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Development of White-Light Emitting Active Layers in Nitride Based Heterostructures for Phosphorless Solid State Lighting

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Table of Contents

Executive Summary	3
I. Introduction – Technical Background	5
I.a Introduction	5
I.b Luminescence Process in the Active Layer	6
I.c Technical Basis of the Proposed Material Design	7
I.d Milestones	10
I.e Research Methodology	12
I.f Conclusions	12
II. Rare Earth Ion Activated Nitride Powders	13
II.a Introduction	13
II.b Synthesis and Optimization of Nitride Powders	13
II.c Spectroscopic Measurements	16
III. Pulsed Laser Deposition of GaN: RE ³⁺ Thin Films and Characterization	34
III.a Introduction	34
III.b PLD Process	34
III.c PLD Deposition and Characterization of GaN:RE ³⁺ Thin Films	35
III.d Conclusions	39
IV. Designing the MOVPE Reactor	40
IV.a. Design and Assembly of the MOVPE Reactor	40
IV.b Hardware Upgrades	42
IV.c Choice of Precursors	44
V. Deposition and Characterization of GaN:RE ³⁺ Thin Films by MOVPE	51
V.a Introduction	51
V.b Structural Characterization of Thin Films Deposited by MOVPE	51
V.c Fluorescence Measurements of Undoped Films	58
V.d Measurement of Fluorescence from RE ³⁺ in GaN Thin Films	63
V.e Conclusions	69
VI. Modeling and Luminescence Mechanism	71
VI.a Introduction	71
VI.b Luminescence Mechanism	71
VI.c Oxygen Defects in GaN	75
VI.d. Location and Stability of RE ³⁺ in Nitride Hosts	82
VI.e Saturation of Emission from RE ³⁺	86
VI.f Conclusions	88
VII. Conclusions	91
VIII. Recommendations	95
VIII.a Core Level Research	95
VIII.b Developmental Research	97
Appendix	99

Executive Summary

This report provides a summary of research activities carried out at the University of California, San Diego and Central Research of OSRAM SYLVANIA in Beverly, MA partially supported by a research contract from US Department of Energy, DE-FC26-04NT422274. The main objective of this project was to develop III-V nitrides activated by rare earth ions, RE^{3+} , which could eliminate the need for phosphors in nitride-based solid state light sources. The main idea was to convert electron-hole pairs injected into the active layer in a LED die to white light directly through transitions within the energy levels of the $4f^n$ -manifold of RE^{3+} .

We focused on the following materials: Eu^{3+} (red), Tb^{3+} (green), Er^{3+} (green), Dy^{3+} (yellow) and Tm^{3+} (blue) in AlN, GaN and alloys of AlN and GaN. Our strategy was to explore candidate materials in powder form first, and then study their behavior in thin films. Thin films of these materials were to be deposited on sapphire substrates using pulsed laser deposition (PLD) and metal organic vapor phase epitaxy (MOVPE). The photo- and cathode-luminescence measurements of these materials were used to investigate their suitability for white light generation. The project proceeded along this route with minor modifications needed to produce better materials and to expedite our progress towards the final goal.

The project made the following accomplishments:

1. red emission from Eu^{3+} , green from Tb^{3+} , yellow from Dy^{3+} and blue from Tm^{3+} in AlN powders,
2. red emission from Eu^{3+} and green emission from Tb^{3+} in GaN powder,
3. red emission from Eu^{3+} in alloys of GaN and AlN,
4. green emission from Tb^{3+} in GaN thin films by PLD,
5. red emission from Eu^{3+} and Tb^{3+} in GaN thin films deposited by MOVPE
6. energy transfer from host to RE^{3+} ,
7. energy transfer from Tb^{3+} to Eu^{3+} in AlN powders,
8. emission from AlN powder samples codoped with (Eu^{3+} , Tb^{3+}) and (Dy^{3+} , Tm^{3+}),
9. white emission from AlN codoped with Dy^{3+} and Tm^{3+} .

We also extensively studied the stabilities of rare earth ions in GaN, and the nature of oxygen defects in GaN and its impact on the optical properties of the host material, using first principles method. Results from these theoretical calculations together with fluorescence measurements from the materials essentially proved the underlying concepts for generating white light using RE^{3+} -activated nitrides.

For this project, we successfully built a horizontal MOVPE reactor and used it to deposit thin films of undoped and doped nitrides of GaN and InGaN, which is a very significant achievement. Since this reactor was designed and built by in-house experts, it could be easily modified and reassembled for specific research purposes. During this study, it was successfully modified for homogeneous distribution of rare earth ions in a deposited film. It will be an ideal tool for future research involving novel thin film material concepts.

We examined carefully the suitability of various metal organic precursors for incorporating RE^{3+} . In order to avoid oxygen contamination, several oxygen-free RE^{3+} precursors were identified. Both oxygen-free and oxygen- containing metal organic

precursors were used for certain rare earth ions (Eu^{3+} , Tb^{3+} and Er^{3+}). However, the suitability of any particular type of precursor for MOVPE deposition was not established during this study, and further study is needed.

More intensive research in the future is needed to improve the film quality, and eliminate the separation of rare earth oxide phases during the deposition of thin films by MOVPE. The literature in the area of the chemistry of rare earth ions in nitrides is almost nonexistent, in spite of the significant research on luminescence of RE^{3+} in nitrides. Consequently, MOVPE as a method of deposition of RE^{3+} -activated nitrides is relatively unexplored.

In the following sections of this report, the outcomes from this study are described in detail. The present investigations have clearly validated the underlying concepts for generating white light within the LED die itself and its importance for fabricating a new generation of solid state light sources. Yet, significant research is still needed to transform these concepts into products.

Section I. Introduction - Technical Background

I.a Introduction

This three-year long project from 10/1/2004 to 12/31/2007 was supported by a US Department of Energy Grant, DE-FC26-04NT4227. It was based on a proposal for exploring novel active layer materials for fabrication of a novel architecture for nitride base solid state light (SSL) sources, which obviate the need of phosphors to convert UV light emitted by a LED source to white light. The white light is generated directly from the LED device by using an activated thin film of a semiconducting alloy as the active layer in a heterojunction design. Generation of white light within the LED architecture was the kernel of this proposal. The key to a successful implementation of this architecture is the development of a novel semiconducting material that efficiently converts the electron-hole (e-h) pairs to white light.

This project focused on developing thin films of GaN activated by suitably chosen rare earth ions, RE^{3+} . These activators are to be selected based on their ability to convert the e-h pairs in the host lattice to visible radiation. The thin films of these materials could be integrated in a double heterojunction structure shown in Figure 1.a as an active layer.¹

A double heterojunction uses two semiconducting materials with differing band gaps. The material with the larger band gap is used as the confinement layers or claddings, which could be doped to yield p- and n- type semiconductors. The active layer between the confinement layers has a smaller band gap. Thus, in the forward bias application, when the electrons and holes are injected into the active layer, they cannot diffuse back to the confinement layers because of their larger band gap. In Figure 1.b, we have shown the energy band diagram of the confinement layers and the active region in the real space, which illustrates the electron confinement process just described.

In the proposed LED-based SSL design using a double heterojunction architecture (Figure 1), the active layer sandwiched between two carrier-confining layers converts the electrons and holes injected into this region into white light. In the present construct, a part of the emission would come as the characteristic LED emission (Process 1) via direct e-h radiative recombination, and the other would be generated by the activator ions sensitized by the e-h pairs (Process 2). The sensitization process involves nonradiative energy transfer from the e-h pairs to an activator ion, which results in the excitation of the activator ion from the ground state E_g to an excited state, E_1 . Next, the activator ion relaxes nonradiatively from the energy state, E_1 to the emitting state, E_1' . This relaxation process leads to the Stokes shift that enables emission of a red or green photon from the activator ion. By suitably choosing the type and concentration of activator ions, one could generate white light directly from the active layer by wavelength mixing of the light from the direct e-h recombination process and sensitization of the activator ions. We will refer to this architecture as the phosphor-less double heterojunction LED design (PDH-LED). Since the photons emitted by the activator ions suffer from significant Stokes shift, they escape through the active and confinement layers without significant re-absorption by the host lattice; this is a significant advantage of the current design over the other designs discussed earlier.

Figure 1. (a) Typical LED heterostructure design; (b) Fluorescence from the active layer either by direct recombination of e-h pairs or via energy transfer to an impurity ion. Process 1 corresponds to direct e-h radiative recombination. Process 2 describes a nonradiative energy transfer from an e-h pair to an activator ion. Process 3 describes schematically radiative transition of the activator ion following a nonradiative relaxation to the energy level, E_1' from E_1 . Processes 1 and 2 convert the energy of an e-h pair to a Stokes-shifted emission from an activator ion.

I.b Luminescence Process in the Active Layer

Light is generated in the active layer by recombination of the injected e-h pairs. In III-V nitride semiconductors, emission from e-h pairs occurs almost near the band edge with insignificant Stokes shift. This is the main advantage of SSL lighting. The recombination of the e-h pairs results in the emission of a narrow band spectrum with a full width at half maximum (FWHM) of ~ 5 -10 nm. This narrow band, monochromatic emission has to be converted to multiple band emissions to generate white light; this is the conventional approach of designing SSL LEDs.

There are two interesting observations from phosphor physics that support the concept of a new class of materials that could be used for “white light” emitting active layers. First, most phosphors that have high quantum efficiency when the impurity ions are excited directly and exhibit efficient band edge fluorescence when undoped, usually yield high quantum efficiency near the band edge.² Furthermore, all the LEDs are known to have high internal radiative transition probabilities. Fluorescence from Tb^{3+} , Sm^{3+} , Dy^{3+} , Er^{3+} and Tm^{3+} from thin films of GaN and AlN^{3,4} have been reported. Thus, the literature on the fluorescence of RE^{3+} ions in nitride hosts appears to be very promising for developing novel III-V materials activated by RE^{3+} ions that could lead to emission of white light.

Second, sensitization by exciting the host lattice directly is a well-known scheme in phosphor technology. In the case of photo-luminescence (PL), host lattice absorption is usually strong, and energy transfer could be very efficient. However, the exact nature of sensitization is not well understood and is the subject of considerable interest for generating a luminescent active layer. The process of sensitization by a host is believed

to proceed through emission from a self-trapped exciton. If the emission band due to a self-trapped exciton (STE) has a good overlap with the excitation peak of an emitting ion, the host can serve as a good sensitizer. However, there are at least two drawbacks associated with this approach: the STE emission occurs at considerably lower energies than the absorption due to a large Stokes shift, and nonradiative transitions at energies higher than the band gap dominate due to trapping of free electron and hole pairs at the surface and defects prior to the formation of a self-trapped exciton. The latter is not of serious concern for this project, since the LED chips are increasingly available with significantly less microscopic and macroscopic defects as evidenced in reported high internal quantum efficiencies of LEDs over the last few years. In the case of the former, the III-V semiconducting materials are known for their small Stokes shift.

White light generation by multiple dopants is not new. The most commonly used fluorescent phosphor, fluoro-chloro apatite that revolutionized the fluorescent industry in the 1950's, is activated by Sb^{3+} and Mn^{2+} to produce a broadband white light.⁵ Thus, in view of the reported fluorescence from various RE^{3+} in III-V nitride semiconductors, it may be reasonable to expect that with a nitride thin layer suitably codoped or multiple thin layers in which each layer fluoresces monochromatically, white light could be generated in the active layer upon e-h recombination.

The critical tasks for this project were to identify the rare earth ions that would fluoresce efficiently in a nitride host, to understand the mechanism of fluorescence near the band edge excitation, to use this understanding to modify the composition of nitride semiconductors by alloying nitrides of Al, Ga and In to optimize this fluorescence, and finally deposit thin layers of these materials epitaxially on a suitable substrate and to test their performance.

We assumed throughout this project that observations from PL could be extended to fabricating "white light" emitting active layers and designed the experiments to test the response of candidate materials accordingly. We did not consider it to be necessary to test the candidate materials in LED devices. When a material is excited near or above the band edge, e-h pairs are also created within the host lattice. Emission from the impurity ions will occur if nonradiative energy transfer from the e-h pairs to the activator ions occurs efficiently. Thus, excitation of the host near the band edge could be used as a good predictor of its performance in an electroluminescent device. As an alternative, cathode luminescence (CL) was also used to excite the RE^{3+} in nitride hosts.

I.c Technical Basis of the Proposed Material Design

This project was based on three basic concepts: 1. sensitization of RE^{3+} by the host; 2. optimization of the performance of a host- RE^{3+} combination by band gap engineering; and 3. using powder performance as an indicator of thin film behavior. These concepts are discussed next in some detail.

Sensitization refers to a process of energy transfer from one excited ion to another via a nonradiative path. In many fluorescent materials, sensitization of the activator ion is necessary for a better absorption of the exciting radiation. The green emitting LaPO_4 phosphor activated by Tb^{3+} is a good example.⁶ The first allowed absorption band of Tb^{3+} corresponding to $4f^8 \rightarrow 4f^7 5d$ transition lies at a too high energy to make 254 nm

excitation effective. Ce^{3+} are incorporated for an efficient absorption of the 254 nm radiation from a Hg-discharge. For this purpose, Ce^{3+} is a suitable sensitizer ion whose $4f \rightarrow 5d$ transition band overlaps the 254 nm emission from the discharge.

The cross relaxation energy transfer (Figure 1.B, Process 2) is essentially an electron-electron correlation process. The theory of energy transfer by multipole-multipole interactions or exchange interaction electrons located at two different ions was initially formulated by Forster⁷ and Dexter.⁸ Later Kushida⁹ explicitly investigated the energy transfer process between two rare earth ions. The selection rules are summarized in Table 1.

Table 1. Selection rules for energy transfer between two rare earth ions involving states within the f^n -manifold

Nature of multipole at A	Nature of multipole at B	Selection rule for A		Selection rule for B	
		J=0	$J_i \neq 0$	J=0	$J_i \neq 0$
electric dipole	electric dipole	$ \Delta J =2,4,6$	$ \Delta J \leq 6$	$ \Delta J =2,4,6$	$ \Delta J \leq 6$
electric dipole	electric quadrupole	$ \Delta J =2,4,6$	$ \Delta J \leq 6$	$ \Delta J =2$	$ \Delta J \leq 2$
electric quadrupole	electric dipole	$ \Delta J =2$	$ \Delta J \leq 2$	$ \Delta J =2,4,6$	$ \Delta J \leq 6$
magnetic dipole	magnetic dipole	$ \Delta J =1$	$ \Delta J \leq 1$	$ \Delta J =1$	$ \Delta J \leq 1$

Another critical component of the sensitization process is the transfer rate since it must compete with the radiative relaxation rate of the sensitizer. In the case of GaN, the life time of e-h pairs is of the order of 1.0×10^{-8} s. The radiative rate is typically 10^3 to 10^6 s^{-1} for the $4f \rightarrow 4f$ transitions.

The dipole-dipole transfer rate between a rare-earth ion and an e-h pair can be written in terms of the oscillator strengths of the optical transition connecting the initial and final states of the cross relaxation. This is expressed as:

$$P_{AB}^{dd} = (2/3)(2\pi/\hbar)(e^2/R^3)^2(3\hbar/2m_e)^2(1/\omega)^2 f_A f_B S$$

where e is the charge on the electron, $\hbar$ is Planck's constant/ 2π , the average separation of between the activator and sensitizer ions, R is the average separation between an RE^{3+} and nearest Ga^{3+} in Angstroms, m_e is the mass of the electron, ω is the transition frequency on each ion involved in the cross relaxation, f_A and f_B are the oscillator strengths of the transitions for the rare earth ion and the e-h pair, respectively, and S is the overlap of the two transitions. Putting in values for the constants and expressing the transition energy, $\Delta E = \hbar\omega$, in eV, the overlap integral in cm^{-1} , and the ion-ion separation in Angstroms, the transition rate can be shown to be:

$$P_{AB}^{dd} = (1.4 \times 10^{24} f_A f_B S) / (\Delta E^2 R^6).$$

For typical f-f oscillator strengths of 10^{-6} , an estimated oscillator strength of an e-h pair in GaN of $\sim 10^{-2}$, a transition energy of ~ 3 eV and an overlap of 10^{-3} cm⁻¹ of transitions from the rare earth ion and GaN (whose widths at room temperature are taken to be 10 and 500 cm⁻¹ wave numbers, respectively), this yields a rate of $\sim 10^{10}$ s⁻¹ for ions separated by a typical nearest neighbor distance of 2.0 Å. At this rate, the direct recombination of e-h pairs will not be able to compete with energy transfer to activator ions.

We have also not considered explicitly the exchange mechanism, which is significantly faster compared to multipole-multipole interactions. In $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Sb}^{3+}, \text{Mn}^{2+}$, the transfer of energy competes effectively with np $\rightarrow$ ns type of radiative transition from Sb^{3+} . The transfer mechanism has been speculated to be a (super) exchange process. In the energy transfer process from the host to the activator ions, this could play a very important role.

Selection of Alloy Composition and Activator

The energy transfer rate from the host to RE^{3+} depends on the overlap of the host emission bands and excitation peaks of the RE^{3+} , if the transfer proceeds according to the Dexter-Forster mechanism. Therefore, it is important to have a complete picture of the excited states and excitation peaks associated with RE^{3+} . The excitation peaks are either narrow, intraband 4f $\rightarrow$ 4f transitions that are, to a good approximation independent of the host material, or broadband 4f $\rightarrow$ 5d transition and ligand-to-metal charge transfer bands that depend strongly on the host lattice. For nitride hosts with available sites with tetrahedral coordination, such data are not readily available. Therefore, our first objective was to determine the excitation peaks of RE^{3+} in nitride hosts. Since AlN is a large gap material, it was hoped that this host would enable us to probe the excitation peaks of candidate rare earth ions over a wide range of energy.

Once these excitation peaks are identified, the next issue was to modify the host lattice so that band edge emission would overlap with the excitation peaks. The idea was to modify the composition of GaN by alloying it with InN or AlN. In this connection, the available data on the variation of band gap energy with alloy composition was expected to be very helpful. So, it was our plan to optimize the fluorescence yield from the candidate host- RE^{3+} pairs by altering the alloy composition of the host to facilitate increasing overlap of the excitation peaks of the rare earth ions and emission peaks due to near band edge excitation. These studies were planned to be carried out in RE^{3+} doped nitride powders. Although a number of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys were made using the powder synthesis approach, a thorough investigation matching the band edge emission with the excitation peaks of the RE^{3+} was not done.

Thin Film Behavior

Our plan was to test by PL or CL basic energy transfer concepts using powder samples of activated materials. However, it is essential that the fluorescence characteristics of the material were retained when deposited as a thin film. For this purpose, pulsed laser deposition (PLD) and metal organic vapor phase epitaxy (MOVPE) were chosen for the

present study. The PLD method uses a packed powder target and thus, could use optimized powders from the powder study. These thin films could provide preliminary results for further exploration. The MOVPE method is essential for integrating the technology to manufacturing. However, during this study both deposition methods were used concurrently to explore different combinations of RE³⁺-host systems.

I.d Milestones

The goal of this project was to expedite the process of generating a white light source by developing a nitride-based semiconducting material that could be used as an active layer in a double heterojunction design to convert e-h pairs directly to white light. Developing such a material would lead to a more compact, phosphorless design of a light source. Intrinsically it would lead to a more energy efficient source since the light generated by the activator ions would easily escape the device without significant re-absorption. In order to develop such a material and test its applicability in an LED system, the project was carried out in three overlapping phases. The first two phases were of one and one half-year duration, and the last phase was carried over the last two years. The milestones of the three phases were set as follows.

Phase I.

Milestones:

1. Demonstration of efficient emission from activator ions in GaN
2. Demonstration of efficient energy transfer from e-h pairs to the activator ions by photo-luminescence measurements.
3. Demonstration of white light emission from suitable choice of alloy composition and activator ions.

These three milestones were expected to establish the validity of the concept of developing a white light emitting active layer, and the fact that the e-h pairs could be used to excite the activator ions. They were critical for subsequent development of white light emitting active layers from nitride alloys.

Phase II.

Milestone:

1. Demonstration of high efficacy performance of thin films grown by PLD.

The performance of a thin film with selected alloy composition and activator ions was expected to establish that efficacy from plaque measurements could be reproduced by the materials in thin films. Since the actual application in PDH-LED would require the material to be in the form of a thin film, this milestone was necessary to test if the approach taken by this research proposal was technologically feasible and useable in LED SSL design.

Phase III.

Milestones:

1. Establishing the reaction paths for the thin film deposition of candidate materials by the MOVPE method.
2. Demonstration of performance of the thin films deposited by MOVPE method.

The milestone status is summarized in Table 2. Although many of the stated goals are only partially achieved at the end of the project, Table 2 shows significant accomplishments towards designing a white light SSL device without a down-converting phosphor.

