Pulsed laser deposition and characterization of gallium nitride thin films

Massimo Cazzanelli

Submitted for the degree of

Master of Science,

University of Dublin,

Trinity College,

Department of Physics,

September 1998

Declaration

This thesis has not been submitted as an exercise for a degree in any other university.

This thesis is entirely my own work, except for the advice and assistance mentioned in the acknowledgements.

I agree that the library may lend or copy the thesis on request.

Massimo Cazzanelli

August 1998

Ad Alfonso e Massimina.

"... spesso non si tratta di imparare
prima e di agire poi, ma al contrario
di agire e poi imparare,
perche' agire e' imparare."

Mao Tse Tung

Summary

The aim of this project was to investigate the growth process and to assess the electrical and luminescent properties of the gallium nitride (GaN) thin films that we produced.
The growth of the films was performed in different reactive atmospheres with the aim to link the growth conditions to the properties of the material.

Ion probes in the time-of-flight mode were employed to characterize the ion plume- atmosphere interaction in the chamber. Optical reflectometry was used to monitor the growth of the GaN films.

The crystalline properties were studied via x-ray diffraction in the $\theta/2\theta$ and ω-scan (x-ray rocking curves) mode. The structure of the films was characterized via atomic force microscopy (AFM) imaging of the top surface of the films. Scanning electron microscopy of these surfaces was also performed.

Electrical properties of the films in the temperature range 77$\rightarrow$300 K were investigated and an estimation of resistivity, carrier density and Hall mobility of the films was made.

Luminescent properties of the films were investigated in detail on a wide temperature range (7→300 K) using both continuous wave photoluminescence (CW-PL) and time resolved photoluminescence (TR-PL).

The radiative and non-radiative contributions to the recombination process responsible for the light emission from GaN samples were assessed for a wide range of prepared samples. A simple qualitative model explaining the luminescence properties of the films is presented.

Acknowledgements

This work has been done thanks to the help, guidance and suggestions of many people. I would like not only with this lines to acknowledge them.

I would like to thank my supervisor Dr. James G. Lunney for having given me the opportunity to work on this project, for his genuine interest in the work that I did and for his guidance throughout the work.

I would like to thanks Prof. J. M. D. Coey, not only for the financial support during this work but also for the sincere interest in the things I did, even if they were -as they were- quite far from his own scientific interests: I really appreciated it!

Thanks to Dr. John Donegan for his interest and for the useful discussions on the luminescence from GaN thin films.

Thanks to Dr. Lorenzo Pavesi, who putted at my disposal the TR-PL apparatus of the University of Trento.

Thanks to Dr. Kevin P. O'Donnel for the CW-PL measurements and for all the help in writings the papers.

I am very grateful both to the internal and external examiners of this manuscript for their very punctual and competent referee work.

Thanks to Rui P. Borges for the proof reading of the thesis and the precious help in the laboratory.

I would like then to thank all the people of group D, with whom I shared most of my time here in Trinity.

Thanks then to Guido Mariotto,Dr. Igor. V. Chvets, S. Murphy, Ciaran Seoighe and Marie D'Angelo of the STM group.

Thanks to Marc in het Panhuis, who shared with me for one year the apartment in Dublin.

This thesis would have never been started, written and wouldn’t be as it is without the friendship, help, collaboration, corrections, measurements and so on, of Claudio Vinegoni: thanks!

Thanks finally to my father, my mother and my brother, to whom this thesis is due.

Table of Contents

Declaration
Summary
Acknowledgements

Chapter 1 Introduction
1.1 Gallium nitride and group III-nitrides 10
1.2 Pulsed laser deposition of GaN 14
1.3 Overview of chapters 17

Chapter 2 The growth process
2.1 Introduction 23
2.2 Ablation and deposition of GaN 25
2.3 Results and conclusions 35

Chapter 3 Structural and electrical properties of the films
3.1 Characterisation of the films 41
3.2 Atomic force microscopy and SEM 42
3.3 X-ray diffraction 45
3.4 Electrical characterisation 48
3.5 Comparison with other techniques and conclusions 50

Chapter 4 Luminescence of the films
4.1 Introduction 57
4.2 Experimental results 58
4.2.1 Continuous wave photoluminescence 62
4.2.2 Time resolved photoluminescence 69

Chapter 5 Conclusions and suggestions for further work

Appendix A List of publications 80

Chapter 1

Introduction

In this thesis the results of an investigation of the electrical, structural and luminescent properties of pulsed laser deposited gallium nitride thin films are presented.

