



VCU

Virginia Commonwealth University
VCU Scholars Compass

Theses and Dissertations

Graduate School

2011

The Effect of Ambient on Photoluminescence from GaN

Iwona Ruchala
Virginia Commonwealth University

Follow this and additional works at: <https://scholarscompass.vcu.edu/etd>



Part of the [Physics Commons](#)

© The Author

Downloaded from

<https://scholarscompass.vcu.edu/etd/226>

This Thesis is brought to you for free and open access by the Graduate School at VCU Scholars Compass. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.

The Effect of Ambient on Photoluminescence from GaN

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics / Applied Physics at Virginia Commonwealth University.

By

Iwona Ruchala

B.S. in Physics

Uniwersytet Wrocławski, 2008

M.S. in Physics/Applied Physics

Virginia Commonwealth University, 2011

Directors:

Alison. A. Baski, Professor, Department of Physics

Michael A. Reshchikov, Associate Professor, Department of Physics

Virginia Commonwealth University

Richmond, Virginia

May 6, 2011

Acknowledgments

I am grateful to many people for their help, both direct and indirect, in writing this thesis. It would have never have become reality without the help and suggestions of advisors, friends and colleagues.

The only people I can imagine dedicating this thesis to are my parents. They not only supported and encouraged me to start my US education, but they also taught me to believe in myself and follow my dreams. Their frequent phone and skype calls always infused me with courage and comforted me in times of doubts. My two sisters' love, Monia and Kinia. *Bardzo was kocham i dziękuję!*

This thesis would not have been possible without the tremendous help of my academic advisors, Dr. Alison Baski and Dr. Mikhail Reshchikov. They were instrumental in developing the ideas presented in this work and were extremely helpful to me through this time of Graduate Studies. I would like to thank them for their patience, mentorship and the heart that they have given me while working on my thesis and throughout graduate school. Also I would like to acknowledge my friends from physics department especially Nahli, Joy, Rosy, Steven, Joe, Vince, Aric and Michael for the memorable moments. These two years in I value all your friendship very much!

I would also like to acknowledge everyone from the Physics Department at VCU and from the University of Wroclaw especially dr. J. Przeslawskiemu and prof K. Redlichowi with whom I started my physics adventure. I would like to especially thank professors for their enthusiasm and eagerness in sharing their knowledge. Also the staff, especially Mrs. Janice Guyer and Ms. Evelyn Parham who made me feel at home at VCU. A special heart flowing thank-you to those I spent unforgettable writing-thesis time and who put a lot of effort in teaching me English :). The Physics Department would not have been the same without so many wonderful friends of mine that I would especially like to thank . Last, but not least, I thank all my incredible friends from Poland and Richmond, in particular Dagusi, Michalowi, Przemkowi, Eid, Azooz, Steve, Sanja, Marta, Kasi, , Keya, Jamal

Thank you all very very much!

Table of Contents

Acknowledgments.....	ii
Table of Contents	iii
List of Figures	v
Abstract	i
Chapter 1: Literature review	1
1.1 Introduction.....	1
1.2 Surface-related properties of GaN	2
1.3 Photoluminescence in GaN.....	4
1.4 The effect of ambient on PL in GaN.....	5
1.5 The effect of pH in ambient on PL in GaN.....	6
Chapter 1 Figures.....	9
Chapter 2: Experimental details.....	19
2.1 Experimental set up.....	19
2.2 Description of the samples studied in this work	19
2.3: Description of experiments	20
Chapter 2 Figures:.....	21
Chapter 3: Experimental results.....	23
3.1 Photoluminescence of GaN in vacuum and air ambient.....	23
3.1.1 Photoluminescence from as-received GaN	23
3.1.2. Photoluminescence from freshly-etched GaN	23
3.1.3. The effect of oxygen pressure on PL intensity	24
3.1.4. The effect of excitation intensity on PL intensity	25
3.2 The effect of pH in ambient on PL in GaN.....	26
3.2.1. Effect of acid and ammonia vapor on PL from GaN stored in air for long time.....	26
3.2.2. Effect of acid and ammonia vapor on PL from freshly etched GaN	27
Chapter 3 Figures:.....	28

Chapter 4: Discussion	38
4.1: The effect of band bending on PL	38
4.2: Nonradiative recombination at the surface as the reason for PL intensity changes	40
4.3. Comparison of our results with results reported in literature for the effect of pH on PL..	41
Chapter 4 Figures	42
Chapter 5: Summary and Conclusions.....	44
References.....	46

List of Figures

Fig. 1.1: Band diagram for a semiconductor with main electron transitions (on the left) and PL spectrum (on the right) illustrating the origin of the PL Exciton and broad bands.....	9
Fig. 1.2: Schematic band diagram of n-type semiconductor near the surface. Φ is the band bending, W is the depletion region width, and CB is the conduction band minimum.....	10
Fig. 1.3: Band diagram for n-type GaN with front illumination and PL emission from bulk region.....	11
Fig. 1.4: PL spectrum from GaN. a) Undoped GaN in air ambient at room temperature (Ref. 12). b) GaN: Si in air ambient at room temperature (Ref. 6).	12
Fig. 1.5: Schematic illustration of a recombination of the hole bound to a deep-level defect and free electron, causing emission of photons and phonons. (Ref. 13).....	13
Fig. 1.6: Evolution of the YL intensity at room temperature in vacuum and air ambient (Ref. 13).....	14
Fig. 1.7: Evolution of the exciton band intensity in GaN at room temperature in different ambients. (Ref. 17).....	15
Fig.1.8: Yellow luminescence spectra from GaN film in air, HCl and NH ₃ ambient (Ref. 16). .	16
Fig.1.9: Near-band-edge emission spectra from GaN film in air, HCl and NH ₃ ambient (Ref. 16).	17
Fig. 1.10: Energy diagram transition for yellow band and near-band-edge emission in GaN a) in NH ₃ ambient b) in HCl ambient (Ref. 16).	18
Fig. 2.1: Schematics of PL set up.	21
Fig. 2.2: Schematic of cuts for the GaN:Si sample #2015 The piece 17 studied in more detail in this work is labeled as 2015-17.....	22
Table. 2.3 Characteristics of the GaN samples	22
Fig. 3.1: PL spectra in vacuum and air for as-received GaN:Si sample # 2015-2 at room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	28

- Fig. 3.2: PL spectra in air ambient for the following experimental conditions: 1) freshly etched in Aqua Regia/BOE and exposed to 325 nm UV light for 1 h, 2) after exposure to 325 nm UV light during 19 hours. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$. .. 29
- Fig. 3.3: Evolution of exciton PL intensity at 3.42 eV in air ambient for the following experimental conditions: 1) freshly etched in Aqua Regia and BOE, 2) after exposure to 325 nm UV light during 19 hours Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 29
- Fig. 3.4: PL spectra in vacuum ambient after etching GaN in Aqua Regia and after holding it for 1 hour under 325 nm UV light. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 30
- Fig. 3.5: Evolution of PL intensity at 3.42 eV in vacuum for freshly etched sample..... 30
Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 30
- Fig. 3.6: PL spectra in vacuum and air ambient after etching in Aqua Regia and BOE. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 31
- Fig. 3.7: Evolution of PL intensity in vacuum / air /vacuum ambient for GaN sample after etching in Aqua Regia and BOE. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 31
- Fig. 3.8: Dependence of the exciton PL intensity on oxygen pressure measured 24 days after the etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$ 32
- Fig. 3.9: PL spectra (divided by the excitation power density) in air ambient after etching in Aqua Regia and BOE and after consequent exposure for 1 hour to 325 nm UV light. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$ 33
- Fig. 3.10: PL Quantum efficiency for the freshly etched GaN sample for the Exciton, BL and RL bands in vacuum after etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$ 34

Fig. 3.11: PL Quantum Efficiency for the exciton band as a function of the excitation intensity for two sample conditions in air ambient after etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$	34
Fig.3.12: PL spectra in air and HCl acid ambient after 32 min. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	35
Fig.3.13: Evolution of PL intensity for sample placed in HCl vapor. Sample: GaN: Si #2015-17. Before this experiment the sample was stored in dark and air for 1000 days. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	35
Fig. 3.14: PL spectra in ammonia and air ambient. Sample: GaN:Si # 2015-12. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	36
Fig. 3.15: Evolution of PL intensity for GaN sample placed in ammonia vapor.	36
Sample: GaN:Si # 2015-12. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	36
Fig. 3.16: Evolution of PL intensity for sample placed in HCl and ammonia vapor after etching in Aqua Regia and BOE. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$	37
Table 4.1. Comparison of the expected PL quantum efficiency for values of the different band bending in GaN:Si sample with $n = 3 \times 10^{18} \text{ cm}^{-3}$	42
Fig. 4.1: PL spectrum for different excitation power densities in air ambient and room temperature after etching in Aqua Regia and BOE. GaN:Si # 2015-17.	43

Abstract

The Effect of Ambient on Photoluminescence from GaN

By Iwona Ruchala

A thesis submitted in partial fulfillment of the requirements of the degree of Master of Science at Virginia Commonwealth University. Virginia Commonwealth University, 2011.

Major Director: Dr. Alison A. Baski, Chair, Department of Physics

The effect of ambient on photoluminescence (PL) from GaN was studied. We found that the PL intensity in vacuum was nearly four times higher than in air. The PL intensity also increased after etching the sample in Aqua Regia and BOE to remove the native oxide layer. After etching, the PL intensity was very stable in vacuum, but substantially degraded in air ambient. In HCl vapor (low pH), the PL intensity increased as compared to air ambient, while in NH₃ vapor (high pH) it decreased. The quantum efficiency of the exciton and blue luminescence bands increased significantly with increasing excitation power density. This increase could not be explained by reduction of the depletion region width (field effect mechanism), but could be explained by changes in the nonradiative recombination rate at the surface (recombination mechanism). We therefore assume that in vacuum and acid vapor some surface species are desorbed or passivated, resulting in a decreased nonradiative recombination rate and increased PL intensity.

Chapter 1: Literature review

1.1 Introduction

Semiconductors are the foundation of modern electronics. Such devices as transistors, solar cells, diodes, rectifiers, and digital and analog integrated circuits are made of semiconductors. The most important semiconductor material after silicon is probably gallium nitride (GaN). It emits brilliant light and is used to make blue and violet LEDs, as well as laser diodes. It is also the key material for next-generation, high frequency, high-power devices capable of operating at high temperatures. Although the GaN industry is relatively mature, it is important to better understand the source of non-radiation recombination or surface effects.¹ This work is devoted to elucidation of the role of the surface and the effect of the ambient on the electrical and optical properties of GaN.

The optical properties of GaN can be studied by photoluminescence (PL). One of the advantages of this method is that it is a nondestructive technique with no contact and no material modifications. From PL it is possible to obtain useful information about a semiconductor, such as optical quality, presence of radiative and nonradiative defects, energy levels of radiative defects, and more.²

Photoluminescence is the spontaneous emission of light as a result of absorption of electromagnetic radiation. In semiconductors the energy diagram consists of a filled valence band and an empty conduction band. The width of the gap between these two energy bands determines the properties of a semiconductor. GaN with a band gap of 3.43 eV at room temperature³ is called the wide-band gap semiconductor. GaN emits light in the UV (360-400 nm) and visible (400-700 nm) parts of the spectrum, which is another advantage of PL, because detectors are very sensitive in this range. After UV exposure, an electron from the valence band (Fig 1.1) may absorb sufficient energy to be promoted to the conduction band, leaving a hole (positive quasi-particle) in the valence band, i.e. an electron-hole pair is created. This process is very fast, on a time scale of femtoseconds or 10^{-15} s. Photoluminescence is the emission of a photon when the electron returns to the valence band,

directly or via intermediate energy levels. The recombination of electron-hole pairs often occurs through defect states. In an n-type semiconductor, first the hole is captured by a defect. This process is fast (10^{-10} s) and the energy is released in the form of phonons (oscillations of the crystal lattice).