Table 2. Milestone accomplishments

Milestone	Description	Target Date	Status
1.	Demonstration of efficient emission from activated GaN	9/30/05	<ul style="list-style-type: none"> • Demonstrated emission from Eu, Tb, Dy, and Tm in AlN • Eu and Tb in GaN • Report issued
2.	Demonstration of efficient energy transfer to activator ions	3/31/06	<ul style="list-style-type: none"> • Demonstrated energy transfer from: <ul style="list-style-type: none"> - Host to RE³⁺ in AlN and GaN - Tb³⁺ to Eu³⁺ in AlN
3.	Demonstration of white light emission	3/31/07	<ul style="list-style-type: none"> • RGB components identified in AlN • RG components identified in GaN • White light from AlN:Dy³⁺, Tm³⁺
4.	Demonstration of high efficacy of PLD thin films	12/20/06	<ul style="list-style-type: none"> • Demonstrated luminescence from GaN:Tb³⁺
5.	Establish reaction path for thin film deposition	1/31/06	<ul style="list-style-type: none"> • Report issued • Precursors for RE ions identified with/without oxygen ligands
6.	Demonstration of MOVPE thin film performance	9/28/07	<ul style="list-style-type: none"> • Research scale reactor designed and tested • Reactor modified for rare earth deposition • Deposited thin films: GaN, InGaN, GaN:Eu³⁺, GaN:Tb³⁺, GaN:Er³⁺

I.e Research Methodology

The original plan was to explore for the novel material(s) using the following steps:

1. synthesis of activated nitride hosts in powder form
2. demonstration of emission from the activator ions by host sensitization
3. selection of alloy composition and activator ions for optimum performance by modeling and solid state spectroscopy
4. testing of PL properties of thin films produced by pulsed laser deposition
5. testing of PL properties of thin films deposited by MOVPE.

The project proceeded nearly according to the plan just outlined. When problems were encountered, the research plan was modified accordingly to best meet the overall goals of the project. For example, the combustion method for powder synthesis was abandoned for a three-step solution-based method. The outcomes from these research activities are described in detail in Section II- VI. In Appendix 1, we have provided a detailed list of publications and presentations.

I.f Conclusions

During this three year project, a large number of powder samples and thin films were synthesized in order to explore the possibility of using RE^{3+} -activated nitride materials as active layers in SSL sources. The present study showed the validity of the underlying concepts and calls for further study, particularly in the area of rare earth chemistry in nitrides. With a good understanding of the underlying chemistry, high quality films of RE^{3+} -activated nitride thin films with high fluorescence yield could be deposited and employed in a novel SSL design.

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Section II. Rare Earth Ion Activated Nitride Powders

II.a Introduction

In accordance with our original plan, fluorescence from rare earth ions (RE^{3+}) in nitride powders was thoroughly investigated, while the MOVPE reactor was being designed and tested. This approach for developing “white light emitting” nitride materials was adopted since the synthesis of powder samples was expected to be rapid and to enable us to identify composition of nitride hosts activated by RE^{3+} for efficacious emission. The main objectives of the investigations of powder samples were as follows:

- Spectroscopic characterization of fluorescence of RE^{3+} in nitride hosts;
- Identification of corresponding luminescence mechanisms;
- Determination of alloy composition to enhance energy transfer from the host to RE^{3+} ;
- Using optimized powder samples as target materials for depositing thin films using the pulsed laser deposition (PLD) method.

During the course of this study, more than 70 samples of both doped and undoped nitride powders were prepared. Approximately 60 mg of AlN and 0.5 grams of GaN powders, corresponding to ~100% yield, could be prepared from each run. They were systematically analyzed for material quality using X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), and investigated for their fluorescence properties. In the following sections, results from these studies are summarized. More details can be found in publications listed in the Appendix.

II.b Synthesis and Optimization of Nitride Powders

In the initial stage of the project, the synthesis of nitride based semiconductors proceeded with a combination of combustion synthesis and nitridation methods. The combustion synthesis approach is a rapid and highly exothermic technique, and was used to synthesize pure and RE^{3+} activated gallium oxide powders. The oxide powders then underwent nitridation under flowing high purity ammonia gas at 1200°C to convert Ga_2O_3 into GaN. Several GaN and AlGaN samples were synthesized with europium dopants and characterized by XRD and spectroscopic measurements. While these samples exhibited fluorescence from Eu^{3+} , a detailed analysis of the XRD pattern of AlGaN samples did not indicate formation of a solid solution. It is most likely that the nitridation process failed to convert Al_2O_3 to AlN, and thus, an alloy of nitrides of Al and Ga was not formed. For this reason, we chose an alternative synthesis technique in which an aluminum hexafluoride was the precursor for AlN instead of Al_2O_3 . By avoiding an oxide precursor, the oxygen contamination in the nitride product was also reduced.

The alternative synthesis technique was a three-step solution process that involved converting nitrates in solution to hydroxides (Step 1), then hydroxides to fluorides (Step 2), and finally from fluorides to nitrides (Step 3). While both hexafluoride and tetrafluoride were observed during the intermediate step, the final product consisted of pure AlN after nitridation in high purity NH_3 at 900°C for 2.5 hr. The brown body color that was observed for the fluoride precursor due to residual basic nitrate was also

eliminated after nitridation. Once the optimal parameters were established, the same technique was extended to GaN, AlGaIn and AlN doped with rare-earth ions.

In order to improve the purity of our powders, we systematically analyzed the product from each step of the reaction by XRD and EDS for phase purity and oxygen content, respectively. It was discovered that oxygen impurity resulted from:

1. incomplete conversion of hydroxide to fluoride during Step 2;
2. residual water in the fluoride precursor as a result of incomplete drying;
3. water as the washing agent;
4. oxygen from ambient atmosphere during a 12 hr precursor drying period at 200°C, as well as from the atmosphere during nitridation.

To eliminate these sources of oxygen, the following modifications were implemented:

1. excess ammonium fluoride was used to drive the reaction to completion during Step 2;
2. the fluoride precursor was filtered and dried in a vacuum desiccator;
3. the more volatile absolute ethanol was used to quickly evaporate the residual water as the washing agent;
4. a short drying period of 1 hr in nitrogen at 350°C was used;
5. the nitridation system was redesigned to eliminate leaks of air to the system;
6. high purity nitrogen (99.999%) and ammonia (99.9995%) gases were used during nitridation.

The most important step in oxygen reduction was the elimination of residual water from the fluoride precursors. When the precursors were dried at 200°C for 12 hr, water molecules could react and introduce oxygen ions into the lattice of the precursors. Removal of these oxygen ions during nitridation would then be more difficult. Once the 200°C drying step was eliminated, the product nitride consistently had a lower oxygen content and oxygen-to-nitrogen ratio. Another improvement was in the use of absolute ethanol as the washing agent to replace water. The higher vapor pressure of ethanol enhanced evaporation and therefore, reduced the oxygen content. Fluoride precursors washed with ethanol no longer contained oxygen as measured by EDS. These changes allowed the reduction of oxygen in GaN to ~ 4 at% or an oxygen-to-nitrogen ratio of 8%. While the GaN sample still had a light yellow body color, it was visibly improved over commercial GaN powders, which have darker yellow tints and more than 10 at% oxygen.

Synthesis of Pure AlN, GaN and GaAlN Alloy

After successfully synthesizing pure AlN, we measured its reflectance and emission spectra. The best AlN sample showed a band edge near 5.2eV, lower than 6.28eV of pure AlN. Since no secondary phase was detected by XRD, the band edge shift could be attributed to oxygen impurities that shifted the band gap to a lower value. The synthesis conditions were then used to make GaN, GaAlN, and RE³⁺ doped AlN and GaN.

Several GaN samples were synthesized under various drying conditions to minimize oxygen content. It was found that the nitridation step with minimal drying produced the best two samples, with a band edge around 3.45eV. Both samples have

lighter body color compared to a commercial sample. However, both samples that exhibited excitonic emission at 365nm also had a broad defect emission.

GaAlN samples were also synthesized, with the intension of alloying 10 at% and 20 at% Al into the GaN lattice. XRD measurements indicate the final composition to be $\text{Ga}_{0.96}\text{Al}_{0.04}\text{N}$ and $\text{Ga}_{0.8}\text{Al}_{0.2}\text{N}$ calculated by Vegard's law. The reflectance measurements of these samples also showed a shift in band edge toward a shorter wavelength, indicating successful synthesis of an alloy of GaN and AlN.

Synthesis of RE^{3+} Doped Nitride Powders

The solution approach was used to synthesize the following $\text{AlN}:\text{RE}^{3+}$ samples, in which the concentration of dopant is in atomic percent:

- $\text{AlN}:\text{Eu}^{3+}$ (1%), $\text{AlN}:\text{Eu}^{3+}$ (5%), $\text{AlN}:\text{Er}^{3+}$ (1%)
- $\text{AlN}:\text{Dy}^{3+}$ (1%), codoped $\text{AlN}:\text{Eu}^{3+}$ (1%), Dy^{3+} (1%)
- $\text{AlN}:\text{Tb}^{3+}$ (1%), codoped $\text{AlN}:\text{Eu}^{3+}$ (1%), Tb^{3+} (1%)
- $\text{AlN}:\text{Tm}^{3+}$ (1%), codoped $\text{AlN}:\text{Dy}^{3+}$ (1%), Tm^{3+} (1%)
- $\text{AlN}:\text{Pr}^{3+}$ (1%)

Several samples of $\text{GaN}:\text{RE}^{3+}$ were made, in which the dopants were Tb^{3+} , Dy^{3+} , Eu^{3+} , and Tm^{3+} . In addition to $\text{GaN}:\text{Eu}^{3+}$, $\text{GaN}:\text{Tb}^{3+}$ (1%) powder showed fluorescence. XRD of these powders indicated the formation of a single nitride phase. The emission properties of these powders were then further studied.

Several compositions of $\text{GaN}:\text{Tm}^{3+}$ powders were synthesized with the Tm^{3+} concentration of 0.5, 1 and 5 at%; however, no near band edge emission (NBE) or Tm^{3+} emission were observed. Yet, by combining several batches of $\text{GaN}:\text{Tm}^{3+}$ powders, a pressed target for PLD was fabricated and subsequently used to deposit a $\text{GaN}:\text{Tm}^{3+}$ thin film. XRD of the film indicated a randomly oriented polycrystalline structure. When analyzed under cathodoluminescence (CL), a strong NBE was observed. This suggests that the quality of PLD thin films was improved compared to the original powders, and defects were significantly reduced. This result emphasized our reasoning that powders are suitable for the initial investigation of emission properties, but high quality thin films may reveal features not originally observed in even high purity powders. Also, the emission characteristics of the RE^{3+} doped PLD thin films and MOCVD films may be compared.

Composition of Alloy Nitride Powders

EDS was routinely used to analyze the chemical composition of our powders. In combination with XRD and fluorescence measurements, EDS was used to:

1. determine the presence of RE ions in the lattice;
2. compare the oxygen content between each powder sample;
3. determine the gallium and aluminum ion content for alloy samples.

The elemental composition is an average of data from five to eight spots. Comparing the oxygen-to-nitrogen ratio in each nitride powder indicated the relative level of defects. High O/N ratio indicated that RE^{3+} were likely surrounded by oxygen

ions. High Ga/N ratio (> 1.0) suggested nitrogen vacancies. Combined with XRD and the use of Vegard's law, we also determined the amount of aluminum incorporation for alloy samples, and found that drying the precursors in nitrogen was more effective than drying in air to help alloy formation.

II.c Spectroscopic Measurements

The spectroscopic studies focused on four different aspects: defect structure of doped nitrides, effect of alloying and oxygen defects on the band gap, fluorescence from both doped and undoped nitride hosts, and saturation of emission under intense photo-excitation intensity.

Reflectance Measurements and Determination of Band Edge

It is not possible to measure the band gap of undoped nitride powders using standard transmission measurements; therefore, the band gap of both doped and undoped materials were inferred from reflectance measurements. Reflectance as a function of wavelength in the spectral range of 200-500 nm was measured for powder samples pressed to a plaque. The remission function extracted from the reflectance spectrum was used to obtain the band gap of the material. In spite of a weak assumption regarding the invariance of scattering coefficient of the particles with wavelength, the approach described below offers a reasonable estimate of the band gap.

Using the Kubelka-Munk method to describe the reflectance spectrum of a thick plaque, the remission function¹, $f(\lambda)$ as a function of wavelength, λ , is defined as :

$$f(\lambda) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{\mu(\lambda)}{\beta} \quad (1)$$

where R_∞ is the reflectance of an infinitely thick powder sample, μ is the absorption coefficient, and β is the scattering coefficient. Assuming that the scattering coefficient depends weakly on wavelength, the absorption coefficient can be assumed to be proportional to the remission function.

$$\mu = Cf(\lambda) \quad (2)$$

Thus, from the remission function one could easily extract the band gap of the material.

A typical reflectance spectrum of a powder sample, in this case that of undoped AlN is shown in Fig. 1 and the corresponding remission function, μ/β in Figure 2.

Figure 1. Reflectance spectrum of a sample of undoped AlN

Figure 2. Remission function of undoped AlN

The reflectance spectrum clearly shows absorption in the visible region. Two absorption bands are easily noted in Figure 2. These absorption bands clearly show presence of point defects in AlN which absorb in the visible region. Assuming that the scattering coefficient β is constant over the wavelength range between 200 and 300 nm, the direct band gap E_g for AlN:Dy can be calculated according to the relation $(\mu h\nu)^2 \sim h\nu - E_g$. By the extrapolation of a linear regression to $(\mu h\nu)^2 = 0$ in a plot of $h\nu$ vs. $(\mu h\nu)^2$,² the bandgap energy determined for sample SDH014 is 4.68eV as shown in Fig. 3.

Figure 3. Band gap determined from absorption spectrum of AlN powder

Using this approach, the band gaps as well as other absorption features were measured for most of the powder samples. Some of the interesting observations are noted below:

- The powder samples of GaN showed absorption in the visible region. Most of the samples showed yellow body color similar to commercially available samples. This body color has been usually attributed to oxygen defects, O_N . The presence of oxygen in most of the samples has been established by EDS measurements. Annealing did not improve the body color of GaN.
- Typical GaN samples had a band gap of ~ 3.4 eV, which is comparable to that of GaN thin film or single crystal measurements. However, the band edge does not develop sharply as one would expect. We believe that this could be due high oxygen content of the powder samples.
- The powder samples of AlN had band gaps of 4.6-5.2 eV. This is substantially smaller than that reported for AlN of 6.2 eV.³ This lowering of the band gap is attributed to the high oxygen content of the powder samples. From remission measurements, the absorption edge of the undoped AlN sample appears to be shifted to lower energy ~ 5.2 eV (238 nm) compared to the band gap of AlN, ~ 6.2 eV. Trinkler and Brezina⁴ attribute the main PL excitation band in AlN ceramics at 245 nm to oxygen related centers. Considering the nature of chemical bonding of Al and O atoms, the corresponding donor level would have the characteristics of an anti-bonding sp^3 -hybridized state of Al and O, since all the bonding states are fully occupied and belong to occupied states in the valence band. The anti-bonding levels of Al-N belong to the unoccupied conduction band states of the host material. In this sense, this impurity induced donor level due to an oxygen atom substituting for a nitrogen atom can be viewed as a perturbed state at the bottom of the conduction band. At the level of oxygen concentration present (2-10%) in the samples in this study, these localized levels lead to extended states and energy bands.

Since this orbital is obtained due to the lowering of a state from the conduction band, the corresponding energy level will lie close in energy to the bottom of the conduction band, and the associated wave function will have significant overlap with other extended states at the bottom of the conduction band. From first order perturbation theory, it can be easily shown that the first order correction to the wave function will lead to a significant mixture of the donor wave function with the extended states near the bottom of the conduction band. Thus, with increasing oxygen concentration, these perturbed wave functions will overlap through the admixture of the extended states of the host and will start forming an energy band. Unlike the deep level or the localized impurity states, the states associated with oxygen defects will rapidly lead to delocalized states with increasing oxygen concentration. Results from theoretical calculations⁵ to be discussed later support this picture. From this perspective, the host in this study could be considered as a crystalline and homogeneous material having the composition $\text{AlN}_{1-x}\text{O}_x$ ($0.01 < x < 0.05$) with a band gap near 5.2 eV

○ We made several samples of GaN and AlN alloys using a combustion synthesis approach. The formulation was $\text{Ga}_{1-x}\text{Al}_x\text{N}$ with x varying from 0.1 to 0.9. A shift in bandgap was not observed with the change in alloy composition suggesting incomplete conversion of oxides of aluminum and gallium to corresponding nitride alloys (Figure 4). X-ray diffraction measurements and EDS measurements also support this conclusion. The combustion synthesis approach seemed to introduce regions of alumina, which is difficult to convert to AlN during the annealing steps. Based on these results, it was decided to use the solution-based approach for synthesizing nitride powders instead of the combustion method.

Figure 4. Reflectance from a batch of $\text{Ga}_{1-x}\text{Al}_x\text{N}$ alloys with x varying from 0.1 to 0.9.

The reflectance measurements showed that it is indeed difficult to synthesize “high purity” nitride powders. The samples generated during this study are of comparable quality to those generated by other techniques or available commercially, except the

method in which Ga metal is directly converted to GaN using Bi as a catalyst.⁶ The GaN powders produced by this approach appear to be comparable to those of thin films deposited by epitaxial methods.

However, the powders prepared by the solution approach were considered adequate for studying fluorescence from rare earth ions. It was later found that powders made by this approach could lead to high quality thin films by PLD deposition. The PLD films of GaN activated by Tb^{3+} and Tm^{3+} made using this approach will be discussed later.

Emission from Undoped Nitride Powders

For all the samples, photo-luminescence (PL) spectra and photo-luminescence excitation spectra (PLE) were recorded at room temperature and at low temperature, if needed, in order to understand the luminescence processes in nitride hosts. The room temperature PL and PLE spectra were measured with a SPEX DM 3000F spectro-fluorometer with 0.22m SPEX 1680 double monochromators. A 450W Xe-lamp was used as the light source. The photons were detected using a cooled Hamamatsu R928 photomultiplier tube. Both PL and PLE spectra were corrected for the spectral response of the setup. The nitride powder samples were also measured with a pulsed laser. The 248 (KrF) and 351 (XeF) nm lines from a Compex 110 Excimer laser (Lambda Physik) were used as the excitation sources. Various sites for the rare earth ions in nitride powders were studied by site-selective spectroscopy. By carefully tuning the excitation wavelengths using the Xe lamp, the optically active RE^{3+} occupying different sites can be selectively excited.⁷ The excitation wavelengths were selected based on the PLE spectra of a sample.

The cathodoluminescence (CL) spectrum was often obtained for a quick assessment of the quality of the sample. Since electroluminescence was not a part of this project, the focus was on the nature of luminescence upon excitation near the band edge. At this excitation energy, the PL spectrum should reflect the response of a material upon injection of electron and hole pairs (e-h) under forward biasing conditions. Upon exciting near the band edge in a direct gap material, electrons and holes are created which readily recombine to form the e-h pairs or excitons. Once the e-h pairs are formed, the luminescence mechanism does not depend anymore on the nature of production of the e-h pairs. Thus, apart from the fact that efficiency of e-h pair formation upon electron and hole injection into the active layer could be different from the excitation of the host near the band edge, the latter provides a reasonable estimate of the performance of the material under electroluminescence. However, at excitation energies greater than the band gap, the quantum efficiency of the material decreases rapidly due to nonradiative surface recombination due to increasing absorption of radiation near the surface.⁸

A typical emission spectrum from GaN powder at room temperature (RT) shows a sharp, relatively narrow band emission near ~365 nm accompanied by a broad band emission (red band peaking near 700 nm) and a weak blue emission band. The narrow band emission is the excitonic emission, the intensity of which often depends on the quality of the material. Figure 5 shows the emission spectrum for $\text{Ga}_{0.7}\text{Al}_{0.3}\text{N}$ under 320nm excitation at RT. The spectrum is dominated by red defect emission. Locations of various well-identified bands associated with GaN are indicated.

Figure 5. RT emission spectrum of $\text{Ga}_{0.7}\text{Al}_{0.3}\text{N}$

The width of bandgap or excitonic emission is large, about $1,900 \text{ cm}^{-1}$ and is accompanied by an extensive shoulder on the long wavelength side. For 270 nm excitation, the band edge emission either reduces strongly or disappears nearly completely (e.g. $\text{Al}_x\text{Ga}_{1-x}\text{N}$ for $x=0.2, 0.4$ and 0.9).

The broadband emission is mainly due to the rich defect structure of GaN. The defects have been extensively investigated in the literature⁹ and are of considerable interest for improving the performance of nitride based luminescent devices. It is also interesting to note that some of the defects have fast radiative time, which could be revealed by time-resolved spectroscopy. In Fig. 6, the emission spectra of the same material is shown with 15 and 900 ns gate width upon excitation at 248 nm. The blue emission is suppressed at a longer detection time.

The defect structure of nitrides and emission from these defects are very complex. They need to be investigated further in order to understand their effect on the overall performance of GaN and its alloys. In pure GaN powder, defect emission was very strong compared to GaN and AlN alloys. In all of the alloys, we also observed alumina as a secondary phase. It is most likely that the aluminum nitride acts as an oxygen-getter, thus improving the purity of the GaN phase, and thus contributing to reduction in defect emission.