The pulsed laser deposition of the films [1] is performed in a high vacuum (HV) system employing a reactive atmosphere in order to encourage stoichiometric material growth. We investigated the use of both ammonia (NH_3) and of nitrogen (N_2) [2,3], as a reactive gas. Reference samples were grown in ultra high vacuum (10^{-8} mbar) and compared with the HV samples [4]. The interest in this material is due to the recent demonstration of high efficiency light emission (and laser emission) in the blue-ultraviolet range from GaN-based electroluminescent devices (LEDs) and laser diodes (LDs) [5,6]. These devices were all grown via chemical vapour deposition (CVD) techniques. In particular, the first demonstration of blue laser emission from GaN-based structures was achieved with gallium nitride grown by metal organic chemical vapour deposition (MOCVD), but this growth technique employs toxic reactive gases and needs high substrate temperatures. We investigated the possibility of growing good quality luminescent GaN via a physical vapour deposition technique, namely pulsed laser deposition (or laser ablation deposition), aiming to avoid the use of toxic components, to

work at lower substrate temperatures and, possibly, to have a higher deposition rate.

1.1 Gallium nitride and group III-nitrides

The scientific interest in the group III-nitrides, and in particular in GaN, is justified both by fundamental and applicative reasons. Fundamental reasons lie in understanding the peculiar luminescent and electroluminescent properties of nitrides: very high UV light emission efficiency [6] even at very high ($\approx 10^{10}$ cm^{-2}) dislocation density [7], and very high thermal conductivity [8].

The applicative reasons reside in the interest to extend the semiconductor device technology into the blue-UV region of the electromagnetic spectrum, until now not covered by any other semiconductor.[27]

The wurtzite polytypes of GaN, AlN and InN form a continuous alloy system with the direct band gaps taking the values 1.9 eV for InN, 3.4 eV for GaN and 6.2 eV for AlN. The refractive index of GaN is 2.33 (at 1 eV).

Thus a nitride-based device can potentially cover the red to UV region of the electromagnetic spectrum.

GaN can crystallize both in the zincblende (c-GaN) and wurtzite structure (h-GaN), with the wurtzite structure being the most common. The *a* and *c* lattice constants for the wurtzite structure are respectively 3.189 Å and 5.185 Å [7]. Both crystalline structures have a band structure showing a direct optical transition at the Γ-point (**k**=0), this characteristic being one of the

prerequisites to have laser emission from a semiconductor. The direct optical transition takes place between the bottom of the conduction band and the top of the valence band. Near the band gap

