Optical and Electrical Study of the Rare Earth Doped III-nitride Semiconductor Materials

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This dissertation titled
Optical and Electrical Study of the Rare Earth Doped III-nitride Semiconductor Materials

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ABSTRACT

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Optical and Electrical Study of the Rare Earth Doped III-nitride Semiconductor Materials

Director of Dissertation: Wojciech M. Jadwisienczak

The technological advantages of III-nitride semiconductors (III-Ns) have been demonstrated among others in the area of light emitting applications. Due to fundamental reasons limiting growth of InGaN with high Indium content, rare earth (RE) doped III-Ns provide an alternative way to achieve monolithic red, green, blue (RGB) emitters on the same III-Ns host material. However, the excitation efficiency of RE$^{3+}$ ions in III-Ns is still insufficient due to the complexity of energy transfer processes involved. In this work, we consider the current understanding of the excitation mechanisms of RE$^{3+}$ ions doped III-Ns, specifically Yb$^{3+}$ and Eu$^{3+}$ ions, and theories toward the excitation mechanism involving RE induced defects. In particular, we demonstrate and emphasize that the RE induced structural isovalent (RESI) trap model can be applied to explain the excitation mechanism of III-Ns:RE$^{3+}$. Specifically, we have investigated the Yb$^{3+}$ ion doped into III-Ns hosts having different morphologies. The observed emission peaks of Yb$^{3+}$ ion were analyzed and fitted with theoretical calculations. The study of Yb$^{3+}$ ion doped In$_x$Ga$_{1-x}$N nano-rod films with varied indium (In) concentration shown the improvement of luminescence quality from the nanorod due to the presence of Yb dopant. Then we report the optical spectroscopy and DLTS study toward an Eu and Si co-doped GaN and its control counterpart. The Laplace-DLTS and optical-DLTS system developed in this work improved spectrum resolution compared to the conventional DLTS. The high resolution L-
DLTS revealed at least four closely spaced defect levels associated with the Trap B, identified with regular DLTS, with activation energy 0.259±0.032 eV (Trap B1), 0.253±0.020 eV (Trap B2), 0.257±0.017 eV (Trap B3), and 0.268±0.025 eV (Trap B4) below the conduction band edge, respectively. Most importantly, a shallow hole trap was observed at energy 30±20 meV above the valence band edge of the GaN:Si,Eu$^{3+}$ which can be attributed to the RESI hole trap. Furthermore, a study on the Eu$^{3+}$ ion implanted In$_{0.06}$Ga$_{0.94}$N/GaN superlattices (SLs) is reported to illustrate the plausible way of improving the excitation efficiency of Eu$^{3+}$ ion via material engineering. It was concluded that the presence of Eu$^{3+}$ ion in SLs induces an additional compressive stress component modifying the piezoelectric field in SLs active layer giving rise to an extra freedom in material engineering process for efficient energy transfer from the SLs to the Eu$^{3+}$ ion.
DEDICATION

This work is dedicated to my father; Dajun Wang, and my mother; Meng Zhu.
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First, I would like to thank my academic advisor, Dr. Wojciech M. Jadwisienczak for providing me the opportunity to work on his research projects. I appreciate his patient and worthwhile help during my Ph.D. study at Ohio University. The inspiration and encouragement he provided during all stages of my Ph.D. project were crucial and helpful. I also recognized the support by the National Science Foundation (NSF) CAREER Award under contact No. DMR-1056493 he has offered me during my study at Ohio University.

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Finally, I appreciate my parents and grandparents for everything they did for me and their continuous supports of my study at Ohio University.
MAJOR PROJECT OUTCOMES

The scientific, academic and professional outcomes generated during this project are shown below.

Publication:

(a) Major papers with results reported in this dissertation

(b) Contributions to other research projects


Conference presentations/posters on results presented in this dissertation:

• **J. Wang**, V. R. Thota, E. A. Stinaff, W. M. Jadwisienczak, A. Anders, “*Structural and Optical Studies of InGaN/GaN Superlattices Implanted with Eu Ions*”, the 57th Electronic Materials Conference, Ohio State University, Columbus OH, Jun. 2015
• W. M. Jadwisienczak, **J. Wang**, H. Tanaka, J. Wu, R. Palai, H. Huhtinen, A. Anders, “*Optical and Magnetic Properties of GaN Epilayers Implanted with Ytterbium*”, the 6th International Conference on Rare Earth Development and Application, Beijing China, Aug. 2010
• **J. Wang**, W. Jadwisienczak and A. Anders, “*Luminescence Recombination Dynamics of Ytterbium Implanted GaN Epilayers*”, the 52nd Electronic Materials Conference, University of Notre Dame, IN, Jun. 2010
In addition to the above mentioned presentations, I have contributed and delivered two presentations during my PhD term at Ohio University.

- **J. Wang, P. Kuruva, T. Thomas, A. Brant, W. M. Jadwisienczak**, “Optical Characterization of Eu Doped Mixed A-site Perovskite Na$_{0.5}$Bi$_{0.5}$TiO$_3$-Based Red Phosphor”, the 7th International Conference on Rare Earth Development and Application, Ganzhou China, Aug. 2013

- **J. Wang, W. M. Jadwisienczak, A. Podhorodecki, G. Zatryb, J. Misiewicz, J. Wojcik, P. R. J. Wilson, P. Mascher**, “Cathodoluminescence Studies of Silicon Rich Silicon Oxide Doped with Terbium”, the 7th International Conference on Rare Earth Development and Application, Ganzhou China, Aug. 2013

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### LIST OF ABBREVIATIONS

1. III-Ns – III-nitride semiconductors  
2. AFM – Atomic Force Microscopy  
3. CT – Charge Transfer  
4. C-V – Capacitance-Voltage Characterization  
5. DAP – Donor Acceptor Pair  
6. DLOS – Deep Level Optical Spectroscopy  
7. DLTS – Deep Level Transient Spectroscopy  
8. O-DLTS – Optical Deep Level Transient Spectroscopy  
9. EHP – Electron Hole Pair  
10. EPR – Electron Paramagnetic Resonance  
11. I-V – Current-Voltage Characterization  
12. MCTS – Minority Carrier Transient Spectroscopy  
13. MBE – Molecular Beam Epitaxy  
14. MOCVD – Metalorganic Chemical Vapor Deposition  
15. OMVPE – Organometallic Vapor Phase Epitaxy  
16. PLE – Photoluminescence Excitation  
17. SEM – Scanning Electron Microscopy  
18. RESI – Rare Earth Structural Isovalent  
19. RBS – Rutherford Backscattering Spectrometry  
20. XANES – X-ray absorption near-edge spectroscopy  
21. XRD – X-Ray Diffraction
CHAPTER 1: INTRODUCTION

In this chapter, the major outcomes of selected previously reported efforts on optical and electrical characterizations of rare earth (RE) doped III-nitride semiconductors (III-Ns) are reviewed, with special emphasis on the studies related to our current understanding of the excitation mechanisms of RE$^{3+}$ ions, specifically Yb$^{3+}$ and Eu$^{3+}$ ions, doped III-Ns. The emphasis on the importance of studying these materials for practical applications is considered initially. Subsequently, we review the general aspects of typical intrinsic and RE$^{3+}$ ions induced defects in III-Ns. Finally, the identified defects, their plausible origins and their effect on luminescence properties in the studied materials are summarized and linked with the experimental approach of this work.

1.1 Outline

This dissertation is structured in seven chapters. Chapter 1 delivers the motivation of the project, introduces the background of III-Ns:RE$^{3+}$, especially Yb$^{3+}$ and Eu$^{3+}$ ions doped III-Ns, and discusses, in general, the luminescence mechanisms of the RE$^{3+}$ ions in III-Ns. The technological applications’ potential of these materials and the importance of studying them are emphasized. Chapter 2 discusses the theory behind the luminescence of the III-Ns:RE$^{3+}$. The excitation mechanisms related to the RE induced defect and the principle of experimental methods used to characterize the studied materials are discussed. In addition, different types of deep level transient spectroscopy techniques are compared in terms of features and performances. Chapter 3 introduces the samples and experimental setups established during this work. The focus is on the developing DLTS, L-DLTS and MCTS experimental capabilities at Ohio University. Chapter 4 presents the representative
results from a study on Yb$^{3+}$ ion doped GaN nanorod (NR) samples. The optical properties are compared with GaN:Yb$^{3+}$ thin film counterparts grown by different epitaxy techniques. Furthermore, the excitation mechanism of Yb$^{3+}$ ion in GaN is discussed. The second part of Chapter 4 delivers experimental results on Yb$^{3+}$ ion doped InGaN NR samples. The emphasis there is on the observed improvement of luminescence quality from the InGaN:Yb$^{3+}$ NR as a result of the proposed Yb dopant induced gettering effect. In Chapter 5, two projects related to Eu-doped III-Ns are delivered. The first one is the defect study in Si and Eu co-doped GaN epilayers and their reference counterpart using various electro-optical techniques. The defects identified are examined and correlated with the outcomes of optical studies conducted in this and previous works. The plausible Eu$^{3+}$ ion excitation mechanism scheme and luminescence mechanisms are discussed based on the RE structural isovalent (RESI) hole trap model. The second project described in Chapter 5 presents a study focused on Eu$^{3+}$ ion implanted in InGaN superlattices (SLs). Finally, the conclusion of this dissertation and future work are given in Chapter 6 and Chapter 7, respectively.

1.2 Motivation

The photoemission of RE$^{3+}$ ions has attracted enormous research attention for decades due to the fact that their sharp optical emission peaks cover a wide spectral range from visible to infrared. The unique properties of RE$^{3+}$ ions come from the partially filled inner 4$f$ shell that is screened by the outer 5$s$ and 5$p$ orbits. As the result, the intra-4$f$ electronic transitions are hardly affected by the surrounding crystal environment so that the emitted photon energy is nearly independent of the host material. However, due to the fact
that the splitting of the Stark levels of the $4f$ shell depends on the crystal field interaction in the lattice, the host material plays an important role in determining the intra-$4f$ transition probabilities among different $4f$ levels. Also, it was shown that thermal quenching of the RE$^{3+}$ ions emission is a function of band gap energy, thus wide band gap semiconductors are recognized to be better hosts for RE$^{3+}$ ions as compared to the smaller band gap ones.

[1] Among the wide band gap semiconductors, GaN is one of the ideal candidates due to its large band gap energy, high thermal conductivity, good chemical and thermal stability, and break down dielectric strength, respectively. As the GaN growth techniques evolved over the time, the material quality of GaN has been improved significantly during the past decades in terms of, among others, reduction in dislocation density and intrinsic impurities.

[2]–[10] Successful reduction of these two parasitic aspects that hinders the improvement of III-Ns morphology was achieved via different approaches, among which doping with RE elements as intrinsic gettering impurity is the most interesting and novel for our considerations in this work. An example of successful application of RE elements for GaN purification via impurity gettering process during growth was demonstrated by the AMMONO S.A. in Poland, where ammonothermally grown bulk GaN showed remarkable material quality improvement. [11], [12] Thus, we believe like others, that the impurity gettering effect due to RE incorporation can be considered technologically important. In general, one may consider that up to a certain approximation, very similar chemical and physical processes occur in materials’ growth process where RE are used intentionally both for impurity gettering and more conventional luminescence activity. Thus, we assume that
RE elements shall retain their fundamental characteristic properties regardless of the host environment.

Starting from late 1990s, research successfully showed luminescence properties of RE-doped GaN [13]–[16] and demonstrated, although not optimized, optoelectronic devices based on these materials. [17]–[19] Since then, considerable efforts have been devoted to increase the luminescence efficiency of selected RE$^{3+}$ ions by optimizing the doping, improving materials’ quality, devices structure etc. The first successful demonstration of electroluminescent of three primary color from RE-doped GaN devices was done by Steckl et al. [18] They demonstrated that incorporated europium (Eu$^{3+}$) ions, erbium (Er$^{3+}$) ions and thulium (Tm$^{3+}$) ions into GaN could achieve red, green and blue luminescence, respectively. [18] In the meantime, extensive work has been done to understand the excitation mechanism of RE$^{3+}$ ions in III-Ns using both experimental and theoretical approaches. [20]–[27] These works proved to be useful in understanding, up to certain extend, the energy excitation and de-excitation pathways primarily through defects and, consequently, resulted in achieving improved optical performance of the III-Ns:RE$^{3+}$ materials. Most recently, a prototype of GaN:Eu$^{3+}$ based red light emitting diode (LED) was demonstrated by Fujiwara et al. that showed promising performance suitable for commercial applications. [28] To further improve the optical performance of the GaN:Eu$^{3+}$ based devices, one needs to understand the excitation pathway between the host GaN and the RE$^{3+}$ ions by studying the defect energy levels located in the forbidden gap. Recently, successful identification of multiple optical centers in GaN:Eu$^{3+}$ by utilizing the combined excitation emission spectroscopy (CEES) [28] indicated the presence of closely spaced
defect levels critically affecting the energy migration scheme which calls for comprehensive study and understanding. Despite the great success demonstrated by this approach, it was not possible, in our opinion, to unambiguously identify the electrical character of involved defects (i.e. electron vs. hole) associated with the Eu$^{3+}$ ion in each optically active center. This offered an opportunity, which was explored in this project, to contribute to better understanding of the problem by conducting electrical characterization of defects. The *Laplace* deep level transient spectroscopy (L-DLTS) technique used in this work is one of the viable tools to probe and resolve the closely spaced defect energy levels in a material beyond the spectral resolution of typical DLTS. Thus, we combined this approach with other optical and electrical characterization methods discussed in *Chapter 3* to get a better understanding of the role(s) of RE$^{3+}$ ions in the III-Ns as discussed later in this dissertation.

Among the fourteen RE elements, Eu and Yb were selected for investigation in this study. Below we briefly underline our reasoning and motivation in selecting these specific lanthanides doped into III-N hosts when considering only the pivotal and currently unresolved issues.

- Utilizing high In content InGaN semiconductors for red emitters encounters both technical and physical difficulties in terms of precise controlling of In segregation and migration processes during material growth. Instead, the Eu$^{3+}$ ion incorporated into GaN is considered as an alternative approach for achieving red emission [28], [29] for non-phosphor LED applications.
• Multiple optical centers were observed in GaN:Eu$^{3+}$ [22] indicating complex defects distribution in the material that needs to be further investigated using a combination of optical and electrical characterization techniques.

• Despite of significant efforts conducted in the past toward understanding of energy transfer mechanisms between the RE$^{3+}$ ions, in general, and Eu$^{3+}$ ion, in particular, and the GaN host, there exists an urgent need to break through the present bottleneck in our understanding of the energy migration processes for further improvement of GaN:Eu$^{3+}$ based LEDs performance.

• The selection of Yb$^{3+}$ ion doped GaN was motivated by the fact that Yb$^{3+}$ ion has the simplest electronic configuration compared with other lanthanides, and as such can provide a relatively clear path to understand the energy transfer mechanism in other RE$^{3+}$ ions doped III-Ns.

• III-Ns:Yb$^{3+}$ materials hold a technological potential for optoelectronic and spintronic applications as well. [30]–[32]. It was demonstrated that Yb$^{3+}$ ion co-doped with other RE$^{3+}$ ions in many material systems showed the energy upconversion effect that can be utilized in energy harvesting applications. [33]–[36]. Furthermore, Yb$^{3+}$ ion doped in III-Ns showed ferromagnetic behavior at room temperature; however, it is not clear at the present time if the origin of magnetism in these materials is due to spin orbit exchange interaction, local Yb precipitation or structural defect induced by the Yb$^{3+}$ ion.

• Although impressive progress has been achieved in observing emission from RE-doped GaN, the exact excitation mechanisms responsible for RE$^{3+}$ ions intra-4f
electronic transitions in GaN remain incompletely understood. In general, two theoretical models were used to explain the optical and electrical behavior of RE-doped semiconductors, the charge transfer (CT) model [37], [38] and the RESI model. [20], [23] The CT model argues that the excitation (i.e. energy transfer between the 4f-shell electrons and surrounding host) happens through a change in the electronic valence of RE\(^{3+}\) ions (e.g., Eu\(^{3+} \leftrightarrow \text{Eu}^{2+}\)). However, available EPR and optical studies provide no clear evidence that RE\(^{2+}\) ions are involved in studied III-V [39] and III-Ns materials [28], [40], [41]. Although the X-ray absorption near-edge spectroscopy (XANES) study [42] demonstrated the RE\(^{3+,2+}\) ions valence change in persistent phosphors under X-ray excitation, definite explanation of the RE excitation process by CT model in studied III-Ns:RE\(^{3+}\) is still under debate. More discussion on this topic is presented in Section 2.1.2.

Although utilizing DLTS technique as a semiconductor defects study tool has been commonly demonstrated in the past, only a few group reported on the DLTS study focused on RE incorporated into III-Ns. Our motivations for this project was to investigate the RE induced defects in III-Ns by means of variety of DLTS technologies. Also, since defect levels characterized from previous studies showed large deviation in terms of thermal activation energies and capture cross sections, further investigation on this subject is needed. In this work, the high resolution DLTS was used to study the in situ Eu and Si co-doped GaN and its reference counterpart. The samples were provided from Dr. Fujiwara’s research group which successfully demonstrated the world-first GaN:Eu\(^{3+}\) based red LED using OMVPE growth approach.
1.3 Overview of Yb$^{3+}$ ion doped III-nitride semiconductors

The ytterbium has a neutral atom configuration of [Xe] $4f^{14}6s^2$. It becomes a trivalent ion (Yb$^{3+}$) with electronic configuration of [Xe] $4f^{13}$ when doped into III-Ns by losing two electrons from $6s$ orbital and one electron from $4f$ orbital, respectively. Since there is only one unpaired electron left behind at the outermost electronic orbital, the electronic configuration of the Yb$^{3+}$ ion generates the simplest Stark energy levels among other Lanthanides, which are denoted as $^2F_{7/2}$ ground level and $^2F_{5/2}$ excited level. The crystal interaction further Stark-splits the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state manifolds into four and three sublevels, respectively.

Although Yb$^{3+}$ ion has the simplest electronic configuration, it is the least studied among RE$^{3+}$ ions in III-Ns. In the past, extensive studies have been focused on the Yb$^{3+}$ ion doped III-V semiconductors, such as InP and GaAs host, due to the infrared (IR) emission from Yb$^{3+}$ ion. [43]–[48] Those studies, in general, provided useful discussions regarding the excitation mechanism of RE$^{3+}$ ions in semiconductors. It also suggested that doping RE$^{3+}$ ions in wide band gap semiconductors shall result in better optical performance due to the weaker thermal quenching effect. [1] Later on, it was demonstrated that the GaN:Yb$^{3+}$ photoluminescence is indeed relatively weakly thermal quenched. [31] It was shown in this study that the observed complex emission peaks associated with Yb$^{3+}$ ion originate from at least two different optical centers contributing to the splitting of the Stark levels in Yb$^{3+}$ ion. This observation was further supported by the density functional theory calculation. [24] It was concluded that the most stable site a RE$^{3+}$ ion can occupy in III-Ns lattice is the substitutional site to the cation of the III-Ns, e.g., RE$_{Ga}$ in RE doped
GaN. Also, the substitutional RE$^{3+}$ ion site is bound more strongly to nitrogen vacancy (V$_N$) than any other species to form RE$_{Ga}$-V$_N$ complex. [24], [25] Based on these and other studies the crystal-field energy levels of Yb$^{3+}$ ion in GaN [49], [50] and AlN [51] host were calculated and verified by crystal-field calculation and optical spectroscopy. Recently, the characteristic emission peaks of Yb$^{3+}$ ion in GaN nano-rod was also investigated and compared with the same in GaN:Yb$^{3+}$ thin films.[52] It was shown that the presence of some similarities between the lattice locations of Yb$^{3+}$ ion in these hosts, however, with a broadening of the emission lines which was explained by the surface defects. The detailed results and discussion of this study will be presented in Section 4.1.

1.4 Overview of Eu$^{3+}$ ion doped III-nitride semiconductors

As mentioned earlier in this chapter, the III-Ns have their advantages as host material for RE doped LEDs applications due to their wide band gap being transparent to the ultraviolet, visible and infrared emission from RE$^{3+}$ ions. It has been demonstrated in the past that incorporating different RE$^{3+}$ ions into GaN could generate the three primary colors (RGB) when optically or electrically stimulated. [18] Hence, utilizing GaN as a common host for GaN:RE$^{3+}$ based RGB emitters was considered to be an alternative pathway for the next generation of light emitting devices. However, up to now, the GaN:RE$^{3+}$ based emitters gave insufficient optical output due to the inefficient energy excitation process between the host GaN and RE$^{3+}$ ions. Furthermore, as the rapid development of the InGaN based LEDs and laser diodes (LDs) these days, blue and green color LEDs [53], [54] have been successfully demonstrated and commercialized during the past decade. Because of that, the blue GaN:Tm$^{3+}$ and green GaN:Er$^{3+}$ emitters lost their
technological relevance as compared to the InGaN based LEDs in terms of quantum efficiency and optical output power.

Nevertheless, there is technological difficulty in achieving red emission from InGaN based LED technology. It is well known that by changing the In concentration in the InGaN ternary compound, one could tune the band gap from 0.7 eV (InN) to 6.1 eV (AlN) that covers the spectral range from deep UV to NIR. [30], [55] However, in practice, incorporating large amount of In (i.e. x > 30 at.%) to generate red luminescence remains challenging and results in degradation of material quality due to the In migration and segregation. Also, the presence of large lattice mismatch observed in high In content active region of InGaN quantum well structures leads to piezoelectric field induced band bending that degrades the device performance by reducing the recombination probability of EHP.

An alternative way to achieve red emission from III-N based devices is to incorporate europium into the materials. It has been demonstrated that Eu$^{3+}$ ion incorporated into GaN generates red luminescence under optical and electrical excitation. [56], [57] Later on, Fujiwara et al. demonstrated the first low-voltage current-injected p-n structured GaN:Eu$^{3+}$ based red LED operating at room temperature in 2009. [58] Although the quantum efficiency was relatively low, the uniqueness of this device was that the LED was biased with low-voltage current injection at 2.4 V. [29] Since then, efforts have been devoted to improve the performance of the GaN:Eu$^{3+}$ based prototype LEDs by increasing the energy transfer efficiency from the GaN host to the Eu$^{3+}$ ion. It was found that varying the V/III ratio during the material growth process [57] could affect the optical output efficiency due to the modification of gallium related optical centers (i.e. V$_{Ga}$-complex).
More importantly, significant enhancement of red emission was obtained by Mg, Eu co-doping [60][61] or Mg, Si, Eu co-doping [62] into the GaN host due to the formation of preferential Mg induced optical centers (i.e. \(\text{Eu}_{\text{Ga-Mg}}, \text{Eu}_{\text{Ga-VN-Mg-H}}\)). [61], [63]–[65] Since then, continuous progress has been achieved in increasing the quantum efficiency of Eu-doped GaN based red LEDs through the material growth and device structure engineering [45], [22], [46]–[48]. The current state of art output power of these red LEDs is in the sub-mW level comparable to that of a commercial AlGaInP red LED. [28] Most recently, researchers at Osaka University illustrated a 21-fold increase in red photoluminescence by embedding a Eu, O-co-doped GaN layer into a AlGaN/GaN distributed Bragg reflector micro cavity structure in comparison to a reference sample without the micro cavity. [70] The improvement was achieved by the Eu emission lifetime shortening, better control of strain-induced piezoelectric effect, and increasing extraction and excitation field efficiencies, respectively. [70] Although the samples investigated in that work were optically pumped, research showed promising potential in further improving the performance of GaN:Eu\(^{3+}\) based red LEDs through electrical pumping in the future.

Along the path of improving the GaN:Eu\(^{3+}\) based red LEDs performance, efforts have been devoted to understanding the energy transfer mechanisms between the GaN host and the Eu\(^{3+}\) ions by means of defects study. It was confirmed that the defect levels induced by incorporated Eu in GaN played a pivotal role in achieving efficient energy transfer between host and emitting Eu\(^{3+}\) ion centers. Dierolf et al. used a confocal microscopy technique for simultaneous electron and laser beam irradiation [71], [72] combined with
the excitation-emission spectroscopy (CEES) and density function theory calculation [73] to investigate the complex defects in various GaN:Eu$^{3+}$ samples [59], [74]. Those studies, which examined the various excitation energy schemes, resulted in observation of multiple optically activated centers that contribute to the emission of the Eu$^{3+}$ ion involved in various optically active centers. [71], [75] However, there still exists uncertainty regarding the defect energy levels associated with these optically active Eu$^{3+}$ ion centers. In addition, for further improvement of the GaN:Eu$^{3+}$ base LEDs performance, defect energy levels associated with optically active Eu$^{3+}$ ion centers shall be investigated when carriers are electrically injected instead of being optically generated. In the past, deep level transient spectroscopy (DLTS) and Laplace-DLTS (L-DLTS) have been conducted to characterize the defect energy levels induced by Eu implanted to GaN epilayers [76], [77]. It is now well established that there exists multiple luminescence centers in GaN in situ doped with Eu$^{3+}$ ion. Those optical centers have different origins and, in consequence, distinct energy migration schemes determining their optical radiative and non-radiative relaxation processes [28], [59], [71], [78]. The DLTS measurement offers an opportunity to further examine the nature of Eu$^{3+}$ ion induced defects in GaN host as well as to attain complementary quantitative information on involved trap energies and carrier capture cross-sections when material is electrically excited. Also, one can investigate defect energy levels in a more straightforward way using charged carriers (i.e., electron and holes) in contrast to electrically neutral photons involved in the optical investigation.

In this study, the assessment of defects energy levels in Eu$^{3+}$ ions in situ doped GaN epilayer was performed using DLTS, L-DLTS and MCTS techniques on selected samples
extensively investigated by optical spectroscopy in the past by others [28], [59], [64], [68], [78].

1.5 Intrinsic impurities and RE induced defects in GaN

In the past, deep level transient spectroscopy (DLTS) was utilized in analyzing the point defects in GaN. The identified defects showed a large spread in terms of the energy levels across the bandgap of the III-Ns hosts and the corresponding capture cross-section that describes the ability of trapping electrons/holes, due to: (1) the dispersion of growth condition and methods; (2) the Poole–Frenkel effect that lowered the effective barrier of trapped carrier by the electric field; [79] and (3) other possible instrumentation variation among different studies.

In general, the reported defect energy levels in GaN studied using DLTS or similar techniques can be specified in a few groups. Starting with electron traps, relatively shallow electron traps were observed in the energy region from 0.18 eV and 0.30 eV below the conduction band edge ($E_c$). This electron trap was usually associated to $V_N$ or $O_N$ vacancy related defect.[80] Then, literature reports on trap energies positioned from $E_c - 0.48$ eV to $E_c - 0.6$ eV which were attributed to H and C related defects or the $N_{Ga}$ anti-site defect. Furthermore, deep traps with energy at around $E_c - 0.67$ eV, $E_c - 0.81$ eV and $E_c - 1$ eV were also reported that may be related to extended dislocation defect(s). Nevertheless, the origin of the above mentioned electron traps may be still unresolved or under investigation. Unfortunately, there are traps that hold similar energies; however, they may have distinct origins and characteristics (i.e., relevant capture cross-sections), and thus also needs to be further experimentally investigated. On the other hand, the hole traps in $n$-type GaN were
usually identified optically by means of optical-DLTS and DLOS experiments [81][82][83], primarily because they have to be measured from the traps’ minority carrier emission. The hole traps which were also commonly observed in \textit{p}-type Mg-doped GaN are Mg\textsubscript{Ga} [84] and/or Mg-H, respectively. [85] [86] The defect energy levels that were typically reported in the literature are summarized in Table 1.1.

