 6.1. Concentration ($\text{cm}^{-3}$) of the deep levels found in the as-grown and hydrogenated n-GaN films.

<table>
<thead>
<tr>
<th>$E_c - E_t$</th>
<th>As-grown</th>
<th>Hydrogenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58 eV</td>
<td>$4.1 \times 10^{14}$</td>
<td>$\leq 1 \times 10^{13}$</td>
</tr>
<tr>
<td>1.35 eV</td>
<td>$6.0 \times 10^{15}$</td>
<td>$4.8 \times 10^{14}$</td>
</tr>
<tr>
<td>2.64 eV and 2.74 eV</td>
<td>$3.7 \times 10^{16}$</td>
<td>$3.7 \times 10^{16}$</td>
</tr>
<tr>
<td>3.22 eV</td>
<td>$6.6 \times 10^{16}$</td>
<td>$1.0 \times 10^{17}$</td>
</tr>
</tbody>
</table>

The effect of hydrogen incorporation on each level and the implications on possible physical origins of the traps.

### 6.2.1 Passivation of the 0.58 eV level

The 0.58 eV trap concentration has been previously reported to track the residual Mg concentration in n-GaN [8,11] as well as to increase with the Cp$_2$Mg flow rate during growth [12]. Figure 6.1 shows that hydrogenation reduces the concentration of this level from $\sim 4.1 \times 10^{14}$ cm$^{-3}$ to below our detection limit, $\sim 1 \times 10^{13}$ cm$^{-3}$ (Table 6.1). In addition, DLTS depth-profiling down to $\sim 0.3$ µm from the contact showed no trace of this level after hydrogenation. Thus, the behavior of the 0.58 eV trap concentration after H
incorporation is consistent with the formation of Mg-H complexes within n-GaN. These results may indicate that while shallow substitutional Mg acceptors (Mg\textsubscript{Ga}) are known to react with H to create Mg-N-H complexes, Mg impurities may be incorporating at other lattice sites or complexing with other defects (possibly dislocations) that may also react with H. For instance, the origin of the 0.58 eV level may be similar to that of the donor level involved in the blue PL band [13]. Mg\textsubscript{Ga}-V\textsubscript{N} complexes have been proposed to be responsible for this donor level which is found at ~0.4-0.5 eV from the conduction band [13]. If both levels are of the same nature, the blue PL emission should be largely reduced due to H incorporation in the film.

6.2.2 Passivation of the 1.35 eV level

Now, considering the 1.35 eV trap, this level has the closest energy to midgap of all the deep levels present and is thus potentially an efficient R-G center that may impact n-GaN FET's. As a result of hydrogenation the initial 1.35 eV level concentration of ~6.0×10\textsuperscript{15} cm\textsuperscript{-3} is reduced by a factor of ~14 (Figure 6.2(b) and Table 6.1). While the source of the 1.35 eV level is unknown at present, in previous work we have observed that the 1.35 eV concentration tracks the background C concentration in n-GaN [8]. Depth-resolved DLOS on the hydrogenated sample (not shown here for the sake of brevity) showed no variation in the 1.35 eV trap concentration down to ~0.3 \(\mu\)m from the front surface, which indicates that passivation of the 1.35 eV trap penetrated well within the n-GaN layer.
6.2.3 The 2.60-2.80 eV band of states

6.2.3.1 Sharpening of the 2.60-2.80 band of states

The effect of H on the 2.64-2.80 eV band of levels (Figure 6.2) is markedly different from that of the 0.58 and 1.35 eV levels. A shift in the 2.64 eV threshold energy to 2.74 eV is observed but with no change in the trap concentration of this defect band (Table 6.1). Although the 2.64 and 2.74 eV thresholds can be observed in the steady state photocapacitance spectrum (Figure 6.2) before and after H-exposure, respectively, analysis of the photocapacitance transient derivative allows us to determine the onsets more accurately [8,14]. In general, different deep levels will have different emission rates which will cause changes in the photocapacitance transient derivative within different time observation windows [14]. Figure 6.3 shows the derivative of the photocapacitance transients where a sharp onset at 2.64 eV and a step at ~2.80 eV are clearly observed prior to hydrogenation. The fact that the 2.80 eV onset cannot be completely isolated from the 2.64 eV in this analysis is due to their similar electron emission rates. After hydrogenation the 2.80 eV level is still present, but the 2.64 eV threshold shifts to ~2.74 eV (Figure 6.2). This is distinctly seen in the transient derivative analysis (Figure 6.3).

6.2.3.2 Background on V\textsubscript{Ga}-related deep levels

Even though there has been some strong experimental indications that suggest that V\textsubscript{Ga} are responsible for deep levels within the n-GaN bandgap, it has been mostly theoretical calculations that showed the existence of such levels. Among the strongest
Figure 6.3: Photocapacitance transient derivative obtained from a linear regression fitting to the photocapacitance transients obtained within a 5 to 10 s time window. Prior to hydrogenation (solid line) two onsets at 2.64 and 2.80 eV can be observed, whereas hydrogenation (dash-dotted line) causes the 2.64 eV onset to disappear and a new onset at 2.74 eV is revealed. The feature observed before hydrogenation at $E<2.64$ eV is due to the contribution of the 1.35 eV level to the photocapacitance transient. It is not observed after hydrogenation because of the strong reduction in the concentration of this trap.
indirect experimental observations Saarinen et al. [15] reported by means of positron annihilation spectroscopy the direct correlation between the yellow PL band and $V_{Ga}$ in n-GaN. This work taken together with that of Calleja et al. [16] and Polyakov et al. [17], who showed that the yellow PL band intensity is proportional to the concentration of a level found at $\sim E_v + 1$ eV, has suggested that $V_{Ga}$ create a deep level above the valence band. However, it is the theoretical work by Neugebauer and Van de Walle [18,19,20] that clearly substantiates the role of $V_{Ga}$ in the generation of traps within the n-GaN bandgap. This work focused on wurtzite GaN (the stable phase of bulk GaN), but should apply to cubic GaN since only minor differences in the electronic structure and formation energy are found [20]. In order to determine the electronic structure and atomic geometry of the native defects in GaN first-principles total energy calculations were used [18,20]. The formation energy of a defect in different charge states were calculated as a function of the Fermi Energy position in the bandgap. As it is shown in Reference [20] under n-type conditions the formation energy of $V_{Ga}$ is $\sim 5$ eV smaller than that of $V_N$ (which is most likely to form in p-GaN), and much smaller than those of both antisites ($N_{Ga}$, $Ga_N$) and interstitials ($N_i$, $Ga_i$) which are energetically much less favorable to form. Such low energies for the $V_{Ga}$ are due to the fact that this defect can become charged in n-type material which lowers the formation energy. Indeed, for a $V_{Ga}$ the nitrogen dangling bonds are strongly localized [20] producing a weak electrostatic interaction which allows for the low formation energy. In addition, to reduce the electrostatic interaction inside the $V_{Ga}$ an outward relaxation by means of a displacement of the N atoms occurs increasing the distance between the charged dangling bonds. The isolated $V_{Ga}$ acts as a triple
acceptor [20] and has been shown to introduce a deep level at \( \sim 1 \) eV above the valence band [18] (Figure 6.4) which can account for the traps observed in References [16] and [17]. Thus, of all the native defects \( \text{V}_{\text{Ga}}^{3^-} \) will be the most likely to form in n-GaN where electrons are available to help the formation of this defect (in p-GaN \( \text{V}_{\text{Ga}}^+ \) will be very unlikely to form, in agreement with experimental observations that show no yellow PL emission in p-GaN).

\[
\begin{align*}
&\text{E}_c \\
&\vline \quad \vline \quad \vline \quad \vline \\
&\text{E}_F \\
&\vline \quad \vline \quad \vline \quad \vline \\
&\text{V}_{\text{Ga}}^{3^-} \quad (\text{V}_{\text{Ga}}^{-}\text{H})^{2^-} \quad (\text{V}_{\text{Ga}}^{-}\text{H}_2)^{-} \quad (\text{V}_{\text{Ga}}^{-}\text{H}_3) \\
&\vline \quad \vline \quad \vline \quad \vline \\
&\text{E}_v \\
&\vline \quad \vline \quad \vline \quad \vline \\
&(\text{V}_{\text{Ga}}^{-}\text{H}_4)^{2^+}
\end{align*}
\]

Figure 6.4. Schematic of the levels introduced by \( \text{V}_{\text{Ga}} \) and hydrogenated complexes in n-GaN based on theoretical calculations (after Reference [18]).