Both the conduction and valence bands are bent near the surface of GaN because of surface charge (Fig. 1.2). There are several reasons why there is such charge on the surface – it might come from adsorbed molecules, impurities, or native defects, but it might also originate from interface/surface states or defect states, which might be related to the ambient. Usually, the energy bands near the surfaces of n-type semiconductors are bent upward and those of p-type semiconductors are bent downward.

Experimentally, using a Kelvin Probe, it was shown that the work function in GaN increases about 0.1 -0.2 V. This suggests that the Fermi level is moved towards the valence band. This change is explained by the presence of negatively charged dislocations.⁴ The upward band bending in n-type semiconductor is caused by negatively charged species or states that are on the surface.⁵ We can also have positively charged species (or states) but the negatively charged ones outnumber them, so that overall upward band bending is observed. The band bending causes not only a barrier for electrons near the surface, but also results in a depletion region, where a strong electric field sweeps free carriers away and prevents their recombination in the depletion region. The depletion region may therefore strongly affect the electrical properties (reduced conductivity) and optical properties (reduced emission).

1.2 Surface-related properties of GaN

The electrical and optical properties of GaN, as well as those of any other semiconductor, are affected by the surface. Band bending and the resultant depletion region depend on the ambient.^{6,7} Usually, the PL intensity decreases (quenches) due to the presence of the surface. The quenching of PL in GaN is often attributed to an increase of the depletion region width. However, in literature two mechanisms of the surface-related PL quenching can be found: field mechanism and recombination mechanism.⁸

In the field-effect mechanism, PL decreases with increasing depletion region width because there is no recombination of electrons and holes in the depletion region. This first mechanism is radiative and associated with the creation of a luminescence band.⁸ When photons are absorbed in the depletion region, the valence electrons are excited to the conduction band where they are immediately swept to the bulk because of a strong electric field (Fig. 1.3). The electric field can be roughly calculated as the band bending Φ (in Volts) divided by the depletion region width W , or $E = \Phi/(qW)$. For typical values of $\Phi = 1$ eV and $W = 0.1 \mu\text{m}$,^{6,7} the electric field is of the order of 10^5 V/cm. Under this electric field the electron passes through the $0.1 \mu\text{m}$ -wide depletion region in less than 10^{-12} s (with a drift velocity of about 2×10^7 cm/s),⁹ which is insufficient time for an electron or a hole to be trapped by defects or to form excitons. Moreover, excitons will be ripped apart by such a strong electric field. Because of this, there will be no recombination of the electron-hole pair in the depletion region. In other words, the depletion region is a dead layer for PL. Although the width of the depletion region and its variation due to ambient conditions are expected to play a significant role in PL, it will be shown in this work that other reasons, such as ambient-related change in the density of the surface states and/or their modification may play the dominant role in the effect of ambient on PL in GaN.

The effective PL depth d_{eff} can be defined as $2\alpha^{-1}$, where α is the absorption coefficient at the wavelength of the excitation light. Indeed, the excitation light intensity at distance x from the surface decreases exponentially as $\exp(-\alpha x)$. As a result, about 86% of the excitation light is absorbed in the “effective PL region” with a thickness $d_{eff} = 2\alpha^{-1}$ and only 14% is absorbed beyond this region and can be neglected for simplicity. For GaN, $\alpha = 1.2 \times 10^5 \text{ cm}^{-1}$ at 325 nm (HeCd laser)¹⁰ and $d_{eff} \approx 170$ nm. Then, if the depletion region width W is comparable to d_{eff} , the reduction of PL intensity due to the field-effect mechanism may be significant. In this case, the ambient-related changes in band bending (and therefore the depletion region width) would cause significant changes in the PL intensity. In the field-effect mechanism, intensities of all PL bands in the same sample are expected to change by about the same factor in the first approximation.

The second mechanism ignores the depletion region and attributes the reduction of PL intensity solely to the nonradiative recombination of electron-hole pairs at surface states. In this mechanism, an increase in the density of surface states and higher capture cross-section will increase the nonradiative recombination and decrease PL intensity. . In this mechanism, different ambients may increase or decrease the surface state density, as well as their capture characteristics.. For example, atoms or molecules adsorbed at the surface may passivate surface states or increase their carrier-capture ability. The presence of the near-surface barrier for electrons decreases the flow of electrons from bulk to the surface, but does not eliminate it. Although in most cases both the field-effect and surface recombination mechanisms cooperate, contribution of each of them to PL from GaN is unknown.¹¹

1.3 Photoluminescence in GaN

The typical PL spectrum from GaN consists of an exciton band and one or more defect-related bands (Fig 1.4).^{6,12} The exciton peak is due to the annihilation of a free exciton. An exciton is a quasi-particle that consists of an electron and a hole that can move together in the crystal lattice. It is neutral and can freely travel in a crystal unless it is trapped by a defect and becomes a bound exciton. At room temperature (25 meV) such bound excitons can become free again because their binding energy is much smaller (~7 meV). After a short time on the order of nanoseconds, an exciton annihilates spontaneously and emits photoluminescence with an energy corresponding to the exciton peak in the Fig 1.4, which is slightly smaller than the band gap.

The broad PL bands are related to deep-level defects. After excitation of an electron to the conduction band and creation of a hole in the valence band, the hole can be trapped by an acceptor in a short time – about 10^{-10} s. The electrons from the conduction band will then recombine with those holes. After the recombination of a free electron with a bound hole (as illustrated in Fig.1.5), the defect and surrounding atoms relax to a new equilibrium state, and in this process several phonons are emitted. The energy of the emitted photons is then reduced by the phonon energy. Since the number of the emitted phonons is different in

different recombinations (i.e., a statistical process), the observed defect-related PL bands are broad.¹³

In both doped and undoped samples the PL spectrum contains an exciton band at about 3.42 eV. For the spectra measured at room temperature in undoped GaN it is reported that yellow luminescence (YL) appears at about 2.2 eV, as well as a green luminescence (GL) band at 2.5 eV.¹⁴ The YL and GL bands are related to the same defect, a complex consisting of a gallium vacancy (V_{Ga}) and a shallow oxygen donor (O_N). Both the YL and GL bands are observed in freestanding GaN, but the GL bands is not observed in less pure material. The YL band has a nearly Gaussian shape, but precise shape and position are sample dependent. It is still unknown what type of defect and how many defects contribute in this band, but it is established that the transition from the conduction band or from the shallow donor to a deep acceptor is responsible for this band. The GaN growth method plays an important role in the formation of point defects and, therefore, in observing broad bands in the PL spectrum. In undoped or Si-doped GaN samples grown by hydride vapor phase epitaxy (HVPE), it is possible to see a red luminescence (RL) with a maximum at 1.9 eV. For GaN thin films grown by metalorganic chemical vapor deposition (MOCVD) and HVPE, a blue luminescence (BL) band peaking at 2.9 eV is also often observed.¹⁴ This band is usually observed in undoped and Zn-doped GaN. The BL in Zn-doped shows fine structure in pure samples and is attributed to recombination from the conduction band or shallow donors to the Zn-related acceptor. For the undoped GaN and Zn doped the transitions are the same.

1.4 The effect of ambient on PL in GaN

In several publications it was noted that air, as well as pure gas ambients, affect the PL intensity in GaN¹³ and other semiconductors.¹⁵ As shown in Figs. 1.6 and 1.7, PL intensity in GaN can strongly depend on the ambient.¹³ After exposure of the surface to different ambients, the PL changes. For air and oxygen the effect is very similar, with a decrease of PL intensity as compared to vacuum. It was suggested that oxygen adsorption was responsible for changes in both oxygen and air ambient. Nitrogen and hydrogen do not affect the PL

intensity significantly, although the decrease can still be noticed. It was also shown that changes were reproducible.¹³

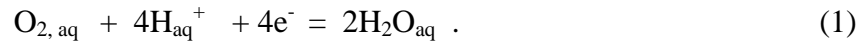
The observed behavior was explained by nonradiative recombination at surface states originating from oxygen, or by an increase of the band bending followed by adsorption of oxygen. Usually, the exciton and YL bands are affected differently; the degree of change varies from sample to sample, though. Desorption of oxygen cannot cause decrease of the PL intensity under UV exposure in air.¹³ The PL intensity usually degraded under UV light in air, contrary to the increase when oxygen desorbed in vacuum under UV light.

1.5 The effect of pH in ambient on PL in GaN

Few experiments on GaN were made in the past showing that PL intensity changes after exposure to HCl or NH₃ vapors.¹⁶ In HCl vapor, the YL band intensity increased while the near-band-edge PL intensity decreased. In ammonia vapor, the YL band intensity decreased while the near-band-edge PL intensity increased. The authors suggested an explanation based on electron exchange between electronic midgap states in GaN and oxygen electrochemical redox couple in adsorbed water film. Other effects such as defect formation, chemisorption, and surface reconstruction could also take place. It is known that a thin layer of water and dissolved air molecules exists at practical surfaces of semiconductors in air ambient and at room temperature.¹⁶ The water and other molecules at the surface and the bulk of a semiconductor may exchange electrons. The Fermi energy is a very important parameter for solids, as well as for electrolyte solutions. It is an 'indicator' showing how the energy levels are occupied by electrons. It is known from thermodynamics that two phases are in equilibrium if their electrochemical potentials are equal. The electrochemical potential of a redox couple in solution is determined by E_{redox} , while the electrochemical potential of the electrons in the semiconductor is determined by the Fermi level E_{F} . If E_{redox} and E_{F} are different, charge redistribution between the semiconductor and solution is required in order to equilibrate the two phases. In the experiment, the electrolyte solution was an adsorbed water film.¹⁶

The PL spectrum in Fig. 1.8 shows the yellow luminescence (YL) band in three ambients. As compared to air ambient, the ammonia reduced the intensity of the YL band, while acid increased it. The opposite trend was observed for the exciton peak, as is shown in Fig 1.9. The following explanation was given in Ref. 16.

The chemical potential for the oxygen/water layer lies between 5.66 and 4.83 eV with respect to the vacuum level,, depending on the pH value of the solution (0 to 14, respectively).¹⁶ In air ambient, the Fermi energy E_F in the adsorbed water film is determined by the oxygen redox couple:



In equilibrium the electrochemical potential U and the electron energy of the redox couple μ_e have a relation known as the Nernst equation:

$$\mu_e = -4.44 + (-1) (+1.229) + 0.0592/4 [4\text{pH} - \log_{10}(\text{P}\text{O}_2)] . \quad (2)$$

The pH changes depending on the ambient. The energy range for the chemical potential of the oxygen redox couple varies from -5.66 eV at pH = 0 to -4.83 eV at pH = 14. For the conditions of experiment described in Ref. 16, the calculated energy changes from -5.6 to -5.01 eV, and with approximate range of midgap state centered 2.2 eV below the conduction band, both are located in the same range as is shown in Fig. 1.10.

The air ambient provides a source of acceptor/donor O_2 molecules, and during this exposure to air the Fermi level of a semiconductor and the electron energy of the oxygen redox couple have to be in equilibrium (causing band bending). The pH of the ambient determines the energy of electron on the surface. If $E_f > \mu_e$, electrons from the bulk move to the water film until equilibrium is achieved.

It is explained in Ref. 16 that for the NH_4OH solution at pH = 11, midgap states up to $E \approx -5$ eV are filled with electrons and that is why the YL transition is less intense, while the

near-band-edge emission intensity is stronger (due to competition between two recombination channels). For acid, the electron energy in water decreases. As a result, in HCl vapor the defect-related midgap states are filled up to $E \approx -5.6$ eV, and for this reason the YL intensity increases and the near-band-edge intensity decreases due to the competition of two recombination channels (Fig. 10). In this work, the near-band-edge emission was attributed to transitions from shallow donors to the valence band and not to excitons.