In addition to the intrinsic defects existing in GaN, one can expect that RE dopant induces extra defects into the material as well. While some of them may contribute to the energy transfer process as energy migration intermediate states, others could degrade the luminescence efficiency acting as non-radiative recombination centers. The RE induced defects in III-Ns have been investigated by a few groups [76], [77], [87]–[90] in the past by means of DLTS, L-DLTS and DLOS. However, the reported characteristic values of RE induced defects were largely dispersed and strongly depended on III-Ns materials growth technique (\textit{e.g.}, HVPE, MOCVD, MBE) and post-growth processes conditions (\textit{e.g.}, implantation, thermal treatment). The RE induced defect levels in GaN reported in the literature are summarized in Table 1.1. It shall be noted here that in the past RE\textsuperscript{3+} ions were usually implanted to III-Ns rather than \textit{in situ} doped. Because of that, many defects identified in the RE implanted GaN were attributed to the implantation induce lattice damage, which brought extra complexity to the problem. For this reason, in this study, samples selected for DLTS investigation were RE \textit{in situ} doped GaN (\textit{see} sample information in \textit{Section 3.1}).
Table 1.1 Review of intrinsic defects in undoped GaN and RE-doped GaN reported in the literature.

<table>
<thead>
<tr>
<th>Electron Trap</th>
<th>$E_c - E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{17}$ cm$^2$]</th>
<th>Material</th>
<th>Origin</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{Er2}$</td>
<td>0.188</td>
<td>56</td>
<td>GaN:Er</td>
<td>$E_{Er2}$-V$_N$</td>
<td>[89], [91]</td>
</tr>
<tr>
<td>$E_{Pr2}$</td>
<td>0.19</td>
<td>56</td>
<td>GaN:Pr</td>
<td></td>
<td>[91]</td>
</tr>
<tr>
<td>$E_{Eu1}$</td>
<td>0.19</td>
<td>26</td>
<td>GaN:Eu</td>
<td>$E_{ Eu1}$-V$_N$</td>
<td>[77], [88]</td>
</tr>
<tr>
<td>$E_{Eu2}$</td>
<td>0.22</td>
<td>38</td>
<td>GaN:Eu</td>
<td>Eu implantation related</td>
<td>[88]</td>
</tr>
<tr>
<td>$E(0.27)$</td>
<td>0.27±0.01</td>
<td>8±2×10$^2$</td>
<td>V$_N$</td>
<td></td>
<td>[77], [81]</td>
</tr>
<tr>
<td>$E_{Er1}$</td>
<td>0.3</td>
<td>180</td>
<td>GaN:Er</td>
<td>V$_N$</td>
<td>[89], [91]</td>
</tr>
<tr>
<td>$E_{Pr1}$</td>
<td>0.28</td>
<td>200</td>
<td>GaN:Pr</td>
<td></td>
<td>[91]</td>
</tr>
<tr>
<td>--</td>
<td>0.36</td>
<td>8.1×10$^4$</td>
<td>GaN:Eu</td>
<td>Eu implantation related</td>
<td>[87]</td>
</tr>
<tr>
<td>TE2</td>
<td>0.37</td>
<td>2.8</td>
<td></td>
<td></td>
<td>[92], [93]</td>
</tr>
<tr>
<td>$E_{Pr4}$</td>
<td>0.39</td>
<td>300</td>
<td>GaN:Pr</td>
<td></td>
<td>[91]</td>
</tr>
<tr>
<td>$E_{Er4}$</td>
<td>0.41</td>
<td>280</td>
<td>GaN:Er</td>
<td>Er related</td>
<td>[89], [91]</td>
</tr>
<tr>
<td>$E_{Eu4}$</td>
<td>0.49</td>
<td>710</td>
<td>GaN:Eu</td>
<td>Eu implantation related</td>
<td>[88], [92]</td>
</tr>
<tr>
<td>$E_{Er3}$</td>
<td>0.6</td>
<td>500</td>
<td>GaN:Er</td>
<td>$N_{Ga}$</td>
<td>[89], [91]</td>
</tr>
<tr>
<td>$E_{Pr3}$</td>
<td>0.61</td>
<td>500</td>
<td>GaN:Pr</td>
<td></td>
<td>[91]</td>
</tr>
<tr>
<td>$E_{Eu5}$</td>
<td>0.60</td>
<td>670</td>
<td></td>
<td>Intrinsic</td>
<td>[88], [93]</td>
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<tr>
<td>$E(0.61)$</td>
<td>0.61±0.02</td>
<td>1±1×10$^3$</td>
<td></td>
<td></td>
<td>[81]</td>
</tr>
<tr>
<td>$E_{Eu3}$</td>
<td>0.68</td>
<td>8.1×10$^8$</td>
<td>GaN:Eu</td>
<td>Eu implantation related</td>
<td>[88], [92]</td>
</tr>
<tr>
<td>$E_{Eu6}$</td>
<td>0.77</td>
<td>5.2×10$^3$</td>
<td>GaN:Eu</td>
<td>Eu implantation related</td>
<td>[88]</td>
</tr>
<tr>
<td>E8</td>
<td>0.89</td>
<td>39</td>
<td></td>
<td></td>
<td>[94]</td>
</tr>
<tr>
<td>E9</td>
<td>1.22</td>
<td>4.3×10$^3$</td>
<td></td>
<td></td>
<td>[94]</td>
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Table 1.1 Continued

<table>
<thead>
<tr>
<th>Hole Trap</th>
<th>$E_v + E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{-17}$ cm$^2$]</th>
<th>Origin</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>H5</td>
<td>1.76</td>
<td>$1.2\times 10^5$</td>
<td>GaN:Tm</td>
<td>[94]</td>
</tr>
<tr>
<td></td>
<td>1.59±0.12</td>
<td>GaN:Er</td>
<td></td>
<td>[90]</td>
</tr>
<tr>
<td>H4</td>
<td>1.19</td>
<td>$230$</td>
<td></td>
<td>[94]</td>
</tr>
<tr>
<td>H1</td>
<td>0.86±0.08</td>
<td>$7.4\times 10^3$-$1.3\times 10^4$</td>
<td>$V_{Ga}$-complex [81], C[93]</td>
<td>[93], [94]</td>
</tr>
<tr>
<td>H(0.85)</td>
<td>0.85±0.05</td>
<td>$3\pm1\times 10^3$</td>
<td>$V_{Ga}$-complex [81], C[93]</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>0.61±0.08</td>
<td>GaN:Tm</td>
<td></td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>0.25±0.03</td>
<td>$500\pm300$</td>
<td></td>
<td>[81], [84], [92]</td>
</tr>
<tr>
<td>H(0.19)</td>
<td>0.19±0.03</td>
<td>$2\times 10^4$-$1\times 10^4$</td>
<td></td>
<td>[81]</td>
</tr>
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CHAPTER 2: THEORY

Initially, in this chapter, we introduce a few fundamental aspects that need to be pay attention when we study the RE$^{3+}$ ions doped in III-Ns. Then, we discuss the theory about the excitation mechanism related to RE induced defects. Subsequently, we consider the principles of variety of deep level transience spectroscopy techniques. Finally, we discuss the selected experimental methods to characterize the defects in studied semiconductors.

2.1 RE doped III-nitride semiconductors

Luminescence from RE$^{3+}$ ions in III-Ns has been considered as technologically advantaged for decades. However, the luminescence efficiency of III-Ns:RE$^{3+}$ material is still deficient due to the complexity of energy transfer between the host material to the RE$^{3+}$ ions. Thus, comprehensive understanding of these mechanisms is considered as important for relevant technology development. The current understanding of RE’s behavior in III-Ns, the excitation mechanism of RE$^{3+}$ ions and the RE induced defects in III-Ns will be discussed in this section.

2.1.1 Gettering effect in semiconductors

The impurity gettering effect has been widely used in semiconductor manufacturing to remove the intrinsic metal impurities from a working layer of e.g., a silicon wafer. [95] For example, metal impurities like copper, nickel and iron are harmful impurities in Si-based devices that degrade the overall device performance. Interestingly enough, it was demonstrated that dislocations and other extended defects are helpful getters that could attract undesirable metal impurities off into the bulk of the material or non-working side of
the wafer if proper thermal treatments and processing steps were followed. [95] To explain this phenomenon, one may consider that those defects in a Si wafer offer the potential for very effective suppression of surface precipitation because they own a smaller energy barrier than that of the wafer surface for attracting the metal impurities. Thus, gettering effect happens due to heterogeneous precipitation. [96]

Furthermore, in the past, the idea of utilizing RE elements as “impurity getters” to gather the undesirable impurities during the growth was applied to liquid phase epitaxy (LPE) of III-V semiconductors (e.g., InP, InGaAsP). [97] It has been demonstrated that incorporating RE elements in the LPE melt purified the III-V material that led to improved PL near band edge (NBE) emission. Specifically, narrower and stronger PL NBE emission was observed in Yb treated InP, InGaAs [98], Er treated InGaAs [99], Gd treated InAs [100] and others [97], respectively, due to the RE elements’ gettering-like effect. Simulation of the RE purification process in LPE growth demonstrated that RE elements in LPE solution favorably gettered shallow donors due to its high chemical affinity to donor impurity [101] (e.g., dysprosium (Dy) as getter in the LPE growth InGaAs [102]). In consequence, reduction of donor concentration or even reverse conductivity type from n-type to p-type usually happened in those materials. [97], [101]

On the other hand, Dwilinski et al. pursued the AMMONO GaN (AM-GaN) technique for growing bulk GaN wafers that required a relatively low growth temperature and pressure as compared to other growth methods. [11] Specifically, this research group has demonstrated that high quality bulk GaN material with remarkably narrowed exciton recombination lines can be achieved when RE elements are introduced during the AM-
GaN growth process. In this specific case, the RE elements were believed to “getter” the oxygen impurities and remain in the ammonia solution as no evidence showed that the RE elements were incorporated as intrinsic impurities into the GaN during growth with concentration being detected using the standard methods. [11] In contrast, Adekore et. al. observed ~1550 nm PL emission from Er$^{3+}$ ion incorporated to AM-GaN material indicating that erbium not only getter oxygen impurity in ammonothermal solution, but also can be incorporated as intrinsic impurities into the GaN lattice and act as emitting center. [103]

Assuming that the RE elements retain the same physical and chemical attributes despite the environment, one can speculate that they can act also as “getters” when incorporated into III-N materials synthesized via different methods. Consequently, it is interesting to question if the improvement of III-Ns material quality after RE doping can be expected or not. In fact, in this work, we observed that the green luminescence from a InGaN NR samples significantly improved after Yb incorporation. Furthermore, a qualitatively similar observation was made for Eu-implanted InGaN SLs. The detailed discussion focused on this subject is delivered in Sections 4.2 and 5.2.2.

2.1.2 The presence of RE$^{2+}$ and RE$^{3+}$ ions in III-nitride semiconductors

In general, RE elements in semiconductors are found in a divalent (2+) and/or trivalent (3+) ionization state defined by the specifics of the RE ion local environment in semiconductor host. In the case of III-Ns doped with RE, the REs are primarily found in a (3+) ionization state; [23], [25], [104], [105] however, it was also reported that the RE$^{2+}$ ions can reside in III-Ns lattice depending on the host specifics (e.g., Eu$^{2+}$ ion in AlN [106]
and GaN [107]). Spectroscopically, the Eu\(^{2+}\) ion emits at about 450 nm (blue), while the dominate Eu\(^{3+}\) ion emission peak is located at ~622 nm (red).

In the past, two theoretical models were used to explain the optical and electrical behavior of RE doped semiconductors, the charge transfer (CT) model [37], [38] and the RESI model. [20], [23] The excitation mechanism of RE in III-Ns explained by the CT model can be understood as the optical promotion of an electron from the semiconductor valence band to a RE\(^{3+}\) ion that changes its valence state from (3+) to (2+) to form a RE\(^{2+}\) ion charge transfer state (CTS). Here, a hole is delocalized over the ligands but is bounded to the RE\(^{2+}\) ion to form an RE\(^{2+}\)+h charge transfer state (CTS). If the CTS is close in energy to the excited state of the RE\(^{3+}\) ion, the excitation process occurs. Figure 2.1 illustrates the simplified configuration coordinate diagram of the CT process, where \textit{parabola a} represents the ground state of an RE\(^{3+}\) ion with an electron in the valence band, and \textit{parabola b} represents an excited state of the RE\(^{3+}\) ion crossing over to the CTS (RE\(^{2+}\)+h).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.pdf}
\caption{Simplified configuration coordinate diagram illustrating the excitation of RE\(^{3+}\) ion through charge transfer process. After Ref. [30]}
\end{figure}
Dorenbos and Van der Kolk [38] considered localization of the lowest $4f^n$ states of divalent and trivalent lanthanides in GaN (see Fig. 2.1) and suggested that Eu$^{2+}$ and Yb$^{2+}$ ions are stable in GaN as their (2+) ground state lies below the conduction band. They argued that this fact was sufficient to make Eu$^{3+}$ and Yb$^{3+}$ ions excited via the CT process. However, the model seems to be invalid for other RE$^{2+}$ ions in GaN, and presumably in all III-Ns, because their ground states are located within the conduction band where the proposed CTS is highly unstable. Furthermore, in principle, the CT model imposes that the RE ions in semiconductors should result in a change of RE ion valence state (e.g., RE$^{3+}$ $\rightarrow$ RE$^{2+}$) due to the CT. In the past there were efforts focused on experimental demonstration of this phenomenon (i.e., CT) using electron paramagnetic resonance (EPR) combined with optical excitation. [39], [105], [108] The good example here is the Yb-doped InP. [39] In this case the EPR spectra were conducted on InP:Yb$^{3+}$ samples with and without optical excitation. It was assumed that the Yb$^{3+}$ and Yb$^{2+}$ ions’ concretions shall change under above band gap excitation due to the CT process resulting in a change of the overall number of electrons on 4f-shell in RE$^{3+}$ ion (e.g., $4f^n$ - $4f^{n-1}$). It was concluded from these efforts that ytterbium is present in the InP host only in (3+) ionization state without unambiguous evidence of the Yb$^{3+}$ ion concentration change due to the stipulated CT process. Furthermore, the EPR investigation toward a GaN:Eu$^{3+}$ phosphor material, which was done by Jadwisienczak et al., showed no clear indication of Eu$^{2+}$ ion presence with and without optical excitation. [109], [110] Furthermore, a recent EPR study of GaN:Eu$^{3+}$ epilayers grown by Dr. Fujiwara’s group at Osaka University, Japan (representative samples were investigated in this work) also has not provided clear evidence of the Eu$^{2+}$ ion presence in
the material due to the doping or optical excitation. [111] Thus, one may assume, when considering the excitation mechanism for RE doped GaN, that the CT process is less probable to occur or at least, to the best of our knowledge, there are not available convincing experimental evidences confirming this process in this and other RE doped semiconductors. [23], [39] It should be emphasized here that the presence of RE$^{2+}$ ions in the III-Ns does not necessarily validate the CT model. This is because the RE$^{2+}$ ions found in III-Ns may attribute their ionization state primarily due to e.g., the surface or lattice imperfection (i.e., specific RE$^{2+}$ ion crystal field environment) rather than the CT state related to the RE$^{2+}$ ion. It is interesting to note, however it is not a detrimental observation, that the RE$^{2+}$ ions are usually observed in III-Ns polycrystalline materials or III-Ns nanoparticle with a large surface to volume ratio. [106], [112], [113] Thus, unless further unambiguous evidence will become available in the future, one should consider the CT model, which the conversion between the RE$^{3+}$ and RE$^{2+}$ ions due to the photon excitation processes with moderate excitation power density, in III-Ns:RE$^{3+}$ with caution.
Figure 2.2 Proposed location of the lowest $4f^n$ states of divalent and trivalent lanthanides in GaN. Optical transitions (arrows) and relevant excited and ground state $4f^n$ level locations (bars) are shown. Reprinted after Ref. [38].

Nevertheless, recently Smet et al. reported the evidence for valence state changes in a SrAl$_2$O$_4$:Eu,Dy persistent phosphors by using the X-ray absorption near-edge spectroscopy (XANES). [42] They argue that some of the Eu ions in the material undergo a valence state change from (2+) to (3+) during the charging by X-ray radiation. The reported data has a rather poor signal to noise ratio in terms of the dynamic change of the XANES peak as a function of X-ray irradiation time; however, serious precautions were exercised to eliminate foreseen ambiguity. Despite that, there still exists the meritorious doubt that the relatively small change of Eu$^{3+} \leftrightarrow$ Eu$^{2+}$ ions population ratio may be caused by the change of Eu local environment during X-ray excitation rather than formation of a
charge state. In addition, in the same study, only the Dy\textsuperscript{3+} ion emission is observed under X-ray excitation (i.e., no Dy\textsuperscript{2+} ions) implying that the excitation mechanism of Dy is not likely to occur via CT model in this material. In another study, Korthout et al. have also indicated the co-existence of Eu\textsuperscript{3+} and Eu\textsuperscript{2+} ions in the Ca\textsubscript{2}Si\textsubscript{4}:Eu phosphor. [114] In this specific case the co-existence of divalent and trivalent Eu ions was primarily attributed to V\textsubscript{Ca} point defects. For every V\textsubscript{Ca} there is a chance to compensate two Eu\textsuperscript{3+} ions in the vicinity of that Ca site. [114] However, even in this case, the co-existence of Eu\textsuperscript{3+} and Eu\textsuperscript{2+} ions cannot be treated as evidence to support the CT model because there is no observed dynamic conversion of valence state upon optical excitation.

Although there are experimental works providing evidence of co-existence of Eu\textsuperscript{2+} and Eu\textsuperscript{3+} ions in the above mentioned materials, it shall be emphasized here that these materials are highly ionic. This situation may create specific conditions required for a less energetic and dynamic RE ion local environment change upon an energetic photon excitation resulting in the reversible change of valence state of a RE ion. Therefore, we can argue that: (1) since much more stable covalent bonding are formed in III-Ns; and (2) experimental observations and theoretical calculations confirmed that RE in III-Ns are primarily in their trivalent ion state [30]; and that (3) there is no other experimental evidence, to the best of our knowledge, supporting conversion of RE\textsuperscript{3+} to RE\textsuperscript{2+} upon optical excitation in III-Ns, we believe the applicability of the CT model to explain the excitation process in III-Ns semiconductors shall be considered with caution.

In the light of the above arguments as well as relying on the fact that RE\textsuperscript{3+} ions preferably substitute for the trivalent cation ions in III-Ns (e.g., Al\textsuperscript{3+}, Ga\textsuperscript{3+}, In\textsuperscript{3+}) [25], we
stipulate after Refs. [23] [25] that they form isovalent RE traps resulting from lattice perturbation due to different ionic radii and electronegativity between them. At the same time, it is conceivable that the substitutional RE impurities also induce defects in the host lattice and thus form complex defects (e.g., Eu\textsubscript{Ga}-V\textsubscript{N}) as illustrated by numerous spectroscopy studies. [28], [40], [41] Discussion on the RE induced defects in GaN and their contribution to the energy transfer processes will be discussed in Section 5.1.

2.1.3 Complex defects in RE doped GaN

Available theoretical studies using density functional theory (DFT) calculations [24], [25] suggested that the RE\textsuperscript{3+} ions show preference for occupying the Ga cation site, either as isolated substitutional or complex intrinsic defects. In the case of Eu-doped GaN, the isolated substitutional RE\textsubscript{Ga} site holds the C\textsubscript{3v} symmetry with the isovalent charge state that suggested to be responsible for the dominated luminescence from Eu\textsuperscript{3+} ion [115] through lattice perturbation due to different ionic radii and electronegativity between Eu\textsuperscript{3+} ion and Ga\textsuperscript{3+} ion. The RE\textsubscript{Ga}-complex defects, on the other hand, result in more complex intra-4f electronic transitions due to breaking the C\textsubscript{3v} symmetry crystal symmetry and relaxing the selection rules even further.

Among RE\textsubscript{Ga}-complex defects, the RE\textsubscript{Ga} defect bonds most frequently to the nitrogen vacancy (V\textsubscript{N}) creating RE\textsubscript{Ga}-V\textsubscript{N} defect complex. This type of complex defect is the most energetically favorable and stable in RE doped GaN. [25] The binding energy of this complex (~0.7 to 1 eV) is sufficiently large allowing that most of the V\textsubscript{N} would remain bound to the RE\textsuperscript{3+} ion even after annealing at temperatures as higher as 1000 °C. [24] Due to the tetragonal structure of GaN unite cell, the RE\textsubscript{Ga}-V\textsubscript{N} complexes can be formed in two
configurations. Assuming that the RE substitutes for the Ga site, the $V_N$ located at one of the three N sites that is placed on the basal plane ($C_{1h}$ symmetry), or the $V_N$ located at the N site along the $c$-axis ($C_{3v}$ symmetry), respectively. It is also known that the RE is slightly displaced from the $c$-axis toward the $V_N$ site when forming $\text{RE}_{\text{Ga}}-\text{V}_N$ complexes in which, e.g., Eu is believed to have the largest displacement among studied lanthanide in Ref. [25]. Thus, it is believed, that the larger stretch of the Eu-N bonds may enhance the intra-4f transition rate.

Furthermore, the $\text{RE}_{\text{Ga}}-\text{V}_N$ complexes are believed to form shallow electron traps at about 0.2 eV below the conduction band edge [24], which may contribute to the $\text{RE}^{3+}$ ion excitation processes as well. DLTS studies of RE-doped GaN confirmed the presence of RE induced electron traps with energy ~0.2 eV below the conduction band edge in GaN:Eu$^{3+}$ [77], [88], GaN:Er$^{3+}$ [89], [91] and GaN:Pr$^{3+}$ [91], respectively. In addition, more defect levels were observed in these materials and believed to be RE induced defects, such as Ga interstitials ($\text{Ga}_{\text{int}}$) or Ga vacancy ($V_{\text{Ga}}$) paired with $\text{RE}_{\text{Ga}}$ complexes, respectively. The $\text{RE}_{\text{Ga}}-\text{Ga}_{\text{int}}$ complex is believed to be hardly generated under equilibrium conditions due to its high formation energy (>20 eV). [25] However, it can be formed under non-equilibrium processes such as the $\text{RE}^{3+}$ ion implantation process, which can explain why more defect levels were identified in the $\text{RE}^{3+}$ ions implanted samples than in RE in situ doped materials. [88], [89] Furthermore, the $V_{\text{Ga}}$ point defect, commonly observed in GaN, can bound to its next-nearest-neighbor $\text{RE}_{\text{Ga}}$ to form $\text{RE}_{\text{Ga}}-\text{V}_{\text{Ga}}$ complex and generate traps in the lower half of the GaN band gap. This complex also effectively breaks the crystal symmetry, holding $C_{1h}$ or $C_1$ symmetry depending on the location of $V_{\text{Ga}}$, thus relaxes the
selection rules resulting in the intra-4f electronic transitions responsible for the observed luminescence.

Recently, Fujiwara and Dierolf [28] reviewed the current findings of Eu$^{3+}$ ion luminescent centers in Eu in-situ doped GaN grown by OMVPE and cataloged different defects as: (1) centers contributing to the Eu$^{3+}$ ion emission and (2) centers that are undesirable in the material. Figure 2.3 shows, in a very generic way, the schematic of four types of defects that could be involved during the Eu$^{3+}$ ion excitation process where type A and B defects contribute to the Eu$^{3+}$ ion emission while type C and D defects are unwanted energy relaxation channels.

![Diagram showing role of different types of defects A–D in the excitation pathway](image)

Figure 2.3 Schematic of role of different types of defects A–D in the excitation pathway after the creation of an EHP. After Ref. [28].

In short, at least eight different optical centers (OMVPE 1-8) were identified in GaN:Eu$^{3+}$ samples by combined excitation-emission spectroscopy (CEES) and site selective spectroscopy studies [71], [72], [75], [116]. The most abundant centers that
contribute to the Eu$^{3+}$ ion emission were labeled as Eu1 (OMVPE 4) and Eu2 (OMVPE 7). The $V_N$ defect is believed to be a type A defect and contributes to the majority Eu1 (OMVPE 4) center as Eu-$V_N$ complex due to the fact that this complex could effectively perturb the lattice symmetry. The $V_{Ga}$ is suggested to work as a type B defect due to the larger distance from Eu site to vacancy when forming Eu-$V_{Ga}$ complex center. Further investigation on samples grown with varied V/III ratio found that $V_{Ga}$ enhanced the excitation efficiency of both Eu1 (OMVPE 4) and Eu2 (OMVPE 7) center and suggested the modification of Eu1 (OMVPE 4) center as $V_{Ga}$-Eu-$V_N$ complex. Furthermore, same impurity can work either as a beneficial defect or an unwanted defect such as magnesium dopant, respectively. It has been widely reported that incorporating Mg in GaN:Eu$^{3+}$ could effectively enhance the Eu$^{3+}$ ion luminescence [60], [61], [63], [78] in which Mg$^{2+}$ ion works as acceptor (type B defect) and forms a donor-acceptor pair (DAP) with the $V_N$ defect in the vicinity of the Eu$^{3+}$ ion. On the other hand, activation of the isolated Mg acceptor by low energy electron-beam irradiation (LEEBI) or thermal annealing has a detrimental effect on the Eu$^{3+}$ ion emission that makes the Mg to be also a type D defect. [28][64]

We would like to note here that Eu-doped GaN samples studied in this project were grown by Prof. Fujiwara at Osaka University and are considered to the best of our knowledge as similar to the materials studied extensively by Professor Dierolf’s group at Lehigh University and discussed in this section.
2.1.4  Magnesium doped GaN:Eu$^{3+}$

$P$-type doping of GaN is of paramount importance for violet-blue LEDs and LDs applications. It is typically achieved using Mg as acceptor in $p$-type GaN because of its lowest ionization energy (~245 meV) resulting in achievable practical hole concentration ~$10^{19}$ cm$^{-3}$ at 300 K. [84] Recently, Eu doped $p$-type GaN attracted attention due to the significant enhancement of Eu$^{3+}$ ion emission upon Mg doping [60], [61], [63], [78] or Si and Mg co-doping [62], respectively; however the first report on this phenomenon was reported by Kim et al. for selective enhancement of 1540 nm Er$^{3+}$ ion emission centers in Er-implanted GaN by Mg co-doping. [117] Anyhow, the enhancement of red emission from Eu$^{3+}$ ion was investigated further [64], [78] giving rise to the postulate that Mg acceptor forms DAP in the vicinity of Eu$^{3+}$ ion, hence increasing the energy transfer efficiency. Specifically, the Mg acceptor associated with hydrogen and Eu-V$_N$ complex donor forms Mg-Eu-H-V$_N$ (Mg/Eu1) [64] DAP structure facilitating energy migration to 4f-shell of Eu$^{3+}$ ion in the Eu1 and Eu2 optical centers. [78] In addition to this, there exists a V$_{Ga}$-Eu-V$_N$ complex center from which energy can be transferred to the same optical centers. These experimental observations were validated with the theoretical predictions implying that increasing concentration of RE$_{Ga}$-V$_N$ complexes in $p$-type GaN [24] shall result in formation of larger amount of desirable DAP structures. However, further investigation toward these proposed DAP structures is still needed.