When H is also available during the formation of a \( \text{V}_{\text{Ga}} \) some of the electrons trapped at the N-dangling bonds may be substituted by H atoms which bond to the N [18]. Indeed, following a similar theoretical approach to that mentioned above, Van de Walle calculated the formation energy and bandgap position of the \( \text{V}_{\text{Ga}}^{-}\text{H}_n \) complexes [18]. From a qualitative perspective, since the lengths of N-H bonds are quite small (\( \sim 1.01 \) Å)
and the radii of the Ga and N atoms are only ~1.26 and 0.75 Å, respectively, where the Ga is surrounded by four N in the tetrahedral sites, it is likely that several H atoms can occupy the V_{Ga} site bonding to the N atoms. Van de Walle's calculations show that this is the case. If one H complexes to the triple acceptor V_{Ga}^{3-}, it contributes with an extra electron and thus V_{Ga}-H only requires two electrons to get filled, and acts as a double acceptor. In V_{Ga}-H_{2} each H contributes with an electron, leading to a single acceptor. However H-H repulsion occurs and causes a lowering of the symmetry by means of a deviation of the N-H bonds from the <111> directions. A larger deviation is found for V_{Ga}-H_{3} and V_{Ga}-H_{4}, which become a neutral and a single donor complexes, respectively. As shown in Figure 6.3 hydrogenation by one and two H atoms of the V_{Ga} causes a shift of the energy level by ~0.1 eV each closer to the valence band, whereas the V_{Ga}-H_{3} level is found right above the valence band, and the V_{Ga}-H_{4} level below the valence band edge (therefore passivated) [18]. However, not all V_{Ga}-H_{n} complexes are equally likely to form. In n-type GaN both V_{Ga}-H and V_{Ga}-H_{2} have lower formation energies than V_{Ga}, and will thus form if H is present, whereas V_{Ga}-H_{3} and V_{Ga}-H_{4} have higher formation energies (likely due the energy required by the above mentioned deviation in the N-H bonds due to the H-H interaction) and are not likely to form. Thus, the hydrogenated V_{Ga} complexes that are likely to form remain electrically active (with deep levels within the bandgap), implying that V_{Ga} cannot be passivated by H.
6.2.3.3 Origin of the 2.60-2.80 eV band of states

Based on the discussion presented in the previous section, the 2.64, 2.74 and 2.80 eV levels (0.8, 0.7 and 0.62 eV above the valence band) are most likely related to the yellow PL emission. Moreover, summarizing those results: (1) \(V_{\text{Ga}}^{3-}, (V_{\text{Ga}}-H)^{2-}\) and \((V_{\text{Ga}}-H_2)^-\) are more likely to form than \((V_{\text{Ga}}-H_3)^0\) and \((V_{\text{Ga}}-H_4)^+\) in n-GaN; (2) \(V_{\text{Ga}}^{3-}\) creates a level at \(~1\) eV above the valence band, and \((V_{\text{Ga}}-H)^{2-}\) and \((V_{\text{Ga}}-H_2)^-\) complexes each shift this energy by \(~0.1\) eV closer to the valence band. This behavior is remarkably similar to that observed for the 2.60-2.80 eV band of states under hydrogenation (see 6.3.3.1). Thus, we tentatively assign the 2.64, 2.74 and 2.80 eV deep levels to the same defects: \(V_{\text{Ga}}^{3-}, (V_{\text{Ga}}-H)^{2-}\) and \((V_{\text{Ga}}-H_2)^-\), respectively. Prior to hydrogenation the 2.74 eV threshold is probably present but likely obscured by the strong signal from the 2.64 eV level (Figures 6.2 and 6.4), while the 2.80 eV level can be observed indicating the existence of \((V_{\text{Ga}}-H_2)^-\) complexes in the as-grown material. After hydrogenation, the 2.64 eV threshold is no longer observed due to the hydrogenation of \(V_{\text{Ga}}^{3-}\) which forms \((V_{\text{Ga}}-H)^{2-}\) and \((V_{\text{Ga}}-H_2)^-\), consistent with their lower formation energies [18]. Finally we note that prior to hydrogenation the concentration of the 2.64-2.80 eV band is \(~3.7\times10^{16}\) cm\(^{-3}\) which remains unchanged even though the band has “sharpened” to 2.74-2.80 eV. Thus, we conclude that post-growth hydrogenation of n-GaN has a small effect on the acceptor levels likely involved in the yellow PL emission, and these levels remain equally electrically active.
6.2.4 Hydrogen impact on the 3.22 eV acceptor-related level

We now consider the $E_c$-3.22 eV level in detail. A detailed discussion of the physical source for the 3.22 eV level will be presented in next chapter. In that chapter we will show that $\text{Mg}_{Ga}$ defects are directly responsible for this level. Table 6.1 shows a slight increase in the 3.22 eV level concentration as a result of hydrogenation, which is not significant since similar changes across the sample were observed prior to hydrogenation [8]. Thus, post-growth hydrogenation has no apparent effect on the 3.22 eV level concentration. While Mg acceptors prefer to form complexes with H and become passivated in p-GaN [2,3,4,5,6,7], it is not clear from previous reports whether the same effect should be expected in n-GaN [10]. However, our results strongly indicate that H does not passivate $\text{Mg}_{Ga}$ acceptors in n-GaN, where the Fermi level is found close to the conduction band.

6.2.5 Nature of the diffused H species

Based on the cumulative results presented above we can now examine the nature of the H species diffusing into n-GaN during plasma hydrogenation. Theoretical calculations by Neugebauer et al [10] have shown that even though the formation energy of H$^-$ in n-GaN is smaller than that of H$^+$, the migration barrier for H$^+$ in the GaN lattice is only 0.7 eV compared to 3.4 eV for H$, which implies that H$^+$ has a larger mobility. Hence it is possible that even if during hydrogenation both H$^-$ and H$^+$ form at the surface, H$^+$ will diffuse deeper into the n-GaN layer and can account for the effects shown in Figures 6.1, 6.2 and 6.4. This is substantiated by the fact that the carrier concentration did
not change with hydrogenation, which suggests that H\(^+\) did not diffuse and complex with donors. Moreover, accounting for the 2.64 to 2.74 eV shift by means of \(V_{Ga-H_n}\) complex formation implies that H must be present in a positive charge state (H\(^+\)) to react with \(V_{Ga}^{1-}\).

6.3 Conclusions

In summary, we have reported the direct observation of trap passivation by hydrogen in n-GaN. This process occurs differentially: the 0.58 and 1.35 eV traps are drastically passivated, the 2.64 eV threshold is shifted to 2.74 eV with a narrowing of this defect band and the 3.22 eV trap remains unaffected. The interaction of H with these traps also aids in the identification of the defects responsible for the levels. Correlation to previous reports [8] strongly suggests that the passivation of the 0.58 eV level is consistent with Mg-H complex generation. Moreover, the 2.64 to 2.74 eV shift correlates well with a model for the hydrogenation of \(V_{Ga}^{1-}\) to produce \((V_{Ga-H})^{2-}\) complexes [18]. The results reported here also indicate that the acceptors responsible for the 3.22 eV level (~0.22 eV above the valence band) are not affected by post-growth hydrogenation.
6.4 References


CHAPTER 7

TRAPS AND THE ROLE OF Mg IN n-GaN

7.1 Introduction

One of the issues during material growth is the incorporation of undesired impurity atoms in the crystal lattice. These extrinsic defects are indeed commonly found in semiconductors and can be electrically active, thus behaving as carrier traps or recombination-generation centers. Therefore, these impurities can have deep levels related to them that are found in the forbidden bandgap. The incorporation of impurities is an important issue in MOCVD-grown semiconductors. This type of growth is not performed under high vacuum conditions, such as MBE growth, and thus presents a more contaminated environment. This is due to impurities incorporated in the reactants as well as to by-products generated after the chemical reaction that undergoes on the semiconductor surface. In addition, MOCVD growth shows memory effects. Since the reactor walls see the reactant and by-product gases continuously, they getter impurities that can desorb during later growths contaminating the film being grown. This is the case for Mg. This dopant is commonly used in III-nitrides as an acceptor to obtain p-type conductivity. However, Mg also sticks to the walls of the reactor liner as well as to the
sample holder. Thus, during growth of n-type GaN, Mg may be present in the environment and may diffuse into the film affecting the electronic properties of the semiconductor. In this chapter we focus in the impact of residual Mg on deep level formation in n-type GaN. Electron irradiation is also used as a source for point defect generation (Section 7.3), and aids in the identification of the origin of these traps [1].

7.2 Role of residual Mg

In order to investigate the impact of Mg incorporation on the deep levels two samples grown under equal conditions and with identical layer structure (described in Chapter 4) were used for this study. Both samples had a front Schottky contact. This prevents the diffusion effect of Mg from the p+-cap layer into the n-side, which is commonly observed in p+-n GaN homojunctions grown by MOCVD. This effect is clearly seen in Figure 7.1, where SIMS analysis shows a large amount of Mg that has diffused into the n-GaN layer of the p+-n sample (see Chapter 5). The only difference between the contaminated and Mg-free samples was the initial condition of the reactor liner. Whereas in the former the liner had been previously exposed to Mg (during growth of p-GaN), in the latter the liner was etched prior to growth providing a very low concentration of Mg in the environment during growth. Indeed, SIMS analysis of the film grown in the contaminated environment shows a distinct concentration of residual Mg found close to the Schottky sample surface (Figure 7.1) most likely due to desorbed Mg from the reactor liner.
Figure 7.1: SIMS analysis of a p⁺-n and n-Schottky diode grown in a reactor with residual Mg present.
7.2.1 Effect of Mg on carrier concentration

If Mg is introducing levels in the forbidden bandgap, in particular levels close the valence band that could behave as acceptors (such as the $E_c$-3.22 eV level, discussed in Chapters 5 and 6), these should probably have an effect on carrier concentration. This possibility was examined by recording the background carrier concentration for both samples by means of C-V profiling (see Chapter 4). This analysis shows an increase in the carrier concentration from $\sim 10^{16}$ to $\sim 4 \times 10^{16}$ cm$^{-3}$ for the Mg-free n-GaN film. This strongly suggests that Mg must be introducing levels which behave as compensating acceptor centers and trap electrons decreasing the total background carrier concentration $n$, which is given by $n = N_d - N_a$ where $N_d$ would be determined by the concentration of residual donors always found in GaN (most likely $V_N$ and/or O atoms [1,2]), and $N_a$ would be due to the concentration of residual Mg incorporated in the GaN film during growth. Thus, growth under Mg-free conditions provides unintentionally doped n-GaN films with fewer compensating centers and higher electron carrier concentration.