Chapter 1 Figures

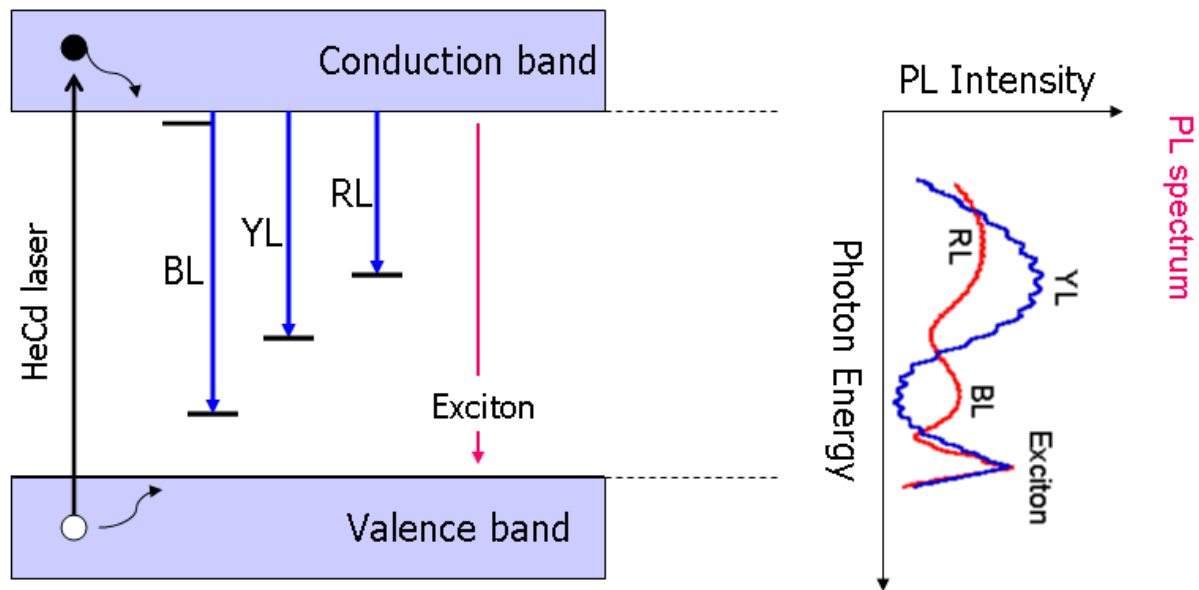


Fig. 1.1: Band diagram for a semiconductor with main electron transitions (on the left) and PL spectrum (on the right) illustrating the origin of the PL Exciton and broad bands.

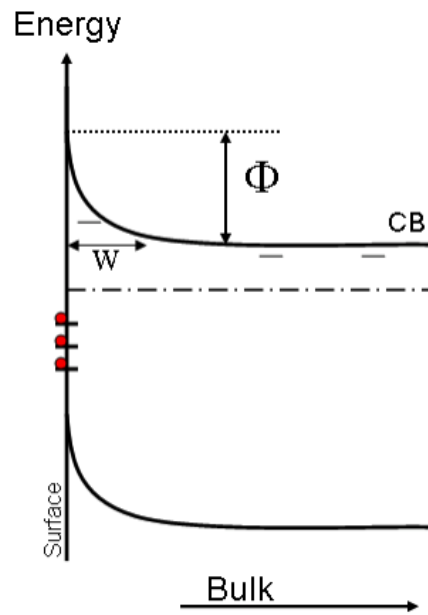


Fig. 1.2: Schematic band diagram of n-type semiconductor near the surface. Φ is the band bending, W is the depletion region width, and CB is the conduction band minimum.

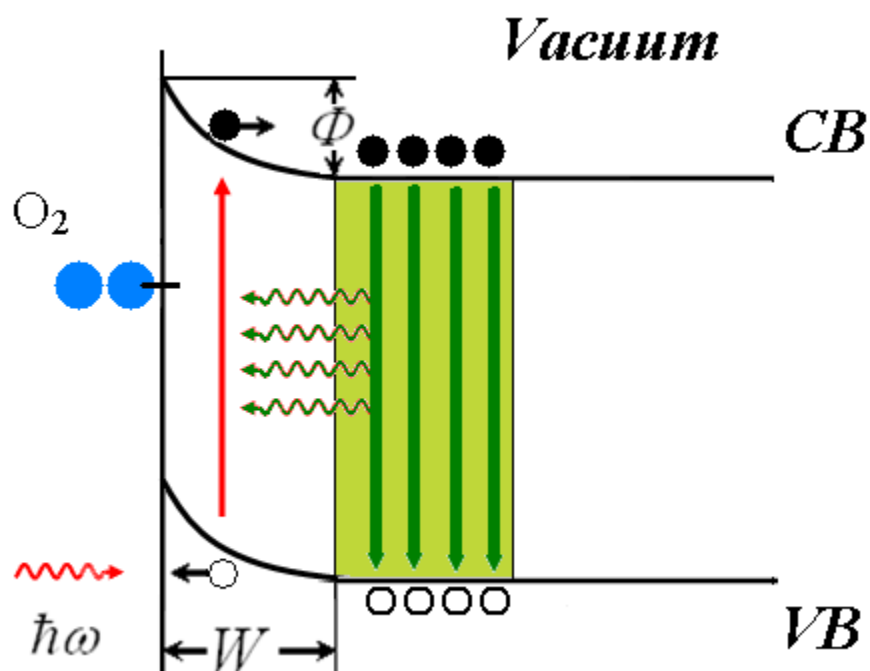


Fig. 1.3: Band diagram for n-type GaN with front illumination and PL emission from bulk region.

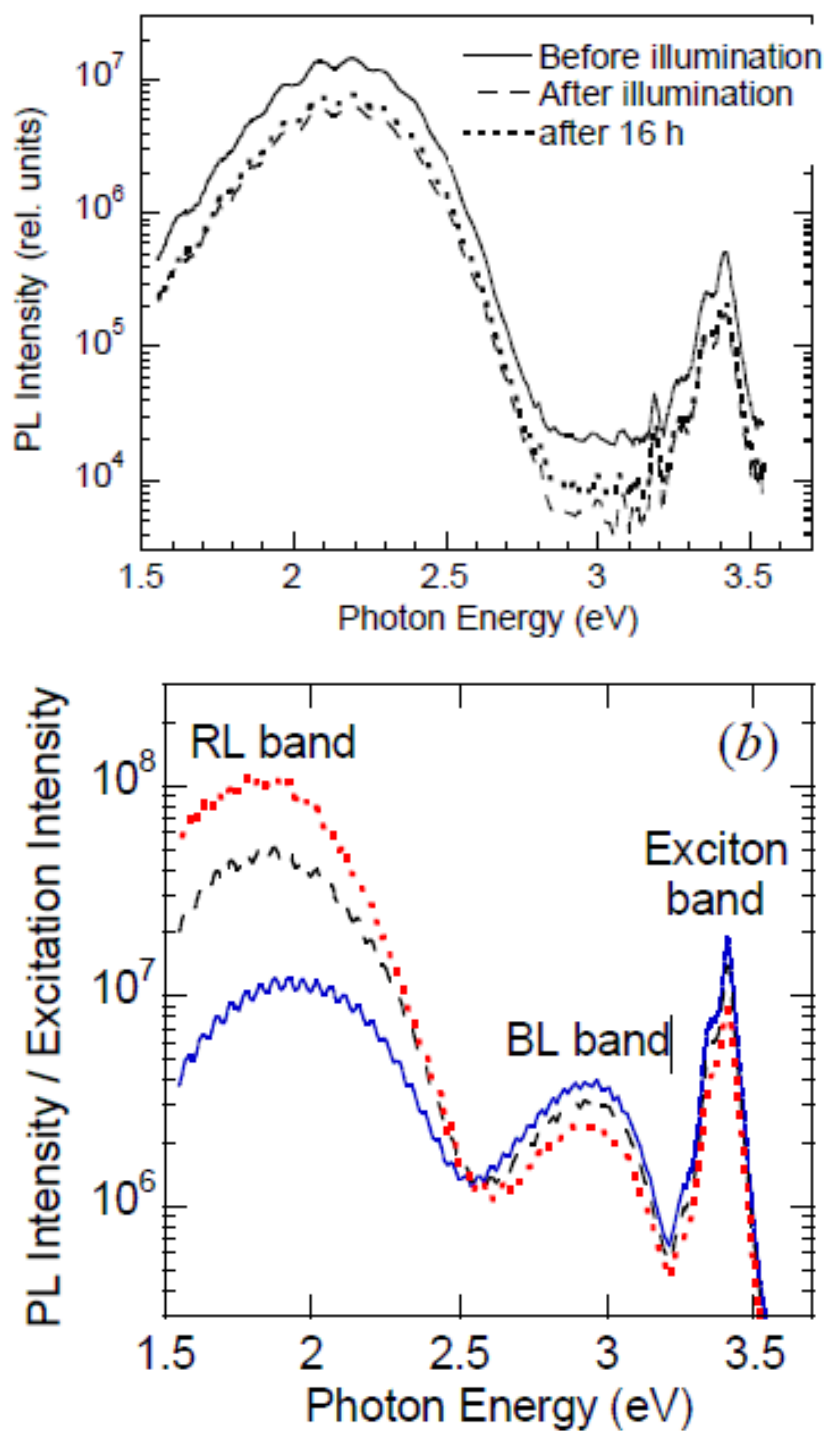


Fig. 1.4: PL spectrum from GaN. a) Undoped GaN in air ambient at room temperature (Ref. 12). b) GaN: Si in air ambient at room temperature (Ref. 6).

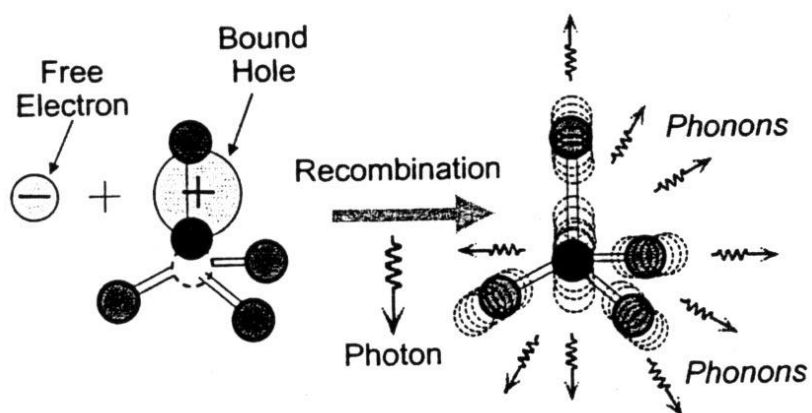


Fig. 1.5: Schematic illustration of a recombination of the hole bound to a deep-level defect and free electron, causing emission of photons and phonons. (Ref. 13).

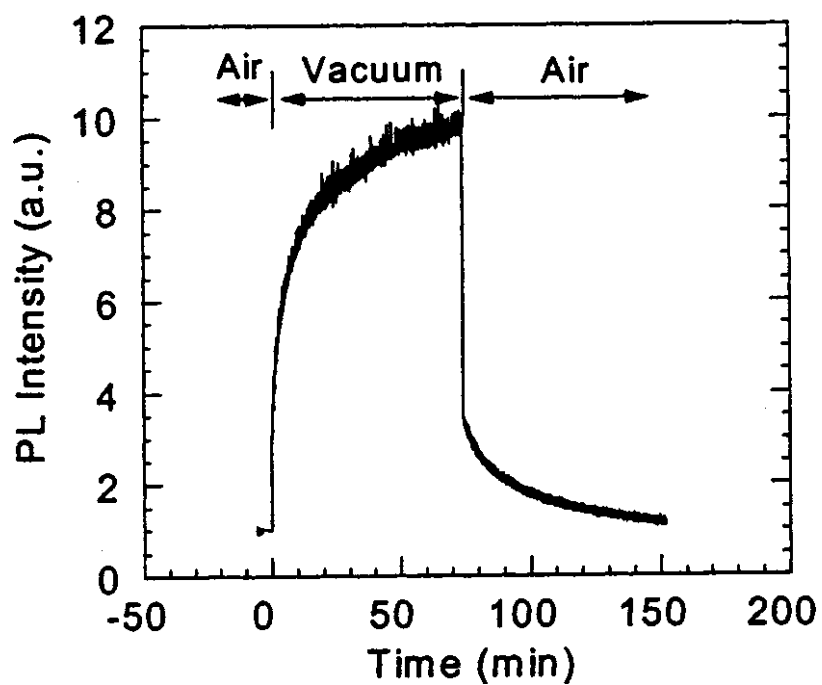


Fig. 1.6: Evolution of the YL intensity at room temperature in vacuum and air ambient (Ref. 13).