There exists alternative possibility explaining why the presence of Mg in Eu-doped GaN enhances 4f-4f transitions luminescence intensity. Let us consider here a RESI trap model to explain optical activity of RE-doped III-Ns. [20], [23] The RESI trap model
describes the energy transfer process between bound exciton and the 4f energy levels in the RE$^{3+}$ ions (see Figure 2.4). Since the RE$^{3+}$ ions are preferably located in the substitutional site of a cation ions in the host III-Ns material, an isovalent RE traps can be generated due to the different covalent radii and Pauling’s electronegativities between the RE$^{3+}$ ions and replaced cation ions. In the case of RE$^{3+}$ ion doped GaN, a RESI hole trap is likely formed because any RE$^{3+}$ ions have larger radii but a smaller electronegativity than Ga$^{3+}$ cation. [20] This RESI hole trap, located near the valence band edge, captures a hole from valence band and consequently attracts an electron by Coulombic interaction to form a bound exciton. Then, the energy of the collapsed bound exciton can be transferred to 4f$^n$ states within RE$^{3+}$ ion by electrostatic perturbation. The RESI model is supported by the theoretical calculations [24], [25] that illustrate the favorable lattice location of an RE$^{3+}$ ion and the possible complex defects related to RE impurities. Thus considering the above arguments, we believe that the applicability of the RESI model to the RE-doped III-Ns, in general, and to the Mg, Eu co-doped GaN in particular, is reasonable.
Figure 2.4 Simplified RESI trap model: (a) formation of RESI hole trap and hole captured by RESI trap; (b) formation of bound exciton; (c) energy transfer from the collapsing bond exciton (effective-mass-like particle) to the 4f core electrons of the RE$^{3+}$ ion; (d) photo emission from the intra 4f transition.

Therefore, assuming that Eu$^{3+}$ ion generate substitutional RESI hole trap in GaN, and that Mg is involved in creating RE complexes as discussed above, one may speculate that there will be a larger probability of capturing a hole liberated from ionized Mg$^{2+}$ ion by RESI hole traps and, in consequence, creating localized bound exciton bounded to RESI hole trap. Thus, the energy transfer from the annihilated bound exciton to the Eu$^{3+}$ ion is expected to be enhanced due to the close proximity effect in accordance with reported experimental results reported for the Mg and Eu co-doped GaN. [60], [61], [63], [78]

In summary of this section, we have considered, in particular, the state-of-the-art of the GaN:Eu$^{3+}$ materials available in the literature and concluded that the excitation of
Eu$^{3+}$ ion in GaN occurs through energy transfer process(es) between the host and Eu$^{3+}$ ion, rather than via CT charge transfer. Thus, we believe that the excitation mechanism of RE$^{3+}$ ions in III-Ns, in general, is attributed to energy transfer processes involving different RE$^{3+}$ ions point defects or complex impurities defects including RESI hole trap as experimentally demonstrated for the first time in Chapter 5.

2.2 Defect characterization techniques

2.2.1 Principle of deep level transient spectroscopy (DLTS)

Deep level transient spectroscopy (DLTS) was first introduced by Lang in 1974 [118]. It is an important method used to study the defect levels (i.e., charge carrier traps) in the semiconductors. Since the carriers trapped at different defect levels in the semiconductor band gap requires different thermal activation energy to liberate charge, the defects information, such as defect concentration, capture cross section and carrier emission rate, can be obtained by measuring the capacitance change of the depletion region in a Schottky diode or p-n junction during a temperature sweep. The semiconductor depletion region under study needs to be reverse biased ($V_r$) at thermal equilibrium so that carrier initially trapped in the defect levels can be depleted until a square-shaped forward bias pulse ($V_p$) superimposed on the reverse bias comes to refill the traps (see Figure 2.5). The pulse width (PW) of this compensating pulse is assumed to be long enough so that all the emptied traps can be refilled with charge carriers. The accuracy of the trap concentration calculation depends on if the trap under investigation is fulfilled by the compensating pulse. Once the forward pulse is gone, the carriers in the traps will then escape with different emission rates based on the ambient temperature and intrinsic trap
properties. Figure 2.6 illustrates the dynamic response of an electron trap in \textit{n}-type Schottky diode before, during and after compensating pulse.

Figure 2.5 Illustration of (a) the applied reverse bias and filling pulse to a Schottky diode; (b) the capacitance changes response to the applied bias; and (c) the sampling time and rate window settings (\textit{e.g.}, the \textit{Sula-DLTS} system).
Figure 2.6 Illustration of the dynamic response of an electron trap in a $n$-type Schottky diode (a) before, (b) during and (c) after a compensating pulse.
The emission rate of the electrons (similar expression can be derived for holes) in an electron trap can be expressed as a function of temperature as shown in Eq. (2.1),

$$e_n(T) = \sigma_n\langle v_n \rangle \frac{g_0}{g_1} N_c \exp\left(-\frac{E_c - E_T}{k_B T}\right)$$

(2.1)

$$\langle v_n \rangle = \sqrt{\frac{3k_B T}{m^*}}$$

(2.2)

$$N_c = 2M_c \left(\frac{2\pi m^* k_B T}{\hbar^2}\right)^{3/2}$$

(2.3)

where $\sigma_n$ is the electron capture cross section, $\langle v_n \rangle$ is the thermal velocity, $g_0$ and $g_1$ are degeneracy terms, $N_c$ is the conduction band density of state, $E_c - E_T$ is the energy difference between the trap level and the conduction band edge (in the case of electron emission), and $k_B$ is the Boltzmann constant. The electron capture cross section as a function of temperature can be expressed as,

$$\sigma(T) = \sigma_\infty \exp\left(-\frac{\Delta E_\sigma}{k_B T}\right)$$

(2.4)

where $\Delta E_\sigma$ is the activation energy of the electron capture cross section and $\sigma_\infty$ is the electron capture cross section at $T = \infty$. Equation (2.1) can be further modified by combining Eqs.(2.2)-(2.4) giving,

$$e_n(T) = \sigma_{na} \gamma T^2 \exp\left(-\frac{E_n}{k_B T}\right)$$

(2.5)

$$\gamma = 2\sqrt{3}M_c (2\pi)^{3/2} m^* k_B^2 \hbar^{-3}$$

(2.6)

where $\sigma_{na} = \frac{g_0}{g_1} \sigma_\infty$ is the apparent capture cross section and $E_n = (E_c - E_T) + \Delta E_\sigma$ is the thermal emission activation energy of electrons.
Figure 2.7 Illustration of a double boxcar technique used to define the rate window. The left-hand side shows capacitance transients at various temperatures, while the right-hand side shows the corresponding DLTS signal resulting from using the double boxcar to display the difference between the capacitance at time $t_1^n$ and the capacitance at time $t_2^n$ as a function of temperature. Please notice that by changing rate windows, the DLTS peak shifts.

Conventionally, a double boxcar technique was introduced to detect the low concentration traps by setting a rate window to the measured capacitance transients. All the carrier emissions happened within this rate window can be filtered to improve the signal to noise ratio (S/N). Figure 2.7 shows that the rate window is determined by setting two
measurement gates $t_1^n$ and $t_2^n$ to the capacitance transient, where $n$ is arbitrary index number indicating different gate settings. The observed capacitances at $t_1^n$ and $t_2^n$ are $C(t_1^n)$ and $C(t_2^n)$, respectively. A DLTS plot is the differences between $C(t_1^n)$ and $C(t_2^n)$ vs. temperature. The peak position of a DLTS plot is determined by the maximum of the time constant $\tau$, which is reciprocally related to the emission rate $e$, through the relationships,

$$\tau = \frac{1}{e}$$

(2.7)

$$\tau_{max}^n = (t_1^n - t_2^n)[\ln(t_1^n/t_2^n)]^{-1}$$

(2.8)

where $\tau_{max}$ is the maximum of the time constant, $n$ is arbitrary index number indicating different gate settings.

To calculate the capture cross section and thermal activation energy in Eq.(2.5), an Arrhenius $\ln\left(\frac{\tau^2}{e_n}\right)$ vs. $\frac{1}{\tau}$ plot is generated by measuring a series of DLTS temperature scans with different gate settings for each scan. The observed $\tau_{max}$ and peak position of each DLTS temperature scan can be plotted as a series of data points on the $\ln\left(\frac{\tau^2}{e_n}\right)$ vs. $\frac{1}{\tau}$ plot. Fitting of these data points results in a straight line. The apparent capture cross section $\sigma_{na}$ of the trap can be obtained from the intercept between the straight line and $y$-axis, and the thermal activation energy $E_n$ of this trap can be derived from the slope of this line. We shall keep in mind that the capture cross section is temperature dependent as shown in Eq.(2.4). So the actual value of the trap activation energy is slightly higher than that of the apparent value. However, the temperature dependence of capture cross section is usually ignorable and a good estimated value can be still obtained based on Eq.(2.5).
The DLTS peak shifts with different gate settings are shown in Figure 2.7. In practice, although the rate window settings can be arbitrarily selected, a fixed $t_2/t_1$ ratio is preferred due to the reason that the term $[\ln(t_2/t_1)]^{-1}$ in Eq.(2.8) becomes a constant. One only needs to consider the $\Delta t = t_2 - t_1$ term when changing the gate settings. Therefore, the trap concentration can be calculated by,

$$N_T = 2(\Delta C(0)/C)(N_D - N_A)$$  \hspace{1cm} (2.9)$$

where $\Delta C(0)$ is the change of capacitance when the filling pulse comes, $C$ is the capacitance under quiescent reverse bias, $N_D - N_A$ is the net donor concentration in the $n$-type material which can be calculated from a capacitance verse voltage measurement.

Assuming the trap concentration is much less than the shallow carrier concentration, the trap concentration can be calculated from the rate window and obtained maximum capacitance transient using the Eq. (2.10),

$$N_T = \frac{\delta C_{\text{max}}}{C_0} 2N_D \exp[\frac{r}{1-r}\ln(r)] \approx \frac{\delta C_{\text{max}}}{C_0} 2N_D r^{\left(\frac{r}{r-1}\right)}$$  \hspace{1cm} (2.10)$$

where $\delta C_{\text{max}}$ is the DLTS peak height, $C_0$ is the steady-state capacitance, $r = t_1/t_2$, respectively.

A modification of Eq. (2.9) has been introduced by Zohta [119] for calculating the deep trap concentration. In this model, a region $\lambda$, defined as the distance from the edge of depletion region to the plane where the Fermi level crossed the deep trap level, was taken into account (see Figure 2.8). The traps in this region are not included into the calculation when using Eq. (2.9) because they are filled with carriers (electrons in this case) and do not contribute to the emission. Consequently, the obtained traps concentration is smaller than the real value. Therefore, the corrected equation is expressed as,
\[ N_T = 2 \left( \frac{\Delta C(0)}{C} \right) N_D \left[ \left( \frac{W - \lambda}{W} \right)^2 - \left( \frac{W_p - \lambda_p}{W} \right)^2 \right]^{-1} \]  \hspace{1cm} (2.11)

and

\[ \lambda = \left[ \frac{2\varepsilon E_F - E_T}{q^2 N_D} \right]^{\frac{1}{2}} \]  \hspace{1cm} (2.12)

where \( W \) and \( W_p \) are the depletion region widths under negative quiescent bias and right after the compensation pulse, respectively. The \( \lambda_p \) is the width of region \( \lambda \) right after the compensation pulse (see Figure 2.8).

Figure 2.8 Schematic diagram showing the presence of region \( \lambda \) in a metal/n-type semiconductor Schottky barrier. \( V_0 \) is the build-in potential defined as the difference between the work function potentials of the metal and the semiconductor. \( V \) is the bias applied to the junction.

Despite that the conventional DLTS is a convenient probe for testing deep energy levels in semiconductor, there are several aspects that can disperse the DLTS signal and
cause inaccurate measurement. One of them is a strong Poole-Frenkel (PF) effect which can lead to a distribution of energies in the depletion region. Due to the Coulomb potential exists around the defect, the presented electric field tilts the band and lowers the carrier emission barrier, giving rise to the DLTS peak shifts toward lower temperature. A double correlation technique (DDLTS) [120] was designed to compensate the PF effect by applying two pulses slightly different in magnitude to charge the traps. Instead of a single correlation (ΔC) method in the conventional DLTS, a second correlation was calculated for the change of capacitances due to the two different filling pulses. This procedure excluded the electric field dependence of the emission rate and improved the general DLTS technique sensitivity.

The other issue that can spread the DLTS signal is the entropy term when calculating the Gibbs free energy (trap activation energy $E_T$) in the DLTS measurement. The Gibbs free energy is related to entropy ($\Delta S$) and enthalpy ($\Delta H$) as,

$$\Delta G = \Delta H - T\Delta S = E_c - E_T$$  \hspace{1cm} (2.13)

where $E_c$ is the conduction band edge and $E_T$ is the trap energy level. Thus, the emission rate in Eq.(2.1) can be written in terms of entropy and enthalpy as,

$$e_n(T) = \sigma_n(\nu_n)X_n N_c exp\left(-\frac{\Delta H_n}{k_B T}\right)$$  \hspace{1cm} (2.14)

and

$$X_n = \frac{g_0}{g_1} exp\left(\frac{\Delta S_n}{k_B}\right)$$ \hspace{1cm} (2.15)

Comparing Eq. (2.1) and Eq. (2.14), one can notice that the entropy term $X_n$ is related to the degeneracy of the system, which can give rise to a larger apparent capture
cross section as much as by a factor of 50. [121] However, such an issue can be remitted mainly for non-degenerate samples.

Furthermore, instrumental effects also induce the unintended DLTS peak broadening if the rate window was not properly selected. Consequently, the DLTS peak width depends on the rate window rather than the physical property of the defect. For instance, a short or un-saturating filling pulse can truncate the lower temperature side of the DLTS peak, pushing the observed peak position towards a higher temperature region.

In addition to the above issues, the most significant limitation of conventional DLTS is the poor spectral resolution that is not able to distinguish closely spaced or overlapped emission rates from different defects. The typical reported theoretical resolution when resolving two capacitance transients is $\tau_1/\tau_2 \sim 8$ (i.e., the ratio of time constant from two defects). [122] In practice, the resolution can be less than $\tau_1/\tau_2 \sim 12$ or $\tau_1/\tau_2 \sim 15$ depending on the rate window design and system used. [123] To overcome the limitation of the conventional DLTS, the Laplace-DLTS method was first introduced by Dobaczewski et al. in 1994 [124] following the entire Laplace-DLTS system developed by the same group [123]. In general, the Laplace-DLTS digitizes the capacitance transient signal and processes the data with a mathematical routine that can separate the closely spaced, multiple emission rates with improved resolution about one order of magnitude as compare to the conventional DLTS.

2.2.2 Principle of Laplace-DLTS (L-DLTS)

The Laplace-DLTS (L-DLTS) technique involves an inverse Laplace transform procedure. This is a mathematical routine, also known as a regularization process, which
is usually used to solve an ill-posed problem (i.e., a problem without unique solution or no solution). The task to separate the closely spaced emission rates obtained from a capacitance transient is such an ill-posed problem. In the past, three mathematical models have been tested in Ref.[123], namely CONTIN [125], FTIKREG and FLOG, respectively. All the models were developed based on the Tikhonov regularization method [126] and showed comparable performance and accuracy. When applying this numerical procedure, one can achieve the resolution of L-DLTS to be improved up to $\tau_1/\tau_2 \sim 2$. [123]

When applying the inverse Laplace transform calculation, it is of importance to collect a capacitance transient with good S/N in order to perform the high resolution L-DLTS analysis. In practice, a desired S/N is larger than 3000, which requires sampling the signal capacitance transient in the order of 5000 times. Since the collection time is relatively long, usually from tens of min. to hrs., the stability of the ambient temperature in the cryostat is critical, especially for shallow defect levels. The typical temperature stability for detecting a 100 meV trap is ±50 mK. [123] Other electronic components that may induce noise need to be considered as well, such as the noise level of the capacitor meter and the stability of the pulse generator.

In this work, the capacitance transient was collected by the isothermal transient spectroscopy (ITS) function integrated with the Sula DDS-12 system. The ITS allows a user to collect a capacitance transient up to 10 s with a minimum time interval of 1 µs. The capacitance transients acquired at the same temperature can be averaged by the ITS software to increase S/N. The averaged capacitance transient was analyzed by a Matlab based Laplace DLTS Analyzer to find the emission rates. Detailed description of the
Laplace DLTS Analyzer and the graphic user interface (GUI) design during the project can be found in Appendix A.

The performance of the developed Laplace DLTS Analyzer was verified with computer simulated capacitance transients. Also, the simulation outcomes were compared with the commercial Sula ITS Analyzer developed by Sula Technology operating on a principle of a different mathematical algorithm. It shall be mentioned here that the standard Sula ITS Analyzer was not routinely available to us for collected experimental data analysis. A representative example used to test the limitation of the developed Laplace DLTS Analyzer is shown in Figure 2.9 (a), where a capacitance transient with 8 exponential components was simulated with S/N = 3000. Figure 2.9 (b) shows the Laplace DLTS Analyzer output that successfully reproduced all 8 emission rates; only peak 3 shows double head, with a standard deviation (error) varied from ~ 4% to 20% in this extreme case. Next, the same simulated transient data was generated and courteously analyzed by Sula Technologies using their ITS Analyzer. Table 2.1 shows outcomes of both simulations. As can be seen, the Sula ITS Analyzer provides extremely accurate results with a very small percentage error. However, in practice, the real number of rates in the measured capacitance transient is unknown and thus any initial analysis requires educated judgment from an experienced user while using the Sula ITS Analyzer. Instead, the Laplace DLTS Analyzer could automatically determine the number of rates in a transient without any initial user judgment. Furthermore, the developed analyzer can simultaneously show the numerical and graphical results in real time, whereas the Sula ITS Analyzer is not offering this option currently. In the most common scenario, the number of emission rates
in a real capacitance transient is less than the simulated extreme case shown in Figure 2.9. The performance of the Laplace DLTS Analyzer, when processing the non-extreme-case data sets containing smaller number of emission rates, was conducted as well and resulted in an averaged error smaller than 10%. As an example of the non-extreme-case, a simulated transient with 4 exponential components and S/N = 500 was analyzed. The results are summarized in Table 2.2.

Figure 2.9 (a) A simulated capacitance transient with 8 exponential components (blue dots) and the analysis fitting result from the Laplace DLTS Analyzer (red line), (b) the graphic output from the Laplace DLTS Analyzer.
Table 2.1 The L-DLTS investigation results of the developed *Laplace* DLTS Analyzer and the Sula ITS Analyzer.

<table>
<thead>
<tr>
<th>Simulated Rate [s]</th>
<th>Laplace DLTS Analyzer</th>
<th>Sula ITS Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate [s]</td>
<td>Error [%]</td>
</tr>
<tr>
<td>$t_1$</td>
<td>0.0002</td>
<td>5.0</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0.0006</td>
<td>8.3</td>
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<tr>
<td>$t_3$</td>
<td>0.0018</td>
<td>6.7</td>
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<tr>
<td>$t_4$</td>
<td>0.0054</td>
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<td>$t_5$</td>
<td>0.0160</td>
<td>16.9</td>
</tr>
<tr>
<td>$t_6$</td>
<td>0.0480</td>
<td>2.5</td>
</tr>
<tr>
<td>$t_7$</td>
<td>0.1440</td>
<td>12.2</td>
</tr>
<tr>
<td>$t_8$</td>
<td>0.4320</td>
<td>9.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simulated Amplitude [V]</th>
<th>Laplace DLTS Analyzer</th>
<th>Sula ITS Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amplitude [V]</td>
<td>Error [%]</td>
</tr>
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<td>1.175</td>
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<td>$A_4$</td>
<td>1.25</td>
<td>1.176</td>
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<tr>
<td>$A_5$</td>
<td>1.25</td>
<td>1.296</td>
</tr>
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<td>$A_6$</td>
<td>1.25</td>
<td>1.310</td>
</tr>
<tr>
<td>$A_7$</td>
<td>1.25</td>
<td>1.329</td>
</tr>
<tr>
<td>$A_8$</td>
<td>1.25</td>
<td>1.323</td>
</tr>
</tbody>
</table>
Table 2.2 The L-DLTS investigation results of a non-extreme case by using the developed Laplace DLTS Analyzer.

<table>
<thead>
<tr>
<th>Simulated Rate [s]</th>
<th>Laplace DLTS Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate [s]</td>
</tr>
<tr>
<td>$t_1$</td>
<td>0.0002</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0.0006</td>
</tr>
<tr>
<td>$t_3$</td>
<td>0.0018</td>
</tr>
<tr>
<td>$t_4$</td>
<td>0.0054</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simulated Amplitude [V]</th>
<th>Laplace DLTS Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amplitude [V]</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1.25</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1.25</td>
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<tr>
<td>$A_3$</td>
<td>1.25</td>
</tr>
<tr>
<td>$A_4$</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Another simulation performed toward testing the accuracy of the developed Laplace DLTS Analyzer was carried out for simulated capacitance transient data having different S/N. Since the S/N in real L-DLTS measurement is usually in the order of a few hundred which is much worse than the suggested S/N (>3000) in Ref. [123], thus it is necessary to test the performance of the Laplace DLTS Analyzer with a smaller S/N. Figure 2.10 shows an example of such simulation when a capacitance transient with 5 exponential components was simulated with S/N = 133. In fact, it is a very noisy transient data that is worse than most of the real world L-DLTS data collected experimentally in this work.
Figure 2.10 (b) shows the Laplace DLTS Analyzer output which successfully reproduced all the 5 emission rates with a standard deviation (error) varied. The errors of three peaks (out of five) are within 5%, while the other two peaks have an error of 21.1% and 43%, respectively (see Table 2.3). The analyzed results obtained from the Laplace DLTS Analyzer were also compared with the Sula ITS Analyzer as shown in Table 2.3. It is seen that better accuracy is achieved using the Sula ITS Analyzer in terms of obtained emission rate values. However, the errors in calculated amplitude values from both analyzers are comparable. Considering the above described tests toward the developed Laplace DLTS Analyzer performance verification, we concluded in the light of the limitations imposed by the chosen regularization method that its performance when dealing with simulated transient data having S/N comparable to the real data results in an overall error no larger than 10%.

Furthermore, it should be noted here that although the Sula ITS Analyzer provides better accuracy in analyzing the simulated transient data which contains a combination of discrete emission rates, the real capacitance transient data may contain continuous emission rates that have a certain distribution. In this scenario, the L-DLTS spectrum obtained from our Laplace DLTS Analyzer could better represent the real distribution of the continuous emission rate when using the shape of the peaks as a guide.
Figure 2.10 (a) A simulated capacitance transient with S/N=133 and 5 exponential components (blue dots), red line shows the analysis fitting result from the Laplace DLTS Analyzer, (b) the graphic output from the Laplace DLTS Analyzer.
Table 2.3 The L-DLTS investigation results of the Laplace DLTS Analyzer and the Sula ITS Analyzer.

<table>
<thead>
<tr>
<th>Simulated Rate [s]</th>
<th>Laplace DLTS Analyzer</th>
<th>Sula ITS Analyzer</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Rate [s]</td>
<td>Error [%]</td>
</tr>
<tr>
<td>$t_1$</td>
<td>0.001</td>
<td>0.00095</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0.003</td>
<td>0.00429</td>
</tr>
<tr>
<td>$t_3$</td>
<td>0.009</td>
<td>0.01090</td>
</tr>
<tr>
<td>$t_4$</td>
<td>0.027</td>
<td>0.02800</td>
</tr>
<tr>
<td>$t_5$</td>
<td>0.081</td>
<td>0.07940</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simulated Amplitude [V]</th>
<th>Laplace DLTS Analyzer</th>
<th>Sula ITS Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amplitude [V]</td>
<td>Error [%]</td>
</tr>
<tr>
<td>$A_1$</td>
<td>2</td>
<td>2.326</td>
</tr>
<tr>
<td>$A_2$</td>
<td>2</td>
<td>2.503</td>
</tr>
<tr>
<td>$A_3$</td>
<td>2</td>
<td>1.178</td>
</tr>
<tr>
<td>$A_4$</td>
<td>2</td>
<td>1.954</td>
</tr>
<tr>
<td>$A_5$</td>
<td>2</td>
<td>2.058</td>
</tr>
</tbody>
</table>

2.2.3 Principle of minority carrier transient spectroscopy (MCTS)

The majority carrier traps usually can be characterized by using regular DLTS with appropriate pulse and rate window settings, such in the case of the electron traps in the $n$-type Schottky diode. However, the hole traps in an $n$-type Schottky diode is hard to be detected with a regular DLTS due to the fact that capacitance change contributed from minority carriers is negligible as compared to the majority carriers’ (electrons)
contribution. Thus, to measure the minority traps in an $n$-type Schottky diode, Peaker et al. introduced in 1979 the minority carriers transient spectroscopy (MCTS) technique [127]. In the literature, this method is also called optical-DLTS (ODLTS). [128] The MCTS involves a modulated above band gap optical excitation superimposed with constant reverse bias applied to the Schottky diode. Before turning the excitation light on, the sample should be kept in dark when applying reverse bias for depleting all carriers from the depletion region. When the excitation light pulse arrives (see Figure 2.11 (a)), the EHPs are generated in the material. The electrons are repelled due to the existing built-in voltage, while the holes can go through the depletion region of the Schottky diode and occupy the defect traps. If the excitation light pulse is long enough, the hole traps in the depletion region are completely filled with optically generated holes. When the light pulse is gone (off) (see Figure 2.11 (b)), those trapped holes are liberated at certain emission rate depending on the ambient temperature. Thus, the trap properties can be characterized with a temperature sweep in the similar way as when using the regular DLTS technique.
Figure 2.11 Illustration of the dynamic response of a hole trap in an n-type Schottky diode during (a) photon excitation (light is on) and (b) after photon excitation (light is off). Reverse bias ($V_r$) is kept as constant during the light on-off cycle.
Although there is an optical excitation source involved in MCTS, it is different from the so called deep level optical spectroscopy (DLOS) in which a tunable below band gap excitation source, rather than above band gap excitation, is used. Specifically, in the DLOS method, the experiment needs to be taken at low temperature to eliminate the capacitance changes due to occurrence of thermal emission rather than optical emission. Since the DLOS measurement relies on the photo-capacitance changes when the excitation photon energy equals the absorption between a defect level and valence band, this process requires large enough photoionization cross-section of the probed defects. [129] However, this is not the case if a defect center is optically inactive. Fortunately enough, the MCTS method overcomes those DLOS method drawbacks and is suitable for characterizing the hole traps in materials investigated in this work. In addition, for electron and hole traps measurements consistency, we have exercised both the DLTS and MCTS techniques as both of them rely on the thermal release of the trapped carriers.

We shall consider now in greater details some precautions when conducting the MCTS experiment. In particular:

1) The pulse width of the excitation light source needs to be long enough in order to allow all the hole traps located in the depletion regions to be filled. In this study, the investigated samples required a laser excitation pulse of 4 s to saturate, presumably, all the hole traps. However, due to the limitation of the Sula DDS-12 system, the longest pulse width (PW) setting was 1 s and the longest rate window setting was 430 ms. Thus, a laser excitation PW of 1 s with a period of 2 s (50% duty cycle) was used for the MCTS experiment, respectively. With this
experimental setting, the calculated trap concentrations may be 10% - 20% smaller than the real value.