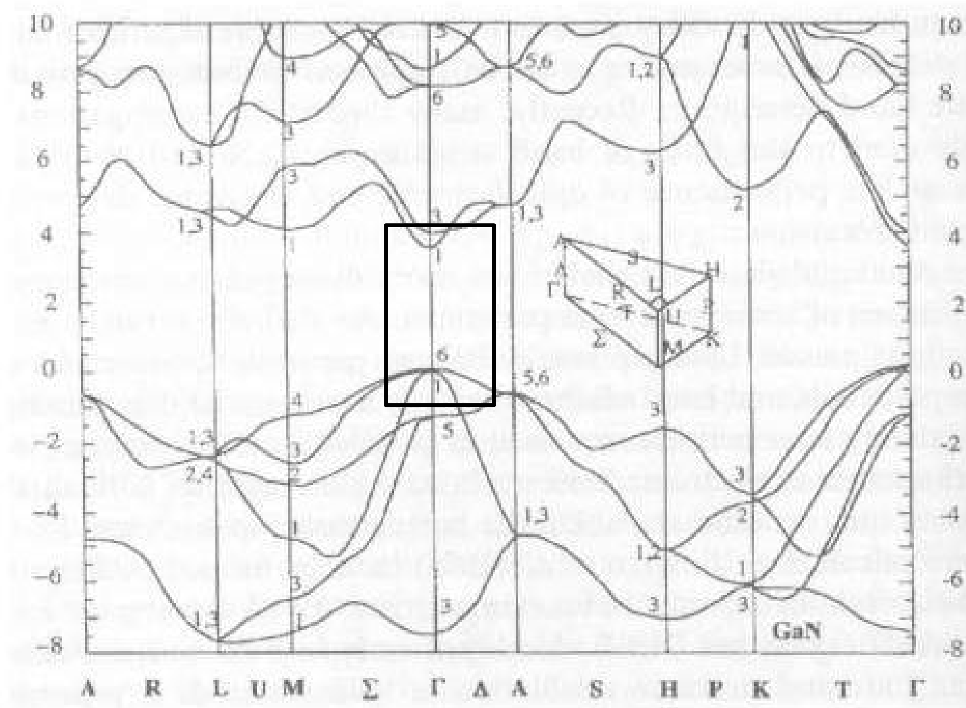


Fig.1.1 Calculated band structure of GaN [7]. The box shown in the figure selects the region of the band structure near the Γ-point; it is presented in greater detail in Fig. 1.2.

edge there are other levels that can lead to lower probability optical transitions. These levels could be defect levels or even excitonic levels.

Excitonic recombination is of particular interest for this work since it will be shown that the pulsed laser deposited GaN has its own luminescence spectrum dominated by the radiative recombination of these structures. An exciton is an electron-hole pair, and the binding energy is due to the Coulomb interaction between them.

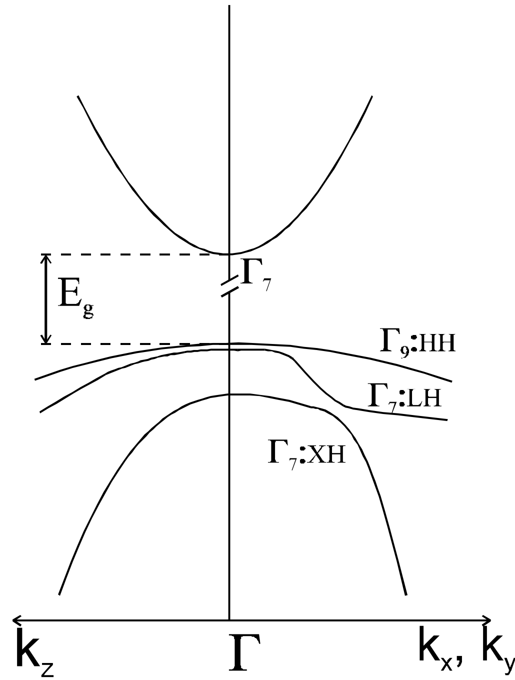


Fig.1.2 Schematic band structure near the Γ-point for wurtzitic GaN [8].

The energy level structure of such an entity is analogous to the hydrogen atom, $E = \frac{-m^* q^4}{2h^2 \mathbf{e}^2} \frac{1}{n^2}$, where m^* is the reduced mass of the exciton, q the charge of the electron, $\mathbf{e}$ the dielectric constant of the material "hosting" the exciton and n is an integer quantum number greater than zero. The exciton energy in the band gap is given by $E = E_g - \frac{-m^* q^4}{2h^2 \mathbf{e}^2} \frac{1}{n^2}$ [9].

The radiative recombination of the exciton consists then in the emission of a photon of energy equal to the energy difference between the energy level of the exciton and the top of the valence band.

Usually in high quality GaN the recorded luminescence is due to free excitons [10], at least at low temperature, i.e. an electron and a hole interacting only via the Coulomb potential. If the sample contains impurities, these can

interact with the exciton creating a binding between the impurity centre and the electron-hole structure: in this situation one refers to “bound excitons”.

The growth of GaN is usually achieved via chemical vapour deposition techniques and, as already stated, the demonstration of blue-UV laser emission was obtained on material grown by metal organic chemical vapour deposition (MOCVD). Employing this growth technique it was possible to solve the early problem of p-type doping of GaN and then to produce p-n junctions that are the basis on which it is possible to build efficient electroluminescent devices [11].

One of the major difficulties in the growth of GaN is the lack of a lattice-matched and thermally compatible substrate for gallium nitride. All the demonstrated devices were grown on Al_2O_3 and the preferred orientations were the (0001),

Typical values of Hall mobility for n-type GaN at room temperature are $\mu_n \approx 600\, cm^2V^{-1}s^{-1}$ (up to $3000\, cm^2V^{-1}s^{-1}$ at 77 K) [15] while for p-type the values are slightly lower [11]. The resistivity of GaN is a parameter that changes with the doping and growth conditions [11].

The other group III nitrides are InN and AlN and their alloys with GaN (InGaN and AlGaN). InN has not received the same attention as GaN mainly because its band-gap (at 1.89 eV) lies in a region of the electromagnetic spectrum already covered by other semiconductors and the intrinsic difficulty in growing this material. Its principal application is, up to now, restricted to use in alloys with GaN and AlN.