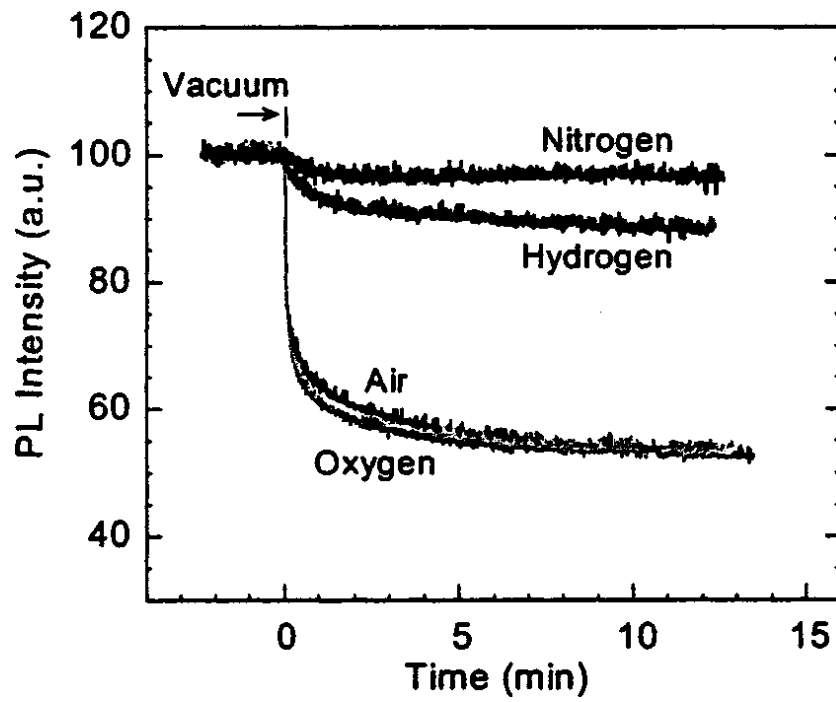


Fig. 1.7: Evolution of the exciton band intensity in GaN at room temperature in different ambients. (Ref. 17).

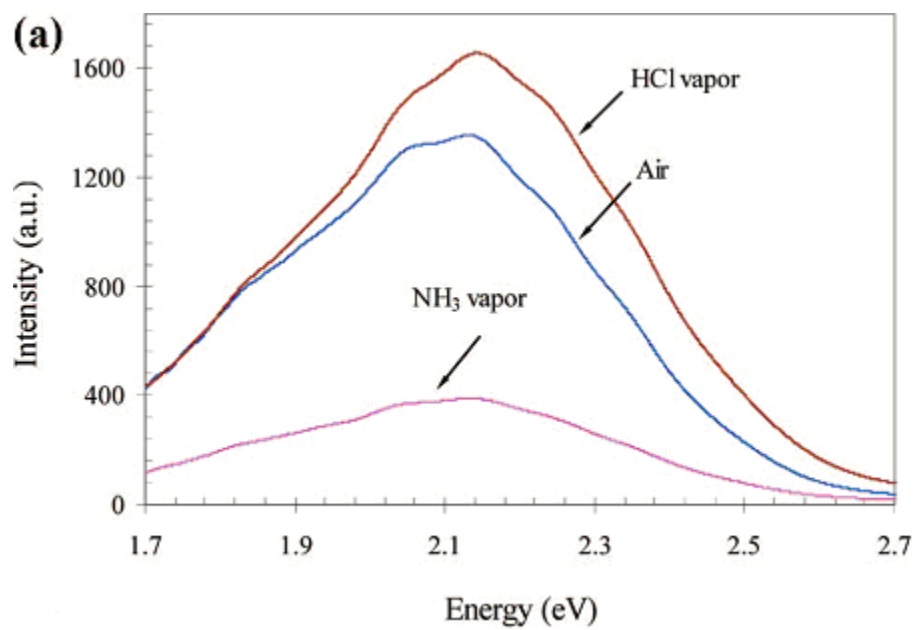


Fig.1.8: Yellow luminescence spectra from GaN film in air, HCl and NH₃ ambient (Ref. 16).

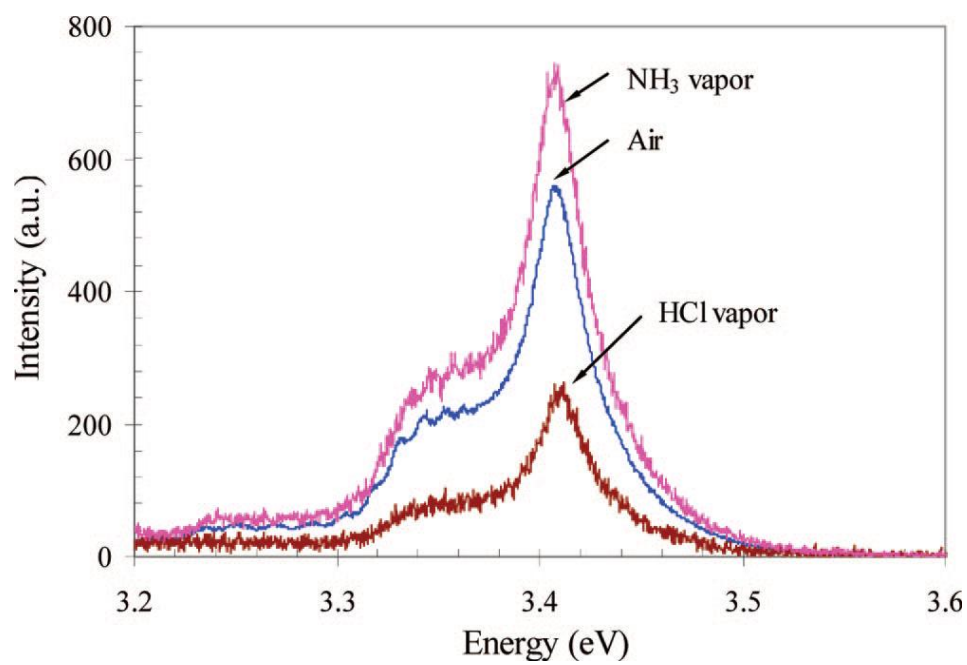


Fig.1.9: Near-band-edge emission spectra from GaN film in air, HCl and NH₃ ambient (Ref. 16).

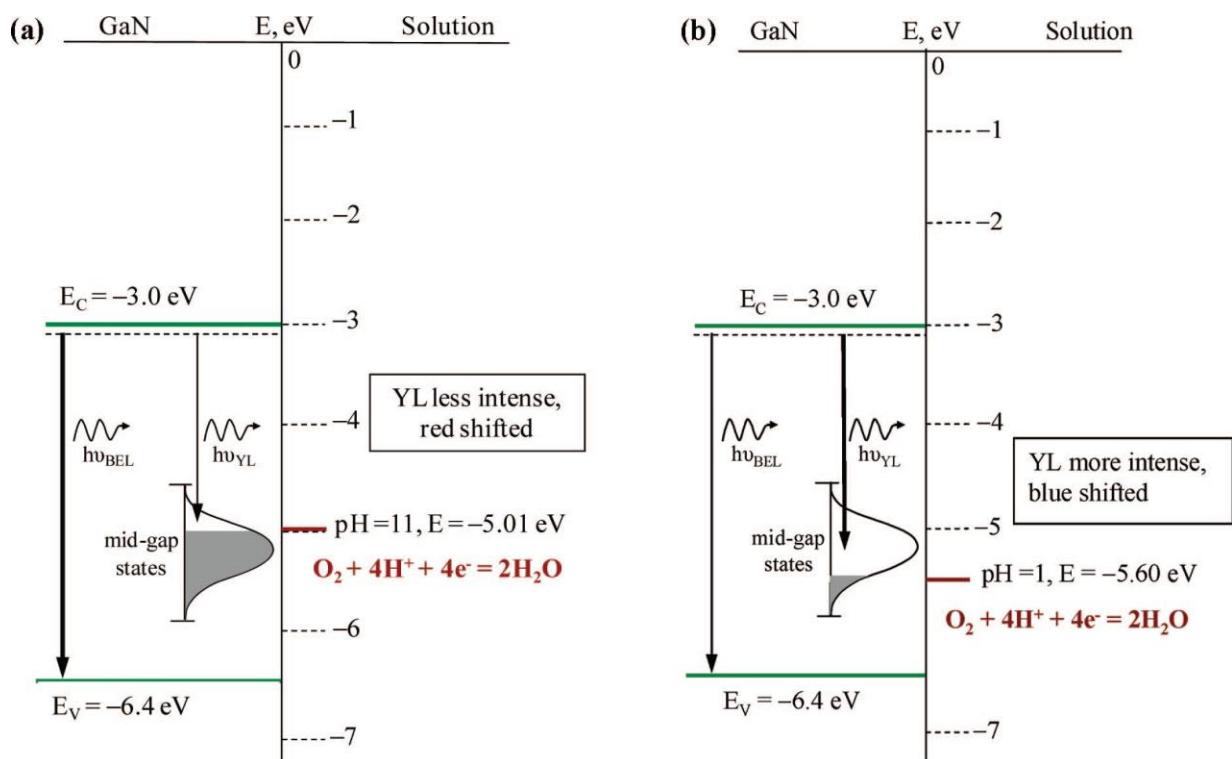


Fig. 1.10: Energy diagram transition for yellow band and near-band-edge emission in GaN a) in NH₃ ambient b) in HCl ambient (Ref. 16).

Chapter 2: Experimental details

2.1 Experimental set up

In our experiments we used a HeCd gas laser as a source of PL excitation. The wavelength of this light is 325 nm, which corresponds to the photon energy of 3.81 eV. The sample was placed in a cryostat for experiments in vacuum, pure oxygen and air, or in a plastic chamber for experiments in acid, ammonia, and water vapors. The laser beam was directed onto the sample. Using 5 filters with different transparency located between the laser and the sample, we could change the laser intensity and measure the dependence of the PL intensity on excitation intensity. The laser power density could be varied from 3×10^{-5} to 0.3 W/cm^2 . Photoluminescence is the spontaneous emission of light in all directions, although we collect only a small part of the emission that is limited by a cone with a base equal to the collecting lens (Fig.2.1). The quantum efficiency of PL was obtained by comparing integrated intensities of the PL bands with those obtained from a calibrated GaN standard.

Since the lens is located at a focal distance from the sample, the collected emission travels as a parallel beam inside the condenser. The right side lens focuses the light into the entrance of the monochromator. Inside the monochromator the light is dispersed into the spectrum and only one wavelength passes through the exit slit. The grating can be rotated to choose the wavelength that exits the monochromator. The light is detected with a high-sensitivity photomultiplier tube (PMT), the cathode of which is cooled to reduce electrical noise.