2) The photon induced EHPs should be predominately generated outside the junction rather than inside the junction to prevent the electron to be captured by the electron trap located in the depletion region. The absorbed photon generated electrons outside the junction are repelled by the built-in electric field, while the holes can diffuse into the junction and become captured by the hole traps. Thus, to verify that the MCTS signal is predominantly due to the hole emission, the I-V characteristic of the studied samples were collected and compared between one measured in dark and another under above band gap laser excitation, respectively. It is expected that the EHPs generated within the depletion region would lead to increase of total current from photon current while EHPs generated outside the depletion region would not. Figure 2.12 shows typical I-V characteristics for investigated samples. It is seen that after exposure to excitation wavelength at 325 nm from He-Cd laser a slight current increase (~1%) was observed. Thus, we have concluded that the EHPs were generated predominantly outside the Schottky junction.
Figure 2.12 I-V curves of GaN:Si,Eu\(^{3+}\) sample measured in dark and under 325 nm pulse laser excitation.

3) In this work, the active region of the investigated samples was kept in between the solid metal contact (top of the structure) and the single face polished sapphire substrate (bottom of the structure), so it was not possible to optically excite the sample either from topside or backward. Thus, the excitation laser light was coupled to epitaxial film from the side of the sample and waveguided laterally along the sample surface as well as was internally reflected between the substrate-epilayer and epilayer-free space interfaces, contributing to excitation of studied material. Since the hole trap in the junction is filled by holes diffused into the junction, the diffusion length of hole needs to be long enough to reach the junction from the
volume of the materials outside the junction. Following Eq. (2.16) and Eq. (2.17), we estimated the hole diffusion length to be about 250 nm [130] at room temperature, which is shorter than the active layer thickness of GaN:Si,Eu$^{3+}$ (500 nm) so that the holes generated outside the junction can diffuse into the junction according to the following expressions,

$$D_p = \mu_p \frac{kT}{q}$$ \hspace{1cm} (2.16)

$$L_p = \sqrt{D_p \tau_p}$$ \hspace{1cm} (2.17)

where $D_p$ is diffusion coefficient of holes, $\mu_p$ is mobility of holes, $k$ is Bozeman constant, $T$ is temperature, $\tau_p$ is the recombination rate and $L_p$ is the diffusion length of holes. Here, we took $\mu_p = 200 \text{ cm}^2/\text{v.s.}$, $\tau_p \approx 0.6 \text{ ns}$, [130] for computing the hole diffusion length.
CHAPTER 3: SAMPLES AND EXPERIMENTAL SETUPS

In this chapter, information of studied samples is summarized along technical discussions on experimental setups developed and used in this work. The theories and principles of each used experimental methods are discussed with emphasis on different types of deep level transient spectroscopy techniques, in terms of their characteristic features and performance parameters. Specifically, in this work, variety of optical spectroscopy techniques were exercised to study the luminescence properties of RE-doped III-Ns. The project focused on understanding the excitation mechanism of RE$^{3+}$ ions via studying the selected RE induced defects by means of optical spectroscopy and electrical defect characterization techniques including deep level transient spectroscopy (DLTS), Laplace DLTS (L-DLTS) and Optical DLTS (O-DLTS). During the project, a DLTS system was built based on the Sula-DDS DLTS unit. [131] The hardware and software used during the experimental work were developed. And their features and functions are described below:

- A helium closed-cycled cryostat was modified by equipping it with a designed sample holders and electrical feedthroughs for DLTS measurement from 10 K to 320 K. A liquid nitrogen (LN2) cooled cryostat was designed and constructed with optical excitation accessibility and temperature scan capability from 78 K to 500 K.

- A Matlab based Laplace DLTS Analyzer and the graphic user interface (GUI) was developed to enable the high resolution L-DLTS analysis that could increase the spectrum resolution up to ten times compared to the regular DLTS technique.
• Optical DLTS (O-DLTS) or minority carrier transient spectroscopy (MCTS) measurement was performed to study the minority traps in the samples by integrating a pulsed optical source to the DLTS system. The MCTS function enhanced the DLTS system capability making it as an effective probe for the minority carrier traps. Otherwise, studying the minority carriers’ traps is very difficult due to expected overwhelming majority carrier emission signal during regular DLTS experiment.

3.1 Samples

During the course of this work a large number of samples were investigated. While selected samples with representative results are reported in this dissertation (see Table 3.1, indicated using bold text), samples that were studied but shown less interesting results or samples that are still under investigation are summarized together in Table 3.1.

Furthermore, samples shown in Table 3.1 are grouped based on the respective type of epilayers. Each group may contain multiple samples that were grown under different growth conditions. Undoped control samples (i.e., without RE dopant) are not listed in the Table 3.1; however, were tested along the RE doped specimens for consistency.

In general, the samples investigated in this work were grown by Dr. Ratnakar Palai’s research group at University of Puerto Rico, or by Dr. Yasufumi Fujiwara’s research group at Osaka University, Japan. Selected samples were prepared or processed prior to characterization at Ohio University, including thermal annealing, dicing, metallization and metal contacts fabrication, and wire bonding, respectively.
Table 3.1 Summary of samples investigated in this work.

<table>
<thead>
<tr>
<th>Group #*</th>
<th>Epilayer</th>
<th>Substrate</th>
<th>Growth Method</th>
<th>RE Dopant</th>
<th>Source of Sample</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GaN</td>
<td>Si (111)</td>
<td>MBE</td>
<td>Yb</td>
<td>U. Puerto Rico</td>
<td>Nano-rod Varied Yb source temperature</td>
</tr>
<tr>
<td>2</td>
<td>AlN</td>
<td>Sapphire c-axis</td>
<td>MBE</td>
<td>Yb</td>
<td>U. Puerto Rico</td>
<td>Varied Yb source temperature</td>
</tr>
<tr>
<td>3</td>
<td>GaN</td>
<td>Sapphire c-axis</td>
<td>MBE</td>
<td>Er</td>
<td>U. Puerto Rico</td>
<td>Varied Er source temperature</td>
</tr>
<tr>
<td>4</td>
<td>GaN</td>
<td>Sapphire c-axis</td>
<td>MBE</td>
<td>Yb, Er</td>
<td>U. Puerto Rico</td>
<td>Varied thickness</td>
</tr>
<tr>
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<td>GaN</td>
<td>Sapphire c-axis</td>
<td>MBE</td>
<td>Yb</td>
<td>U. Puerto Rico</td>
<td>With AlN buffer, Varied buffer layer thickness</td>
</tr>
<tr>
<td>6</td>
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<td>Yb</td>
<td>U. Puerto Rico</td>
<td></td>
</tr>
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<tr>
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<td>MBE</td>
<td>Yb, Er</td>
<td>U. Puerto Rico</td>
<td></td>
</tr>
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<td>MBE</td>
<td>Er</td>
<td>U. Puerto Rico</td>
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<tr>
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<td>MBE</td>
<td>Er</td>
<td>U. Puerto Rico</td>
<td>Varied with indium concentration</td>
</tr>
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<td>MBE</td>
<td>Yb</td>
<td>U. Puerto Rico</td>
<td>Nano column, Varied with indium concentration</td>
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<tr>
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<td>MOCVD</td>
<td>Eu**</td>
<td>Veeco</td>
<td>Superlattice, Varied with indium concentration</td>
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<tr>
<td>14</td>
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<td>Sapphire c-axis</td>
<td>MOCVD</td>
<td>Yb**</td>
<td>CREE</td>
<td>Varied Yb dose</td>
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<tr>
<td>15</td>
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<td>MOCVD</td>
<td>Er**</td>
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<td>Er**</td>
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<td>17</td>
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<td>18</td>
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<td>OMVPE</td>
<td>Eu</td>
<td>Osaka U.</td>
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</tr>
</tbody>
</table>

* Each group may contain multiple samples grown under different conditions. Control sample for each group without RE dopant was investigated but it is not listed in the table.  
** RE ions were implanted into the host material.
3.1.1 \textit{Yb}^{3+} \textit{ion doped GaN samples}

Representative \textit{Yb}^{3+} ion doped GaN samples, which were grown on different substrates (crystal polarity) and/or different growth methods, are selected for comparison from Groups 1, 5, 6, 14 in Table 3.1 and summarized in Table 3.2. The measurement results obtained for these samples are presented in \textit{Section 4.1}.

In Table 3.2 sample \textit{S1} is the control GaN sample of \textit{S2} sample that was grown with the same conditions but without \textit{Yb} doping. Sample \textit{S2} is the \textit{GaN:Yb}^{3+} nanorod (NRs) grown on Si (111) substrate using \textit{EPI 6200 rf} plasma assisted MBE system allowing the \textit{Yb} to be \textit{in situ} doped during the growth process. The growth parameters of \textit{S2} were: base pressure of $10^{-11}$ Torr, nitrogen flux of 0.75–2.0 sccm, \textit{rf} power of 450 W, substrate temperature of 900 °C, Ga cell temperature of 850 °C and \textit{Yb} cell temperature of 350 °C, respectively. The substrates were degreased and etched with a dilute concentration of nitric acid followed by standard cleaning. Subsequently, the substrates were heated 5 °C/min up to 900 °C and held there for 30 min for thermal treatment. Then the temperature was lowered at the rate of 10°C/min to 500 °C. Substrate nitridation process was carried out with 2 sccm N\textsubscript{2} flux for 10–30 min. Finally, the substrate temperature was raised to 900 °C for the growth of \textit{GaN:Yb}^{3+} NRs. The molecular N\textsubscript{2} flux of 0.75 sccm was introduced through the \textit{rf} plasma source of 450 W to produce atomic N to enhance the reaction with Ga and \textit{Yb} on the surface of substrate during the \textit{GaN:Yb}^{3+} NRs growth. Samples \textit{S3} and \textit{S4} are \textit{Yb in situ} doped GaN thin film grown on \textit{c-plane (0001)} and \textit{m-plane (10\textbar10)} sapphire substrates, respectively. Finally, sample \textit{S5} is a \textit{Yb} implanted GaN thin film grown by MOCVD. \textit{Yb}^{3\text{+}} ions were implanted into the GaN with energy not exceeding 150
keV and total dose up to $4 \times 10^{15}$ cm$^{-2}$, respectively. The sample was annealed at 1000 °C for 10 min in the nitrogen gas environment under atmospheric pressure to recover the lattice damage from ion implantation process.

Figure 3.1 shows the representative high resolution scan electron microscopy (HRSEm) images of the GaN:Yb$^{3+}$ NRs (S2). The NRs are vertically aligned with a varying length between 300 nm and 500 nm and an average width of 25 nm, respectively.

Table 3.2 Information on GaN:Yb$^{3+}$ samples investigated in Section 4.1.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
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<td>GaN:Yb$^{3+}$</td>
<td>GaN:Yb$^{3+}$</td>
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<td>MBE</td>
<td>MBE</td>
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<td>Si (111)</td>
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<td>m-sapphire (1010)</td>
<td>c-sapphire (0001)</td>
</tr>
<tr>
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<td>nanorod</td>
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<td>thin film</td>
<td>thin film</td>
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<td>$10^{-11}$</td>
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<td>-</td>
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<tr>
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<tr>
<td>Note</td>
<td>Reference of S2</td>
<td>Yb in situ doped</td>
<td>Yb in situ doped</td>
<td>Yb in situ doped</td>
<td>Yb ion implanted</td>
</tr>
</tbody>
</table>
Figure 3.1 HRSEM images of the GaN:Yb$^{3+}$ NRs (S2): (a) side view and (b) top view. Reproduced after Ref. [52].

3.1.2 Yb$^{3+}$ ion doped InGaN samples

The second group of samples investigated in this dissertation (see Section 4.2) contains the Yb$^{3+}$ ion in situ doped InGaN samples (NRs:Yb$^{3+}$) and their control counterparts (NRs). These samples were grown by Dr. Palai’s group on sapphire (0001) substrate by using an rf plasma assisted MBE, model EPI 620 under high vacuum growth conditions. The base pressure was $\sim 10^{-11}$ Torr and the growth pressure was $8.5 \times 10^{-6}$ Torr. The rf power of 400 W, for the N$_2$ flux of 0.75 sccm, was used to split the N$_2$. The substrate was maintained at a temperature of 900°C for the growth at a pressure of $2.0 \times 10^{-8}$ Torr, where the Ga, In and Yb cells were maintained at the temperatures of 850 °C (Ga), 700 °C (In base), 800 °C (In tip) and 350 °C (Yb), respectively. An undoped InGaN NRs sample was grown under the same condition for comparison purposes. The reference NRs sample showed homogeneous In distribution while an In content gradient was observed in the NRs:Yb$^{3+}$. Because of that, four different regions on the NRs:Yb$^{3+}$ sample were identified and studied individually, named as the NRs:Yb$^{3+}$ region (a), (b), (c), and (d), respectively.
In this way, we have narrow down the In content inhomogeneity and assumed that the In content in each individual region was considered to be homogeneous (±0.23 at.%).

Figure 3.2 shows the surface morphology of the NRs:Yb$^{3+}$ sample. The atomic force microscopy (AFM) image shown in Figure 3.2(a) and the cross-sectional scanning electron microscopy (SEM) image shown in Figure 3.2(b) confirm that studied NRs have an average height in between 420 nm to 450 nm and the diameter of the nanorods varies from 50-60 nm. Figure 3.2(c) shows the high resolution transmission electron microscopy (HRTEM) image of the tip of a single NR with diameter about 15 nm.

Figure 3.2 (a) AFM image of the NRs:Yb$^{3+}$ surface area (5×5 µm$^2$) confirming the growth of vertical nanorods. (b) SEM image of the NRs:Yb$^{3+}$. (c) HRTEM image of a single NR with diameter of 15 nm. Reproduced after Ref. [132].

3.1.3 Eu$^{3+}$ ion doped GaN samples

To avoid possible ambiguity in data interpretation due to the surface defects (NRs) or implantation induced defects in studied RE doped III-N samples we conducted optical and electrical studies using the state-of-the-art Eu, Si co-doped GaN samples (see Section
5.1). Specifically, Eu and Si co-doped GaN (GaN:Si,Eu$^{3+}$, #GN888) and its Eu-undoped control counterpart (GaN:Si, #GN893) were grown by a SR-2000 Taiyo Nippon Sanso organometallic vapor phase epitaxy (OMVPE) system at Osaka University. The epilayers were deposited on a sapphire (0001) substrate using trimethylgallium (TMGa), ammonia (NH$_3$), monomethylsilane (MMSi), and bis (n-propyltetramethyl cyclopentadienyl) europium as precursors for Ga, N, Si, and Eu, respectively. Figure 3.3 (a) shows a schematic diagram of the GN888 structure. As it can be seen, first a low-temperature (LT) GaN buffer layer was grown on sapphire at 475 °C. Then, an undoped GaN epilayer with thickness of 1.7 μm was grown at 1200 °C under atmospheric pressure. Finally, a 500 nm thick GaN:Si,Eu$^{3+}$ layer was grown at 1080 °C under 100 kPa. Detailed description of sample growth condition can be found in Ref. [133]. After the growth, different sizes of ring-shaped Ti (40 nm)/Au (200 nm) Ohmic contacts and circular Pd (40 nm)/Ti (20 nm)/Au (200 nm) Schottky contacts were deposited on the surface by electron-beam evaporation, respectively. General wafer cleaning procedure and deposition consequence has been followed to achieve a good contact quality [132]. The devices tested in this work has a Schottky contact with diameter of 500 μm, space gap in between the Schottky and Ohmic contact was 50 μm (see Figure 3.3 (a)). The sample was then attached to a thin ceramic plate with gold squared pads on it for easy electrical measurements. The 0.1 mil gold wires were than wedge bonded between the contacts on sample and gold pads on the ceramic base by semi-automatic wire bonder (West Bond 7400). The gold pads on the ceramic were in the dimension of 5 mm × 5 mm where external probes can attach to the
pads without direct contact to the samples. Figure 3.3 (b) shows the bonded gold wires on the selected sample.

![Schematic diagram of the sample structure, wire bonding between the contacts on the sample and the gold pads on the ceramic base.]

Figure 3.3 (a) Schematic diagram of the sample structure, (b) wire bonding between the contacts on the sample and the gold pads on the ceramic base.

3.1.4 \textit{Eu}^{3+}\textit{ ions doped InGaN/GaN superlattice samples}

In\textsubscript{0.06}Ga\textsubscript{0.94}N/GaN SLs samples were grown by metal-organic chemical-vapor deposition (MOCVD) on c-plane sapphire (see Section 5.2). The SLs consisted of 25 periods of In\textsubscript{0.06}Ga\textsubscript{0.94}N/GaN grown on a 2.5 \textmu m \textit{n}-type GaN/1.0 \textmu m undoped GaN buffer layer deposited on a sapphire (0001) substrate. The SLs were capped with a 3 \textmu m GaN cap layer. The layer schematic of the SLs is shown in Figure 3.4. The In fraction in the SLs was designed in between 6-7 at.%. The SLs were implanted with Eu ions at 150 keV acceleration energy and a dose of \textasciitilde5.5\times10^{15} \text{cm}^{-2} at room temperature. The simulated depth
profile of europium implantation for the SLs is shown in Figure 3.4 (a). The resulting Eu$^{3+}$ ions concentration in the SLs ranged from $1.4 \times 10^{20}$ cm$^{-3}$ (at surface) to $1 \times 10^{14}$ cm$^{-3}$ (at depth of 144 nm) with the maximum peak concentration of $1.8 \times 10^{21}$ cm$^{-3}$ (at depth of 24 nm), respectively. The SLs and the SLs-Eu were subjected to isochronal thermal annealing in a quartz tube furnace at temperature from 200 °C to 1000 °C in nitrogen ambient. Samples were quickly moved into the furnace hot zone, annealed for 3 min and then rapidly quenched to room temperature with a quenching rate of 400 °C/min. Figure 3.4 shows also the expected PL excitation depth and the resulting concentration of EHPs generated by used laser. It is confirmed that the used excitation light penetrates SL region deeply enough to excite implanted Eu$^{3+}$ ions.
Figure 3.4 (Top) Schematic diagram of the In$_{0.06}$Ga$_{0.94}$N/GaN SLs grown on sapphire. (a) Europium implantation depth profile calculated using the Pearson distribution function reaching peak concentration of $1.8 \times 10^{21}$ cm$^{-3}$ at the 24 nm from surface and $6.7 \times 10^{13}$ at the 144 nm from surface, respectively; (b) Penetration depth profile of the He-Cd laser excitation; (c) Concentration profile of EHPs generated by He-Cd laser with a power density of 0.3 W/cm$^2$. 
3.2 Optical characterizations

Spectroscopy is a powerful technique in assessing materials optical characteristics. High resolution spectroscopy can resolve for example the fine Stark splitting of 4f-4f electronic transitions of the RE elements. It provides useful references to study the 4f electronic level splitting due to crystal field interaction and the symmetry properties of the RE-doped III-Ns at atomic level. [52], [134] In this study, we primarily, investigated the material by means of photoluminescence (PL), PL excitation (PLE) cathodoluminescence (CL), temperature dependent PL/CL (TDPL/CL), and time resolved PL (TRPL).

The generic experimental setup used for optical spectroscopy is shown in Figure 3.5. During a typical spectroscopy experiment samples were mounted on the sample holder that was attached to the cold-finger of a closed-cycle helium cryostat operating in the temperature range from 10 K to 320 K. Samples were excited by different excitation source depending on the type of experiment considered. Typically:

- for regular PL measurement on RE-doped GaN samples, an above band gap excitation provided by a continuous wave (cw) He-Cd laser (325 nm, model IK 3202R-D by Kimmon) was used. The maximum power output of this laser was 25 mW,
- for PLE measurement, samples were excited with a wavelength scan from 300 nm to 700 nm by a 150 W Xenon lamp equipped with a monochromator (CM110). The average excitation power was 2 µW and the narrowest excitation line width was 1 nm,
• CL measurements were conducted with an electron gun (EG) that could generate an electron beam current (~75µA) with maximum of 15 keV acceleration voltage,

• TRPL studies were conducted using when exciting samples with a 358.56 nm frequency doubled Ti:Sapphire laser at 10.5 K. Signal was detected using a standard single photon counting electronics with 500 ps temporal resolution. These experiments were conducted at Dr. Stinaff’s laboratory in the Department of Physics and Astronomy at Ohio University.

Two spectrometer/CCD systems were used for investigating samples’ optical responses. System #1 included an Instruments S.A. spectrometer (model HR320). It has a focal length of 320 mm with Czerny-Turner configuration. Holographic gratings equipped on this spectrometer have 150 gr/mm at 500 nm blaze (grating #1) and 600 gr/mm at 450 nm blaze (grating #2), respectively. The dispersed light from the grating was collected by a charge coupled device (CCD) detector (model PI-Max by Princeton Instrument) with an array of 512×512 pixels with a single pixel size of 24×24 μm. The spectral resolution of this system was ~ 0.6 nm with grating #1 and ~ 0.23 nm with grating #2 at 150 μm entrance slit width. The detector was capable for measuring spectrum range from 300 nm to 1200 nm. The detection system #2 was an Acton 300 spectrometer with three grating options: (1) 300 gr/mm and 500 nm blaze (grating #1), (2) 1200 gr/mm and 300 nm blaze (grating #2), and (3) 1200 gr/mm and 500 nm blaze (grating #3). The CCD camera integrated with this spectrometer was a PI-MAX having 1024×256 pixels. The highest spectral resolution achievable was ~ 0.12 nm when using the system #2 equipped with grating #2 or #3.
Figure 3.5 Generic schematic diagram of optical spectroscopy experimental setup: (1) sample mounted in the closed-cycle helium cryostat connected with (2) helium compressor model SC by HELIX and turbo pump by Pfeiffer model TSH 064D; (3) an electron gun with maximum of 20 keV electron beam acceleration energy for CL measurement; (4) varies of optical excitation source for PL, PLE and TRPL measurements, respectively; (5) optical components used for guiding and focusing the excitation beam and collecting the luminescence from a sample into (6) a spectrometer equipped with (7) CCD camera; (8) the spectrometer and CCD camera were controlled via CCD camera controller (Princeton Instrument model ST-133 in system #1 and ST-133A in system #2, respectively) controlled by (9) computer.
3.3 Electrical characterizations

In this work, a *Sula Technologies DDS-12 DLTS system* (*Sula Technologies*, Ashland, OR, U.S.) was used which consists of a fast capacitance meter, a bias pulse generator, 12 correlators for rate window settings, and a remote computer for data acquisition and analysis. The capacitance meter of the *DDS-12 system* operated at 1 MHz in typical experiments. The pulse generator can generate bias from -13 V to +13 V. There were total of 12 correlators installed on the *Sula DDS-12 system* which can set up 12 different rate windows simultaneously with different initial delay (ID) time. The ID was defined as the time interval between the start of the capacitance transient and the beginning of the sampling windows (*see Figure 2.5 (c)*). The sampling time interval and the sampling time $t_1$ and $t_2$ were designed as *sampling interval* $= 3.6 \times ID$, $t_1 = 2.4 \times ID$ and $t_2 = 7.0 \times ID$. Thus, $\frac{t_2}{t_1} = 2.92 = constant$, and a time constant $\tau_{max} = (t_2 - t_1)[\ln(t_2/t_1)]^{-1}$ is always equal to $4.3 \times ID$. The reason to keep $t_2/t_1 = constant$ and the derivation of $\tau_{max}$ has been discussed in *Section 2.2.1*. Beside the regular DLTS measurement, the *DDS-12 system* was able to conduct capacitance – voltage (C-V), current – voltage (I-V), double-pulse DLTS (DDLTS), constant capacitance DLTS (CCDLTS), isothermal spectroscopy (ITS) measurements and current transient spectroscopy (CTS), respectively.

Any sample designated for electrical characterization could be placed alternatively in one cryostat operating in specific temperature range. Cryostat #1 is an *Advanced Research Systems* model DE-202A close-cycled helium cryostat operating from 7 K to 320 K and cryostat #2 is a homemade liquid nitrogen (LN$_2$) cryostat that operates from ~78 K to 500 K, respectively. We have designed and machined in-house all major components of
the cryostat #2 as well as all sample’s holders used in experiments. The technical drawing of designed LN₂ cryostat is shown in Appendix C. Figure 3.6 shows the pictures of the DLTS system hardware and the LN₂ cryostat #2. Both cryostats were temperature controlled by a Lakeshore 335 temperature controller with temperature accuracy of ± 0.05 K which can fulfilled the requirement of L-DLTS. The Sula DDS-12 spectrometer was equipped with the isothermal transient spectroscopy (ITS) capability to collect the accumulated capacitance transients needed for L-DLTS analysis. Also, both cryostats were equipped with optical windows for optical-DLTS measurements. Figure 3.7 shows a generic diagram illustrating the hardware connections observed in the typical DLTS experiment.
Figure 3.6 Illustration of the constructed experimental setup using *Sula DDS-12 DLTS* system with two cryostats (a); the side view (b) and the front view (c) of the cold finger of the LN$_2$ cryostat with sample mounted on the sample holder.
Figure 3.7 Diagram of DLTS experimental setup: (1) the *Sula DDS-12* system equipped with a pulse generator unit, a capacitance meter unit, a pre-amplifier unit, and an interface to communicate with a computer; (2) sample mounted inside a cryostat that has an optical window; (3) the sample temperature is controlled by a Lake Shore temperature controller Model 335; (4) the capacitance transient signal can be monitored by an oscilloscope; (5) optical excitation source for optical-DLTS measurement, a 325 nm He-Cd laser or a 150 W Xenon lamp equipped with monochromator was used for optical excitation; (6) a mechanical shutter was placed in front of the optical source for pulse operation; (7) a computer was used to synchronize among electronics and provide LabVIEW user control interface.
CHAPTER 4: YETTERBIUM DOPED III-NITRIDE SEMICONDUCTORS

This chapter presents the optical properties of investigated Yb$^{3+}$ ion doped GaN nanorods (NRs) samples and compares them with the GaN:Yb$^{3+}$ thin films grown by different epitaxy techniques. The excitation mechanism of Yb$^{3+}$ ion in GaN is discussed. Furthermore, a recent study of the InGaN:Yb$^{3+}$ NRs material showing improvement of InGaN emission due to incorporated Yb$^{3+}$ ion is presented.

4.1  Yb$^{3+}$ ion in GaN nanorod and thin film structures

In this section, a Yb$^{3+}$ ion in-situ doped GaN NRs sample was investigated by means of PL and CL studies. The focus was on exploring the spectroscopically determined optical centers that contribute to the excitation of Yb$^{3+}$ ion. Furthermore, the Yb emission from these NRs samples is compared to other GaN:Yb$^{3+}$ samples grown on different substrates or with different growth conditions, providing insight into understanding of the excitation mechanism of GaN:Yb$^{3+}$. Some of the results shown in this section have been published in Ref. [52].