7.2.2 Impact of Mg on the DLOS spectrum

Next we focus on the impact that incorporated Mg is having on the deep level spectrum. First, let us compare the DLOS spectra from both the contaminated and Mg-free samples shown in Figure 7.2. Several clear differences between both samples can be observed: (1) the $E_c$-3.22 eV level is no longer present for n-GaN grown under Mg-free conditions, and instead another level at $E_c$-3.38 eV is now observed; (2) the $E_c$-1.35 eV
Figure 7.2: Steady state photocapacitance spectra for the contaminated and Mg-free samples measured at T=300 K.
level seems completely unaffected by the presence of residual Mg during growth; (3) the $E_c-2.64$ eV level also appears in both samples, although the optical threshold is not clear in the spectrum for the Mg-free film. The concentrations of all these levels for the contaminated and Mg-free samples are presented in Table 7.1. Next, we focus on each of these issues individually.

Regarding the $E_c-3.22$ eV level (found at $\sim E_v+0.22$ eV), as it can be seen in Table 7.1, a dramatic change is observed in the DLOS spectrum. This level is not present in the Mg-free sample, whereas for the contaminated sample it shows a concentration of $4.5\times10^{16}$ cm$^{-3}$. It is clear that this level is directly related to the incorporation of Mg in the sample. Indeed, Mg acceptors (i.e. Mg$_{Ga}$) have been observed to generate a level found at $\sim E_v+0.18$ eV as reported by PL measurements on p-GaN [3]. Moreover, this assignment correlates well with the observations from photocapacitance studies by Yi et al. [4] who reported the appearance of a level at $E_c-3.2$ eV as a results of Mg doping of the film. However, we can actually observe this level in undoped n-GaN films due to unintentional incorporation of small concentrations of residual Mg.

The correlation of Mg and the 3.22 eV level is in excellent agreement with the differences observed in background carrier concentration between the contaminated and Mg-free samples. Indeed, as shown in Figure 7.2, the contaminated and Mg-free samples show total electron carrier concentrations of $\sim10^{16}$ and $\sim3\times10^{16}$ cm$^{-3}$, respectively, which, as it was previously discussed, can be explained to result from the smaller concentration of compensating acceptor centers found in the Mg-free sample. All these results taken together indicate that residual Mg found in the MOCVD reactor is diffusing
Table 7.1: Comparison of the deep level concentration (cm$^{-3}$) for the contaminated and Mg-free samples.

<table>
<thead>
<tr>
<th>$E_c-E_t$</th>
<th>n-GaN</th>
<th>Mg-free n-GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35 eV</td>
<td>$6.5 \times 10^{15}$</td>
<td>$4.4 \times 10^{15}$</td>
</tr>
<tr>
<td>2.64 eV</td>
<td>$3.0 \times 10^{16}$</td>
<td>$1.8 \times 10^{15}$</td>
</tr>
<tr>
<td>3.22 eV</td>
<td>$4.5 \times 10^{16}$</td>
<td>-----</td>
</tr>
<tr>
<td>3.38 eV</td>
<td>?</td>
<td>$2.9 \times 10^{15}$</td>
</tr>
</tbody>
</table>
into the GaN film during growth generating Mg\textsubscript{Ga} acceptors which act as compensating centers decreasing the electron carrier concentration in the film. This result will be further validated from the analysis of electron irradiation of n-GaN (Section 7.3) which indicates the 3.22 eV level is related to a point defect, consistent with the assignment to Mg\textsubscript{Ga}.

Even though the Mg-free film does not show the 3.22 eV level, a new optical threshold is now clearly observed at $E_c$-3.38 eV. This level could be found also in the contaminated film, but its threshold may be shadowed by the large signal from the 3.22 eV level. It is unclear what the origin of this level is, but it has also been observed in n-GaN grown by MBE [5], which suggests that it may be related to an intrinsic defect rather than to an impurity and thus could be found in all n-GaN.

The $E_c$-1.35 eV level, however, shows no dependence on the presence of Mg in the film. Both the contaminated and Mg-free samples show a distinct optical threshold at 1.35 eV (Figure 7.2). This result indicates no correlation between this deep level and residual Mg, and is consistent with this level being related to an intrinsic defect. Indeed, this level has been observed in all MOCVD films used for this research (see Chapter 8), as well as on films grown by MBE [5], suggesting an intrinsic source. Further properties of this level will be discussed in Chapter 8.

The behavior of the 2.64 eV level is similar to that of the 1.35 eV level. As it is shown in Figure 7.3, both the contaminated and Mg-free samples show a threshold in this region. However, in the case of the Mg-free film the optical threshold cannot be well resolved, most likely due to the small concentration of this level compared to that of the 1.35 eV. This causes the large capacitance signal from the 1.35 eV level to shadow that of
Figure 7.3: Hole optical cross section for the 2.64 eV level obtained from a least square fitting to the photocapacitance transient derivative within the 0 to 15 s time window. A fill pulse at 2.8 eV during 120 s was used in both cases. Note that the choice of time window does not have an effect on the optical threshold, only on the magnitude of the signal.
the 2.64 eV level, which is reflected in the steady state photocapacitance spectrum. In order to verify that the same 2.64 eV level was present in both samples optical DLOS at T=300 K was performed (see Chapter 2 for a discussion). During this experiment a light source at constant photon energy is used as the carrier pump (in contrast to a change voltage, used in all other DLOS measurements in this work) allowing the change of the initial condition of the trap population from majority to minority carriers. This is immediately followed by the probing beam, which is the same as that used in regular DLOS and allows different energy levels to be probed. For this work a pump beam of 2.8 eV with an exposure time of 120 s was used, while a constant reverse bias V_r=-1 V was applied to the diode. This allowed all traps found between the conduction band edge down to E_c-2.8 eV to be filled with holes prior to the photocapacitance measurement. Under these conditions the 2.64 eV trap should be initially filled with holes (instead of electrons). Thus, during probing illumination there will be a change in the capacitance transient derivative (given by Equation 2.13) which will be proportional to the optical hole cross section (\sigma_h) of the trap, which is a unique signature of a level.

Figure 7.3 shows the DLOS results using optical pumping with both the hole optical cross sections for the contaminated and Mg-free samples. Very similar spectral responses are obtained for \sigma_h indicating that this deep level is the same in both samples. The optical threshold of \sigma_h is at \sim E_c+0.9 eV, in good agreement with that obtained thermally by minority carrier DLTS (Chapter 5) at \sim E_c+0.87 eV. As it was discussed in Chapter 5 this deep level is the same as that observed at \sim 2.64 eV from the conduction band (Figure 7.2) which is observed in both samples regardless of the incorporation of
Mg. It is not clear at this point why the concentration of this level is smaller in the Mg-free film (Table 7.1). However, as it is shown in Chapter 8, n-GaN films grown with the same reactor liner under similar Mg-contamination conditions show very different concentrations of the 2.64 eV level. Thus, there seems to be no direct correlation between Mg and the 2.64 eV level, which is strongly supported by the results from Chapter 6 that indicate that V_{Ga} defects are responsible for this level.

7.2.3 Impact of Mg on the DLTS spectrum

For the DTLS measurements a reverse bias of \( V_r = -1 \) V was used together with 10 ms-long fill pulses at \( V_p = -0.2 \) V. Figure 7.4 shows a DLTS peak in both the contaminated and Mg-free samples which corresponds to the \( E_c - 0.58 \) eV level previously discussed in Chapters 5 and 6. Even though this level can still be resolved for the film grown under Mg-free conditions its concentration decreases by an order of magnitude (Figure 7.4).

As it was discussed in Chapter 5, the concentration of this level is found to be track the concentration profile of residual Mg measured by SIMS in the contaminated sample. These results indicated that the 0.58 eV level was related to a defect that was either introduced by Mg or some other impurity that could incorporate with Mg, or to a defect to which Mg was complexing (such as a V_{N}, as suggested in [6]). The DLTS results from Figure 7.4 show that the concentration of the 0.58 eV level decreases when an environment clean of Mg is used, and support a direct correlation between the generation of the \( E_c - 0.58 \) eV level and the incorporation of Mg in the film.
Figure 7.4: (a) DLTS spectra showing the $E_c - 0.58$ eV level for the contaminated and Mg-free samples for a rate window of 50 s$^{-1}$. (b) Arrhenius behavior of this traps in both films.
7.3 Point defect generation via electron irradiation

Electron irradiation was used to generate point defects in the n-GaN layer with the intent of identifying the origin of some of the traps present in this material (see Chapter 4 for details on the technique). For this study, samples grown under the presence of residual Mg in the MOCVD reactor but with low deep level concentrations were used so as to allow the observation of induced defects in small concentrations. These samples were grown under identical conditions to those of the films discussed in previous sections. A detailed comparison between both sets of samples is presented in Chapter 8, where it is shown that a similar deep level spectrum is present in both cases but with different concentrations.