InN crystallizes in the wurtzite structure and its lattice constants are respectively a=3.53 Å and c=5.69 Å. Its refractive index is 2.9 (at 1 eV) [8].

AlN was studied mainly for its outstanding hardness and high thermal conductivity. Its lattice constants are a=3.11 Å and c=4.98 Å. Its refractive index is 2.15 (at 1 eV). Its use in relation to the photonic applications of III-nitrides has been limited to its alloys with GaN and InN [8].

1.2 Pulsed laser deposition of GaN

The deposition technique employed in this project was a novel deposition technique, namely pulsed laser deposition (PLD) [1,16]. We grew epitaxial thin films of GaN directly on sapphire. In the recent past this technique has been used to prepare high quality thin films of multicomponent oxide ceramics [16]. Very recently it was used successfully to

grow nitrides: TiN [17], BN [18], NbN,[19] AlN, InN [20], AlGaN [21] and GaN [20,22,23].

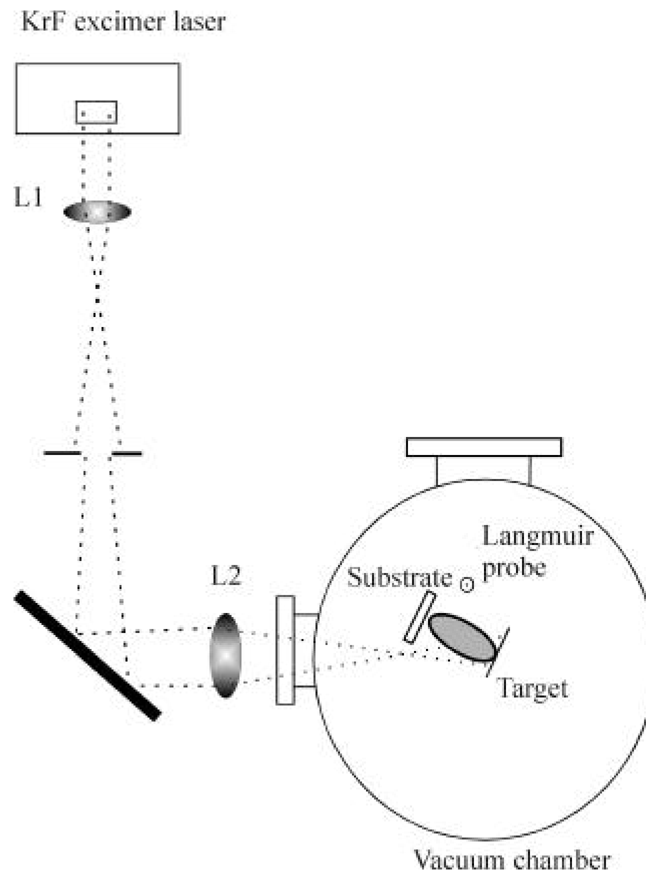


Fig.1.3 Scheme of the pulsed laser deposition system employed to produce the films. The laser wavelength of the KrF laser is 248 nm and its repetition rate is 10 Hz. The beam passes through a first lens at the exit of the laser, which focusses it in a point between L1 and a rectangular pinhole (4×2 mm^2), the beam is then directed through a second lens L2 on the target in the chamber. The final dimension of the spot on the target is controlled in order to have the possibility to tune the total incident fluence on the target, by simply moving the lens L1.

The main advantages of this technique are:

- the non-equilibrium evaporation process produces an intense plasma and transfers the composition of the sputtered target onto the deposited film.
- the high control on the growth rate by adjusting the laser fluence.
- possibility of *in-situ* processing of multilayer heterostructures by using a multiple target carousel.
- reduced growth-temperature at the substrate due to the intrinsic high superficial lateral mobility of the ablated high energy plume.
- possibility to use non toxic gases as the reactive atmosphere during the growth.

Earlier work in our group demonstrated successfully the growth of well-oriented crystalline GaN films on the α-plane of sapphire [22] both in vacuum and in a reactive atmosphere. It was found that the GaN is deposited on this plane of sapphire preferentially along the [0001] direction. In this work the growth of GaN in N_2 and NH_3 atmosphere was also earlier investigated and demonstrated. The present project concerns the production of samples in these already optimized conditions and the characterization of the grown films. A particular attention is paid to understand the mechanism responsible for the UV light emission we observed from the films grown in the N_2 atmosphere [2,3] and for the weak yellow emission of the films grown in ammonia.