2.2 Description of the samples studied in this work

For the studies in this work, we used n-type undoped and silicon-doped GaN grown on c-plane sapphire. Most of the experiments were done on the Si-doped GaN sample obtained from Oxford-TDI (sample 8AV2015 in notation of TDI and 2015 in our notation). The as-

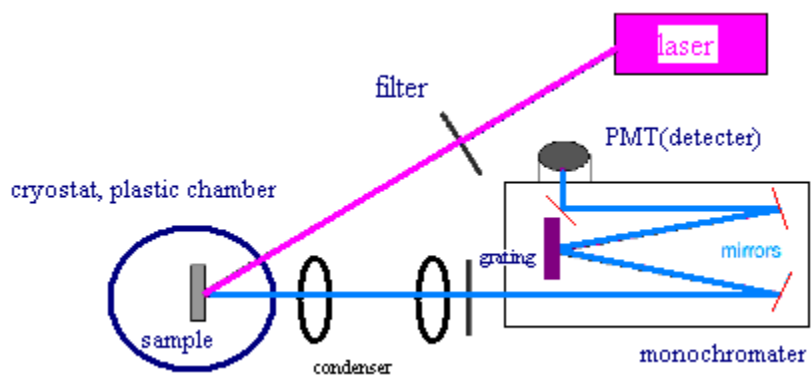
received sample represented a 3-inch wafer with 5 μm -thick GaN grown on one-side polished sapphire substrate. The wafer was cut onto pieces with sizes of about 1×1 cm that were numbered as shown in Fig. 2.2

PL intensity and spectrum were uniform throughout the whole 3-inch wafer. From Hall Effect measurements at room temperature using the Van der Pauw configuration, for sample 2015-9 we determined the electron concentration (3.8×10^{18} cm^{-3}) and electron mobility (130 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). A few other samples grown with different methods and having different types and other parameters were studied. The main characteristics of the samples are listed in the Table 2.1. Unintentionally doped GaN was n-type due to contamination with oxygen which acts as a donor in GaN.

2.3: Description of experiments

All PL spectra and PL transients in time were taken in air, vacuum, acid vapor and base vapor at room temperature. For the air, pure oxygen, and vacuum ($\sim 10^{-5}$ mbar) the sample was placed into an optical cryostat. For experiments in acid and ammonia, we used a plastic chamber to avoid damage of the cryostat and other parts of PL system. A plastic bath with 6 ml HCl with concentration of 50% or ammonium hydroxide NH_4OH with concentration of 28% were placed near the sample on the bottom of the closed chamber.

GaN samples exposed to air have a thin (~ 1 nm) film of native oxide Ga_2O_3 .¹⁷ For some experiments we removed this native oxide layer by using the following procedure. First, the sample was ultrasonically cleaned with acetone and methanol. Then, it was placed in boiling Aqua Regia (HNO_3 and HCL in ratio 1:3) for 15 min and BOE (buffered oxide etch – hydrofluoric acid at high concentration) for 3 min, rinsed with water, and dried with pure nitrogen. It took about 10 min. to transfer the etched sample to the PL set-up while the sample was exposed to air. It is expected that in such a short time oxygen will adsorb at the surface but oxide growth can be ignored. It has to be mentioned that GaN cannot be etched by acids – only native oxide layer is removed but the GaN surface remains unharmed.¹⁸

Chapter 2 Figures:**Fig. 2.1:** Schematics of PL set up.

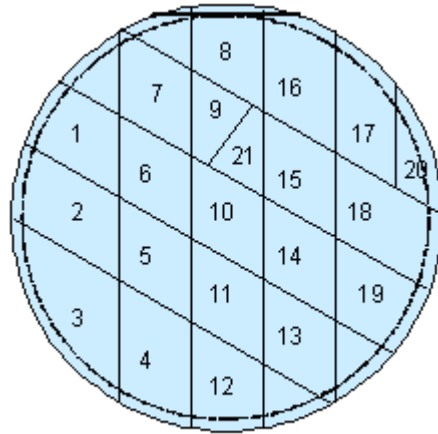


Fig. 2.2: Schematic of cuts for the GaN:Si sample #2015 The piece 17 studied in more detail in this work is labeled as 2015-17.

Table. 2.3 Characteristics of the GaN samples

Sample	Type	Doped	Growth method	Thickness (μm)
2015	n-type	Si	HVPE	5
750	n-type	undoped	MBE	2.5

MBE – molecular beam epitaxy

HVPE – hydride vapor phase epitaxy

Chapter 3: Experimental results

3.1 Photoluminescence of GaN in vacuum and air ambient

3.1.1 Photoluminescence from as-received GaN

The typical PL spectrum from as-received GaN:Si sample 2015 is shown in Fig. 3.1. It consists of the exciton peak at about 3.41 eV, the blue luminescence (BL) band with a maximum at about 2.95 eV, and the red luminescence (RL) band with a maximum at about 1.9 eV. The BL band is attributed to a Zn acceptor appearing in this sample due to contamination.¹³ The origin of the RL band is unknown. It is related to some deep-level defect.

The PL intensity of the as-received sample was not sensitive to changes in ambient: the PL intensity in vacuum and air ambient is about the same for the highest excitation intensity of 0.3 W/cm² (Fig 3.1). Note that for smaller excitation power density (such as 0.00027 W/cm²), we observed a small increase for PL intensity in vacuum. In other GaN samples, PL intensity in vacuum was usually higher than in air ambient, but the percentage of the increase was sample dependent.

3.1.2. Photoluminescence from freshly-etched GaN

After etching GaN in Aqua Regia and BOE, the PL became much more sensitive to ambient. This can be seen from Figs. 3.2 and 3.3. In air environment under UV laser exposure we observed an increase in the exciton PL intensity during the first couple minutes (Fig. 3.3). Then, the PL intensity slowly decreased. After 19 hours of illumination the PL intensity stopped changing. The above etching is known to remove the native oxide. However, in air ambient oxygen is expected to adsorb fast at the surface. We assume that in first minutes the

UV exposure cleaned the surface from the adsorbed oxygen (PL intensity increased) and then it caused adsorption of oxygen or the growth of an oxide layer (PL intensity decreased). It is known that oxide with properties different from the native oxide grows on the GaN surface when it is exposed to UV light in air ambient for several hours.¹⁹ It can be seen from Fig. 3.2 that the changes due to etching and UV exposure took place in the entire spectral region. Namely, the PL intensity increased after the etching but then slowly decreased after long UV exposure.

Our next experiment was conducted in vacuum, for the GaN:Si sample (#2015-17) etched again in Aqua Regia and BOE. In vacuum, the PL intensity did not change under UV exposure during 1 hour (Figs. 3.4 and 3.5). After 6 hours of UV exposure, the PL intensity increased by only 7%. We do not expect that longer exposure to UV might change PL intensity, since 6 hours produced almost no change. After 3 days of keeping the sample in vacuum, pure oxygen was introduced, and several experiments with alternating vacuum and oxygen ambient were conducted as discussed below.

3.1.3. The effect of oxygen pressure on PL intensity

Figures 3.6 and 3.7 show the evolution of the exciton PL intensity for the etched GaN sample when the vacuum was replaced with oxygen. Then the oxygen was the evacuated and the vacuum was replaced with air ambient. It is clear that PL intensity in vacuum is much higher than in air or oxygen ambient, and the behavior of PL intensity in air and oxygen is very similar.

We also measured the dependence of the exciton PL intensity on oxygen pressure (Fig. 3.8). Note that the absolute value of the pressure might be underestimated because the pressure gauge was attached close to the vacuum turbo pump and not to the cryostat.

3.1.4. The effect of excitation intensity on PL intensity

The dependence of PL spectra on the excitation intensity is shown in Fig. 3.9. In this figure the PL intensity is divided by the excitation intensity. No change in PL intensity in Fig. 3.9 corresponds to its linear increase with the excitation intensity or constant quantum efficiency. The exciton and BL band intensities change in a similar way (an increase in Fig. 3.9 corresponds to a superlinear increase of their intensities with excitation power), while the RL band demonstrates the opposite behavior (its decrease in Fig. 3.9 corresponds to a sublinear increase with excitation intensity).

Figures 3.10 and 3.11 show the PL quantum efficiency (which is basically the ratio of PL intensity to the excitation intensity) in vacuum and air ambients as a function of excitation power density in the freshly etched and illuminated sample. Figure 3.10 shows the dependence of the quantum efficiency of PL for each band on excitation power density in vacuum for the freshly etched sample. The quantum efficiency of the exciton and BL bands in the freshly etched GaN sample increased by a factor of 2 with increasing excitation intensity from 3×10^{-5} to 0.3 W/cm^2 (Fig. 3.10). The RL band quantum efficiency decreased, which can be explained by the partial saturation of the PL intensity of the defect-related band, with an increasing excitation intensity. This happens due to a limited number of defects and the large lifetime of related luminescence. When a defect becomes saturated with photogenerated holes due to its very long PL lifetime, it is not able to capture new holes and these holes recombine via other recombination channels. From time-resolved PL experiments the lifetimes of the BL and RL bands at room temperature were estimated as $0.1 \mu\text{s}$ and $150 \mu\text{s}$, respectively. The very long lifetime of the RL band explains why it saturates at low excitation intensities.

The PL quantum efficiency in the freshly etched sample that was kept in air rises very much with the excitation intensity, at least for the exciton and BL bands (Fig. 3.11). The exciton PL quantum efficiency increased by a factor of 5 when the excitation intensity was increased from 3×10^{-5} to 0.3 W/cm^2 . After 19 hours of UV exposure, the magnitude of the rise substantially decreased (Fig. 3.11).

3.2 The effect of pH in ambient on PL in GaN

3.2.1. Effect of acid and ammonia vapor on PL from GaN stored in air for long time

The sample was placed in a plastic chamber for these experiments. First, the PL spectra at different excitation intensities were measured in air ambient. Then, the measurement of the evolution of the exciton PL intensity was initially taken in air ambient. After a few minutes the monochromator slit shutter was closed for a minute, and during this time a bath with HCl acid or ammonia was introduced into the chamber and put under the sample. As soon as the chamber was closed, the slit shutter was opened, and the measurement of the time dependence of the exciton PL intensity was continued. Evolution of the exciton PL intensity for the GaN sample #2015-17, when HCl was introduced for the first time, is shown in Fig. 3.13. The PL intensity in air was 9×10^4 counts, and it jumped to 1.1×10^5 counts in HCl vapor. Then it slowly increased during the first 15 minutes, after which a faster increase began. After 15 min, instead of tracking the exciton PL intensity only, the whole PL spectrum was measured repeatedly, at different excitation intensities, and points in Fig. 3.13 show the PL intensity for the exciton band in the same units and same conditions as it was measured in the “Time domain” mode. The whole spectrum in Fig. 3.12 indicates that the increase in PL intensity occurred not only for the exciton peak.

In ammonia vapor, the exciton PL intensity decreased (Fig. 3.15). The PL intensity decreased in ammonia vapor for the whole spectrum – similarly for the BL and exciton peak (Fig.3.14). The time evolution for the exciton peak represents a drop up to 50% and saturation after about 22 min. The data were taken on the sample 2015-12 that had not previously been exposed to the laser light. The number 12 indicates that it is another piece from the wafer 2015 (Fig. 2.2). We can compare the data because we expect the same

properties for all the pieces. Although, it might be also true that the history of the sample, (i.e., storage in air, exposure and etching in Aqua Regia) might change the behavior of the sample. Future experiments must be taken though.

3.2.2. Effect of acid and ammonia vapor on PL from freshly etched GaN

For vacuum ambient and freshly etched samples we observed an increase in PL intensity. The GaN:Si sample 2015-17 was etched in Aqua Regia and BOE in order to remove the native oxide layer and was then rinsed with DI water as well as dried with nitrogen. Immediately after the etching (10 min) the experimental data were taken. The intensity of the exciton peak as a function of time is shown in Fig. 3.16. In contrast to the immediate increase of PL intensity in HCl vapor for the GaN sample stored in air for long time before changing air ambient to HCl vapor ambient (Fig. 3.14), for the freshly etched GaN sample we did not see any significant increase in PL intensity during the first 7 min. However, after about 10 min the PL intensity started rising abruptly and increased by 4 times after 30 min. The exposure to ammonia did not show a large decrease in PL intensity, although the trend was always the same – the intensity was smaller in NH_3 vapor.