4.1.1  Yb$^{3+}$ ion emission spectrum in different GaN hosts

Figure 4.1 (a) - (e) shows the PL spectra of S1-S5 samples measured at 11 K. The reference NRs S1 sample shows an excitonic emission peak at 371 nm, and a broad band peaking at \( \sim 680 \) nm due to intrinsic impurities and point defects. The GaN:Yb$^{3+}$ NRs (S2) also shows the excitonic emission but with multiple peaks at around 370 nm that overlapped by the broad defect related “yellow band”. The characteristic Yb$^{3+}$ ion emission peaks originating from intra-4f electronic transitions \( (^{2}F_{5/2} \rightarrow ^{2}F_{7/2}) \) were observed around 1000 nm in S2, S3, S4 and S5; however with different spectral components. To further
study the Yb$^{3+}$ ion emission spectra among different samples, the high resolution PL measurement was conducted at 11 K. The observed spectra are shown in Figure 4.2 in which the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of the Yb$^{3+}$ ion in different samples can be clearly compared. The position of the three dominate peaks of $S2$ are marked using the dashed line in Figure 4.2 and the corresponding intra-4f electronic transitions are illustrated in the inset as an energy level diagram.
Figure 4.1 (a) - (e) PL spectra of GaN:Yb$^{3+}$ $S1$ – $S5$ samples measured at 11 K.
Figure 4.2 High resolution PL of Yb$^{3+}$ ion emission in different GaN hosts. The peak position of the three primary peaks observed in the NRs sample (S2) was marked using dashed lines. The inset shows the $^2F_{5/2} \rightarrow ^2F_{7/2}$ electronic transitions corresponding to three primary PL peaks of S2.
The excitation mechanisms involved when excited with photons having energy larger than band gap (PL) or free electrons by impact excitation/ionization (CL) are different [135], (see also discussed in Section 5.2.3). Excitation by energetic electrons in CL produces emission via all possible luminescence mechanisms available in semiconductor. Thus, the CL measurement could generate a spectrally richer spectrum since it can involve all the luminescence channels available. The calculated Stark energy levels splitting and the experimentally observed energy levels of GaN:Yb\(^{3+}\) epilayers (S5) and GaN:Yb NRs (S2) are summarized in Table 4.1. Figure 4.3 shows the high resolution CL spectrum of Yb\(^{3+}\) ion emission from the NRs (S2) measured at 11 K. As can be seen, more peaks are observed as compared to the high resolution PL spectrum shown in Figure 4.2. Peak deconvolution using multiple Gaussian-Lorentzian fitting was applied to distinguish between overlapping peaks by curves (see dashed lines in Figure 4.3).

The theoretical calculation and numerical simulation of the splitting of the Stark energy levels of Yb\(^{3+}\) ion in S2 was done in collaboration with Dr. Dammak’s research group from the Université de Sfax, Tunisia. [52] The obtained 12 deconvoluted CL emission peaks were then assigned to the multiplet Stark energy manifold of \(^2F_{5/2}\) and \(^2F_{7/2}\), respectively. The excited Stark levels \(^2F_{5/2}\) have three splitting energy levels numbered as \(F_5, F_6, F_7\), while the ground state \(^2F_{7/2}\) has four splitting energy levels numbered as \(F_4, F_3, F_2, F_1\). The electronic transitions among these energy levels in S2 are summarized in Table 4.2. Furthermore, we have established in our previous work that the Yb\(^{3+}\) ion in the GaN epilayers most likely occupy two major optical centers, which are the substitutional Yb\(_{Ga}\) and the complex V\(_N\)-Yb sites, respectively [50], [136]. Based on those studies, the observed
Yb$^{3+}$ ion emission peaks in S2 were denoted to the rare earth induced structural isovalent (RESI) trap and complex (complex V$_N$-Yb) centers. The calculated Stark energy levels splitting and the experimentally observed energy levels of GaN:Yb$^{3+}$ epilayer (S5) and GaN:Yb$^{3+}$ NRs (S2) are summarized in Table 4.1.

Figure 4.3 (a) High resolution CL spectrum of Yb$^{3+}$ ion emission in NRs (S2) measured at 11 K, (b) the deconvoluted Yb$^{3+}$ ion spectrum using multiple Gaussian-Lorentzian functions. Dashed lines indicate deconvoluted individual peaks indexed from 1 to 12. Reproduced after Ref. [52].
Table 4.1 Experimental and calculated crystal-field energy levels (in cm\(^{-1}\)) of Yb\(^{3+}\) ion doped GaN NRs (S2) and Yb\(^{3+}\) ion doped GaN epilayer (S5). Reproduced after Ref. [52].

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<th>Exp. val. (^c) [cm(^{-1})]</th>
<th>Cal. val. (^d) [cm(^{-1})]</th>
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<tr>
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<td></td>
<td></td>
<td>(F_3)</td>
<td>271</td>
<td>275</td>
<td>276</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_2)</td>
<td>200</td>
<td>193</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Complex (V(_N)-Yb)</td>
<td>(^2F_{5/2})</td>
<td>(F_7)</td>
<td>-</td>
<td>-</td>
<td>10752</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_6)</td>
<td>10647</td>
<td>10649</td>
<td>10650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_5)</td>
<td>10490</td>
<td>10500</td>
<td>10498</td>
</tr>
<tr>
<td></td>
<td>(^2F_{7/2})</td>
<td>(F_4)</td>
<td>414</td>
<td>424</td>
<td>424</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_3)</td>
<td>358</td>
<td>365</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_2)</td>
<td>310</td>
<td>300</td>
<td>299</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F_1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Stark levels splitting of the manifold levels \(^{2S+1}L_J\).
\(^b\) Experimental energy levels observed from previous work [50], [137] for GaN:Yb\(^{3+}\) epilayers (S5).
\(^c\) Experimental energy levels observed in the NRs sample (S1).
\(^d\) Calculated crystal field energy levels of Yb\(^{3+}\) ion incorporated in GaN NRs corresponding to different optical centers (RESI and defect-complex).
Table 4.2 CL emission peaks of $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ transition of GaN:Yb$^{3+}$ NRs (S2) shown in Fig. 4.3 Reproduced after Ref. [52].

<table>
<thead>
<tr>
<th>Line</th>
<th>Wavelength [nm]</th>
<th>Wave Numbers [cm$^{-1}$]</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1015.74</td>
<td>9845</td>
<td>$F_5 \rightarrow F_3$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>2</td>
<td>1014.40</td>
<td>9858</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1007.25</td>
<td>9928</td>
<td>$F_5 \rightarrow F_2$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>4</td>
<td>1000.90</td>
<td>9991</td>
<td>$F_7 \rightarrow F_4$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>5</td>
<td>996.02</td>
<td>10040</td>
<td>$F_7 \rightarrow F_3$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>6</td>
<td>992.46</td>
<td>10076</td>
<td>$F_5 \rightarrow F_4$ (V$_{N}$-Yb)</td>
</tr>
<tr>
<td>7</td>
<td>987.95</td>
<td>10122</td>
<td>$F_7 \rightarrow F_2$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>8</td>
<td>986.68</td>
<td>10135</td>
<td>$F_5 \rightarrow F_3$ (V$_{N}$-Yb)</td>
</tr>
<tr>
<td>9</td>
<td>985.71</td>
<td>10145</td>
<td>$F_6 \rightarrow F_1$ (Yb$_{Ga}$)</td>
</tr>
<tr>
<td>10</td>
<td>980.30</td>
<td>10201</td>
<td>$F_5 \rightarrow F_2$ (V$_{N}$-Yb)</td>
</tr>
<tr>
<td>11</td>
<td>978.00</td>
<td>10225</td>
<td>$F_6 \rightarrow F_4$ (V$_{N}$-Yb)</td>
</tr>
<tr>
<td>12</td>
<td>977.14</td>
<td>10234</td>
<td>-</td>
</tr>
</tbody>
</table>
4.2 Yb$^{3+}$ ion in InGaN nanorods sample

In this section, Yb$^{3+}$ ion *in situ* doped InGaN NRs samples were investigated. It showed a promising improvement of luminescence properties of near band edge (NBE) emission of InGaN, in terms of the FWHM of the emission peak and the thermal stability. Some of the results and discussion presented in this section have been published in Ref. [132], [138].

4.2.1 *Determination of Yb and In concentrations in InGaN:Yb samples*

Although an approximated In content in InGaN can be estimated from the chemical composition intentionally observed during the growth process, it is pivotal to know the real In concentration in developed material for better understanding of investigated processes. To achieve this goal different experimental techniques were conducted and the results are compared in the following paragraphs.

First of all, the X-ray diffraction (XRD) spectrum were measured by a *Bruker* XRD system with θ-2θ geometry for all the sample/regions. The recorded XRD spectra of the Yb$^{3+}$ ion *in situ* doped InGaN NRs (NRs:Yb$^{3+}$, #DPG216) (all regions) and the reference undoped InGaN NRs (NRs, #DPG219) show peaks around 34° corresponding to the InGaN (0002) direction (*see Figure 4.4*). It can be seen that undoped NRs doesn’t show clear phase separation, while obvious double-head peaks were obtained from the NRs:Yb$^{3+}$. The XRD peak deconvolution using Voigt’s distribution functions revealed three sub-peaks in undoped and two sub-peaks from doped NRs specimens (*see dotted lines in Figure 4.4*). The two sub-peaks in the reference NRs are positioned at 34.52° (Peak 1) and 34.13° (Peak 2), respectively. However, the peak positions of the three sub-peaks in the NRs:Yb$^{3+}$ are
varied with In content among regions. Peak 1 (34.70°) and peak 2 (34.20°) positions and intensities have not changed among regions, while peak 3 increased in intensity and shifted toward smaller angle from region (a) to region (d) in the NRs:Yb$^{3+}$ by 0.15°. This demonstrates that the composition of the NRs:Yb$^{3+}$ gradually changes from (a) to (d) region due to the In content ($x$) change in In$_x$Ga$_{1-x}$N [139]. Furthermore, the presence of peak 4 at 31.2° due to the InN (0002) direction indicates existence of In-rich regions in both types of NRs samples.

Figure 4.4 XRD spectra of the InGaN:Yb$^{3+}$ NRs and the InGaN NRs samples. Dotted lines represented components of deconvoluted XRD spectra.
Furthermore, the elemental composition of the films was measured via Rutherford backscattering spectroscopy (RBS) using a 4.5 MV tandem accelerator. Alpha beams with incident energy of 6.5 MeV were used in the analysis. Results of the elemental composition of In and Yb are given as ratios normalized to the Ga concentration. The RUMP software package was used in the analysis of the films. The RBS results are shown in Figure 4.5 and the obtained In to Ga ratio (In/Ga) in studied samples is summarized in Table 4.3. The observed In/Ga ratio in the NRs:Yb$^{3+}$ varies from 14/100 to 22/100 in different regions, while the Yb/Ga ratio was constant across the same sample.

![RBS spectra](image)

Figure 4.5 RBS spectra of InGaN:Yb$^{3+}$ NRs (lower spectrum) and undoped InGaN NRs (upper spectrum).
Table 4.3 Summary of the compositional data obtained from RBS analysis and band gap energies estimated using Vegard’s law.

<table>
<thead>
<tr>
<th></th>
<th>InGaN:Yb$^{3+}$</th>
<th></th>
<th>InGaN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>region (a)</td>
<td>region (c)</td>
<td>region (d)</td>
</tr>
<tr>
<td>In/Ga</td>
<td>14/100</td>
<td>18/100</td>
<td>22/100</td>
</tr>
<tr>
<td>Yb/Ga</td>
<td>9/100</td>
<td>9/100</td>
<td>10/100</td>
</tr>
<tr>
<td>x</td>
<td>0.1138</td>
<td>0.1417</td>
<td>0.1667</td>
</tr>
<tr>
<td>y</td>
<td>0.073</td>
<td>0.0709</td>
<td>0.0758</td>
</tr>
<tr>
<td>$E_g$ [eV]</td>
<td>2.36</td>
<td>2.25</td>
<td>2.21</td>
</tr>
</tbody>
</table>

It has been discussed already in the Section 2.1.3 that the most stable lattice site the Yb$^{3+}$ ion can occupy in the III-Ns is the substitutional site of a trivalent cation [25]. Thus, we consider here that the InGaN:Yb$^{3+}$ NRs as a quaternary semiconductor, In$_x$Ga$_{1-x-y}$Yb$_y$N, where the $x$ and $y$ values can be calculated based on the In/Ga and Yb/Ga ratios obtained from the RBS and the modified Vegard’s law formula as shown in Eq. (4.1) [140],

$$E_g(x,y) = xE_{g,InN} + yE_{g,YbN} + (1 - x - y)E_{g,GaN} - b_{GaYbN}y(1 - y)$$

$$- b_{InGaN}x(1 - x) - b_{InYbN}xy + (b_{GaYbN} + b_{InGaN})xy$$

$$- Cxy(1 - x - y)$$

where $E_{g,InN} = 0.7$ eV and $E_{g,GaN} = 3.4$ eV are band gaps energies of InN and GaN, and $E_{g,YbN} = 0$ eV assuming that YbN is metallic [141], [142]. The bowing parameter for InGaN was assumed to be $b_{InGaN} = 2.98$ eV [143]; however the bowing parameters for GaYbN and InYbN ternary alloys were not found in the literature. Thus, we assumed their values to be $b_{GaYbN} = b_{InYbN} = b_{InGaN} = 2.98$ eV in the NRs:Yb$^{3+}$ sample regions (a) and (c). A smaller
value of $b_{\text{InGa}N} = b_{\text{InYb}N} = 2.29$ eV, when keeping $b_{\text{GaYb}N} = 2.98$ eV, was considered for the NRs:Yb$^{3+}$ sample region (d) due to the fact that the band gap bowing parameter reduces as the In content increases [144]. The $C$ parameter in Eq. (4.1) is a constant and intentionally set to be zero since the expected significance of the last term in Eq. (4.1) is negligible. The predicted band gap energies of the In$_x$Ga$_{1-x}$Yb$_y$N NRs quaternary alloys in region (a) through (d) are summarized in Table 4.3. The observation of increasing $x$ values in the NRs:Yb$^{3+}$ sample between regions (a) through (d) confirms the presence of In content gradient in this sample, which is in agreement with the peak 3 shifts trend observed in the XRD spectra.

4.2.2 *Narrowing of the InGaN:Yb$^{3+}$ NRs emission bandwidth and temperature dependent behavior*

Figure 4.6 (top) shows photo images of the characteristic color emissions from different regions on the NRs:Yb$^{3+}$ sample. The lower part of the Fig. 4.6 shows PL spectra of the NRs:Yb$^{3+}$ (spectra (a)-(d)) and its undoped NRs counterpart (spectrum e) measured at 11 K, respectively. Single dominate PL peak was observed from all the samples/regions, corresponding to the near band edge (NBE) emission of InGaN NRs as seen in Figure 4.6. The NBE peak position red-shifted from 554.9 nm (green) to 602.8 nm (orange) across the NRs:Yb$^{3+}$ regions (a) to (d) due to the In content increase. Although the Yb$^{3+}$ ion emission was overwhelmed by the strong NBE emission of InGaN NRs, the characteristic luminescence transition lines between the Stark energy levels of $^2F_{5/2}$ and $^2F_{7/2}$ multiplets, which results from the 4f-shell transition in Yb$^{3+}$ ion, were observed between 970 nm and 1040 nm (*see* Figure 4.6 bottom right), similarly to the Yb-doped GaN NRs case [145].
This fact indicates the successful incorporating of Yb$^{3+}$ ions into the InGaN lattice. Furthermore, the Yb$^{3+}$ ion emission spectra collected for the NRs:Yb$^{3+}$ sample at varied In content regions are similar without substantial peak position shift, indicating there is no significant modification of crystal field in the vicinity of Yb$^{3+}$ ion among different regions.

Figure 4.7(A) shows evolution of PL peak energy as a function of temperature for the NRs:Yb$^{3+}$ and undoped NRs samples. The S-shaped luminescence intensity variation as temperature changed was observed from all the investigated InGaN NRs samples similar to previous reports [146], [147]. The reason of this abnormal PL peak position change with temperature is accounted typically to two competing processes: (1) the band gap widening at lower temperature, and (2) the thermal excitation of localized exciton at higher temperature. These two effects can be described by the band-tail state model [148] together with the Varshni’s model using expression shown in Eq.(4.2),

$$E(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} - \frac{\sigma^2}{(k_B T)}$$

(4.2)

where band gap variation as the function of temperature was determined by the Varshni parameters $\alpha$ and $\beta$. The band gap at $T = 0$ K ($E_g(0)$) and the exciton localization energy ($\sigma$) can be found by fitting the higher temperature part of the S-shaped PL peak energy profiles as shown in Fig. 4.7(A). The obtained $E_g(0)$ values agreed very well with the estimated band gap $E_g$ values obtained using the modified Vegard’s law (see Table 4.4).
Figure 4.6 (top) (a)-(d) Photo images of color emission from the InGaN:Yb$^{3+}$ NRs and (e) the undoped InGaN NRs at 11 K. (bottom left) PL NBE peaks of the NRs:Yb$^{3+}$ (solid lines) and the undoped NRs (dotted line), (bottom right) PL spectra of Yb$^{3+}$ ion collected from different regions on the NRs:Yb$^{3+}$ sample. Spectra were normalized and artificially shifted upward for clarity.
Figure 4.7 (A) Temperature dependence of NBE peak energy for different regions on the NRs:Yb$^{3+}$ sample (circles) and from reference NRs (triangle). Fitting curves to Eq.(4.2) are shown as dashed lines. (B) NBE bandwidth (FWHM) changes for the NRs:Yb$^{3+}$ sample (dots) and the reference NRs (squares) as a function of temperature.

Table 4.4 Band-tail model fitting parameters summary when using Eq.(4.2).

<table>
<thead>
<tr>
<th></th>
<th>region (a)</th>
<th>region (b)</th>
<th>region (c)</th>
<th>region (d)</th>
<th>InGaN NRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g(0)$ [eV]</td>
<td>2.32</td>
<td>2.27</td>
<td>2.25</td>
<td>2.21</td>
<td>2.60</td>
</tr>
<tr>
<td>$\alpha$ [meV/K]</td>
<td>0.23</td>
<td>0.32</td>
<td>0.62</td>
<td>0.83</td>
<td>2.07</td>
</tr>
<tr>
<td>$\beta$ [K]</td>
<td>426</td>
<td>456</td>
<td>672</td>
<td>632</td>
<td>452</td>
</tr>
<tr>
<td>$\sigma$ [meV]</td>
<td>23</td>
<td>31</td>
<td>34</td>
<td>36</td>
<td>67</td>
</tr>
</tbody>
</table>
It was found that the largest exciton localization energy was for the reference NRs sample ($\sigma = 67$ meV) and was twice as large as the average $\sigma$ values for different regions of the NRs:Yb$^{3+}$ sample. These estimates are supported by the observed PL peak energy temperature profiles showed on Figure 4.7 where the strongest S-shaped PL peak energy fluctuation is for the undoped NRs. Furthermore, it was observed that the exciton localization energy was increased with increase In content in all the NRs:Yb$^{3+}$ regions. This effect is typically associated with the argument that larger In content causes stronger band gap fluctuation due to the formation of In-rich regions or In clusters [149]. On the other hand, as evidenced in this work, incorporation of Yb into the InGaN lattice relaxes the exciton localization energy, hence reduces the amplitude of the S-shape NBE band peak energy fluctuation profile. In addition, as shown in Figure 4.7(B), the FWHM of the NBE band for all the NRs:Yb$^{3+}$ sample regions are almost as twice smaller as compared to the reference undoped NRs sample at any measured temperature. It may indicate that the Yb incorporation improved the uniformity of the In distribution in the material. Furthermore, we believe that the narrowing of FWHM as temperature decreasing is due to suppression of the exciton localization effect.

Although this phenomenon is not fully understood at the present, one may speculate that the Yb$^{3+}$ ion may attract the intrinsic defects (e.g., $V_N$) as well as intrinsic impurities in the InGaN during growth and form the complex defects. Thus, this process may mimic, in general, the gettering effect typically observed in semiconductor phase purification [6] (see also discussion in Section 2.1.1); however other phenomenon like e.g., improved indium add-atoms surface diffusion during the growth process can be critically considered.
as well. Anyhow, one may speculate that the observed improvement of optical properties in InGaN:Yb$^{3+}$ NRs with increased In content results from reduction of the defective regions density in InGaYbN host lattice (e.g., In clustering, $V_{\text{In}}$, $V_{\text{In}}-V_{\text{N}}$) manifested by significant reduction of observed band gap fluctuation. Consequently, the Yb doping leads to a more homogeneous redistribution of In ions in InGaYbN material, which is a very desirable aspect in improving the overall quality of InGaN growth technology.
Figure 4.8 Power dependent PL of integrated Yb emission intensity from the InGaN:Yb$^{3+}$ NRs region (d) (triangles), integrated NBE emission intensity of the same sample region (d) (dots), and integrated NBE emissions intensity of the undoped NRs sample (squares). All intensities are normalized with respect to the strongest NBE emission. Inset shows the PL spectra of NBE emission of the NRs:Yb$^{3+}$ sample region (d) exited with 0.9 mW and 41 mW, respectively.

Furthermore, power dependent PL measurement of the NRs:Yb$^{3+}$ was studied by exciting the samples/regions with a 488 nm Argon ion laser offering larger density photons excitation. Figure 4.8 illustrates the integrated PL intensity changes as a function of laser excitation power. The NBE emission intensity for both the NRs:Yb$^{3+}$ and the reference NRs samples linearly increases with the laser power increase at the same rising pace (i.e.,
the same slop). However, the integrated PL intensity of Yb\textsuperscript{3+} ion emission seems to be less excitation power dependent than the NBE emission. This observation may suggest that a large portion of the excitation energy contributes to the NBE emission rather than to excite Yb\textsuperscript{3+} ions due to the much faster NBE excitation processes as compared with the energy migration between the host and the Yb\textsuperscript{3+} ion centers. Thus, the inefficient excitation process of Yb\textsuperscript{3+} ions makes observed luminescence less excitation power dependent. In addition, considering the NBE emission peaks position in the NRs:Yb\textsuperscript{3+} sample region (d) excited with optical power changing from 0.9 mW to 41 mW shown in Fig.4.8 inset, one can observe a clear narrowing of the emission peak bandwidth and peak position blue-shift of ~3 nm. These facts once more confirm that the band gap fluctuation is due to inhomogeneous distribution of In clusters. We expect that in the In rich regions of InGaN, the band gap narrowing effect occurs and that EHPs recombination, generated after excitation photon absorption, results in the NBE emission peak broadening and red-shift. As the excitation energy becomes stronger the population of the generated EHPs increases. They fill the band edge minima energy states and starts to recombine at higher energy states simultaneously leading to the observed blue-shift of the NBE emission peak.
4.2.3 *In concentration dependent radiative life time*

Figure 4.9 shows PL decay curves measured for the NRs:Yb$^{3+}$ NRs and its undoped counterpart at 10 K. The PL decay curves were fitted with a double exponential decay function and obtained decay time components are shown in Figure 4.9 for each sample/region. It is seen that the undoped NRs shows faster PL decay as compared to any region in the NRs:Yb$^{3+}$. This fact supports the observation that larger exciton localization energy results in shorter radiative life time as it was expected in the case of the undoped NRs where In-cluster size and concentration are expected to be larger than in the NRs:Yb$^{3+}$ material. Furthermore, it is seen that the PL decay time increases from region (a) to region (d) of the NRs:Yb$^{3+}$ with In content increase. This fact is in contrast to the observed change of the expected exciton localization energy. The detailed mechanism responsible for this matter is unclear yet; however it may be related to the presence of RE structural isovalent (RESI) traps [20] in the NRs:Yb$^{3+}$ sample. We believe that the luminescence of RE$^{3+}$ ions in III-Ns when excited above band gap originates, among other energy transfer mechanisms, from the energy transfer between the III-Ns host and the 4$f$ levels in the RE$^{3+}$ ion via the bound exciton recombination. Thus, the formation of RESI traps may lead to a slower NBE PL decay time in the NRs:Yb$^{3+}$ having higher In content due to the more complex energy transfer process involved.
Figure 4.9 PL decay curves for the InGaN:Yb$^{3+}$ NRs and the undoped InGaN NRs measured at 10 K. PL decay times $\tau_1$ and $\tau_2$ were obtained by fitting experimental curves with double exponential decay function. All curves are artificially shifted for clarity.
Figure 4.10 PL decay curves of the InGaN:Yb$^{3+}$ NRs sample region (c) measured at different emission wavelength. PL decay times $\tau_1$ and $\tau_2$ were obtained by fitting experimental curves with double exponential decay function. All curves are artificially shifted for clarity.

Figure 4.10 shows the PL decay monitored at different luminescence wavelength of the InGaN:Yb$^{3+}$ NRs sample region (c). It is seen that the obtained decay times increase as the monitoring wavelength shifts toward longer wavelength side of the PL peak. The similar observation was found for other regions of the NRs:Yb$^{3+}$ and the undoped NRs samples (not show here). It agrees with the previous observation that: (1) the PL decay time is longer at the In content richer regions (regions that emits at longer wavelength); (2)
the PL peak broadening is due to the band gap fluctuation results from the inhomogeneous
distribution of indium.

4.3 Summary

In this chapter, we reported on the optical properties of in situ Yb-doped GaN NRs and Yb-doped InGaN NRs grown by MBE. In the case of GaN:Yb$^{3+}$ NRs, the optical properties of which is compared with other Yb doped GaN thin films grown on different substrate or grown by different epitaxy techniques. The Yb emission peaks observed from high resolution PL and CL are investigated in terms of theoretical fitting and analysis. The excitation mechanism of Yb$^{3+}$ ions in GaN is discussed.

In the case of the Yb-doped InGaN NRs it was observed that the amplitude of the “S-shaped” temperature dependent PL peak energy reduced and PL peak line width narrowed by factor of two as compared with the undoped InGaN NRs. It was concluded that observed phenomena are related to the exciton localization energy decrease. Furthermore, the PL decay lifetime was found to be longer in the InGaN:Yb$^{3+}$ NRs, which further supports its the claim that observed improvement of the optical properties is the exciton localization energy related. Finally, we speculated that the feasible Yb gettering effect in the NRs:Yb$^{3+}$ and the presence of RESI trap in these materials can affect the exciton localization energy as well.
CHAPTER 5: EUROPIUM DOPED III-NITRIDE SEMICONDUCTORS

The first section of this chapter focuses on the defect level characterization of a GaN:Si,Eu$^{3+}$ and its reference GaN:Si by means of DLTS, L-DLTS and MCTS. These electrically identified defect levels in GaN:Si,Eu$^{3+}$ are examined and correlated with the optical studies conducted in this work and previous work. A distribution of defect levels in the GaN:Si,Eu$^{3+}$ bandgap is proposed and plausible luminescence excitation channels are discussed. In the second section we present a spectroscopic study of Eu$^{3+}$ ion in InGaN SLs.

5.1 Defect study of Eu$^{3+}$ ion in situ doped GaN

5.1.1 Photoluminescence results

In this section, a Si and Eu co-doped GaN epilayer (GaN:Si,Eu$^{3+}$, #GN888) and its control sample (GaN:Si, #GN893) were investigated by means of optical spectroscopy. Figure 5.1 shows the PL spectra of GaN:Si,Eu$^{3+}$ and GaN:Si samples measured at 11 K. The PL emission from the Eu$^{3+}$ ion dominates the visible spectrum, with the strongest emission peak at 622 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ intra-4f transition. Relatively weak near band-edge emission (NBE) at ~355 nm is observed, together with the donor-acceptor pair (DAP) recombination peak, and phonons replicas structure between 360 nm and 410 nm. The typically observed host defects related “yellow” emission band is not seen in GaN:Si,Eu$^{3+}$ indicating a good control of intrinsic impurities during the growth process. Reference GaN:Si shows the dominant NBE and DAP bands structures only. High resolution PL spectra of the NBE region for both samples are shown in Figure 5.2 where the spectra are normalized and artificially shifted up for clarity. It is seen that the NBE
band of GaN:Si is a combination of one dominant peak and shoulders on both sides. Since the GaN:Si is intentionally doped with Si, the dominant peak at 355.7(7) nm (3.48(5) eV) is assigned to a neutral donor bounded exciton (D°X). The shorter wavelength side shoulders are assigned to free excitons B (FX_B, 353.9(4) nm or 3.50(3) eV) and A (FX_A, 355.0(1) nm or 3.49(2) eV), respectively, while the longer wavelength side shoulder is attributed to neutral acceptor bound exciton (A°X, 357.4(7) nm or 3.46(8) eV). [150] The peaks in between 360 nm and 410 nm are phonon replicas of FX_B, FX_A and D°X with multiple longitudinal optical (LO) phonons (92 meV). The observed excitonic peaks’ assignment is based on the experimental observation and calculations reported in the literature [151]–[153], while further assessment of their origin requires time resolved luminescence analysis, which is beyond the scope of this work.
Figure 5.1 PL spectra of GaN:Si,Eu$^{3+}$ (solid red line) and GaN:Si (dot blue line) at 11 K.