Overview of chapters

Chapter 2

A description of the growth process of pulsed laser deposited GaN both in NH_3 and in N_2 reactive atmospheres is presented. Ion probes curves in the optimized conditions are discussed [25]. *In-situ* reflectivity curves for the samples grown in NH_3 at low pressure ($\approx 2\times10^{-3}$ mbar), are presented and qualitatively discussed [26].

Chapter 3

The experimental methods used to characterize the films are described. A particular emphasis is given to the results of atomic force microscopy (AFM), electrical measurements, x-ray diffraction both in the $\theta/2\theta$ and in ω-scan (x-ray rocking curves) modes.

Chapter 4

The luminescence properties of the films are presented and discussed. A comparison between the continuous wave photoluminescence (CW-PL) and time resolved photoluminescence (TR-PL) is proposed and a qualitative model allows us to explain the luminescence of the films.

Chapter 5

The conclusions resulting from the work in this thesis are presented, and possible developments for further work is considered.

References

[1] D. B. Chrisey, J. S. Horwitz, C. M. Cotell, R. E. Treece and P. C. Dorsey, NRL Review **282**, (1995) 73. T. Venkatesan and S. M. Green, The Industrial Physicist, **1**, (1996) 22. F. X. Rong, Appl. Phys. Lett. **67**, (1995) 1022. C. Phipps and R. W. Dreyfus, in *Laser Microprobe Mass Analysis* (John Wiley & Sons, New York, 1994). J. T. Dickinson, D. R. Ermer, J.-J. Shin and S. C. Langford, Appl. Surf. Sci. **127-129**, (1998) 7. M. E. Taylor and H. A. Atwater, Appl. Surf. Sci. **127-129**, (1998) 159.

[2] M. Cazzanelli, D. Cole, J. Versluijs, J.F. Donegan and J.G. Lunney, submitted to Mat. Sci. & Eng.B .

[3] M. Cazzanelli, D. Cole, J.F. Donegan, J. G. Lunney, P.G. Middleton, K.P. O'Donnell, C. Vinegoni, L. Pavesi, submitted to Appl. Phys. Lett.

[4] D. Cole, J. G. Lunney, F. P. Logue, J. F. Donegan, J. M. D. Coey, Mat. Sci. & Eng.B, **48** (1997) 631.

[5] S. Nakamura, T. Mukai and M. Senoh, Appl. Phys. Lett., **64** (1994) 1687.

[6] S. Nakamura, M. Senoh and T. Mukai, Jpn. J. Appl. Phys. **30**, L1708 (1991); S. Nakamura, T. Mukai and M. Senoh, *ibid.* **30**, L1998 (1991). R. Dingle and M. Ilegems, Sol. State Commun. **9**, (1971) 175. J. I. Pankove, J. E. Berkeyheiser, H. P. Maruska and J. Wittke, Sol. State Commun. **8**, (1970) 1051. M. A. Kahn, D. T. Olsen, J. M. Van Hove and J. N. Kuznia, Appl. Phys. Lett. **58**, (1991) 1515. D. L. Camphausen and G. A. Connell, J. Appl. Phys. **42**, (1971) 4438. I. G. Pichugin and D. A. Yas'kov, Inorg. Mater. **6**, (1970) 1732. A. M. Zykov and G. K. Gaido, Sov. Phys. Semicon. **6**, (1972) 154. Y. M. Suleimanov, I. G. Pichugin

and L. A. Marasina, Sov. Phys. Semicon. **8**, (1974) 537. T. Sasaki and T. Matsuoka, J. Appl. Phys. **64**, (1988) 4531. M. A. Kahn, J. N. Kuznia, J. M. Van Hove, D. T. Olsen, S. Krishnankutty and R. M. Kolbas, Appl. Phys. Lett. **58**, (1991) 526. T. Sasaki and S. Zembutsu, J. Appl. Phys. **61**, (1987) 2533. J. M. Hvam and E. Ejder, J. Lumin. **12/13**, (1975) 611. R. D. Cunningham, R. W. Brander, N. D. Knee and D. K. Wickenden, J. Lumin. **5**, (1972) 21. W. Goetz, D. B. Obermann and J. S. Harris, Jr., Mat. Res. Soc. Symp. Proc. **378**, (1995) 324.