Two different irradiation doses, $5 \times 10^{15}$ and $1 \times 10^{16}$ cm$^{-2}$, with 1 MeV electrons were used for this study. A small electron energy was chosen in order to minimize excessive damage to the film and to the Schottky contacts from the bombardment of electrons [1]. Indeed, the devices showed similar I-V and C-V behaviors before and after irradiation. These results show a distinct increase in the concentration of both the band of states at 2.6-2.8 eV and the 3.22 eV level (Figure 7.5). The increase in concentration of the 2.6-2.8 eV band can be explained to result from point defect generation during electron irradiation [7]. As it was discussed in Chapter 6 this band of states is likely related to $V_{Ga}^{3+}$ and related H-complexes, which together with the effect of electron irradiation substantiates the role of point defects such as $V_{Ga}^{3+}$ in the formation of the
Figure 7.5: Steady state photocapacitance spectra from n-GaN prior and after 1 MeV electron irradiation measured at $T=300$ K. Both the band of states at 2.6-2.8 eV and the deep level at 3.22 eV show concentrations that increase with e-irradiation.
2.64-2.80 eV band of levels. Irradiation seems to specially have an impact on the 2.80 eV threshold. Indeed, Figure 7.6 shows the same effect for a different diode on the same sample, where the increase in the photocapacitance signal after 2.80 eV can be easily observed. This behavior could possibly be explained to arise due to the formation of V$_{Ca}$ hydrogenated complexes during irradiation. Thus, V$_{Ca}$ may be forming and could react with residual H present in the sample to generate hydrogenated complexes. However, the concentration of this level did not increase proportionally with irradiation dose (Table 7.2), as it would be expected for an ideal point defect generation process, and indeed it can be seen in Figure 7.5 that the second irradiation with a higher dose did not produce any measurable changes in the concentration of the 2.60-2.80 eV band of states. Thus, we cannot conclude yet that point defects were generated during irradiation, and further experimental analysis is required.

Electron irradiation also has a strong impact on the concentration of the 3.22 eV level [7]. As shown in Figure 7.6, and summarized in Table 7.2, the concentration of this level increased by a factor of $\sim$2 for changes in the electron dose from 5x10$^{15}$ and 1x10$^{16}$ cm$^{-2}$. Following the above discussion regarding the 3.22 eV level, it is most likely that electron irradiation may be generating V$_{Ga}$ (as discussed in the previous paragraph). This would allow some of the residual Mg found in the film to occupy these sites, producing an increase in the concentration of the electrically active acceptors responsible for the 3.22 eV level. Indeed, as it is shown in Table 7.2, the concentration of this level increased proportionally to the electron dose, indicating that there is a one to one correlation.
Figure 7.6: Steady state photocapacitance spectra from n-GaN prior (dash-dotted line) and after electron irradiation (solid line) measured at $T=300\,K$. A clear change in the threshold at $E_c-E_i=2.80 \, eV$ can be observed as a result of e-irradiation.
between the number of irradiated electrons and the number of generated 3.22 eV-related traps. Thus, this deep level has to be related to a point defect, most likely MgGa.

The increase of the 3.22 eV level with electron irradiation could also apparently be explained to arise from the activation of acceptor atoms which are already in a Ga site but which may be found partially electrically passivated. For example, H may be initially bonding the acceptor center responsible for the 3.22 eV level, and these bonds could be broken as a result of irradiation. However, as it was shown in Chapter 6 and in contrast to p-GaN, incorporation of H in an n-GaN film has no effect on the 3.22 eV level-related acceptors. Thus, we must rule out this possibility.

<table>
<thead>
<tr>
<th>$E_c-E_t$</th>
<th>As-grown</th>
<th>$\Phi=5\times10^{15}$ cm$^{-2}$</th>
<th>$\Phi=10^{16}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.60 eV</td>
<td>0.21</td>
<td>0.75</td>
<td>0.72</td>
</tr>
<tr>
<td>3.22 eV</td>
<td>1.52</td>
<td>3.39</td>
<td>6.66</td>
</tr>
</tbody>
</table>

Table 7.2: Effect of electron irradiation on the concentration ($x10^{15}$ cm$^{-3}$) of the 2.60 and 3.22 eV levels.
7.4 Conclusion

In this chapter we have presented direct evidence that the Mg memory effect has an impact on deep level spectrum of n-GaN. Films grown by MOCVD in reactors which have been previously exposed to reactant gases with Mg show a distinct residual amount of this element. The presence of residual Mg generates a measurable trap concentration at Ec-3.22 eV. This level is not observed under Mg-free conditions. Moreover, it has an effect on the background electron concentration \(n\) of the contaminated film, decreasing \(n\) via a carrier compensation mechanism. Electron irradiation strongly supports these results, and shows that the concentration of the 3.22 eV trap increases proportionally to the dose, suggesting point defects are being generated and are responsible for this trap. This effect can be explained to arise from the generation of \(V_{Ga}\) during irradiation together with the diffusion of residual Mg into these sites, which creates electrically active \(Mg_{Ga}\) acceptors. Thus, we can conclude that the 3.22 eV level is due to \(Mg_{Ga}\) point defects.
7.5 References


CHAPTER 8

TOWARDS THE IDENTIFICATION OF PHYSICAL SOURCES FOR THE ELECTRICALLY ACTIVE DEFECTS IN n-GaN

8.1 Introduction

Once the deep level spectrum for n-GaN has been established in Chapters 5 through 7, we now focus on the role that extended vs. point defects are having on the generation of these traps. We attempt to understand how these deep levels may be behaving as R-G centers and whether these centers are associated with TDs or point defects. Indeed, the role of point defects and TDs in deep level generation within the bandgap of n-GaN is presently controversial, but it is clear that it is of great importance because of the impact that these defects and associated traps can have on nitride devices [1,2]. As it was discussed in Chapter 1, the high TD density is believed to be partially responsible for the limitations observed in the performance of GaN devices. For example, a combination of CL and atomic force microscope (AFM) studies on GaN buffer layers has demonstrated that GaN regions associated with TDs have reduced optical bandgap emission intensity [3], whereas AFM and scanning capacitance
microscope experiments showed that negative charge is present in the vicinity of TDs [4]. Both of these results imply that high TD density regions show high non-radiative recombination, in essence, carrier recombination at traps [5]. Indeed, carrier mobilities in heteroepitaxial n-GaN grown on sapphire have been shown to follow a model where Coulomb scattering by negatively charged extended defects found perpendicular to the current path is the predominant scattering process [6]. This effect can be explained to result from either the TD acting as a trap itself, or because the TD can enhance the formation of point defects and other related complexes that may act themselves as carrier traps. However, at this point, TDs have not been experimentally observed to generate deep levels within the n-GaN bandgap that could account for such behavior.

As we also discussed in Chapter 1, the impact that point defects in nitrides have in trap generation is even less understood. Even though theoretical studies have reported that different vacancies and interstitials may be responsible for levels found within the bandgap of GaN, these studies still require experimental verification [7]. For example, $V_{Ga}$ defects have been theoretically predicted to generate a deep level at $\sim 1$ eV above the valence band and are more likely to form in n-type material [8]. Moreover, positron annihilation measurements have shown that these $V_{Ga}$ defects are associated with the yellow PL band [9], whose intensity correlates with the concentration of the $\sim E_v + 1$ eV deep level [10,11]. This deep level PL emission is observed only in n-type material, which consistent with the lower formation energy calculated for $V_{Ga}$ defects in n-GaN [7].

Thus, in this chapter we have used a combination of DLOS [12] and DLTS to identify the deep level spectrum within the entire n-GaN bandgap, and to study their
capture kinetics properties in order to identify extended vs. point defect behaviors. Then a combination of TEM and EBIC together with post-growth hydrogenation studies have been employed to characterize the structural origin of the defects responsible for the deep levels. This combination allows the identification of traps and their physical origin, and brings some light into the role of point defects and TDs on deep level formation in n-GaN.

8.2 Experimental procedure

For this study two sets of test samples (A and B) both grown on c-sapphire were used. Sample A was grown several months prior to sample B, under identical growth conditions, with similar layer structure and in the same two-flow horizontal MOCVD reactor. Sample B was previously discussed in Chapters 5 through 7 [13], whereas sample A is now analyzed for the first time. The sample structure is discussed in detail in Chapter 4. Details on the DLOS and DLTS experimental conditions can also be found in that chapter.

8.3 Results

8.3.1 Deep level detection and identification in n-GaN

In this section DLTS and DLOS analysis are used to compare in detail the deep level spectrum of samples A and B. A summary of each level and its properties obtained from
the results in Chapters 5 to 7, together with correlation to previous reports, is presented in order to identify possible physical sources responsible for these levels. This will allow a better understanding of the results presented in the following sections, where the structural origin of these levels is discussed by means of TEM and EBIC analysis of these same samples.