Figure 6. Time resolved emission spectrum of $\text{Ga}_{0.7}\text{Al}_{0.3}\text{N}$ at excitation near 248 nm

In contrast to GaN, emission from AlN powders was mostly a broadband emission (Figure 7). The band gap was determined from the reflectance measurements to be near 260 nm. The decrease in band gap compared to AlN single crystals is believed to be due to oxygen contamination. Therefore, the host lattice was probed by exciting at 254 nm. The corresponding emission is most likely due to several point defects, being composed of several bands. The excitation spectrum corresponding to the peak of the broad emission band is also shown in Fig. 7. It clearly reveals that this band could be excited near 300 nm below the band gap energy as well as near 260 nm. The weak peak near 260 nm clearly suggests energy transfer from the host to the defects.

Emission from Nitrides Doped with RE^{3+}

We extensively investigated RE^{3+} -activated nitride powders in order to understand the luminescence process of RE^{3+} in nitride hosts, to identify RE^{3+} and host lattices combinations for generating white light, and to determine optimum compositions for maximizing the efficacy of nitride-based active layers. Results from luminescence measurements from powder samples were intended to be used for “thin film” deposition by metal organic vapor phase epitaxy (MOVPE).

Figure 7. RT emission and excitation spectrum of AlN powder samples. The sharp peak near 350 nm is an artifact of the measurement.

Although the reflectance measurements and the emission spectra from undoped nitride hosts indicated a high oxygen concentration, preliminary measurements of GaN doped with Eu^{3+} showed enhanced emission compared to undoped GaN (Figure 8). We focused on AlN as the host material, because it has a large band gap and thus provided a larger energy regime to probe the multiplet energy level of RE^{3+} . Results from these studies indicated the likelihood of obtaining red, green, yellow and blue emission from Eu^{3+} , Tb^{3+} , Dy^{3+} , and Tm^{3+} ions, respectively. We assumed at the beginning of the study that any ion that fluoresces in AlN would do so in GaN, but we did not find this to be the case. We also did not observe any characteristic intraband $f \rightarrow f$ transition for Er^{3+} in AlN and GaN. We believe that this has to do more with the purity of the material than any other causes since emission in the green due to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ was reported for Er^{3+} in GaN powder recently.¹⁰

We made samples of AlN doped with Eu^{3+} , Pr^{3+} , Tm^{3+} , Er^{3+} , Dy^{3+} and Tb^{3+} . Of these samples, strong intraband $f \rightarrow f$ transitions were observed for Eu^{3+} , Tb^{3+} , Dy^{3+} and Tm^{3+} . The PL spectra for these ions are shown Figures 8-12. Various transitions observed in the PL and PLE spectra are listed in Table 1. More details on the corresponding energy level transitions could be found in the publications listed in the Appendix.

Figure 8. Fluorescence from GaN:Eu (10%) and GaN powder

AlN:Tm³⁺ is considered a candidate for blue emission. ZnS:Tm³⁺ is used as a blue emitter in CRT applications ($^1D_2 \rightarrow ^3F_4$ / $^1G_4 \rightarrow ^3H_6$ ~460 nm). Figure 9 compares the room temperature PL spectra of AlN:Tm³⁺ with that of an undoped AlN sample excited at 250 nm using a Xe lamp. It is interesting to note that defect emission is substantially quenched in the presence of Tm³⁺ indicating efficient energy transfer from the host to the rare earth ions. The spectroscopic assignments of the emission peaks are indicated in Fig. 9. The strongest emission with the peak wavelength of 792 nm is attributed to the $^3H_4 \rightarrow ^3H_6$ transition of Tm³⁺. The blue emission near 481 nm is assigned to the $^1G_4 \rightarrow ^3H_6$ transition, which is of interest for generating white light when UV-emitting GaN is used as a host. Unfortunately this transition is weak compared to the spin allowed infrared transition, $^3H_4 \rightarrow ^3H_6$. In addition to these two major peaks, there are two other peaks assigned to $^1D_2 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3H_4$ transitions near 360 nm and 655 nm, respectively.

Table 1. Summary of RE³⁺ intra-configurational transitions from AlN. The transitions of interest for white light generation are highlighted.

RE ³⁺	λ (nm) at room temperature	Transitions Assignments
Dy	452	$^4M_{21/2} - ^6H_{13/2}$
	476	$^4M_{21/2} - ?$
	485	$^4F_{9/2} - ^6H_{15/2}$
	575	$^4F_{9/2} - ^6H_{13/2}$
	669	$^4F_{9/2} - ^6H_{11/2}$
	757	$^4F_{9/2} - ^6H_{9/2}, ^6F_{11/2}$
	349	$^6H_{15/2} - ^6P_{7/2}, ^4M_{15/2}$
	364	$^6H_{15/2} - ^4P_{3/2}, ^6P_{3/2}$
	380	$^6H_{15/2} - ^4M_{19/2}$
	390	$^6H_{15/2} - ^4I_{13/2}, ^4K_{17/2}$
	402	$^6H_{15/2} - ^4M_{21/2}$
	424	$^6H_{15/2} - ^4G_{11/2}$
	452	$^6H_{15/2} - ^4I_{15/2}$
	475	$^6H_{15/2} - ^4F_{9/2}$
Tm	356	$^3H_6 - ^1D_2$
	481	$^3H_6 - ^1G_4$
	655	$^3H_4 - ^1G_4$
	792	$^3H_6 - ^3H_4$

Tb	378	${}^7F_6 \rightarrow {}^5D_3$
	416	${}^7F_5 \rightarrow {}^5D_3$
	435	${}^7F_4 \rightarrow {}^5D_3$
	484	${}^7F_6 \rightarrow {}^5D_4$
	542	${}^7F_5 \rightarrow {}^5D_4$
	585	${}^7F_4 \rightarrow {}^5D_4$
Eu	621	${}^7F_3 \rightarrow {}^5D_4$
	364	${}^7F_0 \rightarrow {}^5D_4$
	378	${}^7F_0 \rightarrow {}^5L_7, {}^5G_2$
	465	${}^7F_0 \rightarrow {}^5D_2$
	526	${}^7F_0 \rightarrow {}^5D_1$
	536	${}^7F_1 \rightarrow {}^5D_1$
	592	${}^5D_0 \rightarrow {}^7F_1$
	610	${}^5D_0 \rightarrow {}^7F_2$
	655	${}^5D_0 \rightarrow {}^7F_3$
	707	${}^5D_0 \rightarrow {}^7F_4$

Figure 9. PL spectrum from Tm^{3+} in AlN. The broad band emission is due to AlN host.

The $^5D_4 \rightarrow ^7F_5$ transition in the yellow-green region from Tb^{3+} has often been utilized as the green component in white light emitting blends of luminescent materials. Figure 10 shows the room temperature PL spectra of an AlN:Tb sample excited at 250 nm. The narrow band f→f intra-configurational transitions associated with the Tb^{3+} appear to be superimposed on a background emission from the host lattice. Although emission from the defects in the host lattice is stronger than that for Tm^{3+} , the emission from Tb^{3+} appears to be quite efficient. Various emission peaks have been given spectroscopic assignments (Table 1) by comparisons with data from the literature for AlN:Tb.^{11,12} The strongest emission near 542 nm is attributed to the $^5D_4 - ^7F_5$ transition of Tb^{3+} . This transition will be useful for application of this material as a yellowish green emitter in solid state lighting applications.

Figure 10. PL spectrum of Tb^{3+} in AlN

Figure 11 shows the room temperature PL spectra of an AlN:Eu sample. In contrast to other samples discussed, the emission from the defect states appears to be quite strong with 250 nm excitation. Nevertheless in the spectral range from 550 nm to 700 nm, one observes sharp multiplet transitions within the f-manifold. Upon exciting Eu^{3+} directly at 464 nm, corresponding to a transition from the ground level, 7F_0 to an excited level, 5D_2 , a well resolved spectrum for Eu^{3+} in AlN is obtained with almost no defect emission. In Table 1, a list of observed f→f transitions for Eu^{3+} in this sample is provided.

In Fig. 11 the strongest emission with the peak wavelength near 610 nm is attributed to the hypersensitive $^5D_0 - ^7F_2$ transition of Eu^{3+} . This transition is particularly interesting for application of this material as a red emitter in solid state lighting applications. The peak energy for this $^5D_0 - ^7F_2$ hypersensitive transition in GaN has been reported at energies varying within 10 to 15 nm depending on the method of preparation. It is usually observed at 621-622 nm in GaN:Eu³⁺ and AlN:Eu³⁺ thin films. In contrast, its location near 612 nm is indicative of oxygen in the neighborhood of Eu^{3+} in AlN. For a detailed discussion on the controversy surrounding the location of the $^5D_0 - ^7F_2$ transition, refer to Ref. 13.

Figure 11. Emission from AlN:Eu³⁺ in AlN upon excitation near 250 nm

Figure 12 compares the room temperature PL spectra of an AlN:Dy³⁺ sample and an undoped AlN sample excited at 250 nm using a Xe lamp.¹⁴ The PL spectrum of AlN:Dy³⁺ is dominated by a strong yellow emission at 575 nm, which is attributed to the hypersensitive $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition. The defect emission from the host is effectively quenched in AlN:Dy³⁺. For LED applications, it is of particular importance to harvest all the e-h pair energies through the Dy³⁺ luminescent center when e-h pairs are created either electrically under forward bias conditions of a LED hetero-structure or direct photo-excitation by photons with energies exceeding the band gap energy. However, with increasing excitation intensity under pulsed laser excitation conditions, emission from defects dominates the spectrum.¹⁴

Figure 12. PL spectrum of AlN:Dy³⁺

Emission from Codoped Samples of AlN

One can generate white light by codoping with rare earth ions capable of emitting in blue, green and red part of the spectrum upon excitation near the band edge. This concept was further explored for three different combinations of rare earth ions in AlN host: AlN: Tb³⁺, Eu³⁺, AlN: Eu³⁺, Dy³⁺ and AlN: Dy³⁺, Tm³⁺. To the best of our knowledge, the only other attempt to co-dope a nitride host was by Lee et al.¹⁵ In our case, we obtained simultaneous emission from AlN:Eu³⁺, Tb³⁺ and AlN: Dy³⁺, Tm³⁺ samples. In the case of AlN sample codoped with Dy³⁺ and Eu³⁺, we observed emission only from Dy³⁺ ions. The absence of fluorescence from Eu³⁺ in this sample could be due to very low concentration of Eu³⁺.

Figures 13 (a) and (b) show the room temperature PL spectra of an AlN sample codoped with Tb³⁺ and Eu³⁺. The narrow band f-f intra-configurational transitions associated with both Tb³⁺ and Eu³⁺ are clearly observed. The spectrum between 300 and 600 nm [Fig. 13(a)] is dominated by the intra-configurational f-f shell transitions of Tb³⁺, while between 580 and 750 nm [Fig. 13(b)] the f-f transitions involving Eu³⁺ are clearly observed.

It was also observed from the PLE spectra for Eu³⁺ that Eu³⁺ could be excited by energy transfer from Tb³⁺ in addition to being directly excited by the host. As we observed from the singly doped samples, energy transfer from host to Tb³⁺ or Dy³⁺ is more efficient than that for Eu³⁺. Therefore, energy transfer from Tb³⁺ to Eu³⁺ subsequent to excitation of Tb³⁺ due to host excitation will be very helpful in optimizing the host for Tb³⁺ excitation and then one could codope with Eu³⁺ for simultaneous green and red emission.

Figure 13 a. Emission from Tb^{3+} in AlN codoped with Tb^{3+} and Eu^{3+}

Figure 13 b. Emission from Eu^{3+} in AlN codoped with Tb^{3+} and Eu^{3+}

White-light emission was obtained from a co-doped AlN:Dy(1%), Tm(1%) sample. Dysprosium and thulium-related emissions have been observed under CL for the AlN:Dy(1%), Tm(1%) sample, as shown in Fig. 14. The peak assignments have been made according to those previously observed in AlN:Dy(1%) (SDH014) and AlN:Tm(1%) . The estimated color coordinates for the codoped AlN sample are $x=0.437$ and $y=0.424$ with correlated color temperature of ~ 1300 K (Figure 15). The spectral shape was manually extracted from Figure 14. However, XRD measurements as shown in Fig. 16 indicate the possible presence of Dy_2O_3 and/or Dy_2N_3 , suggesting that oxygen impurity might be needed for luminescence from the dopant.

Figure 14. CL spectra of AlN: Dy³⁺, Tm³⁺ compared with PL spectra of AlN:Dy³⁺ and AlN:Tm³⁺

Figure 15. CIE chromaticity diagram x,y. The color coordinates of AlN: Tm, AlN: Dy and AlN:Dy, Tm indicated by blue triangle, red square and green circle, respectively.

Figure 16. XRD measurements indicate the presence of AlN along with Dy₂O₃ and Dy₂N₃ phase

Fluorescence from RE³⁺ in GaN

From our investigation of fluorescence from RE³⁺ in AlN, it was clear that the candidate ions for red, green, blue and yellow emission are Eu³⁺, Tb³⁺, Tm³⁺ and Dy³⁺. Therefore, it was decided to make GaN powders using these earth ions as the activator ions. Samples of GaN activated with Eu³⁺ and Tb³⁺ ion showed PL spectra similar to those with AlN host. However, with Dy³⁺ and Tm³⁺ doping, fluorescence which could be definitively attributed to Dy³⁺ or Tm³⁺ was not observed.

A very intriguing observation was made with respect to GaN. When we could reduce significantly oxygen defects using an ethanol wash, the rare earth ions did not fluoresce. It appears that oxygen is necessary to incorporate RE³⁺ into the nitride lattice. This was also confirmed with the AlN: Dy³⁺, Tm³⁺ sample as discussed. A similar observation has been also made by Hara et al.¹⁶ and Torvik et al.¹⁷

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Section III. Pulsed Laser Deposition of GaN: RE³⁺ Thin Films and Characterization

III.a Introduction

Our original approach to explore the behavior of thin films deposited by pulsed laser deposition (PLD) technique involves using rare earth activated nitride powders as targets. Structural and fluorescence data from such thin films were expected to be helpful in defining film characteristics for the MOVPE deposition techniques. We used this approach to deposit several films of GaN:Tm³⁺ and GaN:Tb³⁺. While the GaN:Tm³⁺ films did not show any fluorescence from Tm³⁺, GaN:Tb³⁺ films showed characteristic green emission near 546 nm due to 4f→4f transition under CL excitation.

III.b PLD Process

During this work Dr. Nestor Perea-Lopez and Dr. Gustavo Hirata from Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Ensenada, Baja California, México helped us to deposit films by PLD technique with their equipment at their laboratories. A schematic drawing of the PLD unit is shown in Figure 1.

Figure 1. Schematic diagram of the PLD system

In order to deposit a thin film, the corresponding powder was pressed into a circular disk and mounted on the rotating target stage. The reaction chamber was maintained in high vacuum. A YAG:Nd pulsed laser source irradiated the target at 355 or 532 nm. This caused the target material to evaporate and condense on the heated substrate across the chamber, mounted on the rotating heating stage. Sapphire single crystal oriented along the <001> direction was chosen as the substrate. The quality of the film depends on the laser power, substrate temperature, rotation of the target and substrate, deposition time, and ambient temperature and pressure. The deposition parameters for GaN:Tb³⁺

and GaN:Tm³⁺ films reported are listed in Table 1. After a thin film was deposited, it was further annealed at 1000°C in NH₃ in order to remove any residual oxygen.

Table 1. PLD parameters for GaN:Tb³⁺ and GaN:Tm³⁺ thin films

RE dopant	Tm	Tb
Substrate type	GaN/Al ₂ O ₃	GaN/Al ₂ O ₃
Laser power (mW)	300, 250	300, 250
Laser wavelength (nm)	355	532
Laser spot radius (cm)	0.15	0.2
Laser rep rate (Hz)	3	10
Surface fluence (J/cm ²)	0.444, 0.370	0.239, 0.199
Deposition time (min)	22, 20	2
Vacuum before (Torr)	1x10 ⁻⁵	1x10 ⁻⁵ , 7x10 ⁻⁶
Vacuum during dep. (mTorr)	400	100
N ₂ pressure (mTorr)	400	100
Target-substrate dist. (mm)	40	40
Target rotation (rpm ccw)	24	20
Substrate rotation (rpm cw)	8	5
Substrate temperature (°C)	650	650

III.c PLD Deposition and Characterization of GaN: RE³⁺ Thin Films

GaN:Tm³⁺

While several compositions of GaN:Tm³⁺ powders were synthesized, no near band edge emission (NBE) or Tm³⁺ emission were observed. Combining several batches of GaN:Tm³⁺ powders, a pressed target for pulsed laser deposition (PLD) was fabricated, and was subsequently used to deposit a GaN:Tm³⁺ thin film.

Two GaN:Tm films were deposited by PLD from a pressed powder target. The target was made by mixing batches of powder from the solution method, pressing into a pellet, and annealing at 1200°C in NH₃. The films were deposited onto sapphire substrates in an ultra high vacuum chamber using an Nd:YAG laser at 355nm. The target was rotated at 24 rpm, while the substrate was rotated at 8 rpm. During deposition, the substrate was heated to 650°C. Following deposition, the GaN: Tm³⁺ films were annealed again at 1000°C in NH₃.

As shown in Fig. 2 and 3, XRD reveals a less textured film for Film 1 than Film 2. While the films are expected to grow along the <001> direction, Film 1 shows a somewhat preferred <101> direction. Since the only difference in growth conditions between the two films is the laser power strength, this suggests that lower laser power produced a thinner but a more textured film.

Figure 2 XRD pattern of GaN:Tm³⁺ Film 1 made by PLD.

Figure 3 XRD pattern of GaN:Tm³⁺ Film 2

The CL spectra for both samples from the center of the sample are shown in Figure 4. The band edge emission can be clearly observed at 367 nm. This suggests that the crystallinity of PLD thin films was improved compared to the original powders, and defects had been significantly reduced from the powders. However, we did not observe luminescence at 463nm, 466nm, and 479nm from Tm³⁺ reported earlier for GaN prepared by an ion implantation approach.¹ The dominant transition $^1G_4 \rightarrow ^3H_5$ which is expected between 770-840 nm was not observed. In addition to the band edge emission, some minor peaks were observed at about 422 and 446 nm. The source of these emissions could not be definitively identified in the absence of strong $^1G_4 \rightarrow ^3H_5$ due to Tm³⁺. However, these peaks are close to $^3P_1 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_4$ of Tm³⁺ calculated using energy levels of Tm³⁺ in AlN.² The sharp peak observed at 695 nm is due to the sapphire substrate. Some Eu contamination has been observed on Film 2 as a result of handling

and not as a result of synthesis. It suggests that GaN:Eu³⁺ thin films may be fabricated by the PLD method.

Figure 4 CL emission from center of GaN:Tm films made by PLD

When the corners of both films were examined, a strong peak at 228 nm was observed in Film 1 (shown in Fig. 5). However, a broader peak was observed at 256 nm in Film 2. These emissions below the band edge could be from the substrate, as the 695 nm peak in Fig. 4 is also much more intense relative to that in Fig. 3, suggesting that the deposited layer is thinner near the substrate edge. The band edge emission relative to the background has also been reduced, showing some additional peaks at 305, 320, 422 and 446 nm. The peak at 684 nm for both films may be an instrumental artifact.

Figure 5 CL emission from a corner of GaN:Tm films made by PLD

GaN:Tb³⁺

Two GaN:Tb³⁺ films were fabricated at 300mW and 250mW laser power at a lower N₂ pressure and shorter deposition time than GaN:Tm³⁺ films. A preferred growth in the <001> direction can again be seen in Fig. 6. Lower laser power also produced a more oriented film, where peaks in the <100> and <101> direction are lower in intensity than the film fabricated at higher power.

Figure 6 XRD pattern of GaN:Tb films made by PLD with 300mW and 250mW laser power.

CL emission for the film fabricated at 250mW is shown in Fig. 7. Various transitions originating from 5D_4 level of Tb^{3+} are indicated including the classical green transition to the 7F_5 level. These transitions were also observed in the source powder, with the exceptions of the NBE at 370nm. This indicates that the lower defect level in the film improves the quality of the material. When compared to the $GaN:Tm^{3+}$ film, however, it has much lower band edge emission intensity even at higher excitation voltage and current. This is indicative of more efficient energy transfer from the GaN host to Tb^{3+} than to Tm^{3+} , thereby reducing its band edge emission. The results demonstrate the possibility of using $GaN:Tb^{3+}$ as the green emitter in a white light source.

Figure 7 CL emission of GaN:Tb film made by PLD at 250mW.

III.d Conclusions

Deposition of thin films using PLD started in the final year of the project. Our investigation was limited only to two types of thin films. However, our experience shows that this method together with a reliable method of powder synthesis provides a useful approach to making thin films on a shorter time scale and of quality comparable to MOVPE deposition method. In our opinion, this approach could be used to explore the parameter space of thin films in an efficient manner for optimizing thin film behavior. These results should then be implemented in the deposition process by the MOVPE method.

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Section IV. Designing the MOVPE Reactor

IV.a Design and Assembly of the MOVPE Reactor

One of our main objectives has been to dope RE ions into nitride-based semiconductor films using a metal organic vapor phase epitaxy (MOVPE) method which is the preferred technique for modern LED chip manufactures. The primary motivation for employing an MOVPE deposition method is to facilitate a smooth technology transfer as it is the preferred technique for modern LED chip manufactures. Since doping with RE ions occurs as the nitride deposition progresses, it should be relatively easy to integrate RE doping into existing nitride growth processes.