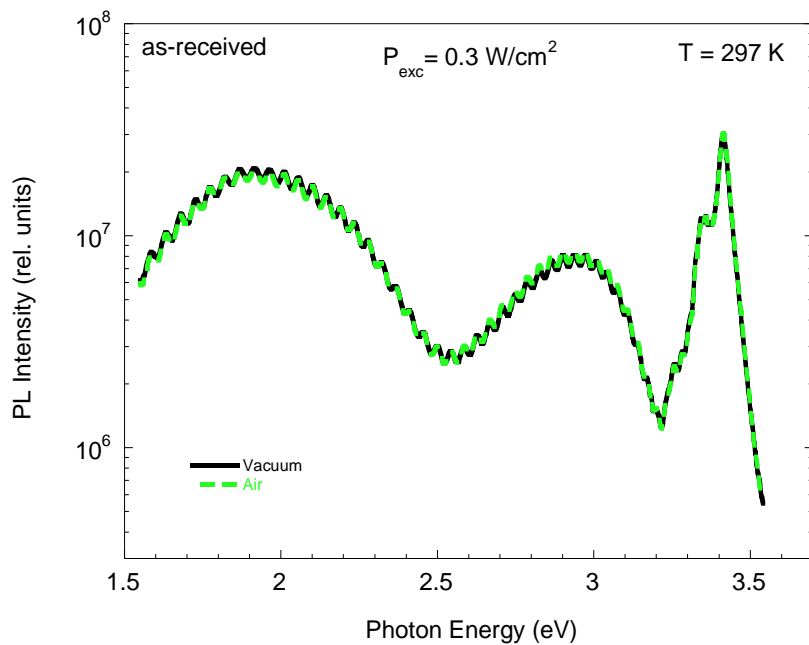
Chapter 3 Figures:

Fig. 3.1: PL spectra in vacuum and air for as-received GaN:Si sample # 2015-2 at room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

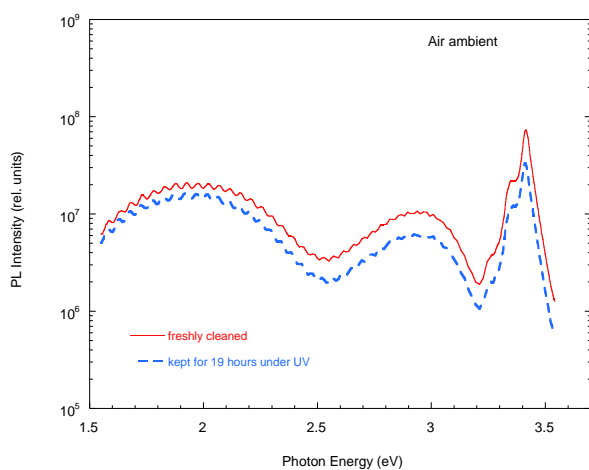


Fig. 3.2: PL spectra in air ambient for the following experimental conditions: 1) freshly etched in Aqua Regia/BOE and exposed to 325 nm UV light for 1 h, 2) after exposure to 325 nm UV light during 19 hours. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

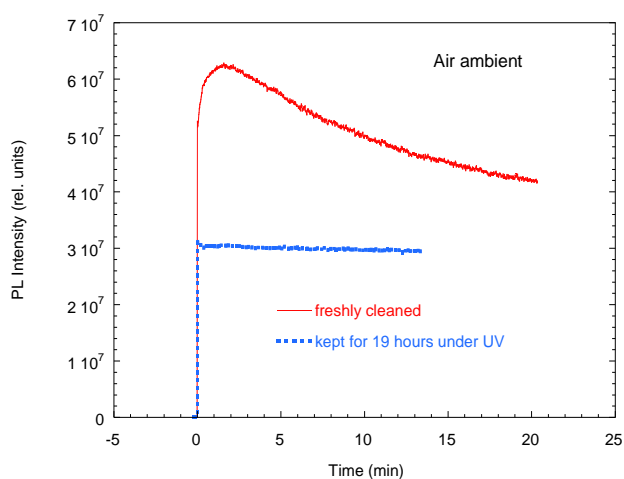


Fig. 3.3: Evolution of exciton PL intensity at 3.42 eV in air ambient for the following experimental conditions: 1) freshly etched in Aqua Regia and BOE, 2) after exposure to 325 nm UV light during 19 hours. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

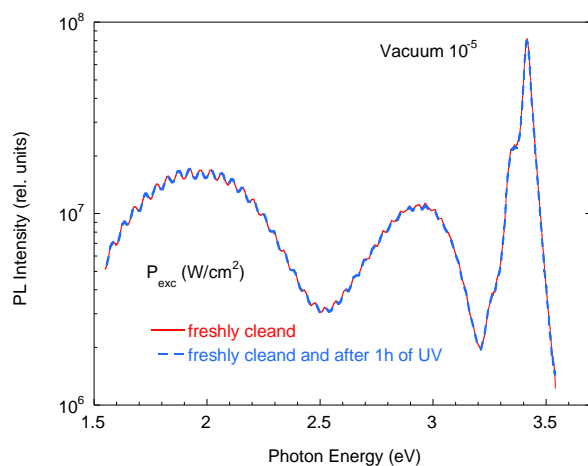


Fig. 3.4: PL spectra in vacuum ambient after etching GaN in Aqua Regia and after holding it for 1 hour under 325 nm UV light. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

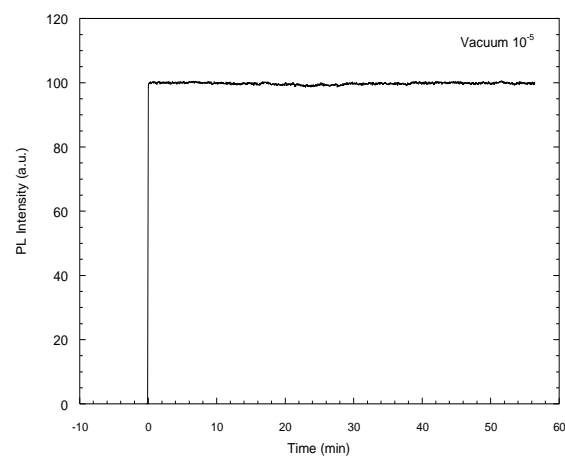


Fig. 3.5: Evolution of PL intensity at 3.42 eV in vacuum for freshly etched sample. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

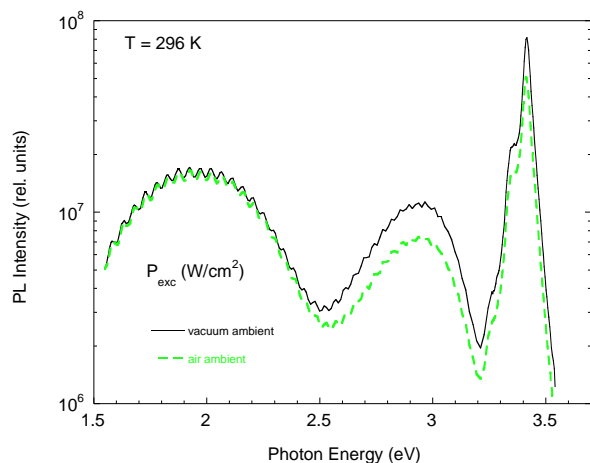


Fig. 3.6: PL spectra in vacuum and air ambient after etching in Aqua Regia and BOE. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

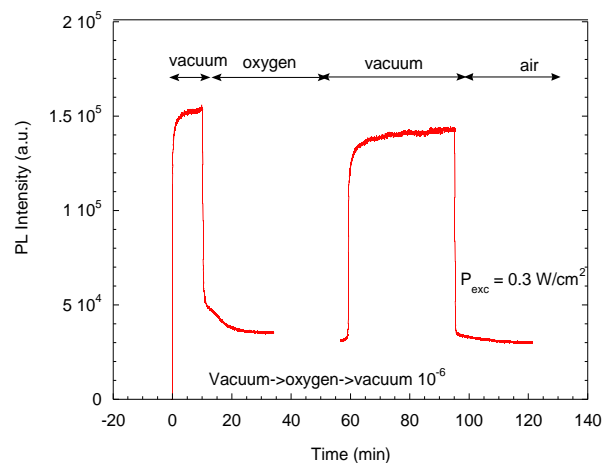


Fig. 3.7: Evolution of PL intensity in vacuum / oxygen / vacuum / air ambient for GaN sample after etching in Aqua Regia and BOE. Sample: GaN:Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

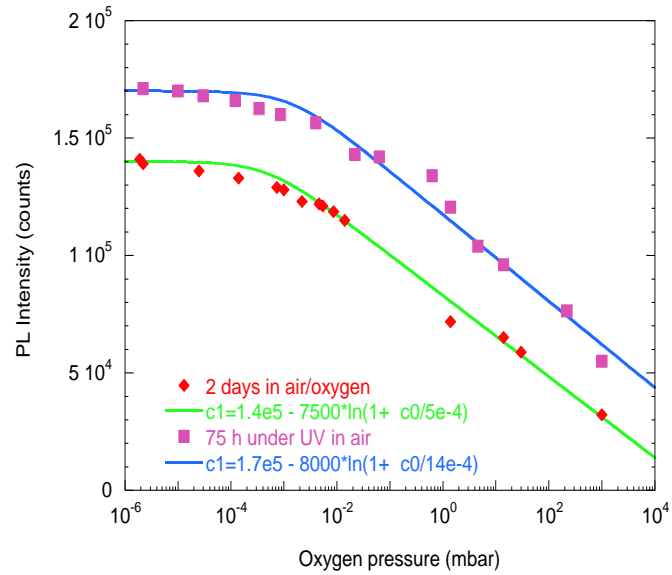


Fig. 3.8: Dependence of the exciton PL intensity on oxygen pressure measured 24 days after the etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

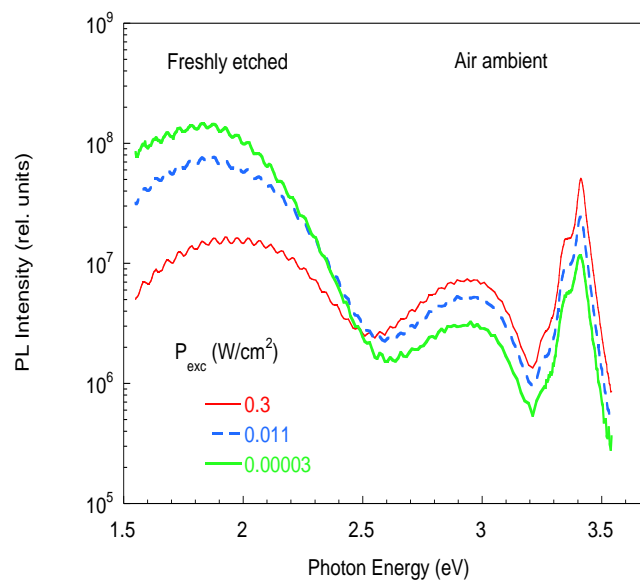


Fig. 3.9: PL spectra (divided by the excitation power density) in air ambient after etching in Aqua Regia and BOE and after consequent exposure for 1 hour to 325 nm UV light. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$.

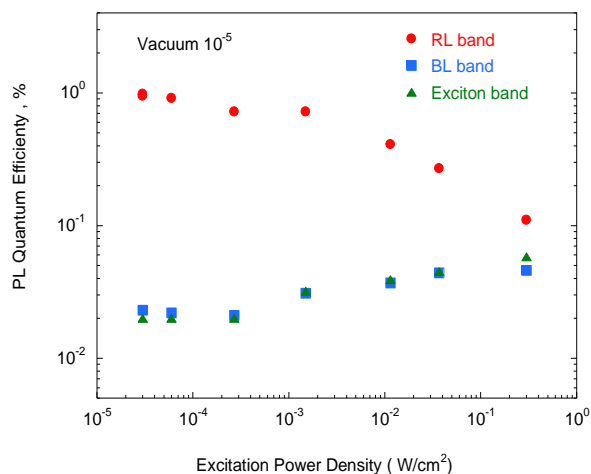


Fig. 3.10: PL Quantum efficiency for the freshly etched GaN sample for the Exciton, BL and RL bands in vacuum after etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$.