Both test samples A and B present deep levels in the n-GaN layer at $E_c - E_t = 0.58 - 0.61$, $1.35$, $2.60 - 2.64$ and $3.22$ eV (Figures 8.1 and 8.2). In addition, sample A shows two other deep levels at $E_c - E_t = 1.0$ and $3.04$ eV (Figure 8.2). The source for the $1.0$ eV level is at this time unknown although previous photocapacitance reports [14] have shown a similar level but did not identify its origin.

8.3.1.1 The $0.58$, $0.61$, $1.35$, and $2.60 - 2.64$ eV levels

First, let us discuss the results from DLTS data shown in Figure 8.1. As shown in this figure, under minority carrier injection conditions (fill pulse $V_p > 0$) a hole trap (negative peak) is found at $E_v + 0.87$ eV with a hole capture cross section of $\sim 6 \times 10^{-14}$ cm$^2$ in both samples A and B. This hole trap is the same level as that observed by DLOS at $E_c - (2.60 - 2.64$ eV) [15] (Figure 8.2) and that reported by Polyakov et al. [16] with equal energy and capture cross section. Because of the dependence of the minority carrier DLTS signal on total injected current the total hole trap concentration cannot be calculated. However, under equal injection conditions on both samples the concentration of this hole trap is much smaller in sample A than in sample B (height of negative peak in Figure 8.1),
Figure 8.1. DLTS spectra from samples A and B. The positive and negative peaks correspond to electron and hole traps, respectively. The hole trap is the same as that observed by DLOS at $E_c-(2.60-2.64)$ eV. The inset shows the Arrhenius behavior for these traps.
<table>
<thead>
<tr>
<th>$E_c-E_f$</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58 eV *</td>
<td>~</td>
<td>2.7x10^{14}</td>
</tr>
<tr>
<td>0.61 eV *</td>
<td>3.6x10^{14}</td>
<td>~</td>
</tr>
<tr>
<td>1.35 eV</td>
<td>5.2x10^{14}</td>
<td>1.79x10^{15}</td>
</tr>
<tr>
<td>2.60-2.64 eV</td>
<td>6.6x10^{14}</td>
<td>2.32x10^{16}</td>
</tr>
<tr>
<td>3.22 eV</td>
<td>1.0x10^{15}</td>
<td>3.06x10^{16}</td>
</tr>
<tr>
<td>TD density</td>
<td>8x10^8 cm^{-2}</td>
<td>8x10^8 cm^{-2}</td>
</tr>
</tbody>
</table>

* The 0.58 and 0.61 eV levels are different traps as evidenced by their different capture cross section: ~1x10^{-15} and ~9x10^{-17} cm^2, respectively.

Table 8.1: Comparison of concentrations (cm^{-3}) for the deep levels found both in samples A and B.

consistent with the much smaller concentration of the 2.60-2.64 eV level in sample A (see Table 8.1).

The DLTS spectra also shows two electron traps found at $E_c$-0.58 eV [15] and $E_c$-0.61 eV in samples B and A, respectively (Table 8.1). However, the capture cross sections of both levels are quite different: ~1x10^{-15} cm^2 and ~9x10^{-17} for the 0.58 and 0.61 eV levels, respectively. This difference is implied by the shift in temperature of the DLTS peak for a given rate window, and indicates that both levels are related to different traps. Indeed, because of the similar Arrhenius behavior, the 0.61 eV trap is likely the same as the E3 level initially reported for HVPE-grown n-GaN [17], which was also observed in
MOCVD-grown n-GaN after N<sup>2+</sup> implantation [18]. Since this level was shown to subsequently anneal out by means of rapid thermal anneal [18], it is most likely that the 0.61 eV trap is related to a point defect or a complex of point defects. However, the 0.58 eV level is likely the same as the E2 trap which has been previously observed in both HVPE [17] and MOCVD-grown n-GaN [19] as well as in MOCVD-grown n-AlGaN [20].

Both the 0.58 and 0.61 eV level show similar depth-profile concentration behavior, and indeed neither level can be detected for V_p<0 (i.e., away from the p<sup>+</sup>-side of the junction). As discussed in References [15] and [21] for the 0.58 eV level, such change in concentration tracks the residual Mg-profile in the n-side of the junction measured by SIMS (both samples show equivalent Mg SIMS profiles). This behavior is consistent with the increase in 0.58 eV trap concentration observed for higher Cp2Mg flow rates [22]. Because of their bandgap position, one or both of these levels may be related to that observed by Kaufmann et al. [23] which was ascribed to the blue PL band, for which Mg-V<sub>N</sub> complexes were proposed.

Next, we focus on the results from DLOS analysis. Figure 8.2 shows deep levels at E<sub>c</sub>-E<sub>t</sub>=1.35, 2.60-2.64 and 3.22 eV for both samples. The physical origin for the 1.35 eV level [13,15] is unknown at this time, but of all the levels observed in these samples it is the closest to mid-gap suggesting it is the trap that is most likely to behave as a recombination-generation center, and thus could have an impact on device performance by providing a current leakage path. Regarding the 2.60-2.64 eV level, there is experimental evidence that indicates it may be related to V<sub>Ga</sub> native defects and related
Figure 8.2. Steady state photocapacitance spectra from samples A and B performed at T=300 K.
complexes with donors [13,24,25]. This level also matches earlier reports, in which the concentration of this trap was found to be directly proportional to the yellow PL emission in MOCVD n-GaN [10,11]. These results also agree with the work of Saarinen et al. [9] where the yellow PL band has been associated to \( V_{Ga} \) defects by means of positron annihilation spectroscopy. Thus, we can conclude that the 2.60-2.64 eV levels are likely related to \( V_{Ga} \) and could play a role in yellow PL emission.

8.3.1.2 The 3.04 and 3.22 eV levels

As shown in Figure 8.2 the 3.04 eV level is only observed in sample A. However, it is likely that this trap is also found in some concentration in sample B but its optical threshold may be shadowed by the large signal from the 2.64 eV level whose concentration is significant in this sample (Table 8.1). The 3.04 eV level may be that reported by Yi et al. [14] at \( E_c-3.1 \) eV which was observed in n-GaN when Mg was incorporated in the film. Some evidence for the origin of the 3.04 eV level can be extracted from the behavior of the DLOS spectra obtained on different regions across the sample. In this type of spectrum every step corresponds to the optical threshold of a deep level and the height of the step is proportional to the concentration of the level. Details on DLOS and on the analysis and determination of these parameters can be found in References [12] and [26], and applied in particular to n-GaN in Reference [15]. Figure 8.3 shows the DLOS spectra for diodes 1 cm apart from each other across sample A where changes in the concentration of the deep levels by as much as a factor of 2-3 are observed. These changes are consistent with possible depletion of the gas sources flowing
across the sample during MOCVD growth as suggested by the absence of such behavior in MBE-grown n-GaN [27].

As shown in the inset of Figure 8.3, the concentrations of both the 3.04 and 3.22 eV levels increase proportionally across the sample. This behavior suggests that the physical sources responsible for the 3.04 and 3.22 eV may be related. These results can be understood if we look at previous results for the 3.22 eV level. Indeed, as it was discussed in Chapter 7, analysis of n-GaN grown in a Mg-free reactor and of electron irradiation on this sample shows that the 3.22 eV level is related to residual Mg acceptors (MgGa), i.e., extrinsic point defects [25]. Thus, it is likely that either some kind of impurity introduced by the Mg source or Mg itself introduces the Ec-3.04 eV level. In addition, the concentration of the 2.60 eV level changes inversely to that of the 3.22 eV level. This decrease can be explained to result from Mg substituting into VGa defects. Indeed, since the 2.60 eV level has been previously assigned to VGa [13], the increase in the 2.60 eV level concentration across the sample may be due to more Mg incorporating into a VGa site causing a decrease in the 3.22 eV level concentration due to a depletion of the available Mg.

8.3.2 Structural origin of the deep levels

We now use a combination of TEM and EBIC measurements to investigate the origin of the differences in deep level concentration in samples A and B (Table 8.1). Indeed, even though the 1.35, 2.60-2.64 and 3.22 eV levels are found in both samples
Figure 8.3. Comparison of steady state photocapacitance spectra for three diodes found 1 cm apart from each other across sample A (T=300 K). The inset shows the deep level concentrations for the three diodes.
they are present with very different concentrations. All these traps are present at much higher concentrations in sample B than in sample A. In addition, the 0.61 eV level is observed only in sample A whereas the 0.58 eV level is only observed in sample B.

The first key result is that plan-view TEM analysis shows equal TD density (within experimental error) for both samples A and B (Figure 8.4), \(~8 \times 10^8\) cm\(^{-2}\). This result indicates that the differences in concentration for the 1.35, 2.64 and 3.22 eV levels shown in Table 8.1 most likely cannot be accounted for by the TD density.