High resolution PL spectrum of Eu$^{3+}$ ion emission from GaN:Si,Eu$^{3+}$ is shown in Figure 5.3. The observed emission lines are due to the Stark effect splitting of 4$f$ electrons energy levels caused by the crystal field. It should be noted here that the spectrum shown in Figure 5.3 is in good qualitative agreement with the one reported in Ref. [28] for Eu-doped GaN, which makes us believe that the studies conducted here compared with different previous reports are reasonable and realistic. Figure 5.3 insert shows the thermal quenching dependence of Eu$^{3+}$ ion emission from GaN:Si,Eu$^{3+}$ at 622 nm measured from 10 K to 300 K. It is nonlinear and shows a shoulder at ~160 K. The thermal activation energies were obtained by fitting separately the thermal quenching data to the equation
show in the plot inset, for lower temperature region (10 K – 160 K) and higher temperature region (160 K – 300 K), respectively. The estimated thermal activation energies in lower and higher temperature regions are $\varepsilon_1 = 12.7$ meV and $\varepsilon_2 = 233.1$ meV. Here, we assume that the thermal activation energy ($\varepsilon$) is the energy required to release the hole ($\varepsilon_1$) from the exciton trapped on Eu$^{3+}$ ion RESI trap [20], [23] or electron ($\varepsilon_2$) trapped by defect or complex defect induced by incorporated Eu$^{3+}$ ion. [24], [88] These thermal activation energies are believed to be associated with the shallow hole trap and donor trap(s) induced by Eu$^{3+}$ ions residing in different local host environments as will be argued later.
Figure 5.2 High resolution PL spectra of GaN:Si,Eu$^{3+}$ (red) and GaN:Si (blue) measured at 11 K. The NBE peaks and their phonon replicas separated by multiple LO phonon (92 meV) are labeled.

Figure 5.4 shows the PLE spectrum of GaN:Si,Eu$^{3+}$ when emission was monitored at dominate Eu$^{3+}$ ion emission peak at 622 nm (see Figure 5.4 inset). It is seen that luminescence intensity drops sharply when excited below GaN band gap absorption edge (i.e., ~ 355 nm). A longer wavelength PLE spectrum shoulder between 360 nm and 390 nm is related to the shallow defect levels in the host material. No PL emission from Eu$^{3+}$ ion was observed in spectral range between 400 nm to 565 nm. The PL emission with
excitation wavelength longer than 565 nm is attributed to excitation through optically active centers as reported previously in the CEES experiment. [6] Recently, a detailed analysis of these centers assessed using site-selective excitation spectroscopy with fine excitation resolution was reported. [28], [63], [154] However, in our opinion, the specific energies of these defects with respect to the forbidden gap edges cannot be unambiguously assessed from these characterizations. Thus, there is opportunity to further examine this issue using DLTS or others charge transport measurement techniques.
Figure 5.3 High resolution PL spectra of Eu emission from GaN:Si,Eu$^{3+}$ (red line) measured at 11 K. Inset shows temperature dependent of PL peak at ~ 622 nm. The thermal activation energy at lower temperature region and higher temperature are obtained from the fitting of equation shown in the plot. The fitting curves are expressed as dashed lines.
Figure 5.4 PLE spectrum of GaN:Si,Eu$^{3+}$ measured at 11 K. Inset shows the PL intensity monitored at 622 nm.

5.1.2 Defect levels identified by deep level spectroscopy techniques

5.1.2.1 I-V and C-V results

The electrical properties of the Schottky diodes investigated in this study were characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurement. Figure 5.5 (a) shows the I-V curve of GaN:Si,Eu$^{3+}$. The ideality factor ($n$), series resistance ($R_s$) and leakage current ($I_{\text{leak}}$) were calculated as $n = 2.5$, $R_s = 10 \ \Omega$, and $I_{\text{leak}} = 10 \ \text{mA} \ @ \ V = -2 \ \text{V}$, respectively. The ideality factor indicates the diode performance and the value of it usually lays in between 1 and 2. For an ideal diode, the ideality factor equals to 1. A larger ideality factor could result from the series resistance of the junction due to inhomogeneous
metal contact, interface states or defects. In the past, the $n$ value of $n$-type GaN Schottky diode were reported in a wide range from 1.04 to ~ 6 at room temperature.[81], [155]–[157] The leakage current of the devices used in this study meets the requirement of Sula DLTS system which requires a leakage current smaller than 100 mA at any given reverse bias during measurement.

Figure 5.5 (b) shows the C-V characteristic of GN888 under reverse bias measured at 300 K. The built-in voltage ($V_{bi}$) and the net carrier concentration ($N_D - N_A$) can be determined from the linear fit of the rewritten C-V relation as shown in Eq. (5.1),

$$\frac{S^2}{C^2} = \frac{2(V_{bi} + V)}{\varepsilon_s \varepsilon_0 q (N_D - N_A)}$$

(5.1)

where $S$ is the area of the Schottky contact, $\varepsilon_s$ is the permittivity of the semiconductor and $\varepsilon_0$ is the permittivity in vacuum. The value of $V_{bi}$ and $N_D - N_A$ were calculated as $V_{bi} = 2.1$ V and $N_D - N_A = 4.8 \times 10^{17}$ cm$^{-3}$, respectively, from the intercept to the x-axis and the slope of the linear fitting (see inset of Figure 5.5 (b)). The value of net carrier concentration was used to calculate the trap concentration identified from the DLTS experiment as described in Section 2.2.1.

The value of above mentioned parameters of GaN:Si were calculated from the I-V and C-V measurement shown in Figure 5.6 (a) and (b), indicating a similar electrical performance between the two samples.
Figure 5.5 (a) I-V and (b) C-V characterization of GaN:Si,Eu$^{3+}$ sample.

Figure 5.6 (a) I-V and (b) C-V characterization of GaN:Si sample.
5.1.2.2 DLTS results

The DLTS measurement was conducted by applying a reverse bias of $V_r = -2$ V upon the Schottky devices with filling pulse $V_p = 0$ V and pulse width $t_p = 2$ ms. The DLTS spectrum of GaN:Si,$\text{Eu}^{3+}$ that measured with different rate windows was shown in Figure 5.7. Three dominate DLTS peaks were observed in GaN:Si,$\text{Eu}^{3+}$ that are assigned to be electron traps. The thermal activation energies of these defect levels were calculated from the fitting of the *Arrhenius* plot shown in Figure 5.8 as 0.11±0.03 eV (Trap A), 0.29±0.04 eV (Trap B), and 0.49±0.06 eV (Trap C) below conduction band edge $E_c$, respectively. The corresponding capture cross section ($\sigma_n$) and trap concentration ($N_T$) were summarized in Table 5.1.

The DLTS spectrum measured for GaN:Si was shown in Figure 5.9 that revealed one electron trap at the same position as Trap C in GaN:Si,$\text{Eu}^{3+}$ and one hole trap that was not seen in the DLTS spectrum of this material. The thermal activation energies of this hole trap was calculated from the *Arrhenius* plot shown in Figure 5.10 as 0.28±0.03 eV (Trap D) above the valence band edge $E_v$. The capture cross section ($\sigma_n$) and trap concentration ($N_T$) of traps identified in GaN:Si were also summarized in Table 5.1.
Figure 5.7 DLTS spectrum of GaN:Si,Eu$^{3+}$ measured with different rate windows.
Figure 5.8 The Arrhenius plot that calculated the thermal activation energy and capture cross section of traps identified in GaN:Si, Eu$^{3+}$ with linear fitting shown as red lines.
Figure 5.9 DLTS spectrum of the reference GaN:Si sample measured with different rate windows.
Figure 5.10 The Arrhenius plot that calculated the thermal activation energy and capture cross section of traps identified in GaN:Si with linear fitting shown as red lines.
Table 5.1 Defect levels identified in studied samples by conventional DLTS measurement.

<table>
<thead>
<tr>
<th>Trap</th>
<th>$E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{-17}$ cm$^2$]</th>
<th>$N_T$ [$\times 10^{15}$ cm$^{-3}$]</th>
<th>$E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{-17}$ cm$^2$]</th>
<th>$N_T$ [$\times 10^{15}$ cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$E_c$ - 0.11±0.03</td>
<td>0.69</td>
<td>4.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>$E_c$ - 0.29±0.04</td>
<td>25</td>
<td>5.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C</td>
<td>$E_c$ - 0.49±0.06</td>
<td>3.2</td>
<td>1.6</td>
<td>$E_c$ - 0.49±0.06</td>
<td>7.0</td>
<td>20.3</td>
</tr>
<tr>
<td>D</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>$E_v$+0.31±0.04</td>
<td>56</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Trap A and B in GaN:Si:Eu$^{3+}$ are believed to be Eu-related defect levels, while Trap C may origin from the nitrogen anti-site (N$_{Ga}$) defect [158], [159]. Although different capture cross sections and trap activation energies were observed from traps A and B, their similar trap concentration may lead to the conclusion that both traps were attribute to the same luminescent center, i.e., Eu1 (OMVPE 4), but with distinct excitation efficiencies that was demonstrated in previous optical study. [78] It is known from theoretical considerations that the $V_N$-Eu$_{Ga}$ complex defect in GaN:Eu$^{3+}$ could originate from two different centers depending on where the $V_N$ sits in the tetrahedral structure of a unit cell. In principle, a $C_{3v}$ or $C_{1h}$ symmetry can be formed when a $V_N$ is located along the crystallographic c-axis direction right above the Eu$^{3+}$ ion or in one of the three equivalent nitrogen sites, i.e., off c-axis positions, respectively. [25] This typically leads to observation of different optical excitation efficiency of these two optical centers. The capture cross-sections observed from our DLTS study agrees with the optical excitation efficiency study reported in Ref. [78].
5.1.2.3 Laplace-DLTS results

Figure 5.11 shows the high resolution L-DLTS spectrum of GaN:Si:Eu$^{3+}$ measured from 155 K to 200 K. It reveals multiple peaks that represent the different emission rates of Trap A and B identified from DLTS experiment. The thermal activation energy and capture cross section of these traps were calculated based on the linear fitting of the temperature evolution of the L-DLTS peaks shown in Figure 5.12. It is found that one electron trap with activation energy of $0.103\pm0.020$ eV below the conduction band edge corresponds to the Trap A peak observed in the DLTS spectrum. Also, at least four closely spaced trap levels, named here as Trap B1 ($E_c - 0.259\pm0.032$ eV), Trap B2 ($E_c - 0.253\pm0.020$ eV), Trap B3 ($E_c - 0.257\pm0.017$ eV) and Trap B4 ($E_c - 0.268\pm0.025$ eV), respectively, are found to be associated with the Trap B peak observed in the DLTS spectrum. The identified defect levels have comparable activation energies but different capture cross-sections and trap concentrations (see Table 1). Among the four closely spaced traps (Trap B1-Trap B4), Trap B3 has the largest concentration ($1.9\times10^{15}$ cm$^3$) that is more than three times larger than that of the Trap B1 ($0.6\times10^{15}$ cm$^3$). While Trap B1 has the smallest concentration, it has the largest capture cross-section ($2.5\times10^{-15}$ cm$^2$) among other traps ($e.g.$, $10^{-16}$-$10^{-17}$ cm$^2$). The differences in capture cross-sections and trap concentrations presumably leads to different optical excitation efficiency of the specific Eu$^{3+}$ ion related trap that can explain the variety of observed luminescence peaks intensity of intra-4$f$ transitions originating from different Eu$^{3+}$ ion optically active centers reported in the CEES study [28]. We assume that the observed multiple defect levels can originate from the different energetically favorable location of $V_N$ associated with Eu$_{Ga}$ as well as a
possible formation of donor-accepter pair (DAP) of $V_N-V_{Ga}$ that bond to $Eu_{Ga}$. The later complex defect involves a minority trap level $V_{Ga}$ and as such can be effectively studied by minority carrier transient spectroscopy (MCTS) [160] or deep level optical spectroscopy (DLOS) study [161] (future work).

Figure 5.11 L-DLTS spectrum of GaN:Si:Eu$^{3+}$ measured from 155 K to 200 K.
Figure 5.12 The Arrhenius plot obtained from L-DLTS spectrum shown in Figure 5.11.

The trap’s activation energy and capture cross section are calculated from the linear fitting shown as dash line.
The L-DLTS measurement was conducted from 292 K - 310 K to characterize the Trap C in GN888. The L-DLTS spectra are shown in Figure 5.13 and the Arrhenius plot analysis of trap properties is shown in Figure 5.14. The L-DLTS spectra of Trap C are dominated by a single emission rate, but with certain distribution, indicating that this defect level (Trap C1) may be caused by extended defect rather than single isolated point defect. Furthermore, a less intense peak (Trap C2) on the left hand side to the Trap C1 starts to rise with temperature increase. The origin of the Trap C2 is unclear at this time, and in consequence it was not taken into account as a contribution to the Trap C, due to the nature of ill-posed L-DLTS analysis that peaks with very small amplitude and large temporal distribution may be artificial resulting from the noisy tail of capacitance transient. The capture-cross sections and the thermal activation energies of defect levels obtained from L-DLTS measurement and analysis are summarized in Table 5.3.
Figure 5.13 L-DLTS spectrum of GaN:Si:Eu$^{3+}$ measured from 292 K to 310 K.
Figure 5.14 The Arrhenius plot obtained from L-DLTS spectrum shown in Figure 5.13.

The trap’s activation energy and capture cross section are calculated from the linear fitting shown as dash line.

The hole trap (Trap D) in GaN:Si is further studied by L-DLTS measurement from 205 K to 230 K that gave rise to two peaks with different emission rates as shown in Figure 5.15. The activation energies of these two traps are calculated from the Arrhenius plot shown in Figure 5.16 as $E_v + 0.284$ eV (D1) and $E_v + 0.258$ eV (D2), respectively. The corresponding concentrations and capture cross-sections are comparable to each other.
indicating that the cause of these traps is similar in nature. Although the origin of these traps is unclear at present, hole traps with similar properties were reported previously in $n$-type GaN and their origin was attributed to the carbon related defects, such as $C_N$ or $C_N$-complex. [39, 40]

Figure 5.15 L-DLTS spectrum of GaN:Si measured from 205 K to 230 K.
Figure 5.16 The Arrhenius plot obtained from L-DLTS spectrum shown in Figure 5.15. The trap’s activation energy and capture cross section are calculated from the linear fitting shown as dash line.

### 5.1.2.4 MCTS results

The MCTS measurement was conducted by applying a constant reverse bias of $V_r = -2$ V to the Schottky diode. A 325 nm cw He-Cd laser was pulsed by mechanical shutter to excite the sample at a duty cycle of 50% with optical pulse width $t_{opt} = 1$ s. The respond time of the mechanical shutter is faster than 1 ms so that the initial delay of the capacitance
transient caused by the shutter can be ignored with the rate window settings used in this study (4.3 ms – 430 ms).

The MCTS spectrum of GaN:Si:Eu$^{3+}$ was shown in Figure 5.17. Two dominant peaks are observed at ~60 K and ~330 K, named as TH1 and TH2 (in GaN:Si:Eu$^{3+}$) hole traps, respectively. Similar to the previously discussed cases, the temperature evolution of the emission rates of these hole traps is plotted and fitted with a linear function to find out the trap properties (see inset of Figure 5.17). Trap TH2 (in GaN:Si:Eu$^{3+}$) is located at 0.84 eV above the valence band edge with capture cross section of $2.1 \times 10^{-14}$ cm$^2$. This trap was commonly found in GaN in the past. [81], [93], [94] The origin of this trap is attributed to the gallium vacancy related complex (V$_{Ga}$-complex) defect. A defect labeled TH2 (in GaN:Si) was also observed in the GaN:Si reference material and shared similar properties as shown in Figure 5.18. Also, the L-LDTS detected hole trap (Trap D) observed in GaN:Si is the same as trap TH3 that was found in MCTS measurement. The hole traps identified from the MCTS experiment are summarized in Table 5.2.
Figure 5.17 MCTS spectrum of GaN:Si,Eu$^{3+}$ measured with $V_r = -2$ V, $t_{opt} = 1$ s, $\tau = 8.6$ ms (left) and $\tau = 0.43$ s (right). The inset shows the *Arrhenius* plot of obtained two hole traps and their electrical properties.
Figure 5.18 MCTS spectrum of GaN:Si measured with \( V_r = -2 \) V, \( t_{\text{opt}} = 1 \) s, \( \tau = 0.43 \) s.

The inset shows the Arrhenius plot of obtained two hole traps and their electrical properties.
Table 5.2 The hole traps identified from MCTS measurement.

<table>
<thead>
<tr>
<th>Trap</th>
<th>$E_T$ [eV]</th>
<th>$\sigma$ [×10^{-17} cm$^2$]</th>
<th>$N_T$ [×10^{15} cm$^{-3}$]</th>
<th>$E_T$ [eV]</th>
<th>$\sigma$ [×10^{-17} cm$^2$]</th>
<th>$N_T$ [×10^{15} cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH1</td>
<td>$E_v+0.03\pm0.02$</td>
<td>0.01</td>
<td>13</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TH2 (GN888)</td>
<td>$E_v+0.84\pm0.04$</td>
<td>2100</td>
<td>2.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TH3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>$E_v+0.30\pm0.03$</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>TH2 (GN893)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>$E_v+0.85\pm0.04$</td>
<td>3200</td>
<td>2.2</td>
</tr>
</tbody>
</table>

5.1.3 Correlation to optical centers identified by optically site-selective spectroscopy

Table 5.3 summarizes the electron and hole traps identified in this work and defect levels observed from other $n$-type GaN and Eu-doped GaN samples that reported in the literature. A band gap energy diagram of GaN is draw in parallel to the 4f electronic levels of the Eu$^{3+}$ ion (see Fig. 5.19). The defects listed in Table 5.3 are placed into the band gap diagram according to their energies.

We emphasize here that the TH1 trap in GaN:Si:Eu$^{3+}$ is a shallow hole trap and to the best of our knowledge was not reported in the literature. We assume, at present, that this trap observed after doping with Eu in GaN:Si:Eu$^{3+}$, and not being observed in the GaN:Si grown under the same growth conditions, is a Eu induced hole trap. We believe that RE$^{3+}$ ions, in this case Eu$^{3+}$ ion in GaN:Si, are most likely to form RESI hole trap. [20], [23] In such a case, first, a hole is attracted by a short range localized potential developed at Eu$^{3+}$ ion site due to the ionic radii and electronegativity differences between Eu$^{3+}$ ion and Ga$^{3+}$ cation it substitutes for, then, an electron e.g., from the conduction band is
attracted through Coulombic interaction to form a bound exciton. During the MCTS experiment, since the electrons generated by above bandgap optical excitation are repelled away from the polarized junction, only the holes can diffuse into depletion region of the Schottky device under investigation. Thus, if there are no electrons available to form bound excitons in the depletion region, the holes that are captured by the RESI hole traps can only go back to the valence band at certain temperature satisfying the thermal activation energy requirement of a hole liberation. In consequence, the hole emission from such Eu$^{3+}$ ion RESI traps can be observed when conducting MCTS measurement.

Furthermore, the fact that the calculated thermal activation energy from fitting of the temperature dependent PL data in the lower temperature region ($\varepsilon_1 = 12.7$ meV, see Figure 5.3 inset) is close to the hole trap energy ($E_{v}+30 \pm 20$ meV) determined from the MCTS experiment supports further the concept [20], [23] that RESI hole traps shall be created in the studied GaN:Si,Eu$^{3+}$ material. Considering that the hole capturing by the “empty” RESI trap and the subsequent formation of a bound exciton associated with the RESI trap, establishes the beginning of the energy transfer process (e.g., this is one of the possible energy transfer processes between the GaN host and the Eu$^{3+}$ ion), we would like to emphasize that the observation of TH1 shallow hole trap validate in general the RESI trap model. [30, 31] Furthermore, the estimated thermal activation energy from temperature dependent data fitting in the higher temperature region ($\varepsilon_2 = 233.1$ meV, see inset Figure 5.3) suggests the existance of another competitive energy transfer channel that may involve the donor bound excitons associated with the Eu$^{3+}$ ion defects induced electron traps (Trap B1-B4). In general, the $\varepsilon_2$ energy of Traps B1-B4 corresponds quantitatively to
the thermal activation energy required to release the electron from the ionized donor level. Assuming that the isolated Eu\textsubscript{Ga} subsitutional site results in formation of a RESI hole trap whereas the donor levels are attributed to the various Eu\textsubscript{Ga}-V\textsubscript{N} complexes, one may speculate that the energy transfer from a RESI hole trap collapsing bound exciton shall be more efficient than via the Eu\textsuperscript{3+} ion induced defect complex donor bound exciton. Reasoning here is that the RESI hole trap bund exciton is stronger localized with respect to the 4f-shell electrons system than in the case of the Eu\textsubscript{Ga}-V\textsubscript{N} complex where it can be somehow delocalized due to various posions of the Eu\textsuperscript{3+} ion in the complex. It was reported that the dominant luminscence peak of Eu\textsuperscript{3+} ion in GaN is attributed to the isolated Eu\textsuperscript{3+} ion center, rather than to Eu\textsuperscript{3+} ion complex center. [115] This conclusion supports further the RESI trap model proposal when applied to the GaN:Si,Eu\textsuperscript{3+} material. Thus, we believe, that although both engery transfer processes, from a RESI hole trap bound exciton and from a Eu\textsubscript{Ga}-V\textsubscript{N} complex induced donor bound exciton, coexist and dominate in different temperature regions in studied here sampels, the first one shall offer more efficient energy transfer disarable for enhancing red emission from Eu\textsuperscript{3+} ion doped GaN. This, in general, can be true for any RE\textsuperscript{3+} ion doped III-Ns; however further experimental studies are required.
Table 5.3 Electron and hole traps in GaN:Si,Eu$^{3+}$, GaN:Eu$^{3+}$ and $n$-type GaN identified in this work and from the literature.

<table>
<thead>
<tr>
<th>Electron Trap*</th>
<th>$E_c - E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{-17}$ cm$^2$]</th>
<th>$N_T$ [$\times 10^{15}$ cm$^{-3}$]</th>
<th>Origin</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.11±0.03</td>
<td>0.69</td>
<td>4.3</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work, [92]</td>
</tr>
<tr>
<td>$E_{Eu1}$</td>
<td>0.19</td>
<td>2.6×$10^1$</td>
<td></td>
<td>Eu$_{Ga}$-VN</td>
<td>[77], [88]</td>
</tr>
<tr>
<td>$E_{Eu2}$</td>
<td>0.22</td>
<td>3.8×$10^1$</td>
<td></td>
<td>Implantation related</td>
<td>[88]</td>
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<tr>
<td>$E(0.27)$</td>
<td>0.27±0.01</td>
<td>8×$10^2$±2×$10^3$</td>
<td>0.016</td>
<td>V$_N$</td>
<td>[77], [81]</td>
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<tr>
<td>$B$</td>
<td>0.29±0.04</td>
<td>2.5×$10^1$</td>
<td>5.3</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work</td>
</tr>
<tr>
<td>$B1$</td>
<td>0.259±0.032</td>
<td>2.5×$10^2$</td>
<td>0.6</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work, [93]</td>
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<tr>
<td>$B2$</td>
<td>0.253±0.020</td>
<td>4.4×$10^1$</td>
<td>1.3</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work, [93]</td>
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<tr>
<td>$B3$</td>
<td>0.257±0.017</td>
<td>1.4×$10^1$</td>
<td>1.9</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work, [93]</td>
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<tr>
<td>$B4$</td>
<td>0.268±0.025</td>
<td>4.3</td>
<td>1.5</td>
<td>Eu$_{Ga}$-VN</td>
<td>this work, [93]</td>
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<tr>
<td>$TE2$</td>
<td>0.37</td>
<td>2.8</td>
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<td>[92] [93]</td>
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<tr>
<td>$E_{Eu4}$</td>
<td>0.49</td>
<td>7.1×$10^2$</td>
<td></td>
<td>Implantation related</td>
<td>[88] [92]</td>
</tr>
<tr>
<td>$C$</td>
<td>0.49±0.06</td>
<td>3.2</td>
<td>1.6</td>
<td>N$_{Ga}$ [158], [159]</td>
<td>this work</td>
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<tr>
<td>$E_{Eu5}$</td>
<td>0.60</td>
<td>6.7×$10^2$</td>
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<td>Intrinsic</td>
<td>[88] [93]</td>
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<tr>
<td>$E(0.61)$</td>
<td>0.61±0.02</td>
<td>1×$10^3$±1×$10^3$</td>
<td>0.03</td>
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<td>[81]</td>
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<tr>
<td>$E_{Eu3}$</td>
<td>0.68</td>
<td>8.1×$10^9$</td>
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<td>Implantation related</td>
<td>[88] [92]</td>
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<td>$E8$</td>
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<td></td>
<td>[94]</td>
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<td>$E9$</td>
<td>1.22</td>
<td>4.3×$10^3$</td>
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<td>[94]</td>
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Table 5.3 Continued

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<tr>
<th>Hole Trap*</th>
<th>$E_v + E_T$ [eV]</th>
<th>$\sigma$ [$\times 10^{-17}$ cm$^2$]</th>
<th>$N_T$ [$\times 10^{15}$ cm$^{-3}$]</th>
<th>Origin</th>
<th>Ref.</th>
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<td>H5</td>
<td>1.76</td>
<td>$1.2 \times 10^5$</td>
<td></td>
<td></td>
<td>[94]</td>
</tr>
<tr>
<td>H4</td>
<td>1.19</td>
<td>$2.0 \times 10^2$</td>
<td></td>
<td></td>
<td>[94]</td>
</tr>
<tr>
<td>H1</td>
<td>0.86±0.88</td>
<td>$7.4 \times 10^3 \pm 1.3 \times 10^4$</td>
<td>V$_{Ga}$-complex [81], C [93]</td>
<td>[93], [94]</td>
<td></td>
</tr>
<tr>
<td>H(0.85)</td>
<td>0.85±0.05</td>
<td>$3 \times 10^3 \pm 1 \times 10^3$</td>
<td>2</td>
<td>V$_{Ga}$-complex [81], C [93]</td>
<td>[81]</td>
</tr>
<tr>
<td>TH2(GN893)</td>
<td>0.85±0.04</td>
<td>$3.2 \times 10^3$</td>
<td>2.2</td>
<td>V$_{Ga}$-complex [81], C [93]</td>
<td>this work</td>
</tr>
<tr>
<td>TH2(GN888)</td>
<td>0.84±0.04</td>
<td>$2.1 \times 10^3$</td>
<td>2.1</td>
<td>V$_{Ga}$-complex [81], C [93]</td>
<td>this work</td>
</tr>
<tr>
<td>D</td>
<td>0.31±0.04</td>
<td>56</td>
<td>6.1</td>
<td></td>
<td>this work, [92]</td>
</tr>
<tr>
<td>TH3</td>
<td>0.30±0.04</td>
<td>14</td>
<td>12</td>
<td></td>
<td>this work, [92]</td>
</tr>
<tr>
<td>D1</td>
<td>0.284±0.036</td>
<td>46</td>
<td>3.4</td>
<td></td>
<td>this work, [92]</td>
</tr>
<tr>
<td>D2</td>
<td>0.258±0.036</td>
<td>3.5</td>
<td>2.6</td>
<td></td>
<td>this work, [92]</td>
</tr>
<tr>
<td>H(0.25)</td>
<td>0.25±0.03</td>
<td>500±300</td>
<td>0.5</td>
<td></td>
<td>[81] [92]</td>
</tr>
<tr>
<td>H(0.19)</td>
<td>0.19±0.03</td>
<td>$2 \times 10^4 \pm 1 \times 10^4$</td>
<td>0.5</td>
<td></td>
<td>[81]</td>
</tr>
<tr>
<td>TH1</td>
<td>0.03±0.02</td>
<td>0.01</td>
<td>13</td>
<td></td>
<td>this work</td>
</tr>
</tbody>
</table>

*The electron and hole trap’s notation are kept the same as they appeared in the literature.
The optical and electrical properties of Eu³⁺ ion in GaN epilayers have been presented in this section. The L-DLTS and MCTS measurements developed in this study provided a powerful tool of defect characterization for GaN:Eu³⁺, and in general, III-Ns:RE³⁺ semiconductors.