Our plan was to construct an MOVPE system that would be capable of depositing Group III nitrides using typical process conditions, but which would also be flexible enough to allow sufficient modification of the growth conditions to enable RE doping of the films. For this purpose, an MOVPE nitride deposition system was designed and built that would simulate the operation of a commercial system but which also could be reconfigured relatively easily in order to explore a wider range of deposition parameters.

The system is essentially a single-substrate chemical reactor with the reactant gases flowing horizontally from left to right at atmospheric pressure as shown in Fig. 1. The deposition reactions occur within a custom-built quartz vessel in which the sapphire substrate (approximately 1 cm x 1 cm) is mounted on a wedge-shaped SiC-coated graphite susceptor. The susceptor, which is radiatively heated by two infrared heating lamps located outside of the quartz vessel, has a well bored into its downstream end for the insertion of a temperature-sensing and controlling thermocouple. The thermocouple itself is sheathed in a closed quartz tube so that it is not exposed to the reaction-chamber environment, but yet extends deeply enough into the body of the susceptor to accurately measure the temperature of the susceptor. To the extent that the quartz reactor is transparent to the infrared radiation, only the susceptor is directly heated. The heated susceptor, in turn, then heats the deposition substrate with which it is in contact. Such a reactor is described categorically as a “cold wall” reactor, even though natural convection processes will typically lead to wall temperatures higher than the ambient temperature. When the susceptor and substrate are heated to approximately 1000°C, as is typical, all other surfaces within the reactor are well below this temperature, and chemical reactions are expected to occur only at the surface of the growing film.

Figure 1. Quartz reactor vessel with susceptor and substrate

The quartz reactor vessel, including the susceptor and substrate, is the most critical component of the MOVPE reactor. Because of the subtle fluid dynamics issues that are described below, we have chosen to adopt a reliable design based on the literature and on the experience of Dr. Bing Han who assembled the reactor. The quartz vessel which contains the susceptor and substrate is a two piece construction with a clamped O-ring seal for loading and unloading the sample. The geometry of the quartz reactor vessel is such that the process gases enter via a 0.5 inch OD inlet tube which then flanges out into a 1 x 1 inch square cross-section tube where the susceptor is located (see Figure 1). The angle at which the inlet tube flanges out to the square tube must be small enough to allow relatively laminar gas flow across the quartz surfaces in this transition zone. The angle of the wedge-shaped susceptor defines the angle at which the laminar flowing process gases approach the growing film. This angle affects depletion of reactants as the process gases eventually reach the farthest (more downstream) regions of the growing film. If the substrate were horizontal (i.e. parallel to the gas flow stream), significant depletion of reactants would occur towards the extreme end of the substrate. The wedge-shaped susceptor allows a gradual constriction of the gas flow cross-section, resulting in an increasing gas velocity which serves to reduce the boundary layer thickness of gas near the film surface enough to allow increased reactant diffusion, thus compensating for depletion. Additionally, the cross-section of the quartz tube is large enough that the gas flow lines diverted by the wedge-shaped susceptor geometry remain laminar. Otherwise, turbulence and eddy currents could result. Because investigating the complexities of these fluid dynamics issues was beyond the scope of this project, a proven design was adopted as used in other published research on the deposition of nitrides via MOVPE.

The rest of the system hardware is dedicated to providing the appropriate gas mixtures for delivery to the quartz reactor vessel at a controlled and predetermined rate. Here, most of our efforts were spent customizing the system to create GaN deposition conditions that are compatible with RE doping. Although we have made undoped InGa_N films, the deposition of which will be a critical part of future development phases, the following discussion of the MOVPE reactor design will be restricted to the RE doping of GaN.

Our process for GaN film deposition follows relatively standard methodologies. Ammonia is used as the source of N and is supplied in “research grade” quality in the form of standard gas cylinders from commercial suppliers. Trimethylgallium (TMGa) is used as the source of Ga and is obtained in very high purity by commercial suppliers, in our case, packaged in a 150 ml stainless steel “bubbler”. High purity hydrogen is used as both the “carrier gas” to transport precursors from their respective bubblers and also as the “push gas” to appropriately dilute the other process gases, as well as to adjust the overall gas flow velocity. The system is also equipped with high-purity nitrogen to be used as a carrier gas and push gas for InGa_N deposition and as a vent-line purge gas. All gases are purchased in “research grade” purity and supplemented with an in-line purifier.

Figure 2. Simplified schematic of a standard GaN configuration with a RE precursor delivery line.

Between the gas cylinders and the quartz reactor vessel is a relatively complex labyrinth of tubing, valves, and mass flow controllers (MFC). Figure 2 shows a simplified schematic of a standard GaN configuration along with our preliminary RE precursor delivery line design. Fortunately, both TMGa and ammonia have sufficiently high vapor pressures at 25°C. However, all of the RE precursors do not. Thus, the RE bubblers and all downstream gas lines must be heated to temperatures high enough to obtain workable vapor pressures, but not so high as to promote premature thermal decomposition of the precursors. Uniform heating of the gas delivery lines was accomplished by wrapping with standard heating tape and then over-wrapping with fiberglass-based insulating tape. This must be done with extreme care so as to avoid “cold spots” that might cause precursor condensation within the heated gas delivery lines.

Two families of RE precursors have been used which will be discussed in more detail in the next section. The RE precursors with isopropylcyclopentadienyl ligands typically are used as liquids, with melting points about 60°C and use temperatures about 80°C. The RE precursors with beta-diketonate ligands typically are used as solids (by sublimation), with melting points about 185°C and use temperatures about 135°C. Hence, the precursor containers are typically heated to about 80°C and 135°C, respectively, and the corresponding delivery lines are maintained at 10°C to 20°C above these temperatures.

IV.b Hardware Upgrades

Various hardware upgrades were made throughout the duration of the project so as to optimize the delivery of the RE precursors to the reactor. Figure 3 represents a summary of these configuration changes:

- In order to be able to increase carrier-gas flow rates through the RE bubblers, pre-heating coils were fabricated and installed at the inlet of each bubbler. Pre-heating coils were also installed in other high-flow sections of the system to ensure that all gases mixing with the RE-containing gases were pre-heated to the same temperature before mixing so as to prevent condensation of the precursor.

- Lower-range mass flow controllers were installed in parallel with the existing (original) TMGa and ammonia mass flow controllers. A lower delivery rate of TMGa enables a slower film growth and consequently a higher RE-to-Ga ratio. The lower flow rate of ammonia was necessary to achieve the high Ga-to-N ratio required for Eu doping.

- It was found that to obtain sufficiently high RE-precursor vapor pressures, the use of temperatures in excess of the temperature limits of our Epifold manifold (in which the other process gases were mixed and controlled) was required. Therefore, a system of valves was assembled to allow the RE-precursor delivery lines to combine with the main gas stream at a point downstream of the manifold.

- It was found that RE precursors, particularly the beta-diketonate types, did not mix well with the TMGa/ammonia gas mixture. Therefore, a static mixer was installed.

Figure 3. MOVPE system upgrades to better accommodate RE doping

IV.c Choice of Precursors

One advantage of MOVPE over many other epitaxial techniques is the independent control of the molar flow of the different precursors. This, however, implies the availability of suitable precursors for each element of interest. Ideally, these precursors should be either gases (e.g., hydrides of column V elements such as NH_3 , PH_3 , or AsH_3) or liquids with high vapor pressure, which enables their transport in the gas line using a high purity gas as the carrier. Thus, solid and liquid precursors must be volatile at operating temperatures and pressures, and if heating is required to obtain a sufficient vapor pressure, thermal stability of the precursor over prolonged time is necessary.

In general, MOVPE precursors should possess the following desirable properties:

- High purity
- Substantial volatility at process temperatures
- Long-term thermal stability at bubbler or sublimator temperatures
- No self-decomposition at deposition temperatures
- Must adsorb or react with surface sites and release the desired element (and only that element)
- Must not etch the substrate or the growing film
- Availability at a reasonable price
- Should be safe to handle and preferably non-toxic

In the following sections, the precursors for the different reactants and dopants are discussed.

Precursor for Nitrogen

The most commonly used nitrogen precursor is ammonia (NH_3). However, it has a high thermal stability, which necessitates that III-V nitrides be grown at temperatures over 1000 °C. The high growth temperature restricts the choice of substrate materials (which must be physically and chemically stable at the growth temperature) and makes implementation of the nitride growth process more difficult (e.g., requiring the use of specially designed heaters). In an effort to decrease the growth temperature, less stable precursors, including hydrazine (N_2H_4),¹ asymmetric dimethylhydrazine [$\text{H}_2\text{N}_2(\text{CH}_3)_2$, 1,1-dimethylhydrazine],² and hydrogen azide, or hydrazoic acid (HN_3),³ have been used by different groups. These precursors, however, are generally either very toxic or have quite low vapor pressures. The low precursor pressures, combined with the high equilibrium nitrogen pressures over III-V nitrides, result in the formation of a high density of nitrogen vacancies and/or excess group III element deposition (e.g. Ga droplets). Consequently, NH_3 was chosen as the nitrogen precursor in the present study. It is interesting to note that NH_3 has been the precursor of choice for almost all III-V nitride-based commercial optoelectronic device structures.⁴

Precursors for Group III Elements

The alkyl-aluminum/gallium/indium sources are most often used as the metalorganic precursors for the group III elements because of their high vapor pressures and stabilities. The stability increases from In to Ga to Al. All the three precursors can be stored for indefinite periods at room temperature prior to use. The trimethyl sources are most often used due to their higher vapor pressures (plotted in Fig. 4) and greater stabilities. However, in reduced-pressure reactors, the use of triethylgallium and triethylaluminum have been found to result in significantly reduced carbon concentrations in GaAs and AlGaAs, since they pyrolyze without producing highly reactive CH_3 radicals, which are believed to be the main source of carbon in the epitaxial layers.⁵ A ball and stick diagram of a trimethyl precursor is shown in Fig. 5.

Figure 4. Temperature dependence of the vapor pressures of trimethylaluminum, trimethylgallium, and trimethylindium.

Figure 5. Structure of the trimethyl-metal precursors for aluminum, gallium, and indium.

Precursors for Rare Earth Elements

Unlike for group III elements where the suitable precursors have been thoroughly researched and are well-established, choosing the rare earth precursor remains a challenge. The vapor pressure of RE metal-organic precursors is typically very low. This makes the control of precursor delivery a significant challenge for several reasons, including the elevated source temperatures needed to increase vapor pressures, the changing surface area of the solid precursor material as it is consumed, and precursor condensation on colder internal surfaces of the upstream manifold, the reactor wall, and the downstream gas delivery system. (For solid metal-organic precursors, channels start to form where the precursor has been depleted. As time passes, the channels widen and the gas starts to travel at a high velocity through them without coming in contact with the precursor, or the precursor surface area exposed to the carrier gas decreases.)

The rare-earth precursors that have been used most often in the MOVPE deposition of III-V materials can be classified as either organometallic (in which the rare-earth atom is bonded directly to one or more carbon atoms) or non-organometallic (in which there are no metal-carbon bonds). The most widely used organometallic precursors are the so-called cyclopentadienyls which contain two or more cyclopentadienyl groups (5-member olefinic carbon rings, as shown in Fig. 6) bonded to the central metal atom. The non-organometallic precursors that have most often been used are the so-called β -diketonates in which each β -diketone ligand is bonded to the central metal atom via two metal-oxygen bonds (an example of which is shown in Fig. 7). These two classes of precursor compounds are separately described below.

Figure 6. Tris(isopropylcyclo-3,5-pentadienyl)erbium(III)

Figure 7. Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)Dysprosium(III)

1. β -Diketonates

The β -diketonate-type metal chelates are known for their volatility and were originally synthesized for the separation of metals by fractional sublimation and gas chromatography. In the 1970s they were utilized for the first time in CVD depositions.^{6,7} The good thermal stability and volatility of the β -diketonates make them suitable for metalorganic chemical vapor deposition, where high deposition temperatures or additional energy are required to promote gas-phase or surface reactions.

The β -diketone used most frequently with rare earth ions is 2,2,4,4,-tetramethyl-3,5-heptanedione (abbreviated as 'thd'). The anionic form of the compound coordinates with the central metal ion via the two oxygen atoms, as shown in Fig. 7. Neuhalfen et al. used $\text{Er}(\text{thd})_3$ as the rare-earth precursor in the preparation of Er-doped $\text{In}_{1-x}\text{Ga}_x\text{P}$ via atmospheric pressure MOVPE with TmIn and TMGa and the Group III element precursors.⁸ In this work, the precursor was heated to between 120 and 160 °C in order to obtain a sufficiently high rare-earth-compound vapor pressure. Later, Hara et al.⁹ have successfully employed the Tb analog, $\text{Tb}(\text{thd})_3$, to prepare Tb-doped GaN, also via atmospheric pressure MOVPE. In this case, the precursor (contained within a stainless-steel vessel) was heated to 150 °C, resulting in a $\text{Tb}(\text{thd})_3$ vapor pressure of about 9×10^{-2} mm Hg. Pan et al, subsequently used $\text{Eu}(\text{thd})_3$ as the rare-earth source in the preparation of GaN:Eu, with the Eu-containing precursor maintained at a temperature of 135 °C (resulting in a $\text{Eu}(\text{thd})_3$ vapor pressure of about 3×10^{-3} mm Hg).^{10,11}

Oxygen is believed to be responsible for the yellow color often apparent in GaN powders.¹² A shallow donor in GaN, oxygen also has a strong influence on the background n-type conductivity.¹³ The question arises, therefore, as to the possible introduction of oxygen impurities into the growing film originating from the decomposition of the rare-earth precursor molecule. This possibility was discussed by Hara et al. in their paper on the deposition of Tb-doped GaN.⁹ Torvik et al.¹⁴ previously reported that the Er luminescence in GaN:Er is considerably enhanced by the presence oxygen (as well as fluorine). In other work, it was found that Er^{3+} -related photoluminescence and cathodoluminescence from GaN:Er was only observable in samples that had been codoped with O.^{15,16} Similar effects have been observed in GaAs:Er where the excitation mechanism of the Er atom was assumed to be via the nonradiative recombination of an exciton bound to an Er atom substituting for Ga associated with two O atoms.^{17,18}

2. Cyclopentadienyls

Cyclopentadienyl compounds, which have at least one direct metal-carbon bond to the C_5H_5 ligand (see Fig. 3), were first synthesized in the 1950s. Since then, reactions of cyclopentadienyl reagents have been applied for almost every element. The main application of these compounds is their use as catalysts in the polymerization of olefins by Ziegler-Natta polymerization processes. However, as many of the cyclopentadienyl compounds are both volatile and thermally stable, they are also suitable for use as precursors in MOVPE. The physical properties (most significantly vapor pressures and melting points) of the cyclopentadienyl may be changed dramatically by substituting alkane groups in place of one or more of the hydrogen atoms on the 5-member ring. This effect is demonstrated in Tables 1 and 2 for cyclopentadienyl compounds of terbium and erbium, respectively.

Table 1
Melting Points of
Terbium Cyclopentadienyls

Compound	Melting Point (°C)
TbCp ₃	315
Tb(Me ₄ Cp) ₃	175
Tb(i-PrCp) ₃	76

Table 2
Melting Points of
Erbium Cyclopentadienyls

Compound	Melting Point (°C)
ErCp ₃	287
Er(n-BuCp) ₃	96
Er(i-PrCp) ₃	69

Since it is preferable to employ bubbling (i.e., evaporation at a liquid/gas interface) rather than sublimation (evaporation at a solid/gas interface) as a means of bringing the rare-earth precursor into the carrier-gas stream, and since lower source temperatures (less than about 100 °C) are preferred, cyclopentadienyl compounds with an alkyl group (most often an isopropyl group) substituted for one of the hydrogen atoms on each cyclopentadienyl ring are most often used as MOVPE rare-earth precursors.

Yb(i-PrCp)₃ has been used successfully in the deposition of InP:Yb.¹⁹ InP:Er and GaAs:Er layers, obtained using Er(i-PrCp)₃ as the Er source, displayed higher crystal quality and photoluminescence intensities than those obtained using less volatile erbium cyclopentadienyl compounds.^{20,21,22} However, Taguchi et al.²³ have reported that C is doped with Er when GaAs:Er is grown via MOCVD. (The Er and C atoms seemed to form complexes in the GaAs host, which were not electrically active.) Finally, Tm(i-PrCp)₃ has been used successfully as the rare-earth precursor for doping of GaAs, GaP, GaInP, and InP by MOVPE.^{21,24}

The GaN depositions reported here were carried out via atmospheric-pressure MOVPE using NH₃ and TMGa as the precursors for nitrogen and gallium, respectively. The rare-earth dopants were introduced using 2,2,6,6-tetramethyl-3,5-heptanedionate or isopropyl-cyclopentadienyl compounds, depending upon availability and compatibility with the overall process conditions. Equilibrium vapor pressures for Er(i-PrCp)₃, Eu(thd)₃, and Tb(thd)₃ are plotted in Fig. 8 for temperatures ranging from 85 to 220 °C.

Equilibrium Vapor Pressure vs Reciprocal Absolute Temperature for Rare Earth Precursors

Figure 8. Equilibrium vapor pressure vs. reciprocal temperature for rare earth precursors.

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Section V. Deposition and Characterization of GaN:RE³⁺ Thin Films Deposited by MOVPE

V.a Introduction

The MOVPE reactor discussed previously was used to deposit thin films of GaN, InGaN, and GaN:RE³⁺ (RE³⁺=Tb³⁺, Eu³⁺ and Er³⁺). Terbium and europium are multivalent. While terbium can exist in valence states of 3 and 4, europium exists in valence states of 2 and 3. Thus, incorporating trivalent europium and terbium ions into a nitride lattice require very different deposition conditions, a fact rarely discussed in MOVPE literature, and that we learned during the course of this study. For Er³⁺, this situation does not exist.

There are only one publication each on MOVPE deposition of GaN: Tb³⁺¹ and GaN: Eu³⁺² and a couple of publications on GaN:Er³⁺.³ The literature is marked by the conspicuous absence of any details on the MOVPE deposition processes, and we had to develop conditions of deposition of these rare earth activated GaN thin films by trial and error. Fluorescence and EDS measurements were used in a complementary manner to identify MOVPE deposition parameters.

In the course of this study we succeeded in obtaining several GaN: Eu³⁺ films and GaN:Tb³⁺ films that exhibited emission from the rare earth ions under PL and CL conditions, respectively. While thin films of GaN: Er³⁺ showed significant incorporation of Er³⁺ ions from SIMS and EDS measurements, no significant green emission at 537 and 558 nm emissions from ²H_{11/2} and ⁴S_{3/2} to ⁴I_{15/2} levels, respectively, were observed.⁴ Strong IR emissions at 1.0 and 1.54 μm due to transitions from ⁴I_{11/2} and ⁴I_{13/2} to the ground state ⁴I_{15/2} reported for MOVPE grown films³ were not explored further. In the following discussions, we will not discuss any further results involving GaN:Er³⁺ thin films.

A thin film of poor quality could easily show poor performance under photo-excitation due to its defect structure, which could lead to misleading conclusions. Therefore, all the thin films were routinely analyzed for elemental composition, secondary phases, morphology, and crystal structure using a variety of techniques available at Osram-Sylvania and UCSD. In the following sections, we discuss results from structural and spectroscopic measurements of these films.

V.b Structural Characterization of Thin Films Deposited by MOVPE

X-ray Diffraction Method

Most of the thin films were deposited on the (0001) surface of sapphire. A typical deposition process involved nitridation of the alumina substrate, low temperature deposition of a GaN buffer layer, and finally deposition of a GaN layer at 1035 °C. Both InGaN and GaN:RE³⁺ layers were deposited on top of a GaN buffer layer.

For ideal epitaxial growth, one should observe 002 diffraction near 2θ value of 34.75° (see Figure 1). This peak position depends on the composition of GaN, and shifts towards lower values of 2θ as in the case of alloys of GaN and InN, commonly referred

to as InGaN. This shift is often utilized to extract the composition of InGaN using Vegard's law. Additional diffraction peaks that could be attributed to GaN appear due to deposition of crystallites along different directions. When the crystallites do not grow epitaxially, random orientations are observed, and the film has a frosty, white appearance.

For this work, only one thin film of InGaN was deposited. In this case, multiple peaks appeared near the dominant peak of 34.7° due to GaN (Figure 2). This clearly indicated the presence of InGaN of varying InN and GaN composition.

X-ray diffraction patterns from GaN:Eu³⁺ and GaN:Tb³⁺ films were found to be more complex. In addition to 002 peaks, 100 and 101 diffraction peaks were also observed indicating random orientation of crystallites on the GaN substrate. The randomly-oriented crystallites probably contribute to the whitish-to-yellowish body color due to multiple scattering. Additionally, the presence of a broad peak near low diffraction angles is also indicative of diffraction from an amorphous structure. However, no change in the location of the 002 peak was observed indicating the absence of any massive lattice relaxation due to incorporation of rare earth ions. The corresponding GaN:Eu³⁺ film showed characteristic Eu³⁺ emission.