Figure 8.4. Plan-view TEM images from samples A and B. Equal TD densities were obtained for both samples (\(~8 \times 10^8\) cm\(^{-2}\)).
However, it must be considered that even though the TD density is similar, those differences could be related to a difference in the electrical activity of the TDs in each sample due to, for instance, H incorporation and passivation [28] during MOCVD growth. Investigation of this possibility was undertaken by comparing EBIC images obtained from both samples. As it was discussed in Chapter 4, during an EBIC experiment, an electron beam is focused and scanned across the diode while the induced diode current is recorded [29]. The electron beam generates electron-hole pairs at the junction that can drift across it and get collected, producing a measurable current (light region in the EBIC images). However, when a recombination center is present, electrons-hole pairs can recombine non-radiatively causing a decrease in the collected current at that point (dark spot in the image).

As shown in Figure 8.5, under identical experimental conditions similar EBIC images are obtained from samples A and B. The quality of the images is low due to the p⁺-cap layer found on top of the n-GaN layer that causes a clouding effect, but qualitatively both samples present a similar pattern. As it will be discussed in the next section, the close agreement between the density of dark spots encountered in the EBIC images to the TD density measured by TEM strongly suggests that the regions where TDs are found, or the TD cores themselves, are behaving as recombination centers. Thus, the EBIC analysis helps support the results from TEM, and substantiates the lack of correlation between the 1.35, 2.64 and 3.22 eV traps and the TD density. Taking together the results from TEM and EBIC analysis, we can conclude that the physical sources for the 1.35, 2.64 and 3.22 eV levels found in both samples A and B are likely point defects.
Figure 8.5. EBIC images for samples A and B at T=300 K. The black dots correspond to TDs found at the depletion region. The cloudiness of both images is caused by the top p⁺-cap layer.
rather than TDs. As it will be seen in the next section, this assignment will also be made for the 0.58 and 1.35 eV levels, whereas, as discussed in the previous section, the 0.61 eV level has already been associated to a point defect [18]. Moreover, the correlation of the 3.22 eV level to MgGa⁺ acceptors made in the previous section is consistent with this assignment.

8.3.3 Hydrogen passivation of recombination-generation centers

We now use a combination of post-growth hydrogenation and EBIC analysis to further aid in the identification of the physical origin for the traps found in the n-GaN layer. This study was performed on a sample grown immediately after sample B but without the p⁺-cap layer. A Ni 80Å-thick Schottky contact was used instead of an ohmic contact in order to obtain a Schottky junction between the metal and the n-GaN layer. This type of junction was chosen for this study in order to avoid dealing with trapping of H expected within the heavily Mg-doped p⁺-cap layer of the p⁺-n structure studied in the previous section [30]. Thus, this sample structure allows a better observation of the changes that occur in the n-GaN layer as a result of H incorporation. In addition, it allows quantitative EBIC to be performed, avoiding the shadowing effect of the p⁺-cap layer (see previous section). A comparison of the deep level spectrum of the Schottky sample to that of sample B is given in detail in Chapter 5, where it was shown that both samples have identical traps at E_C-E_t = 0.58, 1.35, 2.64 eV and 3.22 eV with similar concentrations, confirming that the deep level spectrum of the bulk n-GaN layer is not affected by
possible interface states or the type of junction used for these experiments. Only the concentration of the 1.35 eV level was observed to decrease (by a factor of ~4) for the p-n diode suggesting it is point-defect related (see Chapter 5).

Post-growth hydrogenation shows three different behaviors of the deep levels [13] (Table 8.2). First, the 0.58 and 1.35 eV levels are strongly passivated by H-incorporation, with their concentration decreasing by a factor of ~30 and ~14, respectively. Second, the 2.64 eV level is shifted to 2.74 eV, but the total level concentration remains unaffected. Finally, hydrogen has no impact on the 3.22 eV acceptor level. As it was discussed in Chapter 6 in detail, the 2.64-2.74 eV shift can be explained to result from hydrogenation of V_{Ga^3} to produce (V_{Ga-H})^{2-} and (V_{Ga-H_2})^{2-} which are more likely to form in n-GaN when H is present. Here we focus on the passivation of the 0.58 and 1.35 eV levels.

<table>
<thead>
<tr>
<th>E_c-E_f=</th>
<th>As-grown</th>
<th>Hydrogenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58 eV</td>
<td>4.1×10^{14}</td>
<td>≤1×10^{13}</td>
</tr>
<tr>
<td>1.35 eV</td>
<td>6.0×10^{15}</td>
<td>4.8×10^{14}</td>
</tr>
<tr>
<td>2.64 eV and 2.74 eV *</td>
<td>3.7×10^{16}</td>
<td>3.7×10^{16}</td>
</tr>
<tr>
<td>3.22 eV</td>
<td>6.6×10^{16}</td>
<td>1.0×10^{17} **</td>
</tr>
<tr>
<td>TD density (from EBIC)</td>
<td>6×10^8 cm^{-2}</td>
<td>6×10^8 cm^{-2}</td>
</tr>
</tbody>
</table>

* 2.64 eV for the as-grown sample, which shifts to 2.74 eV as a result of hydrogenation.
** The apparent increase in the 3.22 eV level concentration is within the concentration distribution found across the sample. Thus, it is most likely not significant.

Table 8.2: Concentration (cm^{-3}) of the deep levels found in the as-grown and hydrogenated n-GaN films.
EBIC was performed on the hydrogenated and as-grown samples under identical conditions by using a constant bias and equal current pre-amplification settings. A low accelerating beam voltage (7 kV) was used in order to probe the junction region close to the metal-semiconductor interface producing a penetration depth of ~0.3 μm and a current of ~2-5x10^-7 A. Figure 8.6 shows the EBIC images for the hydrogenated and as-grown samples. In both cases, analysis of the images produces similar dark spot (recombination center) densities of ~6x10^8 cm^-2, in good agreement the TD density obtained by TEM analysis of ~8x10^8 cm^-2 (see Figure 8.4). Thus, the dark spots are most likely related to the regions surrounding the TDs, or the TD themselves. The fact that a dark spot is observed in the EBIC image for every TD-related region indicates that either the TDs or defects decorating them are behaving as carrier recombination-generation centers. Indeed, since the 2.64 eV level concentration is unaffected by hydrogenation this trap could be found in the TD-related regions and could be behaving as a recombination center. It is also clear from Figure 8.6 that the TD pattern is similar in both samples which, together with the lack of change in the TD density, indicates that the TDs are not affected by post-growth hydrogen incorporation.

Further understanding of the passivation of the 0.58 and 1.35 eV levels can be obtained by analyzing the TD region-background contrast by means of quantitative EBIC [29]. The contrast, c, is defined as

\[ c = \frac{I_b - I_d}{I_b} \]  

(8.1)
Figure 8.6. SEM (top) and EBIC (center and bottom) images for the as-grown and hydrogenated samples at $T=300$ K. Equal TD densities were obtained for both diodes ($\sim 6 \times 10^8$ cm$^{-2}$). The SEM image is included to illustrate the smooth surface morphology of the sample. A similar SEM image was obtained for the hydrogenated sample.
where $I_b$ and $I_d$ are the background and defect intensities, respectively, and can be obtained through analysis of the EBIC image line-scan. In the as-grown sample an average contrast of $\sim 27\%$ is obtained, whereas in the hydrogenated sample it increases to $\sim 53\%$. Thus, the TD regions can be equally observed after hydrogenation and with the same concentration indicating that the electrical activity of these regions remains unaffected by H incorporation. However, as discussed above, the concentration of the 0.58 and 1.35 eV levels were drastically decreased by over an order of magnitude as a result of hydrogenation (Table 8.2), which clearly supports the fact that point defects, rather than TDs, are responsible for both of these levels. The increase in TD region-background contrast as a result of hydrogenation can then be explained to result from a decrease in the electrical activity of the point defects that are uniformly distributed through the sample (and therefore across the background of the EBIC image) and are behaving as recombination centers. This decrease would cause the background region in the EBIC images to become lighter, since less recombination centers are available, increasing the current collected from the background region that in turn would produce an increase in the TD-background contrast. Indeed, the total current collected from the EBIC image area increased from $\sim 2 \times 10^{-7}$ to $\sim 5 \times 10^{-7}$ A for the hydrogenated diode. In addition, these results show that either one or both of the 0.58 and 1.35 eV levels behave as recombination centers, and could have a negative impact on device performance. Thus, the combination of EBIC and hydrogenation analysis indicates that point defects or
clusters of point defects, likely distributed across the sample, are responsible for the 0.58 and 1.35 eV levels and supports the results from the previous section on the 1.35 eV level where a similar physical origin was proposed for this trap.