[7] S. D. Lester, F. A. Ponce, M. G. Craford and D. A. Steigerwald, Appl. Phys. Lett. **66** (1995) 1249.

[8] S. Strite and H. Morcoς, J. Vac. Sci. Technol. B **10** (1992) 1237.

[9] J. I. Pankove, *Optical Processes in Semiconductors*, Dover Editions (1975), pp. 12-16.

[10] J J.S. Im, A. Moritz, F. Steuber, V. Haerle, F. Scholz and A. Hangleiter, Appl. Phys. Lett. **70** (1997) 631.

[11] S. Nakamura, *The Blue Laser Diode*, Springer Verlag editions, (1997), pp. 103-128.

[12] M. Ilegems and H. C. Montgomery, J. Phys. Chem. Solids, **34** (1973) 885.

[13] J. C. Vesely, M. Shatzkes and P.J. Burkhardt, Phys. Rev. B **10** (1974) 582.

[14] R. K. Crouch, W. J. Debnam and A. L. Fripp, J. Mater. Sci. **13** (1978) 2358.

[15] S. Nakamura, Jpn. J. Appl. Phys. **30** (1991) L1705.

[16] *Pulsed Laser Deposition of Thin Films*, edited by D. Chrisey and G. Hubler (Wiley-Interscience, New York, 1994), and references therein.

[17] P. R. Willmott, R. Timm, J. R. Huber, Appl. Surf. Sci. **127-129** (1998) 105.

[18] B. Angleraud, M. Cahoreau, I. Jauberteau, J. Aubreton and a Catherinot, J. Appl. Phys. **83** (1998) 3398.

[19] R. E. Treece, M. S. Osofsky, E. F. Skelton, S. B Qadri *et al.*, Phys. Rev. B **51** (1995) 9536. Y. Hiroshima, T. Ishiguro, K. Esaki, Jpn. J. Appl. Phys. **36** (1997) 2267. G. Cappuccio, U. Gambardella, A. Morone, S. Orlando *et al.*, Appl. Surf. Sci. **109-110** (1997) 399. R. E. Treece, J. S. Horwitz, E. F. Skelton *et al.*, Journ. Sol. St. Chem. **117** (1995) 294.

[20] D. Feiler, R. Stanley Williams, A. A. Talin, H. Yook, M. S. Goorsky, J. Cryst. Growth **171** (1997) 12.

[21] T. Huang and J. S. Harris, Jr., Appl. Phys. Lett. **72** (1998) 1158.

[22] D. Cole, Ph.D. thesis, Trinity College, University of Dublin (1998), *Chapter 4.*

[23] R. D. Vispute, V. Talyansky, R. P. Sharma, S. Choopun, M. Downes and T. Venkatesan, K. A. Jones, A. A. Iliadis, M. Asif Khan and J. W. Yang, Appl. Phys. Lett. **71** (1997) 102.

[24] R. Jordan, Ph.D. thesis, Trinity College, University of Dublin (1997).

[25] M. Cazzanelli, D. Cole and J. G. Lunney, accepted for Poster presentation at 14th ESCAMPIG, Europhysics Conference on Atomic and Molecular Physics of Ionized Gases, 26th-29th August 1998, Malahide, Dublin, Ireland.

[26] The idea of the use of low pressure of ammonia is due to a *private communication* of Dr. R. D. Vispute.

[27] S. Nakamura, Physics World, Feb. 1998, 31.T. Strite, Compound Semiconductor Jan/Feb 1996, 56. W. Xie, D. C. Grillo, R. L. Gunshor, M. Kobayashi, H. Jeong, J. Ding, A. V. Nurmikko, G. C. Hua and N. Otsuka,

Appl. Phys. Lett. **60**, (1992) 1999. D. E. Eason, Z. Yu, W. C. Hughes, W. H. Roland, C. Boney, J. W. Cook, Jr., J. F. Schetzina, G. Cantwell and W. C. Harasch, Appl. Phys. Lett. **66**, (1995) 115. J. Edmond, H. Kong and V. Dmitriev, Inst. Phys. Conf. Ser. **137**, (19949 515. H. Okuyama and A. Ishibashi, Microelec. J. **25**, (1994) 643. K. Koga And T. Yamaguchi, Prog. Cryst. Growth Charact. **23**, (1991) 127. M. G. Craford, Circuits & Devices, (Sept. 1992) 24. H. Sugawara, K. Taya And G. Hatakoshi, Jpn. J. Appl. Phys. **33**, (1994) 5784. S. Nakamura and G. Fasol, 1997, *The Blue Laser Diode* (Springer, Heidelberg).