The X-ray diffraction pattern in Figure 3 from GaN:Tb³⁺ films (Samples 120507 and 080607) show clearly the presence of secondary phases. Two of the secondary phases could be identified as cubic or hexagonal Tb₂O₃ and possibly an amorphous phase of TbO_{1.74}. We could not identify a sharp diffraction peak observed at $2\theta \approx 20^\circ$. The phase of TbO_{1.74} appears to be amorphous and contain a mixture of Tb³⁺ and Tb⁴⁺ of which the latter does not fluoresce. The presence of terbium oxide was assumed to be due to incomplete mixing of the rare earth ion precursors with those of N and Ga, which resulted in an inhomogeneous distribution of rare earth ions. The separation of secondary phases was assumed to be driven by higher concentration of terbium ions at certain spots above the solid solution limit. This prompted redesigning the reactor for better homogeneity as discussed earlier. However, the same secondary phases were observed after the changes to the reactor for better homogeneity were implemented.

Figure 1. X-ray diffraction pattern of a GaN thin film. The peak near 41.9 ° is associated with diffraction form (0006) planes of the sapphire substrate.

Figure 2. X-ray diffraction peaks of InGaN near 2 θ of 34.7°

Figure 3. X-ray diffraction pattern of GaN:Eu³⁺

Figure 4. X-ray diffraction pattern between 16° and 32° for two different samples of GaN:Tb³⁺; the red trace corresponds to a sample deposited with the modified design.

AFM and SEM Images of Thin Films

AFM (Atomic Force Microscopy) and SEM (Scanning Electron Microscopy) images of the thin films were routinely taken to examine the quality and topography of the films as well as any unusual growth patterns. In most cases, hexagonal structure of the micro-crystallites was easily visible for GaN grown using N_2 as the carrier gas (Figure 5). In between the particles, it is easy to visualize open spaces, as the particles grow in size to form continuous thin films. With higher resolution, dislocation pits are visible on the surface of individual crystallites.

Figure 5. AFM images of GaN grown with N_2 as the carrier gas.

A more continuous film pattern is obtained for GaN thin films grown with H_2 as the carrier gas (Figure 6). Here a continuous film with hexagonal pits is observed. This particular thin film was significantly more transparent. Fractal structures (Figure 7) emanating from the hexagonal pits are noticed, particularly in the region where the film thickness is low. It is probably indicative of the nucleation process of thin films when hydrogen is used as the carrier gas.

Figure 6. AFM image of GaN with grown H_2 as the carrier gas.

Figure 7. Fractal structures surrounding hexagonal pits on the surface of GaN thin films.

Elemental Analysis

X-ray Energy Dispersive Spectroscopy (EDS) was the principal method used to characterize the elemental composition of our MOVPE films. Wavelength Dispersive Spectroscopy (WDS) and Secondary Neutral Mass Spectrometry (SNMS) were used on our first films where RE dopant concentrations were low and higher sensitivity was required. However, as film deposition methodologies progressed to reliable dopant concentrations in the range of one percent, EDS became the preferred technique for reasons of convenience.

EDS allows for a focusing within a range of magnifications corresponding to varying spot sizes of analysis. Films were typically first analyzed in relatively low magnification, corresponding to a spot size on the order of 1 mm, in perhaps 10-15 locations, to assess film uniformity on a macroscopic scale. By such methods, observations of RE concentration gradients across the surface of the film allowed us to uncover problems combining the vaporized RE precursors with the main process gas stream (most likely due to the slow diffusion of the large cross-section, high molecular weight precursor species). This observation prompted an equipment modification process which included installation of a “static mixer” and more precise attention to the preheating of combining process gas flows so as to avoid temperature gradients and the possible condensation of precursor species within the gas lines or reactor tube upstream of the substrate. Subsequent films showed marked improvement in macroscopic RE concentration across the surface of the film.

Additionally, the ability to focus EDS analysis down to spot sizes on the order of 1 micron allows a microscopic assessment of RE concentration differences which can be correlated with distinct film morphologies. For example, Figure 8 shows SEM images of the film resulting from one attempt to dope GaN with terbium. Focused EDS analysis allowed us to compare the Tb:Ga ratios of the large crystals (Tb:Ga = 0.015), the underlying layer (Tb:Ga = 0.025), and even the breaks in the underlying layer (which are likely to be exposed substrate or the ‘nucleation layer’). In this case, we surmised that the Tb was largely depositing into the large crystals visible in the SEM images, but not exclusively, as the underlying layer (which is mostly the previously deposited undoped GaN) had also been coated with Tb:GaN. In such cases, one must be careful interpreting measured RE:Ga ratios as the x-rays are expected to penetrate between one and two microns into the film depth and to return an integrated elemental composition. Thus, when measuring a spot on a large crystal, one can assume that the measurement has not been affected by the simultaneous detection of the underlying undoped GaN layer. However, when measuring a spot on the relatively smooth layer visible between the large crystals, it is likely that that measurement reflects the compositions of both the Tb-doped and underlying undoped portions of the 1.5 – 2.0 micron thick layer.

Figure 8. SEM images of a Tb doped GaN MOVPE film showing a range of morphological features (left) and a higher magnification of the larger crystal formations (right). Focused EDS measurements of roughly one micron spot size allow a comparison of Tb:Ga ratios for the various morphological features.

V.c Fluorescence Measurements of Undoped Films

GaN Films with N_2 as the Carrier Gas

The SPEX Fluorolog-2 spectrometer was modified to enable transmission measurements of samples that may emit light by positioning two flat mirrors in the incident and transmitted beams at 45-degrees. Rejecting contributions from fluorescence in the transmitted radiation is normally not possible. All photons originating on the back surface of the sample are collected by the detector. By modifying the spectrometer, we are able to spectrally select the photons of interest and therefore, reject everything but the radiation passing through the sample, more or less in-line with the incident light. Photons reflected and/or strongly scattered by the sample are beyond the reach of the detector.

One such film, Film 080406, was measured for its transmission and luminescence properties at room temperature. Figure 9 shows the absorbance (αx) spectrum calculated from the Beer's law $I = I_0 e^{-\alpha x}$ where x denotes the thickness of the sample. One immediately notices a steep absorption edge at about 350-360nm or 3.4eV where one expects the onset of the band gap crossing transitions in GaN.

Figure 9. Absorption spectrum of F080406. The near-vertical line is for aiding the eye to determine the approximate bandgap energy.

Figure 10 shows the luminescence spectrum of F080406 under 300nm excitation. The band at 363 nm (3.39eV) is most likely of excitonic origin. The width of the band (22nm or about 0.2eV) is not influenced by the resolution of the detection monochromator (about 2-3nm). The position of this emission band agrees well with that reported earlier for GaN.⁵ The full-width at half-maximum (FWHM) appears to be wider by a small amount.

Figure 10. Emission profile of the GaN film F080406 under 300nm Xe-lamp excitation.

The excitation spectrum for the band edge emission is shown in Figure 11. Due to the fairly broad monochromator slits used in this measurement, the leakage of excitation light into the emission detector prevents one from seeing the most critical region close to the band edge, 360nm (as evidenced by a steeply rising curve in this area). The PLE spectrum is relatively featureless, although there is indication of slightly higher efficiency towards the onset of the band edge absorption, as expected on the basis of decreasing nonradiative losses with excitation energy approaching the band gap from higher energy.⁶

Figure 11. Excitation spectrum of F080406, together with the emission profile and the position of the monitoring wavelength indicated.

GaN film Grown with H_2 as the Carrier Gas

Several films of GaN were grown using H_2 as the carrier gas. One such film, F101806, appears transparent to the naked eye and exhibits a weak interference pattern under white light for certain orientations. Indeed, the transmission spectrum presented in Figure 12 shows a steep host absorption edge and also a set of intensity oscillations due to interference from the thin film.

Observation of interference maxima and minima in the transmission spectrum allows one to estimate the film thickness with a reasonable accuracy.^{7,8} The average thickness of this film is estimated to be $\sim 1.2\mu\text{m}$. Similar to the procedure described previously, the band gap is estimated to be 3.41 eV from the variation of α^2 with respect to $h\nu$.

Figure 12. Transmission vs. wavelength for F10182006. Note the pattern of interference maxima and minima in the non-absorbing region.

Figure 13. Emission from F101806 under 300nm excitation (dashed line, no filter; dotted line, cut-on at 350nm) and 350nm excitation (solid line, cut-on at 560nm). The long wavelength structure seen for 300nm excitation originates from second spectral orders, stray light and more defect emission.

The emission spectrum of F101806 shows surprisingly a relatively stronger defect emission. The structure in the long wavelength range peaking at 765nm is probably due to a different defect emission. Excitation spectrum for the defect emission at 545nm is presented in Figure 14. It differs from the one in Figure 10 by additional structure at the band edge (two sharp features at 357nm (3.47eV) and 362nm (3.425eV)). This structure was previously not present for F092906 and needs a more thorough investigation at low temperatures.

Figure 14. Excitation spectrum corresponding to emission at 545 nm for an undoped GaN film, F101806.

InGaN Film

The InGaN thin film (F120106) deposited with H₂ as the carrier gas scatters light noticeably and has a slight brownish coloration. The location of the emission band (Figure 15) is consistent with the higher concentration of In (the peak has shifted from UV to blue) but its width (about 0.6eV) is somewhat larger. It could be due to emission bands originating from separate phases of InGaN as evidenced from the X-ray diffraction pattern.

Figure 15. Emission spectra of F12012006 under 300nm (dotted), 375nm (solid) and 400nm excitation (dashed line). Note the absence of emission for 300nm excitation and the peak shift for 375 and 400nm emissions.

V.d Measurement of Fluorescence from RE^{3+} in GaN Thin Films

GaN:Eu³⁺

The PL spectra discussed here are from two samples having the highest concentrations of Eu of ~0.1-0.2 at % (from the EDS measurements.) Similar to other thin films, these films exhibited a higher concentration of Eu near the substrate edge oriented toward the inlet side of the vaporized rare earth precursors.

Figure 16 shows the PL spectrum for lamp excitation in the 300-330nm wavelength region. The emission yields strong, narrow band transitions in the red at approximately 619, 622, 634, 663 and 665 nm due to Eu^{3+} , in addition to the GaN near-band edge (NBE) luminescence around 360 nm. Though weak, the yellow emission band due to defects can be easily noted. The integrated strength of the Eu^{3+} emission peaks is comparable to that of GaN emission near 360 nm and supports the conjecture that electron-hole (e-h) pairs generated upon excitation at energies equal or greater than the band gap are likely to recombine at Eu^{3+} sites.

Figure 16. Room temperature PL spectrum of GaN:Eu³⁺ thin film in response to excitation at 300-330 nm (Xe-lamp).

The sharp peaks observed at 621-622 nm have been assigned to $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ in the nitride environment in GaN² and AlN.⁹ However, various other wavelength values have also been reported depending on the method of material preparation. This emission is reported to appear at 614 nm in GaN prepared by rf-sputtering¹⁰ or at 611 nm by Hirata et al.¹¹ in GaN powder prepared by a combustion method. Hao et al.¹² report this transition in Ga₂O₃ to occur at 617 nm, while Kitai¹³ assigned $^5D_0 \rightarrow ^7F_2$ emission to a set of lines at 621 nm in Ga_{2-x-y}In_xEu_yO₃ thin film devices. Well-known oxide phosphors of Y₂O₃:Eu, YVO₄:Eu and Y₂O₂S:Eu yield the dominant $^5D_0 \rightarrow ^7F_2$ emission at wavelengths of 612, 619 and 625 nm, respectively.

In our earlier study involving AlN:Eu³⁺ powders, the main transition was observed near 612 nm.¹⁴ Considering that the powder samples used in this study had higher oxygen impurity concentration compared to thin films grown epitaxially, it was assumed that Eu ions segregate in the oxygen-rich regions. Only in high purity powder samples of GaN grown directly from metal precursors has this transition been demonstrated near 621 nm.¹⁵

It is clear that the $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ is found to shift in various host materials and is probably very dependent on the ligands. Observing the $^5D_0 \rightarrow ^7F_2$ transition around 621-622 nm in GaN is not entirely proof by itself of having Eu³⁺ ions incorporated into the nitride lattice. Yet, it is a good indication that these ions are in a similar environment as in high purity GaN powder or thin films. The other prominent lines in Figure 16 have been attributed to $^5D_1 \rightarrow ^7F_4$ transition (at 634 nm) and to $^5D_0 \rightarrow ^7F_3$ transition (around 663-665 nm) of trivalent europium based on the data published in literature.¹⁶

More detailed luminescence in the red part of the spectrum is shown in Figure 17 for low excitation densities (Xe-lamp). Varying excitation wavelength yields multiple

5D_0 - 7F_2 hypersensitive peaks between 619 and 623nm. Upon exciting into sharp excitonic absorption at 360 nm or above the band edge at 330 nm, at least three (major) 5D_0 - 7F_2 lines at 619, 620.4 and 622.4nm and one 5D_1 - 7F_4 emission at 633.8nm are observed. Upon direct pumping at 470 nm through 7F_0 to 5D_2 transition of Eu^{3+} or at wavelengths between that and the excitonic absorption (for example with 380nm excitation), only a single 5D_0 - 7F_2 peak at 622.4 nm is recorded and no radiative relaxation from 5D_1 level at 633.8nm is observed. This behavior is very similar to the one described by Nyein et al. in GaN:Eu under 471nm resonant excitation.¹⁷ It shows clearly the difference between charge carrier (or host-activator energy transfer) mediated and direct excitation of the activator ions.

Figure 17. The main red emission lines of Eu^{3+} in GaN for excitation at 330, 360, 380 and 470 nm (Xe-lamp).

As many as five peaks (some unresolved) due to the $^5D_0 \rightarrow ^7F_2$ transition occur in this work (in Table 1). Complete lifting of Kramers degeneracy due to low site symmetry would also result in five Stark split lines. Thus, the occupancy of multiple activator sites cannot be established by the $^5D_0 \rightarrow ^7F_2$ transition alone. Nevertheless, we find additional support for different activator environments in Figure 18. One of the two GaN:Eu films compared does not exhibit the 620.4nm emission peak for the same 330nm excitation. The europium ions corresponding to $^5D_0 \rightarrow ^7F_2$ wavelength of 620.4nm constitute either a negligible minority or are not excited directly by energy transfer from the host.

In order to confirm the indication of multiple sites by the spectral group of $^5D_0 \rightarrow ^7F_2$ transition, the entire region up to about 700 nm was analyzed with higher resolution. The observed emission peaks are listed in Table 1, along with their most likely assignments. Radiative decay from 5D_0 to 7F_0 involves non-degenerate levels that cannot be further split due to the crystalline field. This is a forbidden transition, yet could occur at a very low symmetry site due to ligand field effects. The presence of multiple peaks instead of a single one in the region of 5D_0 - 7F_0 is a clear indication of europium ions in several different environments. As many as five sites have been found previously in the 570-590nm wavelength interval of the same sample Hömmerich et al.¹⁶ presented high

resolution PL excitation spectra locating peaks at 571, 585.8, 587.9, 588.9 and 589.4nm at liquid helium temperatures in samples grown by MBE. Dierolf et al.¹⁸ determined excitation wavelengths of 570.9, 584.6, 585.5, 587.9, 588.8 and 589.3nm that can be associated with 5D_0 - 7F_0 transition. However, they argue that some of them are replicas due to coupling to phonons that reduces the number of distinct sites to four. We find this region to contain several lines (Table 1), including a broader unresolved transition around 571nm that may contain multiple components. However, it is not clear whether there could be also some contributions from 5D_1 - 7F_3 transitions.¹⁹ These observations suggest that Eu^{3+} ions occupy multiple sites in the GaN films made in this study.

Table 1. Observed emission peaks from Eu^{3+} in GaN

Observed Peaks (nm)	Spectroscopic Assignment
571.0, 583.4, 585.7, 589.0, 591.5, 593.1, 595.0, 595.9	5D_0 - 7F_0 (5D_1 - 7F_3 ?)
599.0, 601.0, 602.0, 605.4	5D_0 - 7F_1 ,
619.0, 620.4, 621.6, 622.4, 625.5	5D_0 - 7F_2
633.8	5D_1 - 7F_4
660.5, 663.0, 665.5	5D_0 - 7F_3
717.5, 718.0	5D_0 - 7F_4

The most probable location for europium is a substitutional gallium site. The rare earth ions occupying Ga site have been confirmed by EXAFS.^{20,21} It has been speculated that interstitial sites near defects or impurities are responsible for more broadened, non-exponentially decaying 5D_0 - 7F_0 emission lines.¹⁷ Also, some of these sites could be located in a secondary phase. However, considering the fact that the peaks between 619 and 623 nm have similar intensities and that no dominant secondary phase is indicated by X-ray diffraction measurements, we believe that all the emitting sites are located in the primary phase of gallium nitride.

GaN:Tb³⁺

Green PL from a GaN:Tb^{3+} film deposited by a MOVPE method was reported by Hara et al.¹ To the best of our knowledge, this is the only reported work in the literature on PL from a GaN:Tb^{3+} film. The green luminescence from a $^5D_4 \rightarrow ^7F_5$ transition from a Tb^{3+} near ~ 545 nm has traditionally been used as the green component for white light generation from a triblend phosphor system. It was therefore a challenge for us to make a green emitting GaN:Tb^{3+} film using MOVPE.

Different synthesis conditions were needed for the incorporation of Eu^{3+} and Tb^{3+} . In order to make a Tb-activated oxide phosphor, a reducing environment is needed in contrast to the oxidizing conditions required for a red emitting Eu^{3+} -activated phosphor. This difference in synthesis conditions is a direct result of the multiple valence states of both the ions.

In order to deposit GaN-Tb^{3+} films using our MOVPE reactor, we used approximately the same conditions as Pan and Steckle² for GaN:Eu^{3+} and by Hara et al.¹

for GaN:Tb³⁺. Hara et al.¹ used a vertical reactor in contrast to our horizontal design. Only with reaction conditions similar to that of Hara et al.¹ did we succeed in producing films of GaN:Tb³⁺ which showed only weak PL and CL responses in most cases. In one of the samples, F121407, a strong CL luminescence was noted, which we will discuss next.

CL from the film, F121407, was measured at 3 – 6 keV at the center as well as the film edge. The film yield transitions of Tb³⁺ originating from the ⁵D₄ state. At lower voltages (3 keV), Tb emission is much stronger than the band edge emission (Fig. 18). Relative to films studied earlier, this film has a much lower defect emission when excited at the same voltage and current (i.e., 3keV, 280 μ A). Spots of orange were also observed due to Eu contamination, around 620 nm. It is unknown whether the contamination is from handling or from the deposition process. The peak at ~330nm near the NBE was also observed in an earlier GaN:Tb³⁺ film (F112907).

Figure 18. A comparison of emission spectra for two different GaN:Eu films, one with two and the other with three distinct ⁵D₀-⁷F₀ transitions around 620nm.

As the excitation source voltage was increased from to 6keV, the band edge along with the defect emission also increased (Fig. 19) at the center of the film. The same is observed at the film edge (Fig. 20). Figure 21 shows a comparison of NBE and Tb emission at increasing excitation voltage at the film edge.

Figure 19. CL emission from film center for 3keV at 280uA.

Figure 20. Comparison of NBE and Tb emission at increasing excitation voltage at the film center.

Fig 21. Comparison of NBE and Tb emission at increasing excitation voltage at the film edge.

It is interesting that even this film does not exhibit any PL; this needs to be understood. Based on X-ray diffraction measurements, we believe that the concentration of Tb^{3+} in GaN is too low because of phase separation of Tb-oxide. A qualitative assessment shows that most of the Tb atoms are in the Tb-rich oxide phases. We need to optimize our reaction parameters to avoid deposition of Tb-oxides and incorporate most of the Tb^{3+} into the GaN.

V.e Conclusions

During this project, we succeeded in producing red emitting GaN:Eu^{3+} films that could be excited by near band edge photo-excitation and GaN:Tb^{3+} films that could be excited by cathode rays, in addition to GaN and InGaN films. At this point, the processing parameters of GaN:Tb^{3+} need further optimization for PL emissions. Most importantly, our work has demonstrated that it is possible to realize green and red emitting GaN thin films using Tb^{3+} and Eu^{3+} as activator ions, respectively. For white light emission, they could be combined with a blue emitting InGaN layer.

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Section VI. Modeling and Luminescence Mechanism

VI.a Introduction

During this study, considerable theoretical and modeling activities were undertaken in order to provide a better insight to the luminescence process of the rare earth ions in nitride hosts and to evaluate their suitability for application as an active layer in a heterostructure design of a solid state light source. First principles calculations were used together with the available experimental data employed for developing a coherent picture of rare earth activated nitrides. The following topics were investigated in detail:

1. excitation process of RE^{3+} in nitride hosts;
2. localization of oxygen donor states in nitrides;
3. structural relaxation, stability of oxidation state, and electronic structure of rare earth ions in GaN;
4. saturation of fluorescence yield of rare earth ions in nitride hosts with increasing excitation intensity.

These topics are of interest from the perspective of optimizing the luminescence properties of GaN:RE^{3+} and are discussed in the following sections.

VI.b Luminescence Mechanism

One of our objectives was to determine the process of excitation of RE^{3+} in nitride hosts and to utilize this knowledge for designing an efficient luminescent system based on nitride hosts. For this reason, the PLE spectra of most of the materials synthesized during this work were measured and analyzed. We have summarized various excitation processes in our publications on AlN:RE^{3+} .^{1,2} A brief summary is provided here.