8.3.4 Capture kinetics of the E_v+0.87 eV level

Investigation of the capture kinetics related to a given trap can shed some light on the arrangement of defects in the n-GaN crystal. In general, two different ideal trapping behaviors can be observed for a distribution of defects. First, let us look at those defects that are found with no ordered distribution in the bulk of the film and that do not interact between themselves (such as isolated point defects), and thus are responsible for an isoelectronic bandgap state. Under these conditions, the trap occupation \( n_T \) after a given fill pulse time \( t_p \) due to trapping of carriers at a point defect found in the depletion region of a junction can be expressed as \[31\]

\[
n_T(t_p) = (n_T(0) - N_T) \exp(-c_n t_p)
\] (8.2)

where \( N_T \) is the total trap concentration, and \( c_n \) is the capture rate. However, for a one dimensional distribution of defect sites, for which neighboring defects can interact (as expected for TDs or point defects decorating dislocation cores), a different trapping behavior is found. For this scenario the accumulation of trapped carriers during the fill pulse generates a local time-dependent Coulombic potential given by \[31\]
where $\phi_0$ and $n_{T0}$ are equilibrium values. Initially, carriers will get trapped with a similar behavior to that of isolated defects. However, eventually the carriers that get captured along this line of defects produce a repelling force against continued trapping of other carriers of the same sign, decreasing the probability of these new carriers being captured. Hence, the capture kinetics deviates from the situation for ideal, non-interacting point defects (Equation (8.2)) and it can be shown that $n_T$ has a different dependence on $t_p$ now given by [31]

$$n_T(t_p) \propto \pi N_T \ln\left(\frac{t_p}{\tau}\right) \quad (8.4)$$

where $\tau$ is a time constant that accounts for the time it takes captured charge to start influencing the Coulombic barrier. Since the maximum change in capacitance ($\Delta C_{\text{max}}$) in a DLTS experiment is proportional to $n_T$, the investigation of the dependence of $\Delta C_{\text{max}}$ on $t_p$ can help the understanding of the arrangement of trap-related defects in a crystal.

Figure 8.7 shows the dependence of the DLTS peak on $t_p$, and the extracted values of the peak height, $\Delta C_{\text{max}}$, as a function of log($t_p$) for the $E_v$+0.87 eV hole trap. As seen in this figure, this hole trap (also observed by DLOS at $-E_C$-2.60-2.64 eV) shows a clear linear $\Delta C_{\text{max}}$ vs. log ($t_p$) dependence consistent with the behavior of an ideal extended defect as given by Equation (8.4). Furthermore, the low temperature side of the DLTS peak associated with this hole trap shifts with $t_p$, whereas the high temperature side
Figure 8.7: (a) Dependence of the DLTS peak with fill pulse time \((t_p)\) for the \(E_v+0.87\) eV hole trap measured at \(V_p=2\) V and \(V_r=-1\) V. (b) DLTS peak height \((C_{\text{max}})\) as a function of \(\log(t_p)\) extracted from (a). A clear linear behavior can be observed, indicating the extended nature of the defect responsible for the \(E_v+0.87\) eV level.
does not (Figure 8.7(a)). This can be understood if we consider a distribution of states, characteristic of an extended defect, where the highest energy states are preferentially filled with holes for short $t_p$ values (during the minority carrier injection fill pulse) [33]. For long $t_p$ values, the lowest energy states found closer to the valence band will also be filled, and will generate a DLTS signal detected at progressively lower temperatures. These long fill pulses will also cause a broadening of the DLTS signal, due to multiple carrier emissions from the band of states to the valence band.

Thus, the behavior of the DLTS signal for the $E_v+0.87$ eV hole trap is consistent with that of a band of states associated with an extended defect. This can be explained with one of two possibilities: (1) point defects are responsible for this trap and are found decorating TDs, or (2), the native TDs act themselves as carrier traps and are responsible for this level. In both cases it is clear that the defects responsible for the $E_v+0.87$ eV trap are arranged in some kind of extended ordered geometry in the crystal, and are found in the TD-related regions.

8.4 Discussion

Let us first review the role that TDs may be playing in the results presented here. Indeed, TDs are known to be detrimental for n-GaN devices since they are responsible for leakage current paths, as evidenced by the results on lasers diodes grown on LEO n-GaN [2]. In addition, as previously mentioned, there are reports that strongly indicate that TDs can act as carrier traps that charge up and cause a decrease in the carrier mobility of n-
GaN [3,5,6]. These experimental results are substantiated by the theoretical work by Leung et al. [32] which indicates the edge TDs may generate deep levels within the n-GaN bandgap. However, as discussed in the previous sections, the TD density as well as the electrical activity of the TD-related regions are similar in both samples A and B, and in principle cannot account for the differences in the concentrations of the 1.35, 2.60-2.64 and 3.22 eV levels. In particular, the results from hydrogenation (8.3.3) show that the 0.58 and 1.35 eV levels are related to point defects or clusters of point defects rather than to TDs.

Even if the deep levels reported here seem to not correlate to the TD density, these defects could play an indirect role in the appearance of such deep levels by having an impact on point defect generation during growth. Indeed, TDs could enhance the formation of point defects surrounding the TD by decreasing their formation energy, as observed in other semiconductors [33]. Thus, point defects that are possibly decorating the TDs could be responsible for some of the effects that TDs have been shown to have on carriers (as discussed above). Indeed, there is a reasonable possibility that V_{Ga} may decorate TDs. Since V_{Ga} are found in negative charged state in n-GaN [24], this would account for the negative charge state assigned to the TDs and/or the areas surrounding them [3,4,6]. Moreover, since the 2.60-2.64 eV level captures both electrons and holes (it is observed both by DLOS and minority carrier DLTS), it could behave as a recombination-generation center creating a path for current to flow through the junction, which could account for the current leakage associated with TDs [2].
The results from 8.3.3 on hydrogenation are consistent with these ideas. They show that, indeed, the concentration of the 2.60-2.64 eV level is unaffected by H-incorporation, correlating with the lack of change of the electrical activity of the TD-related regions in the EBIC image. Moreover, as it was discussed in 8.3.4, the carrier capture kinetics of this level are those of an extended defect, indicating that this trap is likely found along the TDs.

8.5 Conclusion

In summary, we have presented experimental evidence that indicates that the deep levels observed across the bandgap of unintentionally doped n-GaN grown by MOCVD show concentrations which do not correlate with the TD density. These traps are found at $E_c - E_t = 0.58$, 0.61, 1.35, 2.60-2.64, and 3.22 eV with concentrations ranging from $~10^{14}$ to $10^{16}$ cm$^{-3}$. Such lack of correlation is obtained for all these traps from analysis of samples that show equal TD density ($~6$-$8 \times 10^8$ cm$^{-2}$) but very different deep level concentrations. This result is further confirmed for the 0.58 and 1.35 eV levels from hydrogenation-EBIC analysis which shows that H passivates these two traps but has no effect on the TD-related regions, supporting a direct correlation between these levels and point defects or clusters of point defects. This analysis also shows that either one or both of these levels behave as recombination-generation centers. In addition, we observe recombination of carriers in the regions where the TDs are found, indicating there must be a deep level associated with these regions. Indeed, the 2.60-2.64 eV level presents the capture kinetics
behavior of an extended defect, which indicates that this trap is likely found along the TDs, and it is related to either point defects decorating the TDs, or to the TD itself. Moreover, its properties could account for some of the characteristics previously associated with the TDs.
8.6 References


CHAPTER 9

CONCLUSIONS AND FUTURE DIRECTIONS

The goal of this work has been to understand in detail the physical properties of the electrically active defects in n-GaN, and to create a knowledge base that could serve for future understanding of ternary and quaternary III-nitride alloys and related devices. To achieve this goal, it was necessary, first of all, to design and put into place an experimental tool that would allow the study of deep levels throughout the entire bandgap of GaN, something that is not commercially available. This was achieved by designing, setting up and understanding the physics behind DLOS. After this technique was mastered on another wide gap semiconductor (ZnSe), it was applied in detail to GaN homojunctions. Once the basic electronic properties of the deep levels had been established, different experimental analyses, including secondary ion mass spectroscopy, hydrogenation, electron irradiation, transmission electron and electron beam induced current microscopies were used to identify the physical, chemical and structural origins of the defects associated to the deep levels. Special care was maintained throughout this work to account for previous literature results, which in some cases have provided strong support for our own results.
Overall, this work has provided two major breakthroughs: the determination of the deep level spectrum and its electrical properties in n-GaN, and the discrimination of the structural origin of the defects that are responsible for these traps. These results are summarized in the following two sections.

9.1 The deep level spectrum in n-GaN

As it was discussed in Chapters 5 through 8 n-type GaN grown by MOCVD shows a rich deep level spectrum. These traps are found at $E_c - E_t = 0.58$, 0.61, 1.35, 2.64 eV, 3.04 and 3.22 eV with concentrations ranging from $\sim 10^{14}$ to $10^{16}$ cm$^{-3}$, and were observed by combining results from DLOS and DLTS. In the case of the 2.64 eV level, this trap was observed by both techniques, and thus its electrical and optical signatures have been fully determined. A schematic of the deep level spectrum is shown in Figure 9.1.