Chapter 2

The growth process.

2.1 Introduction

Gallium nitride based semiconductors have applications in the field of photonics, in fact their band gap is in the UV-blue range which allows it to extend the spectral range of conventional semiconductor based LEDs and LDs [1,2,3]. A particular interest is dedicated to the growth process of high quality GaN thin films. The growth technique most often employed is MOCVD [3]. Nichia corporation holds the world record for the longest-lived GaN LEDs and LDs. These devices were fabricated from materials grown by MOCVD.[4]

In this chapter we study the deposition and characterization of GaN thin films in different reactive atmospheres via the novel technique of pulsed laser deposition (PLD). The main advantages of this technique are in general those of a physical vapour deposition (PVD) technique, which doesn't involve the use of reactive chemicals and the high deposition rates achieved.

The films of GaN were grown in a high vacuum (HV) chamber. The chamber was equipped with a leak valve to introduce NH_3 or N_2 to study the effects of these gases on the deposition process. The gas pressure for films grown in NH_3 was 0.2 mbar and 0.1 mbar for films grown in N_2. An

additional film was grown in UHV conditions. All the films were deposited on the

α-plane of sapphire. The substrate was heated to a temperature of 600 °C for the UHV-film and to 700 °C for the other two samples. The temperature of the substrate was decided looking for a balance between the necessity of having a sufficient (i.e. allowing a reasonable growth rate) lateral mobility of sputtered species on the substrate surface [11] (that is achieved at high substrate-temperatures) and the necessity of working at low temperature that simplifies a lot the deposition process.

Target pellets were prepared by pressing GaN powders (nominally 99.99% pure) under a pressure of about 7×10^4 N cm^{-2}. The targets were then sintered at 650 °C for about 12 hours in a N_2 atmosphere.

The ablation of GaN was performed using the 248 nm line of an excimer laser, with a pulse width of 23 ns and a repetition rate of 10 Hz. The final fluence on the target was 3.6 J cm^{-2} for the NH_3-film, 2.8 J cm^{-2} for the N_2-film and 1.7 J cm^{-2} for the UHV-film. The laser-beam point of incidence on the target was rotated to avoid the pitting on the surface of the target. The laser fluence mainly influences the growth rate, but increasing it one also obtains a sputtering of micrometric sized particulates of material; this latter being clearly an undesirable effect that has to be minimized. One has then to find a reasonable balance between velocity of growth and presence of particulates in the deposited film.

The ion transport to the target was monitored with a Langmuir probe, and the target substrate separation was 35 mm.

2.2 Ablation and deposition of GaN

The set of samples studied consisted of pulsed laser deposited GaN films grown in N_2, in NH_3 and in UHV (around 10^{-8} mbar). The pressures were respectively 0.1 mbar, 0.2 mbar and UHV.

Before starting the growth, the ion signal of the gallium nitride plume was monitored with a Langmuir probe (see Fig. 2.1) [9]. This technique employs a small metallic electrode, usually a wire (simply a peeled BNC cable), inserted into the plasma. The probe is biased at a certain voltage relative to the plasma, and the current collected by the probe that gives information about the plasma. When negatively biased the probe collects the ions in the plasma and from time-resolved measurements of the collected current (related to the ionic current at the probe) information can be deduced on the plasma ionic density and energy. Typical integrated ion charge on the probe is of the order of tens of nC [22]. It is known [23]when the probe is biased sufficiently negative to obtain an ion saturation current the behaviour of the probe could be approximated as $I(TOF) = N(d, TOF) A\, e\, v$ where I is the current collected by the probe as a function of the time of flight *TOF* of the ions, N is the plasma density depending both on the probe-target separation d (very close to the target-substrate separation that is 35 mm) and the time of flight of ions *TOF*, A is the area of the probe, e the electron charge and v the plasma velocity [24]. In Fig. 2.1 it can be seen the geometry of the experiment: the pulsed laser beam hits the GaN-target and a plume of ablated material (composed by Ga and N ions and GaN particulates) is ejected; in the same

position of the substrate, the ion-probe is inserted and is connected to the external circuitry with suitable electrical connectors for vacuum chambers work. The output signal is sent to a fast oscilloscope through a 0.47 μF capacitor. Typical values for the time of flight of ions for GaN, in the described experimental conditions, are of the order of μs, that leads to

Fig.2.1 Schematic diagram of the Langmuir probe system employed to characterize the GaN plume. The shielded wire was negatively biased at -30 V.

energies of ions of the order of tens of eV (taking into account the masses of the ions produced from the ablated GaN target).