AlN:RE³⁺ powder

In general, four different excitation processes of rare earth ions in AlN were observed from the PLE measurements of AlN:RE^{3+} ($\text{RE}^{3+} = \text{Dy}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$ and Tm^{3+}) powder samples. These processes are listed below:

- direct excitation of RE^{3+} through multiplet levels of $4f^n$ -configuration,
- energy transfer from the excited defect states to RE^{3+} ,
- energy transfer from the host to RE^{3+} ,
- energy transfer from one rare earth ion to another.

The last case was mentioned earlier in the context of energy transfer from Tb^{3+} to Eu^{3+} and will not be discussed further.

We begin with the PLE spectra of Dy^{3+} in Figure 1. Four PLE spectra are displayed in this figure, two corresponding to intra-configurational $f \rightarrow f$ transitions associated with Dy^{3+} at 757 and 575 nm, and two for defect emissions at 530 and 720 nm. Weak, sharp peaks between 300 and 500 nm peaks are attributed to the direct intra-configurational excitation of Dy^{3+} . The assignments for the intra-configurational $4f \rightarrow 4f$ transitions are made by comparisons with data from the literature for $\text{LaF}_3:\text{Dy}^{3+}$.³

One notices that Dy^{3+} could be excited in a broad range of the spectrum from 300 to 560 nm. In this wavelength range, the absorption of photons most likely promotes defects from the ground states to the excited states. The Dy^{3+} are subsequently excited from the ground state via nonradiative energy transfer from the excited point defects. It is obvious from Fig. 1 that at 310 nm Dy^{3+} cannot be directly excited. Nor could the host lattice be excited at this wavelength due to its large band gap. Thus, excitation at 310 nm must involve excitation of the defect states. If this leads to emission from Dy^{3+} , it would suggest energy transfer from the excited defect states to Dy^{3+} . To confirm this conjecture about energy transfer from the defects in excited state to the Dy^{3+} , the PL spectrum of the AlN:Dy^{3+} sample was measured by exciting the sample at an excitation wavelength of 310 nm. The f-f intra-configurational transitions associated with Dy^{3+} are clearly observed in response to this excitation. The relative intensity of the defect emission is higher compared to above band-gap excitation where the excitation wavelength is 250 nm. This is expected considering that the photon energy is resonant with the excitation band of the defects (the PLE band peaked at 310 nm as shown in Figure 1). Similar excitation processes were observed for Tb^{3+} , Tm^{3+} , and Eu^{3+} in AlN powder samples.^{1,2}

The source of perturbation could be oxygen defects occupying the nitrogen sites or RE ions occupying the aluminum sites. In the former case, the 3s-like levels of aluminum ions surrounding the oxygen impurities are lowered into the gap region. In the latter case, the 2p-like levels of nitrogen ions coordinated to the RE ions move into the band gap due to lower Madelung potential experienced by these ions because of the substantially larger Dy-N bond length compared to that of Al-N. Both the processes contribute to the lowering band gap of AlN as observed from the remission measurements. We also observed this broad excitation band peaked around 245 nm in the PLE spectra of samples of AlN doped with other RE ions such as Eu^{3+} , Tb^{3+} and Tm^{3+} . Thus, this excitation peak is probably associated with transitions in the perturbed environment of the RE ions and the transfer of energy from the corresponding excited states to the RE ions is quite efficient. Since defect emission is still observed with 250 nm excitation (Fig. 1), it is possible that excitation of Dy^{3+} proceeds at this wavelength with sequential energy transfers from the host to defects to Dy^{3+} .

Figure 2 summarizes the excitation processes leading to emission from the RE^{3+} in AlN when excited above the band gap. This model describes only the nonradiative energy transfer processes based on a Dexter-Förster mechanism^{4,5} and does not include capture of an itinerant electron and hole by Eu^{3+} . This model is used later to discuss saturation issues in RE^{3+} -activated nitride hosts.

Figure 2. Energy level diagrams of host lattice, defects, and Dy^{3+} . Various energy transfer processes are described by lines with two arrow heads. Radiative and nonradiative transitions are indicated by solid and dashed arrows, respectively.

During this project, we investigated the excitation process of Eu³⁺ in GaN thin films deposited by the MOVPE process. Although occupancy of multiple sites made the study more complicated, the PLE spectra corresponding to 619 and 622 nm revealed many interesting features regarding the excitation process of Eu³⁺ in GaN.

The PLE spectra for 619 nm and 622 nm emissions from ⁵D₀ → ⁷F₂ transition of Eu³⁺ are shown in Figure 3. For comparison, the excitation curve for emission near 560 nm due to lattice defects (most likely the defect center associated with the yellow band) is also presented. The PLE spectra for 619 and 622 nm emissions develop peaks near the band edge of GaN. Thus, if these two emissions are associated with Eu³⁺ at two different sites as we claimed earlier, the excitation peaks for both the centers near 360 nm imply that they are both located in the same GaN lattice. This peak also suggests that the electron transfer process from the host to the Eu³⁺ in GaN is quite efficient. However, the excitation spectrum for the 622 nm emission has another peak at energies below the band gap energy near 400 nm. This peak has been often attributed to a charge transfer transition in the nitride lattice.⁶ In our opinion this cannot be the case for the following reasons. First, this peak is very weak for 619 nm excitation, probably non-existent. Usually, the charge transfer transition is more efficient than host excitation. Secondly, it is also associated with the excitation peak for the defect emission at 560 nm. This excitation peak near 400 nm is quite likely associated with a defect center located near Eu³⁺ emitting at 622 nm. The other alternative explanation could be that one of the occupied sites has a vastly different nearest neighbor coordination structure.

On increasing the excitation energy, the excitation efficiency of europium ions is observed to decrease rapidly. This behavior has often been observed in inorganic (powder) phosphors upon exciting the host lattice at energies higher than the band gap.⁷ It is usually explained in terms of increasing recombination of e-h pairs via surface states.⁸ Radiation above the bandgap energy is absorbed closer to the film or particle surface due to a rapidly increasing absorption coefficient and more free electrons or holes arrive at the surface before any radiative recombination in the bulk can take place. In contrast, the excitation efficiency for the yellow defect emission continues to increase monotonically with increasing excitation energy. It develops a peak near the band edge but keeps on rising at higher energy. The likely explanation for this behavior is that the defect concentration near the surface is very high, thus the radiative transition through defect states compete effectively with non-radiative transitions on the surface states.

Figure 3. Excitation spectra corresponding to emission at 622 nm (dashed line) and 619 nm (solid line) due to Eu^{3+} . The excitation spectrum corresponding to defect emission at 560 nm (dotted line) is shown for comparison. The feature at 470 nm (for the 622nm curve) belongs to direct excitation into $^7\text{F}_0$ to $^5\text{D}_2$ transition of Eu^{3+} .

The most significant conclusion from this measurement is that the europium ions are tightly coupled to the host lattice in the sense that the energy transfer from the host to Eu^{3+} occurs efficiently. Whether the exact mechanism is the Dexter-Forster type^{4,5} of energy transfer or recombination of itinerant electrons and holes at the Eu^{3+} sites needs to be investigated further.

VI.c Oxygen Defects in GaN

Throughout the project, we experienced the problem of unintentional contamination of GaN and AlN powders with oxygen. The oxygen atoms are easily incorporated into GaN because of the relative stability of Ga-O bonds compared to Ga-N bonds. The enthalpy of formation of Ga-O bonds is -545 kJ/mol which is much higher than -110 kJ/mol for Ga-N bonds.⁹ The yellow body color of GaN is attributed to oxygen ions occupying nitrogen sites, O_N . We indeed observed a variation of body color of GaN with different annealing conditions (Figure 4). It has been observed that the GaN lattice can accommodate nearly 25 at% of oxygen without any change in its wurtzite crystal structure or precipitation of a second phase.¹⁰ These observations suggest that the rigid band model for semiconductors with O_N point defect introducing a donor level in the band gap is not adequate to explain the optical properties of GaN at higher oxygen concentrations and that at this level of oxygen contamination, the band structure of GaN is changing appreciably.

Figure 4. Color of annealed GaN powder under flowing nitrogen at 775 °C in carbon- and alumina-muffled furnaces.

Using supercell band structure methods, we have studied modifications of local geometries in the vicinity of $O_N^\bullet$ and the electronic structures of GaN as a function of oxygen concentration.¹¹ The Vienna ab initio simulation package (VASP)¹² and augmented spherical wave (ASW)¹³ approach were used in this work for calculating the band structures of GaN and $\text{GaN}_{1-x}\text{O}_x$ for values of x varying from 0 to 0.5. The local structural relaxations due to incorporation of oxygen atoms at the nitrogen sites were first simulated using VASP. The optimized structural data from VASP were then used as structural input for calculating the electronic structures of GaN with and without oxygen impurities using the augmented spherical wave (ASW) method with a scalar-relativistic correction.

The ASW method uses the atomic sphere approximation with atomic spheres, and empty spheres occupying interstitial positions. A sphere geometry optimization (SGO) algorithm was employed for an optimal choice of empty sphere positions and their radii. The requirement of a minimal basis set in this approach makes it relatively faster compared to VASP for calculating the band structure of a material on a larger k -mesh in the Brillouin zone. In the present case, the basis sets include $\text{O}(2s,2p)$, $\text{N}(2s,2p)$, and $\text{Ga}(4s,4p,3d)$. The v . Barth-Hedin exchange-correlation potential¹⁴ and a $12 \times 12 \times 12$ k -mesh in the full Brillouin zone were applied. Calculations with finer k -meshes and different exchange-correlation potentials indicate this choice to be adequate.

The main objective of this theoretical investigation was to study relaxation in the local geometry, and perturbation of the electronic structure of GaN with increasing oxygen concentration with and without any explicit charge compensating mechanism. Supercell cells with dimensions $1 \times 1 \times 1$ (regular cell), $2 \times 2 \times 2$, $3 \times 3 \times 2$ and $4 \times 4 \times 3$ having only one oxygen atom per cell were used to study the effect of oxygen concentration on the band structure of GaN. This choice of supercells corresponds to a variation of oxygen concentration of 0.5 to 25 at%. The lower limit is still a high level of oxygen impurities compared to impurity concentration in an intentionally doped material, yet not unreasonable for powder samples.

Variation in Local Geometry with Oxygen Concentration

In gallium nitride, both the Ga and N atoms occupy Wyckoff sites 2b with site symmetry ($3m$). Both the atoms are tetrahedrally coordinated to four nearest neighbors. Three of the four bond lengths are 1.941 Å and one is 1.977 Å. This departure from an ideal T_d to C_{3v} site symmetry is easily explained in terms of the sp^3 -hybridization of

gallium and nitrogen atoms. The optimized structure for GaN using VASP (Table1) is in good agreement with experiment.¹⁵

The optimized structures of GaN:O for a regular unit cell, Ga₂NO, a 2x2x2 supercell, Ga₁₆N₁₅O and a 3x3x2 supercell, Ga₃₆N₃₅O are listed in Table 1. The last two columns list a range of the Ga-N and O-Ga bond lengths describing the coordination of Ga and O atoms. The oxygen atoms substituting for nitrogen atoms remain tetrahedrally coordinated. The O-Ga bond lengths vary from 2.02 to 2.08 Å and those for N-Ga from 1.93 to 2.07 Å. The extended x-ray absorption fine structure (EXAFS)¹⁶ measurements showed that the average Ga and ligand bond lengths within the first coordination shell decrease compared to the Ga-N bond length in undoped GaN with increasing oxygen concentration. This discrepancy with experiment could be due to the microstructure of thin films and the partially unsaturated coordination although a four fold coordination was assumed for data fitting.

In this context, it is useful to review the coordinations of Ga and O in gallium oxide, Ga₂O₃. In the α -form,¹⁷ all of the Ga ions are coordinated to six oxygen atoms, and the oxygen atoms to four gallium atoms. There are two sets of bond lengths: 1.921 Å and 2.077 Å. The latter is larger than Ga-N bond length and the former is comparable. In the β -form,¹⁸ there are two types of Ga ions, one tetrahedrally coordinated and the other octahedrally coordinated. The oxygen atoms in contrast are coordinated to three or four Ga atoms. For tetrahedral coordination, the Ga-O bond lengths (1.803-1.853 Å) are shorter than the Ga-N bond lengths. But the bond lengths for the tetrahedrally coordinated oxygen atoms (1.853 Å -2.077 Å) are larger than the Ga-N bond lengths. The latter values are in good agreement with the theoretically calculated O-Ga bond lengths.

Table 1. Optimized structure for GaN:O

Row	Supercell	a (Å)	c (Å)	d _{N-Ga} (Å)	d _{O-Ga} (Å)
1	GaN _{exp.}	3.1891	5.1853	1.942 – 1.977	
2	Ga ₂ N ₂	3.216	5.234	1.965 – 1.973	
3	Ga ₂ NO	3.271	5.531	1.978 – 2.068	2.017 – 2.075
4	Ga ₁₆ N ₁₅ O	3.231x2	5.266x2	1.954 – 1.987*	2.035 – 2.045
5	Ga ₃₆ N ₃₅ O	3.224x3	5.243x2	1.952 – 1.981	2.048 – 2.055
6	GaZnNO	3.233	5.290	1.947	1.946
7	Ga ₁₅ ZnN ₁₅ O	3.223x2	5.243x2	1.931 – 2.016*	2.042 – 2.068
8	Ga ₃₅ ZnN ₃₅ O	3.220x3	5.236x2	1.956 – 1.982	2.052 – 2.071

*nearest neighbours are 4 Ga, next nearest neighbours N or O.

One could argue that the structural optimization results in longer metal ligand bond lengths because charge neutrality is accomplished by accommodating electrons in the conduction band states. There is one excess electron for every supercell which reduces the effective charge on the cations, thus leading to longer bond lengths. In order to test if this is indeed the case, calculations were performed with one Zn atom per supercell occupying a Ga site in addition to an O atom occupying an N-site. The charge compensating atom pairs of Zn and O were deliberately placed far apart from each other in the supercells of $\text{Ga}_{16}\text{N}_{15}\text{O}$ and $\text{Ga}_{36}\text{N}_{35}\text{O}$. The optimized metal ligand bond lengths and the lattice vectors are also listed in Table 1. In these cases, the point defects, Zn'_{Ga} and $\text{O}^{\text{g}}_{\text{N}}$, lead to charge neutral pairs and, thus there are no free electrons. However, the structural parameters for these supercells show the same trend as those without any charge compensating scheme. The bond lengths calculated by these two different approaches differed by less than ~ 0.02 Å.

Variation of Electronic Structure of GaN:O with Varying Oxygen Concentration

The band structures for various supercells studied in this work are shown in Figures 5 and 6 along the symmetry direction, Γ -A-L-H of the Brillouin zone of a hexagonal lattice. The calculated optical band gap is 1.86 eV which is about half the experimental value of 3.4 eV. This discrepancy is associated with the density functional approximation and is discussed extensively in the literature.¹⁹

Figure 5. 1. Electronic band structure of the highest valence bands and the lowest conduction bands for Ga_2N_2 , GaZnNO and Ga_2NO hexagonal unit cells for the symmetry direction, Γ -A-L-H of the Brillouin zone. The Fermi energy E_F is the zero of the energy scale.

In Figure 5, the band structure of GaN is compared with those of Ga_2NO and GaZnNO for the unit cell, $1 \times 1 \times 1$. In Ga_2NO , 50% of N has been substituted by O. Such high levels of oxygen concentration have been experimentally observed, as discussed earlier. GaZnNO is used as a model compound to study the effect of electrons in the conduction band on the electronic structure of the heavily doped system. On comparing

the electronic structures of Ga_2NO and GaN , it is quite obvious that the degeneracy of the lowest energy conduction bands is removed along A-L-H directions. The lowest band bends towards the valence band. This splitting is severe for GaZnNO compared to Ga_2NO . Both the systems have become essentially “metallic” with no energy gap. While the low lying conduction bands show significant dispersion from Γ to A, two high lying valence bands show no dispersion along this direction. These states correspond to electrons in non-bonding p-like states of N. In contrast to these localized states, the corresponding conduction band states are anti-bonding in nature with respect to nearest neighbors and bonding with respect to the second nearest neighbors and exhibit significant dispersion characteristic of truly extended states.

Figure 6. Electronic band structure of the highest valence bands and the lowest conduction bands for $\text{Ga}_{16}\text{N}_{16}$, $\text{Ga}_{15}\text{ZnN}_{15}\text{O}$, $\text{Ga}_{16}\text{N}_{15}\text{O}$, $\text{Ga}_{35}\text{ZnN}_{35}\text{O}$ and $\text{Ga}_{36}\text{N}_{35}\text{O}$ hexagonal unit cells for the symmetry direction, Γ -A-L-H of the Brillouin zone. The Fermi energy E_F is the zero of the energy scale.

The band structures for supercells $2 \times 2 \times 2$ and $3 \times 3 \times 2$ shown in Figure 6 demonstrate the effect of dilution of oxygen impurity on the band structures. We have focused on the bands near the top of the valence band and bottom of the conduction bands. Changes in these regions are critical for the electrical and optical properties of a material. For a better comparison with the undoped GaN , the band structure of pure GaN for a larger unit cell ($2 \times 2 \times 2$) (smaller Brillouin zone) is also included in Figure 6. Comparing GaN and $\text{GaN}:\text{O}$ one sees that no new band appears in the forbidden gap without any dispersion even for largest supercell, which could indicate the presence of a localized donor level in the conventional sense. Therefore, we defined the top of the valence band, E_{VBM} , to the maximum of the bands originating from Ga- and N- bonding states, and the bottom of the conduction band, E_{CBM} , as the minimum of the next band. The difference in energy between the two bands near the Γ -point is chosen to be the band gap, $\Delta E_{\text{CV}} = E_{\text{CBM}} - E_{\text{VBM}}$. Figures 5 and 6 demonstrate that ΔE_{CV} decreases with increasing oxygen concentration. This gap completely disappears for GaN_2O corresponding to 25 at% concentration of oxygen. This is also true for $\text{Ga}_{1-x}\text{Zn}_x\text{N}_{1-x}\text{O}_x$. Thus, this lowering of the gap is not related to occupancy of conduction band-like states. The lowest conduction band states for Ga_2NO and GaZnNO have similar dispersion in the k -space. This similarity is more apparent for lower oxygen concentration.

In addition to E_{CV} the energy separation between the Fermi energy, E_F , and E_{CBM} , $\Delta E_{FC} = E_F - E_{CBM}$ and also between E_F and E_{VBM} , $\Delta E_{FV} = E_F - E_{VBM}$ are listed in Table 2. The value of ΔE_{FC} increases with increasing O concentration since more conduction band states need to be occupied to accommodate electrons freed by the substitution process. However, the quantity ΔE_{FV} indicate a maximum. The non-monotonic behavior of ΔE_{FV} is a result of the different rate of change in the values of ΔE_{CV} and ΔE_{FC} with increasing oxygen concentration.

Table 2. Energy differences (in eV) for GaN:O. $\Delta E_{CV} = E_{CBM} - E_{VBM}$ is the energy between the conduction band minimum E_{CBM} and the valence band maximum E_{VBM} ; $\Delta E_{FC} = E_F - E_{CBM}$ is the difference between the Fermi level E_F and E_{CBM} and $\Delta E_{FV} = E_F - E_{VBM}$ is the difference between the Fermi level E_F and E_{VBM} (half the band gap for semiconductors).

Supercell	ΔE_{CV}	ΔE_{FC}	ΔE_{FV}
(GaN) _{exp.}	3.38		
Ga ₂ N ₂	1.86	-0.93	0.93
Ga ₂ NO	0	3.26	3.26
Ga ₁₆ N ₁₅ O	1.54	1.81	3.35
Ga ₃₆ N ₃₅ O	1.67	1.23	2.90
GaZnNO	0.0	0.0	0.0
Ga ₁₅ ZnN ₁₅ O	1.00	-0.50	0.50
Ga ₃₅ ZnN ₃₅ O	1.67	-0.89	0.89

The shape of the energy bands near the Γ point suggests that electrons associated with O_N^x defects reside in delocalized states in the supercells. The distribution of electron density near the Fermi surface clearly shows that localization progresses monotonically with increasing supercell size or decreasing oxygen contribution. This localization effect was further explored in the xy-plane with 2x2x1, 4x4x1 and 6x6x1 supercells. The corresponding plots of electron density are shown in Fig. 7. It appears that at a higher dilution, for example parts per thousand or parts per million concentration, the electron in the donor state would be more localized near the oxygen site. The donor could be described as O_N^x with the excess electron occupying a state composed of oxygen 3s- and Ga 4s- and 4p-like character yielding an s-like distribution around the defect site. In this sense, this is similar to the electronic distribution of an F-center associated with anion vacancies. The critical density indicating a transition from a delocalized to an extended state could not be determined since the process of localization appears to be a monotonic process.