Regarding the electron traps close to the conduction band, at $E_c - E_t = 0.58$ and 0.61 eV, these present different capture cross sections clearly indicating that they are related to different defects. Indeed, both defects had been observed before in the same GaN film [1]. The 0.58 eV level shows a concentration that tracks the profile of background Mg in n-GaN measured by SIMS, which taken together with its bandgap position suggests that it may be related to that reported in Reference [2] which was ascribed to the blue PL band, and for which Mg-$V_N$ complexes were proposed.
**Related to Mg**

- Mg-V$_n$? (blue PL?)
- $V_{Ga}$ & $V_{Ga-H_n}$ (yellow PL)
- residual Mg$_{Ga}$

$0.58 \text{ eV}$ trap correlates with [Mg]; strongly H-passivated; point defect-related

$0.61 \text{ eV}$ trap = point defect-related

$1.35 \text{ eV}$ trap strongly H-passivated; point defect-related; not related to Mg

$2.64, 2.74 \& 2.80 \text{ eV}$ traps related to $V_{Ga}$, $V_{Ga-H}$ and $V_{Ga-H_2}$ complexes; found in TD-related region

$3.04 \text{ eV}$ trap follows concentration of $3.22 \text{ eV}$ level

$3.22 \text{ eV}$ level due to Mg$_{Ga}$ acceptors

Figure 9.1: Schematic of the deep level spectrum and their properties in n-GaN grown by MOCVD.
The 2.64 eV level is the dominant level and it is always observed in MOCVD-grown n-GaN, even under Mg-free conditions. The region surrounding the 2.64 eV level shows a series of small optical thresholds that make up a band of closely spaced hole traps at $E_c-E_f=2.64-2.80$ eV. This band of states correlates well with a level at $E_v+0.8$ to 1.0 eV which has been ascribed to the yellow PL band [3,4]. Strong evidence for the identification of its physical origin was obtained from its behavior under hydrogen incorporation, which narrows this band of states from 2.64-2.80 eV to 2.74-2.80 eV. This band of states shows a similar energy position within the bandgap to reported calculations of deep levels produced by $V_{Ga}^{3+}$ and $V_{Ga-H}$ complexes [5]. Such calculations have shown that the hydrogenation of $V_{Ga}^{3+}$ to form $(V_{Ga-H})^{2+}$ and $(V_{Ga-H_2})^+$ complexes each shift the level energy by $\sim 0.1$ eV closer to the valence band correlating with the 2.64 to 2.74 eV shift. Thus, we have assigned the $E_c-E_f=2.64, 2.74$ and 2.80 eV levels to $V_{Ga}^{3+}$, $(V_{Ga-H})^{2+}$ and $(V_{Ga-H_2})^+$, respectively. The presence of the 2.80 eV level before hydrogenation indicated the existence of $(V_{Ga-H_2})^+$ complexes in the as-grown material.

Since positron annihilation measurements have associated $V_{Ga}$ defects with the yellow PL band [6], it is most likely that this band of states is related to the yellow PL band.

Details on the characteristics of the $E_c-E_f=1.35$ and 3.22 eV levels are given in the next section.
9.2 Point defects vs. threading dislocations in n-GaN: R-G centers

In addition to the determination of the deep level spectrum, we have presented in this work strong experimental evidence for the identification of the physical origin of these traps and of their electrical behavior.

The first striking result from this research is that we do not observe a direct correlation between the TD density and the concentration of the bulk deep levels in n-GaN. Indeed, while the concentration of the deep levels is found to change from \( \sim 10^{13} \) to \( \sim 10^{16} \) cm\(^{-3}\), the TD density does not present any changes (\( \sim 8 \times 10^8 \) cm\(^{-3}\)). This is in fact a very interesting result, and suggests that TDs may not play a direct role in deep level formation in n-GaN. As we next address, additional analysis showed strong support for this picture.

First, two of the traps, the 0.58 and 1.35 eV levels, have been shown here to be directly related to point defects or clusters of point defects (Chapter 8). Indeed, hydrogenation of n-GaN films shows high electrical passivation of both of these deep levels. However, no changes in the electrical activity of the TD-related regions were observed, and only the electrical activity of the regions away from the TDs were affected by such passivation. These results not only indicate that the 0.58 and 1.35 eV levels are not related to TDs, but they also show that either one or both of them behaves as a recombination-generation center. This result is of great importance because it indicates that point defects or clusters of point defects found away from the TDs can act as current sources and current sinks (i.e. current leakage pathways), behavior that has traditionally been only attributed to TDs in GaN. These point defects could thus have a very
detrimental impact on GaN-based devices. The assignment of the 1.35 eV to point defects is consistent with the fact that this trap anneals out as a result of exposure of the GaN film to a temperature anneal cycle (Chapter 5).

In addition, we have also confirmed the direct correlation between the 3.22 eV level and residual Mg found in the n-GaN due to memory effects in the MOCVD reactor. These Mg atoms substitute into a Ga site to form Mg\textsubscript{Ga} and become electrically active, producing the 3.22 eV level, which behaves as a compensating level. Thus, when n-GaN films are grown in a reactor free of Mg, the background electron carrier concentration increases due to the absence of compensating centers. These results not only indicate that the 3.22 eV level is related to an electrically active point defect, but it also points out the important role that residual Mg found in the MOCVD reactor (as a result of p-type doping of GaN) can have on the electrical properties of GaN devices grown in such reactors. Furthermore, the 0.58 eV level is also highly dependent on the presence of background Mg, and its concentration can be strongly reduced when a Mg-free reactor is used. These results also point out the importance of using Mg-free reactors for growth of nitrides that do not require p-doping (such as AlGaN/GaN FETs).

So the question that remains is, what is the role of TDs in the generation of recombination-generation centers that could account for the current-leakage behavior associated with these defects? We presented evidence in Chapter 8 that shows that the electrical activity of the TD regions is not affected by hydrogen incorporation, and neither was the concentration of the 2.64 eV level. In addition, this level shows the ideal capture kinetics behavior of an extended defect, where the capture of carriers is limited by the
repelling Coulombic force due to previously trapped carriers along the defect. Moreover, the 2.64 eV level behaves as an electron and hole trap, which strongly suggests that it could be related to a R-G center, and could account, at least partially, for the electrical activity observed in the TD-related regions and the electrical properties previously reported and assigned to TDs [7,8,9,10]. Thus, the defects responsible for the 2.64 eV level are most likely found in the TD regions, with their formation in these regions likely enhanced by the strain field that surrounds the TDs.

9.3 Future directions

As we discussed earlier in this chapter, this work has allowed us to establish a baseline for the understanding of the electrically active defects in n-GaN. However, this will be used as a basis for future understanding of more complex nitrides, such as alloys, as well as for the determination of trap impact on device performance. Thus, several areas can be identified as future extensions of this work, and they include:

1) Further understanding of the basic physics of nitrides and materials properties should be developed, with special emphasis on the electrical behavior of extended and point defects. This should involve, first of all, a detailed study of n-GaN grown by lateral epitaxial overgrowth (LEO) on sapphire. A comparison of the wing and window regions, which present low and high TD densities, respectively, will bring light into the role of TDs in deep level formation, and will help establish a definite correlation between extended defects and recombination-generation centers.
2) Another important area that should be addressed is the impact of different growth techniques on the electrically active defects of n-GaN. Even though MOCVD is commonly used to grow GaN, there is increasing interest to understand the properties of GaN grown by MBE. Indeed, the growth of MBE GaN has already been studied in some detail [11], but little information is available regarding its electronic properties and how they compare to MOCVD material. In addition to the understanding of MBE material, this study would allow the identification of defects that are intrinsic to GaN, regardless of the growth technique. This type of knowledge is very important for the development of the different growth techniques and for their application to specific devices.

3) A field that has not been addressed here at all is the impact that different substrate materials have on the electronic properties of GaN. While sapphire is currently commercially used, other materials are receiving increasing attention, mostly SiC. This type of substrate is promising because of its smaller lattice mismatch to GaN, and because of its large thermal impedance, which is very desirable for high temperature microelectronics. Thus, a comparative study of the role of substrates on the electrical defects in GaN would be of great interest for comparison of devices grown on either type of substrate.

4) It is also necessary to study alloy composition in III-nitrides and their electrical properties. Indeed, both Al and In are currently used in nitride devices. In is commonly used to control both the emission wavelength (by changing the bandgap) and the emission efficiency (due to carrier localization) in nitride optoelectronics [12], whereas Al is used for AlGaN/GaN field effect transistors [13]. However, it is well known that the
incorporation of foreign atoms in a crystal can have a strong impact on the electronically active defects of the material, even if such incorporation happens in very small concentrations. This is an issue for all blue III-nitride lasers and light emitting diodes, where In is commonly used in very small amounts to increase carrier localization. Thus, the electronic properties of GaN films should be characterized as a function of In or Al incorporation.

5) As an ultimate goal, the results from this work, together with those from the previous sections, should be applied to the understanding of the impact that electrically active defects have on the performance and properties of III-nitride opto- and micro-electronic devices.
9.4 References


S. Heun, J. J. Paggel, L. Sorba, S. Rubini, A. Bonanni, R. Lantier, M. Lazzarino, B.


A. Hierro, D. Kwon, S. H. Goss, L. J. Brillson, S. A. Ringel, and S. Rubini, E. Pelucchi,

A. Hierro, D. Kwon, S. A. Ringel, L. J. Brillson, A. P. Young, and S. Rubini, E. Pelucchi,

87, 730 (2000).

DenBaars, International Workshop on Nitride Semiconductors 2000, Nagoya, Japan,
September, (2000).


(1993).

B. Hu, G. Karczewski, H. Luo, U. Bindley, and J. K. Furdyna, J. Appl. Phys. 77, 2026


H. Jeon, J. Ding, W. Patterson, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi,

U. Kaufmann, M. Kunzer, M. Maier, H. Oblo, A. Ramakrishnan, B. Santic, and P.