5.2 Eu³⁺ ion in InGaN superlattices

5.2.1 Structural properties of Eu³⁺ ion in InGaN superlattices

Samples studied in this section were Eu implanted InGaN SLs grown by MOCVD. The structural properties of selected SLs:Eu³⁺ and undoped SLs samples were initially investigated using X-ray diffraction (XRD) spectroscopy as reported in Ref. [162].
following we closely reproduce arguments and discussion presented in that study. The SLs characteristic satellite peaks were measured in the vicinity of the (0002) reflection as determined previously [162]. Simulation of the SLs XRD spectra was done based on a fully strained In$_x$Ga$_{1-x}$N sub-layers model using X'Pert Epitaxy software. [163] The as grown SLs were fully strained (pseudomorphic) with the critical thickness (23 nm), significantly exceeding the thickness of an individual In$_{0.06}$Ga$_{0.94}$N QW. Figure 5.20 (a) shows XRD spectra of the as grown SLs and the SLs annealed at different temperatures, together with the simulated SLs. All XRD spectra shown in Figure 5.20 (a) have the zero-order SLs(0) and satellite peaks clearly observed over the scanned range. The (0002) peak of the buffer GaN layer is split due to the existence of two wavelengths in the incident radiation. Such splitting is not observed in the satellite peaks. The SLs(0) peak is resolved from the (0002) GaN buffer layer peak, and the angular positions of satellite peaks are distributed around SLs(0), indicating the presence of a well-defined composition modulation of the studied In$_{0.06}$Ga$_{0.94}$N/GaN SLs along the [0001] direction. The profile of the satellite peaks is constant for all spectra in Figure 5.20 (a) indicating the unchanged interface quality between the QW and barriers in as grown and annealed SLs up to 950 °C. Furthermore, the relative intensity of the XRD satellite peaks is independent of the annealing temperature, indicating a constant quantum well-to-barrier thickness ratio. The simulated XRD spectrum is in good agreement with the experimental results. The estimated thicknesses of a single In$_{0.06}$Ga$_{0.94}$N well and GaN barrier were 2.34 nm and 3.29 nm, respectively [162]. Figure 5.20 (b) shows XRD patterns of the as grown SLs, the as implanted SLs:Eu and the SLs:Eu$^{3+}$ annealed at different temperatures, respectively. It is seen that the XRD spectrum
of the SLs-Eu$^{3+}$ changed due to implantation-induced defects and/or diffusional intermixing of the sub-layer materials. As the result, a less sharp interface quality between the implanted barriers and wells and a non-uniform period along the [0001] direction occur. The satellite peaks are broader and less intense than those of the as grown SLs. The SLs(0, -1) satellite peaks are shifted to lower angles, while the position of SLs(+1) remains unchanged. The top layers of the SLs:Eu$^{3+}$ suffer more degradation and implantation induced defects than those located deeper in the SLs structure due to the existing implantation profile (see Figure 3.4). For layers located deeper in the SLs:Eu$^{3+}$ structure, because the Eu$^{3+}$ ion does not penetrate to that depth, the lattice mismatch of adjacent layers is absorbed by elastic deformation of fully strained In$_{0.06}$Ga$_{0.94}$N sub-layers without forming misfit dislocations, similar to the strain in the as grown SLs. On the other hand, layers closer to the surface suffer more implantation induced displacements prone to the formation of point defects. In consequence, an additional strain to these layers develops. In the near-surface region, the implantation induced expansion is restricted along the normal to the surface direction [0001], while expansion parallel to the plane of growth is not allowed due to the strain to the underlying less damaged layers. This results in a total implantation induced stress over the area, causing bending of the SLs layers along the [0001] direction as it was observed by a non-uniform period of the XRD pattern for the SLs:Eu$^{3+}$ samples. The profiles of the satellite peaks gradually change with progressing thermal annealing. After annealing at 900 °C, a good recovery quality of the SLs:Eu$^{3+}$ structure with the SLs period equal to that of the as grown SLs was achieved. However, the reduction of peak intensity and broadening of satellite peaks indicate less interface
sharpness between the barriers and QW, due to implantation defects as well as thermal diffusion of In and Ga atoms at the In$_{0.06}$Ga$_{0.94}$N/GaN interface.

Figure 5.20 XRD spectrum of (a) the simulated, as grown and annealed SLs and (b) the as grown SLs, as implanted and annealed SLs:Eu$^{3+}$. Reproduced after Ref. [162].

5.2.2 Emission for strained Eu$^{3+}$ ion doped InGaN superlattices

Figure 5.21 shows the representative PL and CL spectra of the SLs:Eu$^{3+}$ annealed at 900 °C and PL of the as grown SLs as reference. It is seen that the PL spectrum of the SLs:Eu$^{3+}$ annealed at 900 °C is dominated by the SLs emission band peaking at 393.2 nm and $^5D_0\rightarrow^7F_2$ intra-4f shell transition of the Eu$^{3+}$ ion at 622 nm superimposed on a modulated broad band centered at ~650 nm. The broad band most probably originates from
the residual implantation induced defects and the observed modulation pattern. The latter screens the less intense emission peaks of the Eu³⁺ ion due to the light interference and waveguiding effect in SLs structure. It was demonstrated in the past that the Eu³⁺ ion occupies two major luminescence centers in the Eu-doped GaN, namely “Eu1”, the substitutional EuGa-intrinsic defect complex (i.e., EuGa-V₅) and “Eu2”, the isolated substitutional EuGa center [164] with distinct excitation mechanisms of the Eu³⁺ ion 4f-shell electrons [165]. Note that the “Eu2” referred in Ref. [164] is different from the Eu2(OMVPE7) labeled in Ref.[28]. We take “Eu1” and “Eu2” defined in Ref. [164] for the following discussion. The PL emission observed from the 622 nm (²⁵D₀→⁷F₂) luminescence associated with these two centers can be distinguished under different excitation photon energies [28]. The above band gap excitation (325 nm) used in this study may result predominately in excitation of the Eu2 center, which gives the 622 nm PL peak as shown in Figure 5.21. However, the Eu1 center should also exist in the material but is overwhelmed by the Eu2 luminescence. The CL spectrum exhibits peaks at 357 nm (GaN buffer layer) and 393 nm (SLs emission peak) in addition to the strong Eu³⁺ ion related emission, i.e., the ²⁵D₀→⁷F₉ transitions with J = 1, 2, 3, 4, respectively [166]. The observed differences in the Eu³⁺ ion optical spectra are due to different excitation mechanisms of optically activated Eu³⁺ ion centers involved in the above band gap PL excitation and electron impact CL excitation [135]. In PL, each absorbed photon with energy higher than the band gap produces a single EHP, while in CL, high energy single electron generates a huge number of “hot” EHPs, reducing the energy from tens of kV to zero. The PL of the Eu³⁺ emission is obtained by an indirect excitation process via energy transfer to the 4fₙ
electron system from EHPs [135]. In electron beam excitation (CL), the Eu$^{3+}$ ions are excited by direct impact with hot electrons, as well as by energy transfer processes from the generated EHPs or by impact excitation (or ionization) involving other impurities (or complex defects), with subsequent energy transfer to the $4f^n$ shell electrons of the Eu$^{3+}$ ion. Generally, the excitation by energetic electrons produces emission via all possible luminescence mechanisms available in semiconductors. Another factor which may play a role in excitation and emission processes is the charged nature of excitation: uncharged photons in PL versus negatively charged electrons in CL. The excitation depth in PL and the concentration of EHP generated by laser are shown in Figure 3.4 (b,c).

Figure 5.21 PL (dash-dot line) and CL (solid line) spectra of the SLs:Eu$^{3+}$ annealed at 900°C. (dash line) PL of the as grown SLs.

°C. (dash line) PL of the as grown SLs.
Figure 5.22 shows SLs emission peak shifts observed for the SLs and the SLs:Eu$^{3+}$ samples as a function of annealing temperature up to 1000 °C. It should be mentioned that the Eu$^{3+}$ ion emission peaks observed between 550 nm to 750 nm do not exhibit any significant position changes (not shown) after annealing in the respective temperature range. It is seen in Figure 5.22 that the PL peak position of both the SLs and the SLs:Eu$^{3+}$ samples undergo subsequent red- and blue-shift as annealing temperature increases. In the case of the SLs (see Figure 5.22(a)), the peak shift is due to two competitive processes evolving in thermally treated SLs structures. The first one is the change of compressive strain in the SLs along with increasing annealing temperature due to the present of the quantum confined Stark effect (QCSE). It tunes the conduction band and valence band of the quantum wells (QWs) leading to a red shift of emission peak [167]. The QCSE originates from the piezoelectric polarization due to lattice mismatch between the well (InGaN) and the barrier (GaN) materials. In case of samples in this study, the piezoelectric polarization induced electric field significantly contributes to the emission peak shift due to that the samples were grown in fully polar direction (c-axis). A detailed analysis of the polarization induced electric field will be given later in this section. The second process is the In migration from the In$_{0.06}$Ga$_{0.94}$N QW layers to the GaN barriers at higher temperature [168], [169], resulting in a blue shift of the emission peak [170]. In addition, the structural inhomogeneity of the SLs may also contribute to the emission peak shift [171]. Similarly, in the case of the SLs:Eu$^{3+}$ emission peak shifts in an analogous way with annealing the temperature (see Figure 5.22 (b)). The emission peaks of both the SLs and the SLs:Eu$^{3+}$ samples contain at least two components, one major peak and one shoulder-like peak. They
were identified as peak #1 (main peak) and peak #2 (shoulder peak) via the peak deconvolution technique and plotted in Figure 5.22. The presence of the shoulder peak indicates the possible uneven distribution of In within a single QW or among different QWs. It worth to mention that the intensity of peak #2 reduces significantly in the SLs:Eu³⁺ samples compared to the SLs samples, giving rise to the emission peak of the SLs:Eu³⁺ samples closer to single component peaks. The reason for this phenomenon is not fully understood yet. But it has been found that by incorporating other RE³⁺ ions (e.g., the Yb³⁺ ion) into InGaN NRs improved the thermal stability and narrowed the line width of the emission peak (see discussion in Section 4.2.2) [172]. Similarly, we observed the improved thermal stability the SLs:Eu³⁺ samples in terms of the PL peak shift as a function of annealing temperature. The maximum peak red-shift of the SLs:Eu³⁺ upon annealing temperature is smaller (11 meV) as compared with the maximum peak red-shift of the undoped SLs (54 meV) (see Figure 5.23(a)). Furthermore, the emission peaks line width of the SLs:Eu³⁺ are, in general, narrower (~0.01 eV in average) than the undoped SLs at any annealing temperature, except the as implanted SLs:Eu³⁺ sample that has a broader peak than the as grown SLs due to the implantation damage of the lattice (see Figure 5.23(b)). The intrinsic defects (e.g., V₅, V₆₆) as well as intrinsic impurities originally presented in the SLs may have been attracted by nearby Eu³⁺ ions during annealing and formed the complex defects. This process is similar in nature to the gettering effect that may result in a semiconductor’s phase purification. [173] Figure 5.24(a) shows the PL intensity of the emission from the superlattice structure of the SLs sample. It is seen that PL intensity decreases with increasing of annealing temperature. This indicates that the
The predominate effect in these samples is the QCSE induced band bending, which separated the wave function of electron and hole further away at higher annealing temperature and reduced the recombination probability and PL intensity, consequently. On the other hand, the PL intensity of the SLs:Eu$^{3+}$ samples shows a growth trend due to the gradually recovery of implantation induced lattice damages. The PL intensity of the Eu$^{3+}$ ion related red emission also increases with annealing temperature indicating a progressive activation of Eu$^{3+}$ ions centers as annealing temperature increases.

Figure 5.22 The PL emission peak shifts of (a) the SLs and (b) the SLs:Eu$^{3+}$ samples as a function of annealing temperature up to 1000 °C. Peak deconvolution reveals two sub peaks for each spectrum.
Figure 5.23 (a) The undoped SLs peak position and (b) the FWHM of the SLs (■) and the SLs:Eu$^{3+}$ (▲) samples at different annealing temperature. The dashed lines are aid to the eye.
Figure 5.24 (a) The undoped SLs samples integrated emission intensity, (b) the SLs:Eu$^{3+}$ samples integrated emission intensity and the integrated Eu$^{3+}$ ion emission after annealing at different temperatures. The dashed lines are aid to the eye.
Figure 5.25 PL decay curves of selected (A) Eu-undoped SLs and (B) Eu-implanted SLs:Eu$^{3+}$ samples. Double exponential decay fitting (dashed lines) were used for each PL decay curve fitting.
Table 5.4 The double exponential decay fitting results of the PL decay of the SLs and the SLs:Eu$^{3+}$ samples.

<table>
<thead>
<tr>
<th></th>
<th>Unimplanted SLs</th>
<th></th>
<th>SLs:Eu$^{3+}$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As grown</td>
<td>Annealed @ 500 °C</td>
<td>Annealed @ 1000 °C</td>
<td>As implanted</td>
<td>Annealed @ 500 °C</td>
</tr>
<tr>
<td>$\tau_1$ [ns]</td>
<td>1.545 ± 0.0067</td>
<td>1.659 ± 0.0081</td>
<td>1.446 ± 0.0073</td>
<td>2.112 ± 0.0305</td>
<td>1.326 ± 0.0092</td>
</tr>
<tr>
<td>$\tau_2$ [ns]</td>
<td>4.341 ± 0.150</td>
<td>3.85 ± 0.0730</td>
<td>4.312 ± 0.083</td>
<td>7.427 ± 0.126</td>
<td>3.843 ± 0.285</td>
</tr>
</tbody>
</table>

TRPL was studied to evaluate the PL decay time of the luminescence from the studied InGaN/GaN SLs layers. Figure 5.25 shows the TRPL results of selected SLs and SLs:Eu$^{3+}$ samples and the double exponential decay fitting (dashed lines) associated with each decay curve. The fitting results of the decay time ($\tau_1$ and $\tau_2$) are summarized in Table 5.4. It can be seen that the decay time of the as implanted SLs:Eu$^{3+}$ (see Figure 5.25 (curve b)) doubled compared with the as grown SLs (see Figure 5.25 (curve a)) due to the change of compressive stress in the SL layers after the Eu$^{3+}$ ion implantation. Comparing the PL decay of the SLs (see Figure 5.25 (curve c)) and the SLs:Eu$^{3+}$ (see Figure 5.25(curve d)) annealed at 500 °C, the former shows slower decay due to the less efficient EHP recombination associated with the presence of larger strain inducing separation of electron and hole wave function. This conclusion agrees with the observation that the PL peak red-shift is larger with annealing temperature in the SLs samples than in the SLs:Eu$^{3+}$ samples. PL decay time are almost identical for both SLs and SLs:Eu$^{3+}$ sample annealed at 1000 °C,
indicating a good lattice recovery from implantation of the SLs:Eu$^{3+}$ sample after thermal annealing.

5.2.3 Plausible excitation efficiency improvement of Eu$^{3+}$ ion by material engineering

To get better understanding to the complex nature of strain induced by Eu$^{3+}$ ion in the SLs, the peak position of SLs emission was modeled by using the finite QW model [174] along with the QCSE before and after implanting Eu$^{3+}$ ions into the SLs. Figure 5.26 illustrates the routine procedure implemented to calculate the SLs peak position and its shift due to Eu implantation. First of all, the peak position of the as-grown SLs was modeled. The lattice constant of In$_{0.06}$Ga$_{0.94}$N layer were first calculated using Vegard’s Law with bowing parameter $b=2.29$ [175]. Then, the piezoelectric polarization (here $98.916\times10^{-3}$ C/m$^2$) and spontaneous polarization (-29.2$\times10^{-3}$ C/m$^2$) of the In$_{0.06}$Ga$_{0.94}$N QW layer were calculated based on the model described in Ref. [176]. Detailed calculation upon the strain induced polarization can be found in Appendix B. The obtained elastic strain values were $\varepsilon_{xx'} = -0.006561$, $\varepsilon_{yy'} = -0.006561$, $\varepsilon_{yz'} = 0$ and $\varepsilon_{zz'} = 0.003407$, respectively. It is known that the positive sign of elastic strain ($+\varepsilon$) indicates that a thin film exhibits tensile strain, while the negative sign ($-\varepsilon$) refers to the presence of compressive strain. The as grown SLs showed a compressive in-plane strain with some tensile strain component along semi $c$-direction. Furthermore, since the piezoelectric field linearly scales with the in-plane strain parameters [176], in the case of In$_x$Ga$_{1-x}$N/GaN quantum structure, the piezoelectric field relaxed the piezoelectricity induced QCSE, consequently, reduced the total polarization induced electric field as shown in Eq. (5.2), where $P_{GaN}^{SP}$ and $P_{z'QW}^{SP}$ are spontaneous polarization of the GaN barriers and InGaN wells, respectively, and $P_{z'QW}^{PZ}$ is
the piezoelectric polarization of the InGaN wells. The denominator of Eq. (5.2) is the dielectric constant taken from Ref. [177]. The calculated total electric field is 0.9465 MV/cm. [167], [177] Finally, the electric field generated in the SLs structure due to polarization was applied to tune the QW’s conduction and valence band by 0.114 eV, giving rise to the peak position of the as grown SLs to value of 3.157±0.005 eV which agrees well with experimentally observed value (3.153 eV).

\[
E = \frac{P_{GaN}^{SP} - P_{z}^{SP}_{QW} - P_{z}^{PZ}_{QW}}{\varepsilon_0 \varepsilon_r} \tag{5.2}
\]

The similar approach was applied to simulate the as implanted SLs:Eu\(^{3+}\) peak position with the following two supplementary assumptions. First of all, based on the implantation profile shown in Figure 3.4, we assumed that the Eu\(^{3+}\) ion concentration is approximately 1 at.% (maximum concentration peak value) across the entire SLs structure. Secondly, we assumed that Eu\(^{3+}\) ions mainly occupy the substitutional Ga\(^{3+}\) (In\(^{3+}\)) sites in the SLs:Eu\(^{3+}\). The Eu\(^{3+}\) ion substitution leads to a change of lattice constant of the SLs:Eu\(^{3+}\) due to the differences in ionic radii among Eu\(^{3+}\) ion (0.185 nm) and Ga\(^{3+}\) (0.126 nm) and In\(^{3+}\) (0.144 nm) cations, respectively. The modified lattice constant \(c\) and \(a\) in the SLs:Eu\(^{3+}\) due to Eu\(^{3+}\) ion are summarized in Table 5.5 together with the lattice constant of InN and GaN. The simulated peak position of the SLs:Eu\(^{3+}\) is 3.160 ± 0.005 eV which corresponds to the peak position in the as-implanted SLs:Eu\(^{3+}\) (3.164 eV).
Table 5.5 Lattice constant $a$ [Å] and $c$ [Å] used in simulation.

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>InN</th>
<th>GaN:1%Eu</th>
<th>In$<em>{0.06}$Ga$</em>{0.94}$N:1%Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ [Å]</td>
<td>3.189</td>
<td>3.54</td>
<td>3.194</td>
<td>3.215</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>5.185</td>
<td>5.705</td>
<td>5.193</td>
<td>5.224</td>
</tr>
</tbody>
</table>

Figure 5.26 Flow chart of the theoretical routine developed to model the SLs emission peak position for the undoped In$_x$Ga$_{1-x}$N/GaN SLs and Eu implanted In$_x$Ga$_{1-x}$N/GaN SLs.
Figure 5.27 (a) The schematic illustration of the energy transfer process between a strained single QW and the Eu$^{3+}$ ion through non-resonant energy transfer. A modified single QW with increased In content resonantly transferring energy to the $^5D_3$ level of Eu$^{3+}$ ion due to implemented strain.

Thus, the simulated emission peak position of the as-grown SLs and the as-implanted SLs:Eu$^{3+}$ shows good agreement with the experimental observation. However, simulations extended on SLs samples annealed at different temperature are beyond the scope of this model. At higher annealing temperature, one needs to take into account the change of the strain as well as the migration of In towards barrier layers. Since both processes happen simultaneously, it is very challenging to simulate the expected peak position unless further experimental data are available like the exact In content in the
individual QW and barrier at different annealing temperature. Recently, Mitchel et al. have demonstrated that atom probe tomography (APT) can be utilized to investigate the doping profiles of the Eu-doped III-Ns quantum structures and quantified the extent of Eu diffusion between the different Eu-doped layers. [40] It was concluded that APT is a suitable technique for this type of analysis because of its ability to spatially resolve features at the nm-scale with a very high sensitivity due to low background levels. Anyhow, in this work, we illustrate schematically the energy transfer process between the SLs and Eu$^{3+}$ ion using a simplified energy diagram model shown in Figure 5.27. Figure 5.27 (a) shows a single QW having the conduction band and the valence band tuned due to strain. Under above band gap excitation, an EHP recombination in the QW region release a photon with energy of 3.154 eV (the case of the SLs:Eu$^{3+}$ annealed 950 °C). This photon energy is ~134 meV larger than the expected $^5D_3$ excited state level energy of the Eu$^{3+}$ ion what makes it less probable to resonantly transfer the photon energy to the $^5D_3$ level of the Eu$^{3+}$ ion without phonons assistance. Thus, the alternative energy transfer process between the SLs to the Eu$^{3+}$ ions may proceed through intermediate energy states located in the energy band gap of the QWs, such as intrinsic defect levels of the InGaN and GaN. Since not all the defects can be involved in energy transfer to the Eu$^{3+}$ ion optically active centers, large amount of excitation energy is dissipated the host as heat. One can conceive that to increase the energy transfer efficiency between host and emitting RE$^{3+}$ ion the following material engineering steps may be undertaken: (1) decease the density of defects which would prevent the radiative energy transfer, in the meantime, create defects that can supply transfer energy to RE$^{3+}$ ion optically active centers. This approach requires precise control of the certain type
of structural defects via optimized growth process. [178] (2) Engineer the strain of the quantum structure layers by changing the width or depth of the QWs and RE-delta doping so that the photon energy generated in the QWs could resonantly match the excited energy levels of the RE$^{3+}$ ions. In the case of the SLs structure studied in this work, the resonant energy transfer to the $^5D_3$ level of the Eu$^{3+}$ ion require deeper QWs. By reversing the simulation process describe earlier, we estimated that by increasing the In content in the InGaN layer to 7.5% and keeping all the other parameters of the QWs unchanged one shall achieve the resonant photon energy matching to the $^5D_3$ level of the Eu$^{3+}$ ion. Figure 5.27 (c) illustrates this case where the photon energy emitted from this QW can resonantly transfer the energy to the Eu$^{3+}$ ion.

5.3 Summary

In this chapter, the defects induced by Eu$^{3+}$ ions in situ doped GaN epilayer were studied by means of DLTS, L-DLTS and MCTS. The high resolution L-DLTS revealed at least four closely spaced defect levels associate with the Trap B, identified with regular DLTS, with activation energy 0.259±0.032 eV (Trap B1), 0.253±0.020 eV (Trap B2), 0.257±0.017 eV (Trap B3), and 0.268±0.025 eV (Trap B4) below the conduction band edge, respectively. A shallow hole trap was observed at the energy of 30±20 meV above the valence band edge. The experimental demonstration of this trap existence corroborates the concept of the RESI hole trap model in rare earth ions doped III-nitrides. In addition, the identified DLTS energy traps were compared with other energy traps reported in the literature.
Furthermore, we studied the effect of the interfaces quality evolution in In$_{0.06}$Ga$_{0.94}$N/GaN SLs due to Eu implantation as a function of post-implantation annealing temperature. It was found that implantation-induced damages do not degrade the SLs structure significantly, and partial SLs structure recovery was achieved by thermal annealing above 900 °C in nitrogen ambient for 300 sec. The optical studies suggested that Eu$^{3+}$ ion in the SLs behaves in the comparable way as the impurity getter in semiconductor resulting in the phase purification of the material. Also, it was concluded that the presence of Eu$^{3+}$ ion in SLs induces an additional compressive stress component modifying the piezoelectric field in SLs active layer. The simulations of the strained as grown SLs and as-implanted SLs successfully reproduced the experimentally observed results when the Eu$^{3+}$ ion strain-induced polarization effect was considered.
CHAPTER 6: CONCLUSIONS

In this project, a combination of optical and electrical characterization methods was used to investigate a variety of RE-doped III-Ns materials, in specific, the Yb$^{3+}$ ion doped GaN NRs and epilayers, the Yb$^{3+}$ ion doped In$_x$Ga$_{1-x}$N NRs, GaN:Si:Eu$^{3+}$ epilayers, and the Eu implanted In$_x$Ga$_{1-x}$N/GaN SLs, respectively.

This dissertation started with the reviewing of our current understanding of the excitation mechanisms of RE$^{3+}$ ions, specifically Yb$^{3+}$ and Eu$^{3+}$ ions in III-Ns. We have also emphasized the importance of studying these materials for practical applications. We have reviewed the fundamental aspects, which in our opinion need to be considered carefully when studying the RE$^{3+}$ ions in III-Ns. Also, we have discussed the theory about the excitation mechanism related to RE induced defects in III-Ns. Furthermore, the principles of variety of deep level transience spectroscopy techniques used to characterize the defects in semiconductors of interest are introduced and discussed.