Variation of the Formation Energy of GaN:O with Oxygen Concentration

Finally we explored the change of the formation energy $\Delta E_{f,n}$ by the process of substituting gradually N with O. Within the same supercell (Ga₃₆N_{36-n}O_n) crystal structure we have calculated the formation energy for the reaction:

with $i = 36$ and $n = 0$ to 3 . The calculation has been performed using the VASP code in the GGA approximation with an energy cutoff of 520 eV and using the tetrahedron method to calculate the total energy. To incorporate the local relaxation of the atoms around the defect, we have optimized the structure taking fixed lattice constants of the pure GaN compound.

Figure 7. Electron density distribution for the lowest conduction (donor) state in the vicinity of the oxygen impurity (for $\text{Ga}_{16}\text{N}_{15}\text{O}$ the state at the Γ point at -1.8 eV, see Figure 2). The density is shown for the planes containing the O and the neighboring Ga. The plots correspond to the 2x2x1, 4x4x1 and 6x6x1 supercells.

The change of the total energy $\Delta E_{f,n}$ as a function of the O concentration is displayed in Figure 8. We have found for the unit cell considered here that isolated O_N defects are energetically favored compared to associated O_N defects. One sees from Figure 8 that the change in the formation energy decreases with increasing n . However, because of the size of the unit cell, we could not increase the number of O atoms any further. For $n > 3$, it is not possible to construct a defect structure of only isolated O substitution defects.

The main objective of this computational investigation was to understand the nature of local geometry and donor states associated with oxygen impurities at nitrogen sites in GaN. Oxygen atoms easily replace nitrogen atoms in GaN and concentration levels can reach almost 25 at% without affecting its wurtzite structure.

Figure 8. Formation energy for the reaction:

Oxygen atoms at nitrogen sites do not affect the local geometries significantly. The observed Ga-O bond lengths in GaN from the EXAFS measurements¹⁶ are in good qualitative agreement with those calculated from theory, although the tendency for shorter bond lengths observed experimentally is not reproduced in the theoretically optimized geometries. This discrepancy is not due to the n-type behavior of the materials as shown from the calculations involving exact charge compensation using Zn-O substitutional couples.

The manner in which the band parameters, such as the Fermi level and energy gap, change with oxygen concentration has been shown. However, the most interesting results from this study concern the nature of localization of the donor state. At the level of dilution investigated in this study, the charge distribution of the electron from the donor impurity O_N^x indicates an extended state. With increasing dilution, this state appears to be localized spatially near the impurity ion with predominantly s-like character similar to F-centers in alkaline halides. It appears that this localization increases monotonically with decreasing impurity concentration.

Optically, these impurity bands will shift the band gap to a lower value. Even with modest oxygen concentration, GaN:O will behave like a material with a smaller optical gap, rather than a host lattice with discrete impurity states. The color variation seen in GaN could be easily explained in terms of these changes in the band structure.

VI.d Location and Stability of RE^{3+} in Nitride Hosts

There are a number of interesting structural, chemical and electronic structure related questions that could be easily probed using first-principles theoretical methods. First, the question of solubility and structural stability with RE^{3+} occupying a Ga^{3+} site is not fully understood. RE ions are not known to occupy sites with tetrahedral coordination in oxides. A RE^{3+} substituting for a Al, Ga or In ion will occupy a site tetrahedrally coordinated to nitrogen atoms. Therefore, it is worthwhile to determine if a RE^{3+} is stable at a tetrahedral site. Second, the ionic radii of Al^{3+} , Ga^{3+} and In^{3+} in

tetrahedral coordination are 0.39, 0.47 and 0.62 Å, respectively, compared to >0.9 Å for a RE^{3+} in typical six-fold coordination.²⁰ This significant mismatch in radii is expected to lead to low solubility and severe structural relaxations. In contrast, only a small shift to a lower diffraction angle, 2θ for the (0002) diffraction peak was observed for Eu- and Tb-doped GaN with almost 2% doping concentration. This suggests that the lattice relaxation accompanying a rare earth ion in a III-V nitride is probably small. Third, it is commonly believed that there is only a single site for the RE^{3+} in III-V nitrides. We have described how multiple sites for RE^{3+} in nitride hosts were indicated by fluorescence measurements. Fourth, the electronic structures of rare earth ions and associated optical transitions in nitrides are yet to be fully explored. It is important to determine the relative location of the 4f-like states due to RE^{3+} in relation to the energy bands of host nitrides. The position of the 4f-like bands indicates the stability of the valence state of these ions.

Most of these questions just described can be analyzed using energy bands calculated by supercell band structure methods and will be useful in understanding the processes of incorporation of RE^{3+} into III-V nitrides and luminescence from these ions. Using supercell band structure methods, we have investigated the electronic structure and associated changes in the band parameters of GaN, 4f→5d transition energies of RE^{3+} in nitride hosts, and local modifications in the neighborhood of rare earth ions. In all cases, it has been assumed that the RE^{3+} substitute for the Ga^{3+} . Relative stability of this tetrahedrally-coordinated site compared to that of other possible coordinations such as cubic nitrides have not been considered since it is not obvious how this could occur in GaN without bringing massive structural changes, not evidenced in the structural measurements.

Theory

The VASP¹² and ASW¹³ methods were used in this work for calculating the local geometries and the electronic structures of GaN and GaN:RE^{3+} for Re=Pr, Nd, Eu, Tb, Dy and Er. First, the local structural relaxations near RE^{3+} at the gallium sites were simulated using a quantum mechanical molecular-dynamic approach implemented in VASP. The optimized structures were then used as input for calculating the electronic structures of GaN and GaN:RE^{3+} by the augmented spherical wave (ASW) method in its scalar-relativistic implementation.

The band structures calculated with both VASP and ASW were almost identical. However, the electronic structure calculated by the ASW method using a minimal, atom-centered basis set lends itself to a simpler interpretation of the electronic states and chemical bonding in term of the valence orbitals. Therefore, we have used the ASW method for analyzing the electronic properties and the chemical bonding for the compounds under consideration.

Lattice Relaxation in the Neighborhood of Re^{3+}

The optimized structures of GaN:RE^{3+} using 3x3x2 supercells consisting of one rare earth ion, thirty five Ga atoms and thirty six nitrogen atoms are listed in Table 1. The RE atoms substituting for gallium atoms continue to be tetrahedrally coordinated.

The nitrogen atoms move away from the RE ions to accommodate these larger ions at the Ga sites. The RE-N bond lengths vary from 2.15 to 2.3 Å, and are in good agreement with the available data from EXAFS measurements.^{21,22} In all the cases, theoretically derived bond lengths are almost half that of the GaN bond length and that expected for RE-N bonds on the basis of ionic radii.

Table 3. Optimized structure for GaN:RE. The experimental lattice constants for GaN are $a = 3.1891$ Å and $c = 5.1853$ Å with Ga-N distances $d_{\text{N-Ga}} = 1.942 - 1.977$ Å. The calculations for GaN:RE have been performed using a supercell $A = 3a$, $B = 3a$ and $C = 2c$, $\text{Ga}_{35}\text{N}_{36}$, and replacing one Ga by a rare earth atom, $\text{Ga}_{35}\text{MN}_{36}$, $M = \text{Pr, Nd, Eu, Tb, Dy}$ and Er . For the pure system $\text{Ga}_{36}\text{N}_{36}$ one finds the optimized structure $A = B = 9.6048$ Å and $C = 10.4125$ Å with $d_{\text{N-Ga}} = 1.956 - 1.962$ Å. For the structure optimization of GaN:RE³⁺ lattice parameters were not changed. The local relaxation of the ions around the RE result in the following M-N distances.

row	Supercell	$d_{\text{N-M}}$ (Å)	$d_{\text{N-M}}$ (Å) (Expt)
1	$\text{Ga}_{35}\text{N}_{36}\text{Pr}$	2.262 – 2.295	
2	$\text{Ga}_{35}\text{N}_{36}\text{Nd}$	2.246 – 2.278	
3	$\text{Ga}_{35}\text{N}_{36}\text{Eu}$	2.260 – 2.304	2.3 (3)-2.5 ²¹
4	$\text{Ga}_{35}\text{N}_{36}\text{Tb}$	2.176 – 2.205	2.2 ²¹
5	$\text{Ga}_{35}\text{N}_{36}\text{Dy}$	2.165 – 2.194	
6	$\text{Ga}_{35}\text{N}_{36}\text{Er}$	2.152 – 2.178	2.23±0.06 ²²

Departure from ideal tetrahedral symmetry was observed for all the rare earth ions. The longest Eu-N bond length of 1.5 Å observed experimentally is comparable to that expected on the basis of ionic radii²⁰ when the ionic radius for Eu³⁺ is corrected for tetrahedral coordination. The longest Eu-N distance obtained from theory is ~2.3 Å. This Eu-N bond length, although smaller than that observed experimentally, is longer than that for any other rare earth ion. It is worthwhile to note that the Er-N bond lengths were determined using a model of six-fold coordination from the EXAFS measurements. In the present calculation, only four-fold coordination has been considered, yet there is good agreement between theory and experiment.

Electronic Structure of RE³⁺ in GaN

In the previous section, we discussed the electronic structure of GaN. In Figure 9, the partial DOS for Eu³⁺ is displayed. For other rare earth ions, namely, Pr, Nd, Tb, Dy, and Er studied during this project, please refer to the publication include in Appendix 1.²³

The position of the RE³⁺ 5d state $\epsilon_{\text{d,up}}$ relative to the position of the host valence states ϵ_{VBM} is almost constant for all RE³⁺ and the relative position of the f states $\epsilon_{\text{f,up}}$ are decreasing for Ce to Gd with increasing atomic number. The 4f-like spin-up states of RE³⁺ move towards the valence bands with increasing atomic number and the difference $\epsilon_{\text{f,up}} - \epsilon_{\text{VBM}}$ decreases on going through the rare earth series whereas $\epsilon_{\text{d,up}} - \epsilon_{\text{VBM}}$ is almost constant ~5.1 eV. For GaN:Eu, in Figure 6, the 4f-like spin-up bands reach the VBM,

$\varepsilon_{f,up} \sim \varepsilon_{VBM}$. For RE^{3+} for which 4f-like spin-up states are completely occupied, the corresponding energy bands for majority spin states overlap energetically with the host valence bands. With increasing spin-down electrons for Tb, Dy and Er, the partially occupied 4f-like spin-down bands exhibit the same trend as for the 4f spin-up states with increasing atomic number. Namely, the 4f spin-down states move towards the VBM going from Tb to Er. However, in all the cases, the partially occupied 4f-like bands appear in the forbidden gap indicating the stability of the valence states of these ions at the substitutional site.

Figure 9. Partial density of states for $GaN:Eu^{3+}$

In a previous paper, a linear correlation between $(\Delta\varepsilon_{f-d})_{calc}$ and $(\Delta\varepsilon_{f-d})_{exp}$ was demonstrated:

$$(\Delta\varepsilon_{f-d})_{exp} = m \cdot (\Delta\varepsilon_{f-d})_{calc} + \varepsilon_{shift}(RE)$$

for the 4f→5d transitions in complex oxides and fluorides.²⁴ We found that m is approximately one; the values for $\varepsilon_{shift}(RE)$ are also listed in Table 4. Using the same value for m in the case of nitrides, the 4f→5d transition energies are calculated and listed in the last column of Table 4. These transitions will occur at higher energies compared to that of the band gap of GaN, but at lower energies compared to that of AlN. Thus in GaN or InGaN, these excitation bands are not expected to play a significant role either in direct excitation or energy transfer from the e-h pairs. It is possible that these transitions could be exploited in designing an active layer based on GaN or AlGaN alloy.

Table 4. Energy difference $(\Delta E_{f-d})_{\text{calc}}$ between the RE partial occupied f and unoccupied d states in $\text{Ga}_{35}\text{N}_{36}\text{RE}$. Fitted energy shift for RE (see text and Ref. 24) and predicted first absorption peak (ΔE_{f-d}) of f to d transitions in GaN:RE .

Row	Supercell	$(\Delta E_{f-d})_{\text{calc}}$	$\epsilon_{\text{shift}}(\text{RE})$	$(\Delta E_{f-d})_{\text{predicted}}$
1	$\text{Ga}_{35}\text{N}_{36}\text{Pr}$	2.9	2.09	5.0
2	$\text{Ga}_{35}\text{N}_{36}\text{Nd}$	3.4	2.35	5.8
3	$\text{Ga}_{35}\text{N}_{36}\text{Eu}$	4.5	1.77	6.3
4	$\text{Ga}_{35}\text{N}_{36}\text{Tb}$	3.8	-	
5	$\text{Ga}_{35}\text{N}_{36}\text{Dy}$	4.4	-	
6	$\text{Ga}_{35}\text{N}_{36}\text{Er}$	5.2	1.03	6.2

There are two important results from this study. First, the location of the 4f-like bands (for the incomplete 4f-shell) in the forbidden gap suggests that the trivalent rare earth ions are stable at the gallium site. It is indeed surprising that a rare earth ion can be stabilized at a tetrahedrally coordinated site in a nitride host, which has never been reported in halide or oxide hosts. It may be related to increased covalency in nitride hosts which is responsible for semiconducting properties of GaN. Second, the 4f→5d transition energies are larger than that of the band gap of GaN. Thus, these absorption bands do not play any significant role in the energy transfer process involving host excitation and subsequent emission from the rare earth ions. It will be interesting to examine the charge transfer bands for some of these ions for which there is almost no experimental data available for the nitride hosts.

VI.e Saturation of Emission from RE^{3+}

Because of the long radiative decay time of the rare earth ions, the possibility of saturation of emission from rare earth ions has been a concern for application of rare earth ion activated nitride as an active layer in a heterostructure design. In a high current situation, the injected e-h pairs may not find enough rare earth ions in the ground state to transfer their energy and thus relax to the ground state via excitonic emission or defect emission. This situation is often described as depletion of the ground state for the activator ions. We have investigated this possibility both for the powder samples of AlN, particularly AlN:Dy^{3+} , and thin films of GaN:Eu^{3+} .

AlN:Dy³⁺

In AlN powder samples, we generally observed two types of radiative centers: point defects, which lead to a broadband transition and rare earth ions with characteristic line transitions. Under lamp excitation above the band gap, the spectrum is dominated by emission from the rare earth ions, and with pulsed laser excitation, the defect emission dominates the spectrum. These emission characteristics indicate that:

1. the rate of energy transfer from the host to the rare earth ions is faster than that to the defects;

2. the concentration of point defects is significantly higher than that for the rare earth ions, which is in agreement with O/N data from EDS measurements;
3. the concentration of rare earth ions in the ground state deplete with increasing excitation intensity.

Using the excitation model described earlier, we developed a kinetic model for the growth of excited states of rare earth ions and point defects. As indicated by the experimental data, it was assumed that both the point defects and the host transfer energy to the rare earth ions and that these transfer rates are higher than the relaxation rates for both the host and point defects via radiative and nonradiative routes. Using these assumptions, the growth of excited states of defects, $N_{d,exc}$ and that for the rare earth ions $N_{r,exc}$ with respect to excitation intensity were studied for excitation energies greater and less than the band gap energy. In Figure 9, the ratio of $N_{d,exc}$ and $N_{r,exc}$ with respect to ground state density N_d and N_r are plotted against intensity of exciting radiation. In the case of complete depletion of ground state, the ratios, $\frac{N_{d,exc}}{N_d}$ and $\frac{N_{r,exc}}{N_r}$ approach unity.

$\frac{N_{d,exc}}{N_d}$ is almost linearly dependent on the excitation intensity when $G/\eta_1 < 1$, while $\frac{N_{r,exc}}{N_r}$ is saturating and approaching 1 with increasing G when $G/\eta_1 > 0.0001$. These results are qualitatively consistent with our preliminary measurements with pulsed laser excitation in which RE ions are saturated at an intermediate excitation intensity $0.0001 < G/\eta_1 < 1$. Similar behavior is also expected upon excitation at energies below the band gap due to direct excitation of the point defects.

Figure 10. Variation of excited states of defects and rare earth ions with excitation intensity. The parameter, G/η_1 has been used as measure of excitation intensity. For details please see Reference 1.

GaN:Eu³⁺ Thin Film

In order to investigate the response of GaN: Eu³⁺ at higher excitation densities, a laser excitation of 10Hz/5nsec pulses was used. The excitation wavelength was chosen near the band edge absorption energy (360nm) which results in generation of electron-hole pairs with low kinetic energy (near the Γ point of the Brillouin zone) and approximately coincides with the effect of electrical excitation (electron-hole injection) before the recombination at activator ions occurs.

Our first observation is the reversal of peak intensities for GaN NBE at 365nm and ⁵D₀-⁷F₂ transitions of Eu³⁺ compared to lamp excitation. This by itself constitutes a reduction in relative activator output of more than an order of magnitude. Figure 11 demonstrates changes in the ⁵D₀-⁷F₂ line intensities of Eu³⁺ from 610 nm to 640 nm for three incident excitation power values with approximately 5mJ/cm² per pulse as the maximum (instantaneous power about 1MW/cm²). The spectra have been normalized to 365nm NBE intensities from GaN host (not shown) while the incident laser excitation is reduced by a factor of 3.5 and 5 using neutral density filters. One immediately notices the falling intensity of this red emission with increasing laser power. This behavior (in Fig. 11a) is suggestive of depletion of the ground state of the rare earth ions and foretells the possibility of saturation of activator emission in rare earth doped materials for high exciton concentration with above the bandgap radiation. In the present case, it is actually expected since both the density of recombination sites (on the order of 10²⁰ cm⁻³ for the Eu activators compared to GaN lattice ions at 10²² cm⁻³) and the excited state decay time (on the order of 10⁻⁹ sec for excitonic emission vs. about 10⁻⁴ sec in case of europium) are less favorable for the red emission compared to NBE. We also note a non-uniformity in GaN:Eu output in response to the laser intensity change (in Fig.11.b). The spectra have been normalized to the peak value of the red emission around 622nm. Since the emission profile is assumed to consist of multiple contributions due to two or more types of europium ions in the GaN lattice, one finds the site giving rise to the 619 nm component to be slightly more sensitive to the excitation density increase. In a crude approximation, this translates into a higher population of the second type of europium ions that are capable of receiving their excitation through the defects.

VI.f Conclusions

In the previous sections, we provided a brief discussion of the various modeling activities undertaken during this project. The following conclusions are of considerable interest for further optimization of GaN:RE³⁺ fluorescent materials for application as active layers.

Figure 11. Excitation power dependent intensity of Eu³⁺ emission: a full laser output (estimated at $\sim 5\text{mJ/cm}^2$, solid line), and its reduction by 3.5 (dashed line) and 5 times (dotted line). The inset shows relative changes in integrated emission intensities.

First, it was shown that, in GaN, the red emission near 620 nm due to $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ occurs upon excitation of the host at energies greater than band gap energy. The excitation peak corresponding to 620 nm emission coincides with that of the band gap of the material. Although the exact microscopic nature of energy transfer process from the host to Eu³⁺ cannot be established, the transition process is essentially non-radiative. The same cannot be said about Tb³⁺ in GaN due to the lack of PL data. Once the deposition conditions for Tb³⁺ are optimized, the excitation process of Tb³⁺ may be established from PLE data. Since photo-excitation above the band gap energy results in generation of e-h pairs, GaN:Eu³⁺ could be used as the active layer component for generation of red light.

In AlN powder samples, we observed that host excitation could lead to fluorescence from Eu³⁺ (red), Tb³⁺ (green), Dy³⁺ (yellow) and Tm³⁺ (blue). It is quite possible that the same behavior would be observed in alloys of GaN and AlN.

Secondly, oxygen contamination is a major problem in synthesis of nitride powders. At the level of impurity concentration, the electronic structure of the nitride host is massively perturbed, which could easily explain the coloration of nitride powders.

Third, our first principles modeling of GaN:RE³⁺ showed that rare earth ions could be incorporated into the nitride lattice without massive lattice reconstruction, a fact corroborated by the XRD measurements. The RE-N bond lengths relax to somewhere in between the GaN bond length and that of RE-N in similar coordination. The energy bands associated with the incomplete 4f-like shell appear in the band gap indicating that the trivalent rare earth ions are quite stable in this lattice. Additionally, no 4f $\rightarrow$ 5d absorption was observed below the band gap energy and therefore, such absorption cannot be utilized in designing a nitride-based fluorescent material.

Finally, saturation of fluorescence yield at higher excitation density was observed. However, considering the fact that the materials studied in this work are not optimized and emission from the rare earth ions persists even at very high excitation density,

depletion of the ground state leading to saturation of fluorescence yield may not be a problem.

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Section VII. Conclusions

The aim of this project was to explore novel active layer materials based on RE^{3+} -doped III-V nitride alloys for the design of phosphorless “white light” solid state light sources. Upon injection of electrons and holes into this active layer under forward biasing, the electron-hole (e-h) pairs recombine at the activator ions and produce characteristic emission from intra-configurational transitions within the $4f^n$ manifold. The rare-earth ions are chosen to produce red, green and blue light for white light generation. The advantages of such an approach in preference to the popular hybrid design, in which the active layer produces either blue or ultra-violet emission and the outer phosphor layer converts these photons for white light, has been discussed earlier.