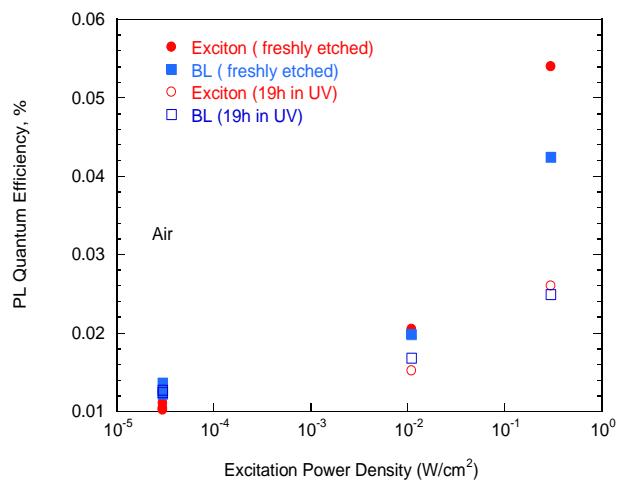


Fig. 3.11: PL Quantum Efficiency for the exciton band as a function of the excitation intensity for two sample conditions in air ambient after etching. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 3 \times 10^{-5} - 0.3 \text{ W/cm}^2$.

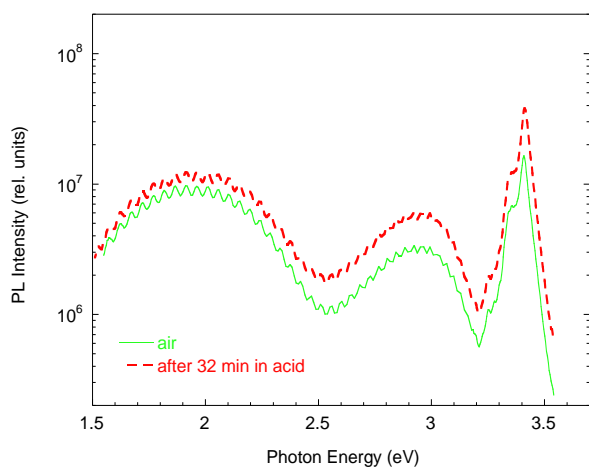


Fig.3.12: PL spectra in air and HCl acid ambient after 32 min. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3$ W/cm²

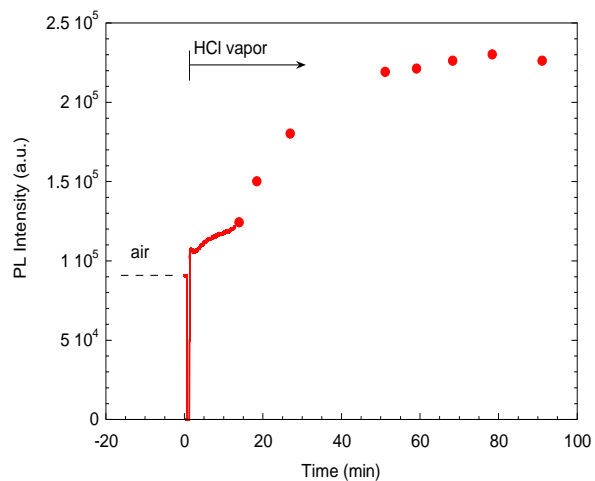


Fig.3.13: Evolution of PL intensity for sample placed in HCl vapor. Sample: GaN: Si #2015-17. Before this experiment the sample was stored in dark and air for 1000 days. Room temperature. $P_{exc} = 0.3$ W/cm².

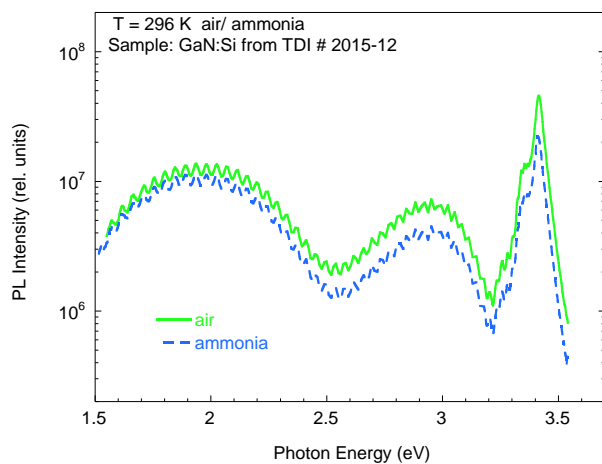


Fig. 3.14: PL spectra in ammonia and air ambient. Sample: GaN:Si # 2015-12. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

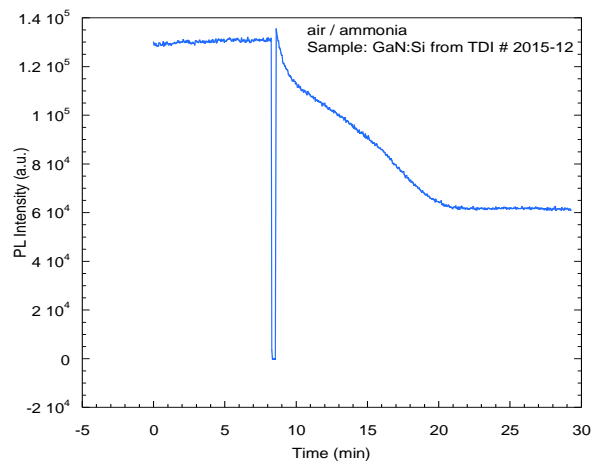


Fig. 3.15: Evolution of PL intensity for GaN sample placed in ammonia vapor. Sample: GaN:Si # 2015-12. Room temperature. $P_{exc} = 0.3 \text{ W/cm}^2$.

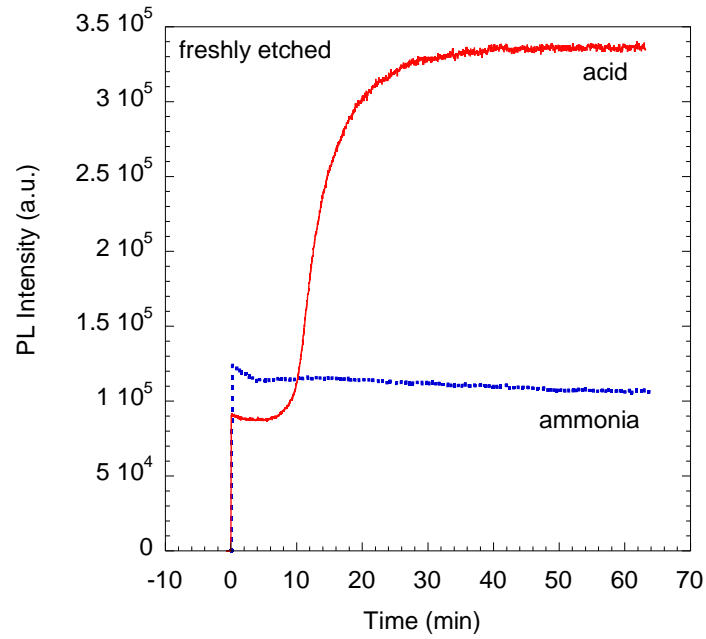


Fig. 3.16: Evolution of PL intensity for sample placed in HCl and ammonia vapor after etching in Aqua Regia and BOE. Sample: GaN: Si # 2015-17. Room temperature. $P_{exc} = 0.3$ W/cm².

Chapter 4: Discussion

4.1: The effect of band bending on PL

In an attempt to explain the changes of PL intensity, we will start with the field effect mechanism. The depletion region width W depends on the band bending Φ and the concentration of uncompensated shallow donors $N_D - N_A$ (which is close to the concentration of free electrons at room temperature) and can be found as²⁰

$$W = \sqrt{\frac{2\Phi\epsilon\epsilon_0}{q^2(N_D - N_A)}} \quad (3)$$

where ϵ is the dielectric constant for GaN ($\epsilon = 9.8$), ϵ_0 is the dielectric constant of vacuum ($\epsilon_0 \approx 8.85 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$), Φ is the band bending ($\Phi = 0.9 \text{ eV}$ in dark), q is charge of electron, and $N_D - N_A \approx n = 3 \times 10^{18} \text{ cm}^{-3}$. As reported by Kelvin probe data,²¹ the decrease of band bending and the depletion region width is due to illumination. We can calculate the PL intensity I^{PL} by integrating PL from the entire bulk region. We will exclude the depletion region, since PL can be ignored due to the strong electric field that separates electrons and holes. In the field effect mechanism, we neglect the nonradiative recombination at the surface. If one accounts for the nonradiative recombination in bulk, a factor less than one must be included in the formula:

$$I^{\text{PL}} = \int_W^D \alpha P_{\text{exc}} e^{-\alpha x} dx = P_{\text{exc}} (e^{-\alpha W} - e^{-\alpha D}) \quad (4)$$

Here D is the GaN layer thickness. We chose a sample (#2015) with a small depletion region compared to the effective depth of the propagation of the laser UV light to demonstrate that the changes in PL intensity cannot be explained by changes in the depletion region width.

We will first calculate the PL intensity in the limit of low excitation intensity (for the value of band bending in dark which is about 0.9 eV), we got value 0.81 from Eq. (4).

We calculated that with changing the excitation power density from 3×10^{-5} to 0.3 W/cm^2 the depletion region width in this sample decreases from 12 to 7.3 nm. Using the equation (4) we can calculate the ratio of the PL intensity to the excitation intensity (I^{PL}/P_{exc}) -which should be proportional to the PL quantum efficiency and equal :

$$\frac{I^{PL}}{P_{exc}} = e^{-\alpha W} - e^{-\alpha D} \quad (5)$$

The second term on the right hand side of this equation, $e^{-\alpha D}$, is about 10^{-26} and can be neglected. In dark (or in the limit of low excitation intensity), the band bending is 0.9 eV, the depletion region is 18 nm, and the ratio I^{PL}/P_{exc} is equal to 0.81. With increasing P_{exc} from 3×10^{-5} to 0.3 W/cm^2 , the band bending decreases from 0.4 to 0.15 eV, the depletion region decreases from 12 to 7.3 nm,⁶ and the I^{PL}/P_{exc} ratio increases from 0.87 to 0.92. All the calculation are summarized in Table 4.1

From the calculations we see that, according to the field-effect mechanism, the PL quantum efficiency is expected to increase by only 5% when the excitation power density is increased 3×10^{-5} to 0.3 W/cm^2 . However, as can be seen from Figs. 3.11 and 4.1, the increase of PL quantum efficiency is about 400%. This result indicates that the field-effect mechanism cannot explain large changes in PL intensity that are observed in our experiments.

Because we obtained also very significant change in the intensity for acid vapor and ammonia, we can conclude that the field-effect mechanism can not explain these results

either (Fig. 3.12 and 3.13). The exciton and BL band intensities change by more than 4 times. We expect that band bending in different ambients does not change much, such as ± 0.2 eV from the used above value of $\Phi = 0.15$ eV at $P_{exc} = 0.3$ W/cm². This expectation value is based on the Kelvin probe data in different ambients, and on available literature information about the surface recombination velocity that mostly affects the surface photovoltage.²¹ However even if we imagine the much large changes (such as $\Phi = 0$ and $\Phi = 2$ eV in different ambients which is actually unreasonable, especially at $P_{exc} = 0.3$ W/cm²), we would obtain from Eq. (5) that the PL intensity can change by at most 27%. This is much smaller than the experimentally observed 400%. Thus, the field effect mechanism should be discarded, at least for the sample studied in this work.

4.2: Nonradiative recombination at the surface as the reason for PL intensity changes

Since the field-effect mechanism cannot explain the experimentally observed large changes in PL intensity with changing ambients or excitation intensity, the second mechanism, namely the surface recombination mechanism should be considered for the explanation of the PL changes.