Subsequently, the Yb$^{3+}$ ion having the simplest electronic configuration among other lanthanides, was investigated when doped into different GaN hosts. The emission spectra of the Yb$^{3+}$ ion were analyzed and fitted with theoretical calculations, supporting the claim of the presence of isolated substitutional Yb$_{Ga}$ and Yb$_{Ga}$-$V_{N}$ complex defects. Furthermore, when studying the In$_x$Ga$_{1-x}$N NRs with varied In concentration, we found interesting behavior demonstrated in studied samples by improved luminescence quality from the NRs due to Yb doping. We have concluded that Yb in studied In$_x$Ga$_{1-x}$N materials acts like a gettering impurity reported in the literatures. The practical aspect of this finding was demonstrated by observation of green to amber color luminescence from these In$_x$Ga$_{1-x}$N...
\text{\textsuperscript{x}N:Yb\textsuperscript{3+}} NRs having lower In content as compared to their reference materials. However, the exact mechanism behind the material quality improvement after RE incorporation requires further investigation.

Subsequently, we reported on the optical spectroscopy and DLTS study toward a Eu and Si co-doped GaN. The L-DLTS and optical-DLTS systems developed in this work improved spectrum resolution as compared to the conventional DLTS. The high resolution L-DLTS revealed at least four closely spaced defect levels associate with the Trap B, identified with regular DLTS, with activation energy 0.259±0.032 eV (Trap B1), 0.253±0.020 eV (Trap B2), 0.257±0.017 eV (Trap B3), and 0.268±0.025 eV (Trap B4) below the conduction band edge, respectively. Most importantly, a shallow hole trap was observed at energy 30±20 meV above the valence band edge of the GaN:Si,Eu\textsuperscript{3+}, which has never been reported before. The experimental demonstration of this trap existence corroborates the concept of the RESI hole trap model in RE\textsuperscript{3+} ions doped III-Ns.

Finally, a study on the Eu\textsuperscript{3+} ion implanted In\textsubscript{0.06}Ga\textsubscript{0.94}N/GaN SLs was reported to illustrate the plausible way of prospective improvement of the excitation efficiency of Eu\textsuperscript{3+} ions via the material engineering approach. It was concluded that the presence of the Eu\textsuperscript{3+} ion in SLs induces an additional compressive stress component modifying the piezoelectric field in the SLs active layer and giving rise to an extra freedom of material engineering for efficient energy transfer from the engineered SLs to the Eu\textsuperscript{3+} ion. In addition, the observed FWHM change of SLs peak suggested, as in the case of InGaN:Yb\textsuperscript{3+} NRs, the possibility of the gettering effect due to Eu incorporation.
CHAPTER 7: FUTURE WORKS

The DLTS, L-DLTS and MCTS techniques exercised in this work are proved to be powerful in characterizing the Eu-doped GaN; however, the same is expected for other RE-doped III-Ns as well. Thus, the developed experimental setups could be utilized in studying, in principle, any semiconductors assuming that proper junction can be fabricated.

We envision a scope of prospective research projects utilizing outcomes of this project as follow:

- DLTS, L-DLTS and MCTS studies on the Mg and Eu co-doped GaN. As described in Section 2.1.4, GaN:Eu$^{3+}$ showed significant enhancement of the Eu$^{3+}$ ion emission upon Mg doping [60], [61], [63], [78]. The enhancement of red emission from Eu$^{3+}$ ion was investigated and explained in details [64], [78], giving rise to the postulate that the Mg acceptor forms DAP in the vicinity of the Eu$^{3+}$ ion, hence increases the energy transfer efficiency. It is also possible that the Mg$^{2+}$ acceptor provides more holes that can be captured by the RESI hole traps, in consequence, enhancing creation of localized exciton bounded to RESI hole trap and thus increasing the energy transfer efficiency due to the close proximity effect. Relying on the fact that the shallow hole trap has been identified in the GaN:Si,Eu$^{3+}$ sample studied in this work, it will be interesting to examine if a similar hole trap forms in the GaN:Mg,Eu$^{3+}$ material and how such hole trap’s properties are varied.

- Interface defect states characterization: the Sula DDS-12 DLTS system is equipped with the constant-capacitance-DLTS (CCDLTS) [179] feature, which can be used to study the defect states at materials’ interfaces like metal-insulator-semiconductor
(MIS) structures or multi-quantum well (MQW) structures. The CCDLTS, together with other DLTS-like methods [180], developed for interface defect study can be applied to study the InGaN/GaN:Eu$^{3+}$ SLs structure reported in this work. It may generate useful information about the changes of defect levels at the interface of the QWs upon Eu$^{3+}$ ion doping.

In addition to the research topics mentioned above, the functionality of the DLTS system can be further explored by adding new features. One possible feature that can be integrated into the existing system is the DLOS option. The difference between the DLOS and the O-DLTS or MCTS techniques developed in this work is that the photon energy excited upon studied materials can be selectively tuned. The DLOS can be realized by using a variable wavelength light source, such as a Xenon lamp or a dye laser, while monitoring the capacitance changes. We have tried the DLOS measurement during this work by tuning a dye laser with converted power output < 1 µW. However, no DLOS signal was observed, due to the insufficient excitation power. Thus, to successfully operate the DLOS measurement, certain precautions need to be noticed: 1) photon flux needs to be strong enough (i.e., use 1000 W Xenon lamp [161]) to achieve a large derivative of photo-capacitance; 2) one needs to collect the derivative of photo-capacitance within a short enough delay after the optical excitation or before the electrical filling; 3) average techniques to increase the S/N need to be considered, similar as conducting the L-DLTS experiment when the collected data analysis strongly depends on the S/N. [181], [182]

The other feature that can be equipped on the current DLTS system is the pressure-driven DLTS. It can be achieved by placing the sample into a diamond anvil cell (DAC)
integrated with the DLTS apparatus. In a typical experiment, the DAC can compress a small (sub-millimeter-sized) piece of material to extreme pressures, typically up to around 10-50 GPa, providing an extra variable for characterizing the defect energy levels in the materials. It has been demonstrated that a pressure-induced donor level in GaAs can be successfully assessed by pressure-induced DLTS. [183] Thus, it is expected that the formation energy of certain defects may change in material under pressure stimulus, and in consequence, one can achieve better spectral resolution as well as better insight into the energy transfer pathway/efficiency in RE-doped III-Ns. Also, the pressure induced lattice distortion can further perturb the local crystal field, resulting in measurable changes of spectroscopic features related to emission from RE$^{3+}$ ions, which is another way to investigate the excitation mechanism of RE-doped III-Ns.
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APPENDIX A: LAPLACE DLTS ANALYZER

A1.1 Background of Laplace-DLTS (L-DLTS) technique

Deep level transient spectroscopy (DLTS) was used to study the defect energy levels located in the semiconductor band gap. The conventional DLTS technique has its limitation in identifying defect levels that are very close to each other due to the poor resolution of the DLTS spectrum. The Laplace-DLTS (L-DLTS) technique introduced by L. Dobaczewski et al. [123] provides an improvement in terms of DLTS spectrum resolution, and hence, makes it possible to distinguish closely spaced defect energy levels. In general, the L-DLTS technique involves an inverse Laplace transform procedure. This is a mathematical routine or regularization process which is usually used to solve an ill-posed problem. The task to separate the closely spaced emission rates associated with defect levels from a capacitance transient measurement is an ill-posed problem. In the past, three mathematical models have been tested (see Ref. [123]), namely CONTIN [125], FTIKREG and FLOG. All the models were developed based on the Tikhonov regularization [126] method and showed comparable performance and accuracy. It expected that by applying this numerical procedure, the actual resolution can be boosted up to $\tau_1/\tau_2 \sim 2$. [123]

A1.2 Laplace DLTS analyzer (Matlab script)

A1.2.1 General facts about the Matlab script used

The original Matlab script was written by Iari-Gabriel Marino and can be downloaded free of charge from www.mathworks.com.
(see here: http://www.mathworks.com/matlabcentral/fileexchange/6523-rilt), which is an online forum for Matlab users. The package of this Matlab script includes a License file (see the end of this appendix). The Matlab script is an emulation of S. W. Provencher’s CONTIN program, written in Fortran language. The CONTIN code written in Fortran can be downloaded from (see here http://s-provencher.com/pages/contin.shtml).

A1.2.2 Modification of the Matlab script

The Matlab script developed here is a part of the Ph.D. dissertation project conducted at Ohio University and sponsored by the National Science Foundation CAREER program No.DMR-1056493. The Matlab script realizes general an inverse Laplace transform calculation. However, it was not designed specifically for solving any L-DLTS problems. Thus it is advised, after the program’s designer claim in the script, that: “The Inverse Laplace Transform is a highly ill-posed problem and is therefore intrinsically affected by numerical instability, i.e., its solution may not be unique, may not exist or may not depend continuously on the data. The g calculated by rilt.m is only one of the possible solutions, and this limit is unavoidable. Changing the parameters, the solution may change too.” Consequently, setting proper initial parameters to allow the simulation to work specifically for solving L-DLTS problems is one of the main modifications of the Matlab script made at Ohio University. The simulation parameters depend on experimental data. Thus these parameters need to be modified or adjusted accordingly. This is achieved by using the graphical user interface (GUI) described in the following paragraphs. An example of the GUI practical application used to analyze selected research data has been published in Ref. [133].
The **GUI** was designed using Matlab R2014a for implementing the Matlab script mentioned above. It enables the user to change the parameters easily without ‘digging’ back into the Matlab script. Also, the **GUI** allows the user to import experimental data file or export the results as *.txt file. Furthermore, using the developed **GUI**, the user who is not familiar with Matlab programming can perform the L-DLTS analysis with relative ease. Figure A1 shows the developed **GUI** window. The six modules of the **GUI**, numbered accordingly in Fig. A1 are briefly described below.

- **Module 1: Data input module**

  In this module, clicking the button “Open file” allows the user to import a *.txt data files with two columns of data, representing x and y data, respectively. The *.txt file needs to be in the same folder as the *Laplace* DLTS analyzer. The selected filename is displayed in the open window on the left. Depending on the type of imported data, it can be either a “decay curve” or “raise curve”. The user can choose “decay” or “raise” option using the “Data shape” selector *(only the “Decay” Data shape is available in the current version).* For large input data files, or if the user wants to reduce the input data size for running a quick evaluation, data can be decimated by the factor entered in the “Decimation” field.
Module 2: Fitting parameters module

Initially, the user needs to define a calculation range by estimating or guessing the possible emission rates (e.g., x-axis range). One can start with a larger parameter range and decrease gradually based on the obtained results. Fitting range is entered from $10^x$ to $10^x$, where $x$ is the power indexes (e.g., from $10^{-5}$ to $10^1$). The calculation will be restricted within the selected range.
Alpha is the most critical regularization parameter needed to be determined using provided data. Large Alpha parameter values will give smoother distribution of output peaks, while smaller Alpha parameter values may point out over fitting.

Iteration determines the maximum number of calculation cycles. The calculation may end before it reaches this number if good fitting conditions were met.

Resolution determines the number of points in the output spectrum. Increasing this number will lead to a longer calculation time. From previous experience, a resolution between 20 and 50 will generate a decent spectrum with a reasonable calculation time.

- Module 3: Weighting function module

This module allows the user to weight the imported data set by increasing the calculation weight of the first xx% by xx times. In case of a data curve that has a very fast initial decay and very noisy decay tail; one can use this module to increase the calculation weight of the initial data points. Note: This Module is disabled in the current version. Weighting is not considered at this point. Testing is in progress to develop this function.

- Module 4: Program control module

This module has three push-buttons – Start, Pause, and Resume. Once all the parameters have been set, the user clicks the “Start” button to initiate the program. During the calculation, a window will pop up to show the calculation progress synchronously (see Fig.A2). Figure A2(a) shows the imported data and fitting curves. Figure A2(b) plots the standard deviation of fitting for each iteration step. Figure A2(c) shows the inverted Laplace transform results. Figure A2(d) shows the normalized residuals of the calculation.
One can click the “Pause” button to pause the program during the run. To continue the program, click the “Resume” button.

- **Module 5 & 6: Data and results display modules**

  The plot in Module 5 shows the imported data (blue circles) and final fitting curve (red line) (*see* Fig. A1). The plot in Module 6 shows the final results of the inverse Laplace transform spectrum. Beside each of the plots are two buttons – Clear and Export. Click the “Clear” button to remove the current plot and reset the figure. Click the “Export” to save the plot as .txt file (*the “Export” buttons are disabled in the current version*). At the end of each run, the program automatically generates two *.txt files, named as “Data and fitting.txt” and “L-DLTS result.txt”, respectively. They are the data files represented in the two plots, respectively. *Note*: these files are overwritten each time the calculation is performed. If you wish to save these results, rename the files prior to the next run.
1.3 Software package

The Laplace DLTS analyzer is packaged in a *.zip file format, which contains four files in total. One of them (ContinTool.exe) are executable Matlab based GUI, two other are license files, and one is an example data file (ITS335K.txt).

To use the Laplace DLTS analyzer

1) Install Matlab Compiler Runtime (MCR) version 8.3 from (http://www.mathworks.com/products/compiler/mcr/) free of charge. Select the

Figure A2 Laplace DLTS analyzer calculation progress window.
right PC OS version depends on your computer. Note: no Matlab installation is required.

2) Double click the ContinTool.exe file to run the GUI. In the file browser, select the ITS335K.txt file in the same folder.

3) Type in parameters as describe earlier in this document.

4) Click “Start” to run the simulation.

5) At the end of the run, two *.txt files will be generated. Note: these files will be overwritten after each consecutive run. Rename or save existing files before the next run.

6) To quit the program, click the “X” located in the top right corner to close the program.
Copyright of the Matlab script

The included Copyright is available in the downloadable code package at


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APPENDIX B: SIMULATION OF STRAIN INDUCED POLARIZATION IN III-NS’ SEMI-POLAR LAYERS

B1.1 Calculations

The procedure of strain induced polarization calculation is followed by using equations and methods in Ref. [176]. The equation number described in this section are kept same as Ref. [176], unless otherwise specified. One issue/typo in Eq. (18a) in Ref. [177] was found and the correction procedure is illustrated below:

Piezoelectric polarization

\[ P_p^z = \begin{pmatrix} e_{15} \varepsilon_{xz} \\ e_{15} \varepsilon_{yz} \\ e_{31}(\varepsilon_{xx} + \varepsilon_{yy}) + e_{33}\varepsilon_{zz} \end{pmatrix} \tag{14} \]

This vector is in the N-coordinate (x, y, z). To transfer it to P-coordinate (x’, y’, z’), need rotation matrix. For rotation along x axis, the matrix is,

\[ R_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix} \tag{a} \]

By multiplying Eq. (a) and Eq. (14), the piezoelectric polarization in P-coordinate can be obtained, where the z’-component of polarization vector is,

\[ P_{pz}^{Lz'} = e_{15} \sin \theta \varepsilon_{yz} + \cos \theta \left[ e_{31}(\varepsilon_{xx} + \varepsilon_{yy}) + e_{33}\varepsilon_{zz} \right] \]

\[ = e_{31} \cos \theta \varepsilon_{x'x'} + \left( e_{31} \cos^3 \theta + \frac{e_{33} - e_{15}}{2} \sin \theta \sin 2\theta \right) \varepsilon_{y'y'} \tag{18a} \]

\[ + \left( \frac{e_{31} + e_{15}}{2} \sin \theta \sin 2\theta + e_{33} \cos^3 \theta \right) \varepsilon_{z'z'} \]

\[ + \left[ (e_{31} - e_{33}) \cos \theta \sin 2\theta + e_{15} \sin \theta \cos 2\theta \right] \varepsilon_{y'z'} \]
Compared with the Eq. (18) in Ref. [176], the third term in this equation is incorrect by using \( e_{33} \) as the first element. Instead, it should be \( e_{31} \) (marked in bold).

The results shown in Fig. 5 and Fig. 6 of the Ref. [176] can be calculated from Eq. (12) and Eq. (13). Then the results shown in Fig. 7 and Fig. 8 of the Ref. [176] can be recalculated from Eq. (18). Figures 5, 6, 7, 8 in the Ref. [176] are successfully reproduced, by MATLAB program shown later in this section, and illustrated in Figs. B1, B2, B3, B4. Thus, the strain induced polarization can be calculated for any given \( x \) value of a In\(_x\)Ga\(_{1-x}\)N epilayer.
B1.2 Simulation results

Figure B1 Elastic strain of In$_{0.2}$Ga$_{0.8}$N on a semi-polar GaN template in P-coordinate.
Figure B2 Elastic strain of In$_{0.2}$Ga$_{0.8}$N on a semi-polar GaN template in N-coordinate.
Figure B3 Piezoelectric polarization for In$_x$Ga$_{1-x}$N on a semi-polar GaN template, $x =$ 0.05, 0.1, 0.15 and 0.2, respectively.
Figure B4 Difference $\Delta P_z$ of the total polarization for $\text{In}_x\text{Ga}_{1-x}\text{N}$ on a semi-polar GaN template, $x = 0.05$, 0.1, 0.15 and 0.2, respectively.
B1.3 Matlab Code

Below is the Matlab script of the calculation procedure of strain induced polarization. The parameters and equations used in the script is followed after Ref. [176].

```matlab
%% InGaN/GaN
% Basic lattice parameters
x=0.2;
a_InN=3.54;
a_GaN=3.189;
c_InN=5.705;
c_GaN=5.185;
a_T=3.189;
c_T=5.185;
a_L=x*a_InN+(1-x)*a_GaN;
c_L=x*c_InN+(1-x)*c_GaN;

% Elastic constants
C_11_GaN=367;
C_11_InN=223;
C_11=x*C_11_InN+(1-x)*C_11_GaN;  % C_11_InGaN
C_12_GaN=135;
C_12_InN=115;
C_12=x*C_12_InN+(1-x)*C_12_GaN;  % C_12_InGaN
C_13_GaN=103;
C_13_InN=92;
C_13=x*C_13_InN+(1-x)*C_13_GaN;  % C_13_InGaN
C_33_GaN=405;
C_33_InN=224;
C_33=x*C_33_InN+(1-x)*C_33_GaN;  % C_33_InGaN
C_44_GaN=95;
C_44_InN=48;
C_44=x*C_44_InN+(1-x)*C_44_GaN;  % C_44_InGaN

% Strain in P-coordinate
theta=0:pi/1000:pi/2;
xigema_xx_pp=(a_T-a_L)/a_L.*(theta./theta);
xigema_m1=(a_T-a_L)/a_L;
s=sqrt((a_L*c_T).^2.*(cos(theta)).^2+(a_T*c_L).^2.*(sin(theta)).^2);
xigema_yy_pp=(a_T*c_T-s)./s;
xigema_m2=xigema_yy_pp;
A_31=C_11.*(sin(theta)).^4+(0.5*C_13+C_44).*(sin(2.*theta)).^2+C_33.*(cos(theta)).^4;
A_32=(C_11.*(sin(theta)).^2+(C_13+2*C_44).*(cos(2.*theta))-
      C_33.*(cos(theta)).^2).*sin(2.*theta);
A_41=0.5.*(C_11-c_13).*sin(theta).^2+2*C_44.*cos(2.*theta)+(C_13-C_33).*cos(theta).^2).*sin(2.*theta);
A_42=(C_11/2+C_33/2-
      C_13).*sin(2.*theta).^2+2*C_44.*cos(2.*theta).^2;
B_31=C_12.*(sin(theta).^2)+C_13.*(cos(theta).^2);
B_32=C_13.*(sin(theta).^4+cos(theta).^4)+(C_11/4+C_33/4-
      C_44).*sin(2.*theta).^2;
```
\[ B_{41} = 0.5 \cdot (C_{12} - C_{13}) \cdot \sin(2 \cdot \theta); \]
\[ B_{42} = 0.5 \cdot (C_{11} \cdot \cos^2(\theta) - (C_{13} + 2 \cdot C_{44}) \cdot \cos(2 \cdot \theta) - C_{33} \cdot \sin^2(\theta)); \]
\[ \xi_{\text{gg}zz_{pp}} = \frac{(B_{41} \cdot \xi_{\text{gg}m1} + B_{42} \cdot \xi_{\text{gg}m2}) \cdot A_{32}}{(A_{31} \cdot (A_{42} - A_{32}) \cdot A_{41})}; \]
\[ \xi_{\text{gg}yy_{pp}} = \frac{(B_{41} \cdot \xi_{\text{gg}m1} + B_{42} \cdot \xi_{\text{gg}m2}) \cdot A_{42}}{(A_{31} \cdot (A_{42} - A_{32}) \cdot A_{41})}; \]
\[ \text{figure(1)} \]
\[ \text{plot}(	heta \cdot 180 / \pi, \xi_{\text{gg}xx_{pp}}, \theta \cdot 180 / \pi, \xi_{\text{gg}yy_{pp}}, \theta \cdot 180 / \pi, \xi_{\text{gg}zz_{pp}}, \theta \cdot 180 / \pi, \xi_{\text{gg}yz_{pp}}) \]
\[ \text{xlabel('theta [degree]');} \]
\[ \text{ylabel('Strain in P-coordinate');} \]
\[ \text{grid on;} \]
\[ \text{% Strain in N-coordinate} \]
\[ \xi_{\text{gg}xx} = \xi_{\text{gg}xx_{pp}} \cdot (\cos(\theta)^2) + \xi_{\text{gg}zz_{pp}} \cdot (\sin(\theta)^2) + \xi_{\text{gg}yz_{pp}} \cdot (\sin(2 \cdot \theta)); \]
\[ \xi_{\text{gg}yy} = \xi_{\text{gg}yy_{pp}} \cdot (\sin(\theta)^2) + \xi_{\text{gg}zz_{pp}} \cdot (\cos(\theta)^2) - \xi_{\text{gg}yz_{pp}} \cdot (\sin(2 \cdot \theta)); \]
\[ \xi_{\text{gg}yz} = 0.5 \cdot (\xi_{\text{gg}zz_{pp}} - \xi_{\text{gg}yy_{pp}}) \cdot \sin(2 \cdot \theta) + \xi_{\text{gg}yz_{pp}} \cdot \cos(2 \cdot \theta); \]
\[ \text{figure(2)} \]
\[ \text{plot}(	heta \cdot 180 / \pi, \xi_{\text{gg}xx}, \theta \cdot 180 / \pi, \xi_{\text{gg}yy}, \theta \cdot 180 / \pi, \xi_{\text{gg}zz}, \theta \cdot 180 / \pi, \xi_{\text{gg}yz}) \]
\[ \text{xlabel('theta [degree]');} \]
\[ \text{ylabel('Strain in N-coordinate');} \]
\[ \text{grid on;} \]
\[ \text{% Piezoelectric tensor} \]
\[ e_{33 \ _{InN}} = 0.73; \]
\[ e_{33 \ _{GaN}} = 0.73; \]
\[ e_{33} = x \cdot e_{33 \ _{InN}} + (1 - x) \cdot e_{33 \ _{GaN}}; \]
\[ e_{31 \ _{InN}} = -0.49; \]
\[ e_{31 \ _{GaN}} = -0.49; \]
\[ e_{31} = x \cdot e_{31 \ _{InN}} + (1 - x) \cdot e_{31 \ _{GaN}}; \]
\[ e_{15 \ _{InN}} = -0.4; \]
\[ e_{15 \ _{GaN}} = -0.4; \]
\[ e_{15} = x \cdot e_{15 \ _{InN}} + (1 - x) \cdot e_{15 \ _{GaN}}; \]
\[ % Spontaneous polarization \]
\[ P_{sp \ _{GaN}} = -0.029; \]
\[ P_{sp \ _{InN}} = -0.032; \]
\[ P_{T \ _{sp}} = P_{sp \ _{GaN}}; \]
\[ P_{L \ _{sp}} = x \cdot P_{sp \ _{InN}} + (1 - x) \cdot P_{sp \ _{GaN}}; \]
\[ % Strain induced polarization \]
\[ P_{L \ _{p2}} = (e_{31}) \cdot (\cos(\theta)) \cdot \xi_{\text{gg}xx_{pp}} + (e_{31} \cdot (\cos(\theta)^3) + 0.5 \cdot (e_{33} - e_{15}) \cdot \sin(\theta) \cdot \sin(2 \cdot \theta)) \cdot \xi_{\text{gg}yy_{pp}} + (0.5 \cdot (e_{31} + e_{15}) \cdot \sin(\theta) \cdot \sin(2 \cdot \theta) + (e_{33}) \cdot (\cos(\theta)^3) \cdot \xi_{\text{gg}zz_{pp}} + ((e_{31} - e_{33}) \cdot \cos(\theta) \cdot \sin(2 \cdot \theta) + (e_{15}) \cdot \sin(\theta) \cdot \cos(2 \cdot \theta)) \cdot \xi_{\text{gg}yz_{pp}}; \]
delta_P_z_p=P_L_pz+(P_L_sp-P_T_sp).*cos(theta);

figure(3)
plot(theta.*180./pi,P_L_pz)
xlabel('theta [degree]');
ylabel('P_L_z [C/m^2]');
grid on;
hold on;
figure(4)
plot(theta.*180./pi,delta_P_z_p)
xlabel('theta [degree]');
ylabel('delta_P_z [C/m^2]');
grid on;
hold on;
APPENDIX C: DESIGN OF THE LN\textsubscript{2} CRYOSTAT

Figure C1 shows the technical drawing of the LN\textsubscript{2} cryostat designed in this work. The cryostat contains three regions separated by stainless steel walls. The region between the outer wall and the inner wall (volume \(A1\)) contains the copper part of the cold finger and all the sensors and probes. This volume is pumped to vacuum (\(\sim 10^{-5}\) Torr) when conducting experiment by a turbo pump. The vacuum between the inner wall and the LN\textsubscript{2} wall (volume \(A2\)) can be vacuumed by a membrane pump to a lower level of vacuum (\(< 10^{-3}\) Torr) so that the LN\textsubscript{2} consumption is significantly reduced. The third region (volume \(A3\)) is the LN\textsubscript{2} reservoir (see light blue area in Fig. C1) with a volume approximately equals to 386 mL. The LN\textsubscript{2} is poured in from the top of the cryostat, while the N\textsubscript{2} vapor escape from the top as well. During the experiment, a pressure release valve can be attached to the top of the cryostat to reduce N\textsubscript{2} gas escape and reduce further LN\textsubscript{2} consumption. The pressure of the LN\textsubscript{2} reservoir can be controlled and monitored by the pressure release valve and a pressure gauge. The LN\textsubscript{2} reservoir is in touch with the rest of the cryostat at the bottom and the top ends via a narrow stainless steel tube with diameter of 0.5 inch, in order to reduce the LN\textsubscript{2} consumption.

The bottom end of the LN\textsubscript{2} reservoir is directly attached to the copper cold finger of the cryostat (orange part in Fig. C1). The cold finger has two sections which are connected by a brass tube, leaving an empty “vacuum gap” in between the two copper parts intentionally as high thermal impedance medium. This design aims to reduce the heat/cold transfer speed between the hot and cold parts of the cold finger. In this way a slower
temperature ramping and thus better temperature control can be achieved. Also, the parameters of thermal impedance can be adjusted to modify the heat exchange efficiency.

The sample holder is attached to the lower part of the copper cold finger that contains a 50 W cartridge heater. Two needle tungsten probes are equipped on the sample holder to reach the contacts on the sample. The temperature is monitored by two thermocouples type K as temperature sensor (T-sensor) with one attached to the sample on the copper sample holder while the other one can be attached to the upper part of the cold finger (see Fig. C1). All electrical leads inside the cryostat are guided along the cryostat side wall and from there go to the electrical feedthroughs. The cryostat is equipped with a quartz optical window, which allow optical excitation getting through and is used for MCTS experiment in this work. The optical window shown in Fig. C1 is rotated 90 degrees from the front view to the side view for clarity purpose.
Figure C1 The technical drawing of the LN₂ cryostat designed in this work.