To test this design concept, we focused on the photo-luminescence (PL) response of the material to excitation near the band edge. Although excitation near the band edge is accompanied by surface losses, these losses are significantly less near the band gap. Most materials exhibit a peak in quantum efficiency near the band edge.¹ The underlying excitation process is very similar to that of emission from an undoped active layer upon injection of e-h pairs. The absorbed photons having energy equal to the band gap or more, generate e-h pairs, which eventually excite the RE^{3+} . Thus, the PL measurements could easily demonstrate whether the e-h pairs would recombine efficiently at the activator sites. In a typical LED-based light source, the e-h pairs are injected from the p- and n-type claddings. Once they are confined to the active layer region, the radiative recombination process should proceed in a manner similar to optical excitation near the band edge. Since our focus was on developing the active layer materials with the PL measurements providing a faster way to evaluate the behavior of these materials upon injection of electrons and holes, no attempt was made during this project to build electroluminescence devices.

Many important issues needed to be addressed so as to test the validity of the proposed concepts. They included doping a nitride host with rare earth ions, testing their response to excitation near the band edge, and, finally, making thin films of these materials by MOVPE or PLD on a sapphire substrate. The project was designed to progress through synthesis of nitride powders and ultimately to thin film deposition with demonstration of their performance in each step.

Several departures from the original plan were made in order to proceed expeditiously towards the final goals. First, it was discovered that combustion synthesis which relied on converting oxides to nitrides through ammonolysis failed to produce nitrides with sufficiently high purity. We therefore moved to a three-step solution approach (nitrates-to-hydroxides-to-fluorides-to-nitrides) and optimized the process for synthesizing nitrides with low oxygen contamination, modified the reactor to eliminate sources of oxygen, and successfully produced GaN, AlN, alloys of GaN and AlN, and nitrides activated by RE^{3+} . The powder samples produced using this process showed significantly better performance upon excitation above the band gap energy, and were used as target materials for thin films of GaN:Tb^{3+} and GaN:Tm^{3+} made by PLD. This approach of making powder for thin films by PLD proved to be an expeditious route to explore alloy and rare earth ion combinations.

Secondly, a horizontal MOVPE reactor was designed, built and tested to epitaxially deposit thin films of GaN and InGaN on sapphire substrates. The reactor design was

based on standard models used in research laboratories. However, many safety features were added to meet industry-level safety standards before it became operational. While the design was adequate for yielding good quality undoped films of GaN, at first it was inadequate for producing thin films of GaN: RE³⁺. The main problem was an inhomogeneous distribution of rare earth ions. The flow of metal organic precursors had to bypass the gas-mixing manifold because of their high vaporization temperature and were introduced downstream just before the inlet to the reactor. The lack of adequate mixing of the precursors for the host and dopants led to an inhomogeneous distribution of RE ions within the deposited films. Therefore, the reactor was modified extensively to achieve a uniform distribution of rare earth ions.

Third, it was realized from powder synthesis that unintentional oxygen impurities are undesirable. They significantly reduce the band edge or excitonic emission, and increase defect emission. Traditionally, metal organic precursors used for rare earth ions include oxygen-containing ligands. In anticipation that this could introduce undesirable problems for emission from rare earth ions, we identified metal organic precursors for the rare earth ions that do not contain oxygen. Subsequently, however, we observed no significant advantage of using such oxygen-free precursors, which remains a mystery. That oxygen may be needed for the incorporation of rare earth ions into nitride lattices has been emphasized by several researchers.² Unfortunately, the rare earth chemistry for MOVPE and the role of oxygen are still very poorly understood.

Fourth, the PLD of thin films using targets from powders synthesized during this study was partly delayed because of our concern about residual oxygen impurities. Subsequently, it was observed that most of these oxygen impurities could be removed during the annealing phase, and the quality of the host materials could be significantly improved. In contrast to the MOVPE process which produced only “one film” per day, the powder-to-thin film via PLD process is a relatively faster process, but was only developed near the end of the project. Overall, we demonstrated the validity of the proposed scheme for designing a “white light source”. Specifically, this study demonstrated that designing a phosphorless white light source with rare earth ion activated nitrides is a feasible concept, but needs more intensive study particularly in the area of rare earth ion chemistry for vapor phase epitaxy.

Our first accomplishment was to demonstrate emission from Eu³⁺, Tb³⁺, Dy³⁺ and Tm³⁺ in AlN powders, Eu³⁺ and Tb³⁺ in powder samples of GaN and alloys of nitrides of Al and Ga, and Eu³⁺ and Tb³⁺ in GaN thin films. Eu³⁺, Tb³⁺, Dy³⁺ and Tm³⁺ activated nitrides could be used as red, green, yellow and blue emitting active layers. However, near infrared emission (³H₄→³H₆) from Tm³⁺ is stronger than the blue emission. It is possible that Tm³⁺ could be made to fluoresce strongly by modifying the alloy composition. The blue emission (⁴F_{9/2} → ⁶H_{15/2}) from Dy³⁺ could also be used as a blue component. Unfortunately, Tm³⁺ and Dy³⁺ ions did not fluoresce in GaN powder samples. Even a PLD thin film made from using GaN:Tm³⁺ did not show any characteristic emission from Tm³⁺. Since Dy³⁺ and Tm³⁺ are known to fluoresce in GaN thin films doped by ion implantation,³ this needs further study.

PLE measurements showed that in AlN, Eu³⁺, Tb³⁺, Dy³⁺ and Tm³⁺ could be excited through excitation by host and defects. The PLE spectrum of GaN:Eu³⁺ thin films shows clearly that energy transfer from the host to Eu³⁺ occurs efficiently. Both defect emission and host emissions are suppressed with emission from Eu³⁺ ions. The

exact nature of the energy transfer process needs to be studied further. However, demonstration of this energy transfer process supports the proposal that these ions could be used as recombination centers for e-h pairs in the active layer.

We also demonstrated emission from AlN:Eu³⁺ and Tb³⁺, and AlN:Dy³⁺ and Tm³⁺. Codoping is necessary to generate white light homogeneously from the active layer. Unfortunately, we observed that the deposition conditions for GaN:Eu³⁺ and GaN:Tb³⁺ thin films by the MOVPE method are significantly different. Thus, a GaN thin film could not be codoped with both of the ions at the same time. Novel deposition conditions must be explored, so as to allow both of the ions to be incorporated simultaneously, requiring a better understanding of rare earth nitride chemistry. Otherwise multiple layers of monochromatically emitting active layers would have to be used for white light generation.

Energy transfer from Tb³⁺ to Eu³⁺ in AlN powders was demonstrated for the first time. Such sensitization processes will make it easier to optimize the alloy composition for efficient energy transfer from the host to the sensitizer ion for efficient emission from the ion pairs. Exploration of such ion pairs should be an important component for further research.

We also explored the possibility of saturation of emission using AlN:Dy³⁺ powder and GaN:Eu³⁺ thin films. In both the cases, the relative intensity of emission with respect to host excitation decreased with increasing excitation intensity. However, this is expected because of the slow decay time of the rare earth ions compared to that of the hosts or defects. Even at a laser intensity capable of producing electron-hole pairs at the same rate as typical diode currents, emission from Eu³⁺ ions could still be observed. In view of the fact that UV radiation is usually absorbed in a thin surface layer (in contrast to uniform distribution of e-h pairs within the bulk) and that the thin films studied are far from being optimized, the saturation issue does not appear to be critical. If further experiments with optimized thin films demonstrate this to be a serious problem, it could be addressed by either changing the concentration of rare earth ions or using thicker layers.

We observed occupancy of multiple sites in AlN:Dy³⁺ and AlN:Tm³⁺ powders and GaN:Eu³⁺ thin films and separation of secondary phases rich in rare earth ions in thin films of GaN:Tb³⁺. The formation of secondary phases limits efficient incorporation of rare earth ions into the nitride lattice. We originally thought that inhomogeneous distribution of the rare earth ions on the surface drives this phase separation. However, even after addressing this issue by modifying the reactor configuration, the problem persisted and needs to be addressed further.

Occupancy of multiple sites is an indication that with increasing rare earth ion concentration the lattice might become increasingly disordered and unstable. The quality of the thin films could deteriorate with increasing rare earth ion incorporation. The underlying kinetics and thermodynamics of multiple-site occupancy needs further investigation.

Our main goal was to demonstrate a thin film capable of emitting white light. We showed that AlN:Dy³⁺, Tm³⁺ is capable of producing this. However, sources of green, red, blue and yellow emission have been identified in an AlN host and green and red emission in GaN. These could either be used as sources of monochromatic radiation or combined together in a multiple-layer structure for white light generation.

In summary, our work has demonstrated the feasibility of designing RE³⁺-activated III-V nitrides for “white light” emission. However, more intense research in the area of the chemistry of rare earth ions in nitrides will be necessary to produce optimized nitride films doped with rare earth ions for white light generation.

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Section VIII. Recommendations

During this project, we demonstrated red, green, blue and yellow emissions from Eu^{3+} , Tb^{3+} , Tm^{3+} and Dy^{3+} in AlN powder, and red and green emissions, respectively, from Eu^{3+} and Tb^{3+} in GaN, in both powder and thin films deposited by MOVPE and PLD methods. Except for GaN: Tb^{3+} which fluoresces under CL, fluorescence from rare earth ions were demonstrated upon exciting the material above the band gap energy. Transfer of energy from the host and defects to the rare earth ions was also demonstrated. Rare earth ion pairs such as (Eu^{3+} , Tb^{3+}) and (Dy^{3+} , Tm^{3+}) fluoresced simultaneously in AlN. More importantly, energy transfer from Eu^{3+} to Tb^{3+} was observed in AlN powders.

While our research has advanced knowledge in this area, there is still relatively little known and understood about rare earth ions in nitride hosts. We had assumed that different nitride hosts would behave similarly since the local coordinations of the rare earth ions are identical in AlN and GaN. To our surprise, Dy^{3+} and Tm^{3+} fluoresced in AlN, but not in GaN, although both of these ions are known to fluoresce in ion-implanted thin films of GaN.¹ Apparently, the observed variances in the performance of RE^{3+} in nitride hosts is dependent both on the intrinsic electronic structure of the host materials and also on the method of preparation of the samples.

In order to integrate nitrides doped with RE^{3+} into optoelectronic structures, such as nitride-based solid-state lighting devices, considerable in-depth research on these materials needs to be done. This research is high-risk and time-consuming, but would take SSL technology to a new level of performance. Such research activities belong to both core level and developmental research outlined by Department of Energy funding guidelines. Our recommendation for future research in this area are categorized accordingly in the following sections.

VIII.a Core Level Research

There are two specific areas that demand further study at the core level: band structure engineering of RE^{3+} doped nitrides and rare earth chemistry for MOVPE deposition of such films.

Band Structure Engineering of RE^{3+} -doped Nitrides

We and many others researchers have demonstrated the following regarding the rare earth ions in nitride hosts:

- most RE ions fluoresce in GaN and AlN hosts;
- emissions from these ions could suitably be combined to generate white light as in fluorescent lamp phosphors;²
- qualitative evidence for efficient emission upon band edge excitation.

However, no quantitative estimates of efficiency are available. Optimization of the rare earth ion doped nitrides has not been undertaken. Further studies in the following areas are necessary to make high quality rare earth doped nitrides for optoelectronics application of these materials:

- manipulating the band gap of nitride alloys for better matching of the band edge emission with the excitation peaks of the rare earth ions;
- identifying RE³⁺ pairs or triplets that would efficiently fluoresce in nitrides and could be combined to produce white light;
- identifying sensitizer ions for RE³⁺ pairs or triplets for minimizing the choice of alloy compositions;
- optimization of rare earth ion concentrations for maximum efficiency and minimization of any saturation effect at high excitation energy intensity;

Although this list appears to be short, the underlying research activities are huge. Large numbers of samples must be prepared and tested, preferably in thin films. In this context, the route taken by the present program is economic, fast and efficient. All the optimizations should be performed in powder samples, synthesized by an approach that minimizes defect structures and impurities, followed by thin film deposition by the PLD approach. We observed that many of the defect and impurity related problems could be minimized by annealing the films deposited by PLD.

Quantitative targets should be established to prescreen the various materials. A good approach might be to use a standard UV emitting InGaN thin film whose quantum efficiency could be compared to those of the promising candidates. Once the most promising candidate materials are identified, the focus of research should be directed towards depositing such layers by the MOVPE approach.

Rare Earth Chemistry for MOVPE Deposition

Needless to say, thin film deposition via MOVPE is the preferred manufacturing method. If standard MOVPE deposition conditions of candidate materials could be established, then the thin film deposition process of RE³⁺-doped materials could be seamlessly integrated into the existing LED fabrication processes.

In spite of the extensive literature on RE³⁺ doped III-V compounds, there is only one publication each for GaN:Tb³⁺³ and GaN:Eu³⁺⁴, and two publications at most for GaN:Er³⁺ utilizing the MOVPE technology.⁵ Most of these publications do not provide a clear description of the deposition conditions employed and reasons for them. Therefore, we had to partially rediscover, by trial and error, deposition conditions for GaN:Tb³⁺ and GaN:Eu³⁺ while trying to reproduce thin films described in Refs. 3 and 4. The deposition conditions are vastly different from those reported earlier.

The question is why? Eu³⁺ and Tb³⁺ are usually incorporated into an oxide lattice using two different conditions, the first in an oxidizing environment and the second in a more reducing environment, because of the multiple valence states of these ions. Other rare earth ions that have multiple valence states are Pr, Ce and Sm. When the desired valence states of two dopants are not electrochemically compatible, they may not be codoped simultaneously!

The environment within a typical MOVPE reactor for nitride deposition is essentially reducing. Therefore, the question is then how to incorporate ions such as Eu³⁺ that may require more oxidizing environments? What will happen then to the quality of the host lattice? Hara et al.³ observed columnar growth of GaN:Tb³⁺, as did we, and also high resistivities for such GaN:Tb³⁺ films.³ Is the high resistivity associated with Tb³⁺ or with the quality of the films?

What is the role of oxygen in incorporating rare earth ions into nitride lattices? The need for oxygen for incorporating rare earth ions into a nitride lattice has been mentioned in the literature.³ We also observed formation of secondary oxide phases of Tb^{3+} in our GaN:Tb^{3+} . Is the precipitation of the secondary phases a consequence of molecular oxygen in the reactor environment or chemically bound oxygen in the precursors molecules?

Questions abound regarding the incorporation of rare earth ions into a nitride lattice, answers to which cannot be found in the literature. These questions indicate the low level of understanding of rare earth chemistry in nitrides. More in-depth research is required to better understand the reaction parameters necessary for incorporating rare earth ions into a nitride lattice and to develop methods for achieving the desired concentration for higher efficacy.

VIII.b Developmental Research

Once the thin films of RE^{3+} -doped nitrides having efficiency comparable to or better than those of commercially available undoped InGaN alloys are fabricated in a reproducible manner, the next important steps will be to integrate this technology with the existing chip fabrication technology and to make devices and test their performance. For successful device generation, the following topics need to be investigated as completely as possible:

- optical and electrical properties of RE^{3+} -doped films,
- saturation characteristics,
- codoping vs. MQW structures for eventual device application.

Optical and Electrical Properties of RE^{3+} -doped Films

As mentioned earlier, the deposition conditions for RE^{3+} -doped films are different from those for pure GaN films. The doping level is usually $\sim 1\text{-}2\%$ which is considerably higher than that of typical dopant levels added deliberately to change the electrical properties of nitride films. Therefore, the quality of the thin films may not be as good as that of the undoped GaN films. In the case of Tb^{3+} and Eu^{3+} activated films, we always observed whitish to slightly colored films in contrast to transparent undoped thin films, implying deposition of micron-size crystallites. We also observed columnar structures of GaN:Tb^{3+} crystals on GaN sub-layers. These conditions might help light to escape from the layer, but also degrade its electrical properties. The optical and electrical properties of the thin films should be investigated simultaneously to produce acceptable thin films for device fabrication.

Saturation of Fluorescence Yield from RE^{3+} -doped Nitride Films

We observed indications of saturation of fluorescence yield with increasing excitation intensity. It is a universal phenomenon when the host lattice is used to transfer energy to the activator ions because of the incompatibility of radiative life time of the host and the activator ions. There are at least two important consequences of saturation of fluorescence yield at high excitation intensity. First, the decrease in fluorescence yield

will lead to a drop in efficacy. This is a serious issue, and we have no quantitative data on this problem. The indications are there that it may not be a severe problem even though our films are not optimized. Second, there will be a color variation with increasing current. This may not be acceptable if the variation in color is perceptible. We strongly recommend that these issues be carefully studied with fully optimized films. The saturation effects could be minimized by varying activator ion concentration or host ion compositions. It could also be reduced using thicker films or multiple films as in multiple quantum well (MQW) structures.

Final Device Configuration

For generating white light, our recommendation is to make thin films codoped with RE-ion pairs or triplets. However, it may not be possible to dope the thin films with more than one rare earth ion because of solubility limits and film quality issues. In this context, it may be helpful to use multiple rare earth doped active layers as sources of monochromatic radiation for generating white light. These structural issues for device applications should be investigated in detail.

Our work has shown that the use of RE³⁺-activated nitrides is a promising approach for creating a new generation of white light sources with better color quality and potentially higher efficacy. We believe that it is an important area of research which should be pursued further. However, considering the fact that it is a relatively high risk area of research, government and industry collaboration will be required in order to develop the appropriate technology.

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Appendix

A.1 External Publications

1. A new method produce rare earth-doped gallium nitride phosphor powders, G. A. Hirata, J. Tao, P. Chen, K. C. Mishra and J. McKittrick, *MRS Symp. Proc.*, **866**, 9.1 (200)
2. A first-principles investigation of the electronic structure of trivalent rare earth ions in gallium nitride, K. C. Mishra, V. Eyert and P. C. Schmidt, *Z. Phys. Chem.*, **221**, 1663 (2007).
3. Localization of oxygen donor states in gallium nitride from first-principles calculations, K. C. Mishra, P. C. Schmidt, S. Laubach and K. H. Johnson, *Phys. Rev. B*, **76**, 035127 (2007).
4. A study of luminescence from Tm^{3+} , Tb^{3+} and Eu^{3+} in AlN powder, B. Han, K. C. Mishra, M. Raukas, K. Klinedinst, J. Tao and J. B. Talbot, *J. Electrochem. Soc.*, **154**, J262 (2007).
5. Investigation of luminescence from Dy^{3+} in AlN, B. Han, K. C. Mishra, M. Raukas, K. Klinedinst, J. Tao and J. B. Talbot, *J. Electrochem. Soc.*, **154**, J44 (2007).
6. Eu^{3+} doped GaN thin films grown on sapphire by pulsed laser deposition, N. Perea-Lopez, J. H. Tao, J. McKittrick, J. B. Talbot, B. Han, K. Klinedinst, M. Raukas, J. Laski, and K. C. Mishra and G. Hirata, Proc. of 7th International Conference of Nitride Semiconductors, Las Vegas, 2007 (accepted)
7. Synthesis of rare-earth activated AlN and GaN powders via a three-step conversion process, J. Tao, N. Perea-Lopez, J. McKittrick, J. B. Talbot, B. Han, K. Klinedinst, M. Raukas, J. Laski, and K. C. Mishra, Proceedings of 7th International Conference of Nitride Semiconductors, Las Vegas, 2007 (accepted)
8. A study of oxygen content in GaN, AlN, and GaAlN powders, J. B. Talbot, J. Tao, N. Perea-Lopez, J. McKittrick, B. Han, M. Raukas, K. Klinedinst, and K. C. Mishra (accepted to *J. Electrochem. Soc.*)

A.2 External Presentations

1. A new method produce rare earth-doped gallium nitride phosphor powders, G. A. Hirata, J. Tao, P. Chen, K. C. Mishra and J. McKittrick, MRS Spring Meeting, San Francisco, CA (2005).
2. Synthesis of GaN and AlN powder via three-step nitrate conversion process, J. Tao, J. Asis, J.B. Talbot, B. Han, K. Klinedinst and K. C. Mishra, The ECS Meeting, Cancun, 2006
3. Investigation of luminescence from Dy^{3+} in AlN, B. Han, K. Mishra, M. Raukas, K. Klinedinst, J. Tao, and J. B. Talbot, The ECS Meeting, Cancun, 2006
4. Localization of oxygen donor states in gallium nitride, K. C. Mishra, P. C. Schmidt, S. Laubach and K. H. Johnson, The ECS Meeting, Washington, 2007
5. Synthesis of rare-earth activated AlN and GaN powders via a three-step conversion process, J. Tao, N. Perea-Lopez, J. McKittrick, J. B. Talbot, B. Han,

- K. Klinedinst, M. Raukas, J. Laski, and K. C. Mishra , 7th International Conference of Nitride Semiconductors, Las Vegas, 2007
6. Eu^{3+} doped GaN thin films grown on sapphire by pulsed laser deposition, N. Perea-Lopez, J. H. Tao, J. McKittrick, J. B. Talbot, B. Han, K. Klinedinst, M. Raukas, J. Laski, and K. C. Mishra and G. Hirata, 7th International Conference of Nitride Semiconductors, Las Vegas, 2007

A.3 Invention Disclosures

1. Rare earth activated nitrides for solid state lighting applications, B. Han, J. Tao, K. Klinedinst, M. Raukas, J. Talbot and K. C. Mishra, Patent Application filed
2. Light emitting diode based on multiple double-heterostructures (quantum wells) with rare earth doped active regions optimized for different colors, M. Raukas, K. C. Mishra and J. Laski , Patent Application filed.