Within this mechanism, we can assume that the density of the surface states and/or properties of the surface states change under different environments. For example, density of oxygen species may increase in air or oxygen ambient as compared to vacuum. On the other hand, the surface recombination velocity (or the capture cross-section of the surface defects) may increase when oxygen is adsorbed at the surface. Considering the behavior of the acid ambient, we can assume that HCl removes some surface states which lead to the decrease of the density of the surface states. On the other hand, it may change their properties (such as passivation of the nonradiative surface defects). In the ammonia ambient, PL intensity decreases, which can be attributed to the creation of some surface defects, or the modification of the properties of the surface defects.

4.3. Comparison of our results with results reported in literature for the effect of pH on PL

Our results and explanations of the effect of acid vapor or ammonia on PL intensity are not consistent with other studies.¹⁶ In Ref. 16 the near-band-edge emission intensity decreased in HCl and increased in NH₃ vapor, which is opposite to the behavior for all the n-type GaN samples studied here. Note that the explanations given in Ref. 16 are controversial and apparently erroneous. First, they attribute the near-band-edge emission to transitions from the shallow donor states to the valence band, while it is well known that this emission is due to annihilation of excitons, and the shallow-donor. Also the valence band transitions are very unlikely in n-type GaN.¹³ Further, they disregard the band bending. If they accounted for it, the band bending would be larger in HCl and smaller in ammonia vapor than in air, because the redox level for acid (-5.60 eV) is lower than that for ammonia (-5.01 eV). Finally, they assume that the YL band consists of multiple energy levels that can be filled with electrons or un-filled depending on the position of the Fermi level. However, the YL band is commonly attributed to a point defect with a single energy level.¹³ In Ref. 16 the authors provide many experimental results and for a number of samples in support of the increase in the YL band intensity in acid vapor (and its decrease in ammonia vapor). However they show only one figure where the near-band-edge emission intensity changes in the opposite direction in these ambients, and say nothing about the statistics for other samples. It also looks suspicious that the spectra for the YL band and the near-bandedge emission are shown in different figures, while their out-of-phase behavior would be more convincing if shown on one figure. Finally, the PL was measured at two locations (Case Western Reserve University and University of Louisville) and in very different experimental conditions (P_{exc} was about 0.4 and 10^4 W/cm² in CWRU and UL, respectively.) For these reasons, the results and explanations presented in Ref. 16 appear to be unreliable.

Chapter 4 Figures

Table 4.1. Comparison of the expected PL quantum efficiency for values of the different band bending in GaN:Si sample with $n = 3 \times 10^{18} \text{ cm}^{-3}$.

Band bending Φ (eV)	Excitation power density, P_{exc} (W/cm^2)	Depletion region width, W (nm)	PL quantum efficiency
0.9 (in dark)	$\rightarrow 0$	18	0.81
0.4	3×10^{-5}	12	0.87
0.15	0.3	7.3	0.92

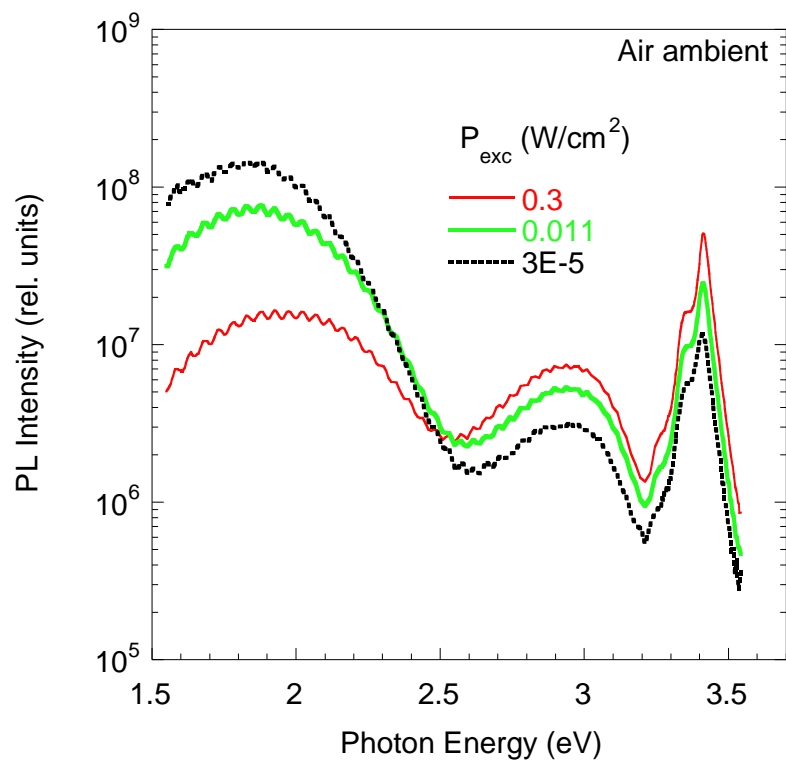


Fig. 4.1: PL spectrum for different excitation power densities in air ambient and room temperature after etching in Aqua Regia and BOE. GaN:Si # 2015-17.

Chapter 5: Summary and Conclusions

We studied the effect of ambient on PL in GaN. We observed a large increase of PL intensity in vacuum and in HCl vapor. Also, etching the sample in Aqua Regia and BOE (to remove a thin native oxide) increased the PL intensity. These changes cannot be explained with the field effect mechanism, because this mechanism predicts changes in PL intensities in different ambients or changes in PL quantum efficiency for different excitation intensities within 5-15% only for the sample studied in this work. In contrast, the experimental data showed an increase in PL intensity by up to 400% under the same conditions. The results, however, can be explained by the surface recombination mechanism.

We observed that the PL intensity from as-received GaN is not sensitive to changes in ambient from air to vacuum and attribute this effect to the presence of a native oxide layer that isolates the GaN surface from ambient. However, after removal of the native oxide by etching in Aqua Regia, the sample becomes very sensitive to the ambient. We observed that in vacuum the PL intensity increased by 3-4 times as compared to air or oxygen. The PL in acid vapor is also very strong, similar to PL intensity in vacuum after etching, whereas the PL in ammonia is slightly weaker than in air.

At least in GaN:Si samples with relatively small depletion region the changes in band bending and in depletion region width due to ambient can be ignored as compared to much larger effective depth of laser light penetration, the depth from which PL originates. For such samples explanations should be based on the surface recombination mechanism. According to this mechanism, nonradiative recombination via surface states competes with PL in bulk region. The origin of these surface states is unknown but it is established that they strongly depend on ambient. We assume that some adsorbed species create these surface states. After removal of the native oxide by etching, the surface states can be partially desorbed in vacuum with aid of UV illumination. In acid vapor these species could be also removed (etched) or

passivated. In both cases the PL intensity increases. In air the species may be adsorbed with the aid of UV illumination. Then PL intensity decreases. With increasing excitation intensity, the nonradiative surface states can be saturated with photogenerated carriers. Then the PL quantum efficiency will increase.

References

- ¹ W. Liu, X. Sun, S. Zhang, J. Chen, H. Wang, X. Wang, D. Zhao, and H. Yang, “Photoluminescence degradation in GaN introduced by light enhanced surface oxidation”, *J. Appl. Phys.* **102**, 076112 (2007).
- ² X. Y. Lee, Ch. Q. Wu, A. K. Verma, R. Ranganathan, and E. Yablonovitch, “Non destructive testing by absolute room temperature Photoluminescence quantum efficiency of gas solar cells”, Conference Record of the 25th Photovoltaic Specialists Conference-1996, Washington DC May 13-17, 1996, page 141 (1996).
- ³ J. F. Muth, J. H. Lee, I. K. Shmagin, R. M. Kolbas, H. C. Casey, B. P. Keller, U. K. Mishra, and S. P. DenBaars, “Absorption coefficient, energy gap, excitation binding energy, and recombination life time of GaN obtained from transmission measurements”, *Appl. Phys. Lett.* **71**, 2572-2574 (1997).
- ⁴ B. S. Simpkins, D. M. Schaadt, and E. T. Yu “Scanning Kelvin probe microscopy of surface electronic structure in GaN grown by hydride vapor phase epitaxy”, *J. Appl. Phys.* **91**, 9924 – 9929 (2002).
- ⁵ B. S. Simpkins, D.M. Schaadt, E. T. Yu, R.J.Molnar, “Scanning Kelvin probe microscopy of surface electronic structure in GaN grown by hydride vapor phase epitaxy”, *J. Appl. Phys.* **91**, 9924 (2002).
- ⁶ M. A. Foussekis, A. A. Baski, and M. A. Reshchikov, “Electrical and optical properties of GaN studied by surface photovoltage and photoluminescence”, *Phys. Stat. Sol. (C)*, in press [as of 5/11/2011 published online as 1–3 (2011) / DOI 10.1002/pssc.201000946].
- ⁷ V. M. Bermudez, “Study of oxygen chemisorption on the GaN(0001)-(131) surface”, *J. Appl. Phys.* **80**, 1190 (1996).
- ⁸ Th. Wolkenstein, G. P. Peka, and V. V. Malakhov, “The influence of adsorption on the luminescence of semiconductors part I. Recombination luminescence”, *J. Lumin.* **5**, 252-260 (1971).

-
- ⁹ M. S. Shur, MRS Symp. Proc. **483**, 15-26 (1998).
- ¹⁰ J. F. Muth, J. H. Lee, I. K. Shmagin, and R. M. Kolbas, H. C. Casey, B. P. Keller, U. K. Mishra, and S. P. DenBaars, "Absorption coefficient, energy gap, exciton binding energy, and recombination lifetime of GaN obtained from transmission measurements", Appl. Phys. Lett. **71**, 2572 (1997).
- ¹¹ M. A. Reshchikov and H. Morkoç, "Luminescence properties of defects in GaN", J. Appl. Phys. **97**, 061301 (2005).
- ¹² M. A. Reshchikov, M. Foussekis, A. A. Baski, H. Morkoç, "Effect of ambient on electrical and optical properties of GaN", Proc. of SPIE Vol. **7216**, 721614-3 (2009).
- ¹³ M. A. Reshchikov and H. Morkoç, "Luminescence properties of defects in GaN", J. Appl. Phys. **97**, 061301 (2005).
- ¹⁴ M. A. Reshchikov and H. Morkoç, "Luminescence from defects in GaN", Physica B **376-377**, 428-431 (2006).
- ¹⁵ C. E. Bleil and A. Albers, "The influence of ambient atmospheres on the exciton emission of cadmium sulfide", Surface Science **2**, 307-313 (1964).
- ¹⁶ V. Chakrapani, Ch. Pendyala, K. Kash, A. B. Anderson, M. K. Sunkara, and J. Angus, "Electrochemical pianning of the Fermi level : mediation of photoluminescence from gallium nitride and zinc oxide", J. Am. Chem. Soc. **130**, 12944-12952 (2008).
- ¹⁷ V. K. Gupta, C. C. Wamsley, M. W. Koch, and G. W. Wicks "Native oxides and regrowth on III-N surfaces", J. Vac. Sci. Technol. B **17**, 1249-1251 (1999).
- ¹⁸ J. R. Mileham, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, R. J. Shul, and S. P. Kilcoyne, "Patterning of AlN, InM, and GaN in KOH-based solutions", J. Vac. Sci. Technol. A **14**, 836-839 (1996).

-
- ¹⁹ M. Foussekis, J. D. Ferguson, X. Ni, H. Morkoç, M.A. Reshchikov, and A. A. Baski, “Effect of UV exposure on the surface charge behavior for GaN”, proceedings of SPIE-The international Society for Optical Engineering, 7602 (2010).
- ²⁰ S. M. Sze, “Physics of semiconductor Devices”, 2nd ed., New York (1981).
- ²¹ M. A. Reshchikov, M. Foussekis, and A. A. Baski, “Surface Photovoltage in undoped n-type GaN”, J. Appl. Phys., Vol. 11, 113535 (2010).