In Fig.2.2 we present typical ion probe signals for samples grown in vacuum and in N_2. This situation differs from the above described situation only for the introduction in the chamber of a reactive gas atmosphere [25-33]. The aim is to improve the growth and the stoichiometry of the deposited GaN film.

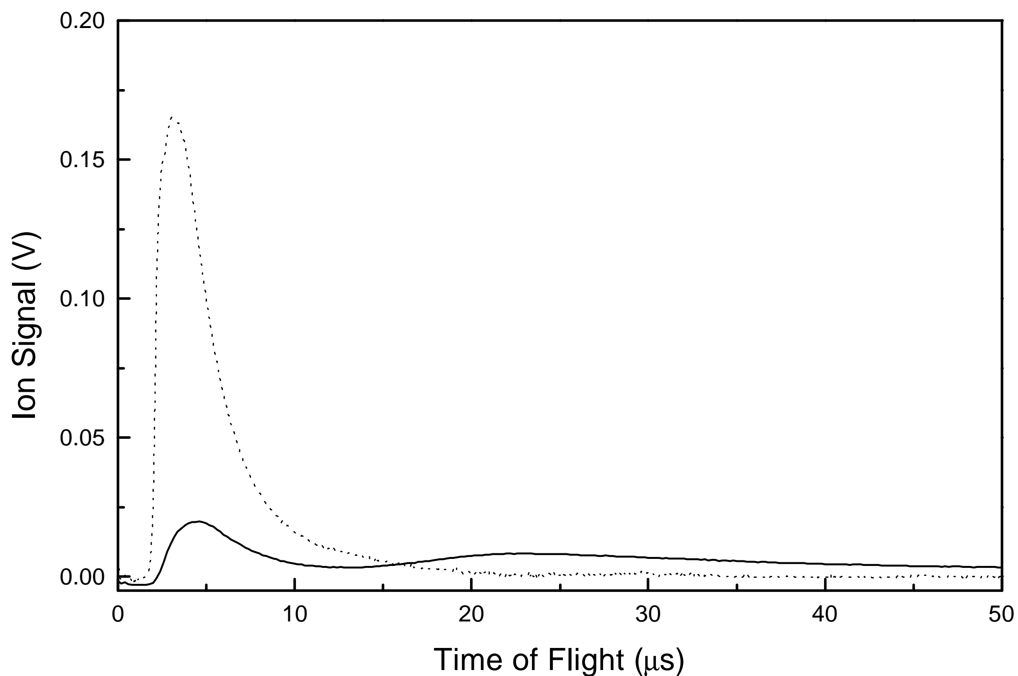


Fig. 2.2 Ion signal, from the Langmuir probe in the chamber, measured for the GaN plume in vacuum (dotted line) and in a 0.12 mbar N_2 atmosphere (full line)

It can be observed that the introduction of the gas in the chamber changes drastically the time of arrival of the ablated species. This is attributed

[5] to the effect of a “shock wave” generated by the ion plume in the atmosphere in the chamber. The energies of ions in the plume in vacuum extracted from the data of Fig.2.2 were respectively 69 eV for gallium and 14 eV for nitrogen ions.

It was found that the best films were obtained when the gas pressure was chosen to give a doubly-peaked ion signal. This kind of signal arises when the ion mean free path is approximately equal to the target-substrate separation [5]. The first peak is due to ions transmitted through the gas, and the second is due to a blast wave launched by ions colliding with the gas [6,7,10].

The film growth was monitored via optical reflectometry. A laser diode (λ=670 nm) was directed to form an angle θ=29 deg. with the film, and the reflected beam from the sample film was detected with a photodiode. As the film grows, the reflectivity exhibits a sinusoidal curve, due to the interference effects related to the thickness of the film. In the ideal situation of no absorption and perfect superficial flatness the curve would be a perfect sinusoidal; the effect of the absorption of the film is to damp the curve around a constant average value, while the effect of the superficial roughness is to decrease this average value monotonically with the time. The theory of optical reflectivity from thin films has been described in details elsewhere [10] and will not be repeated here.

Reflectivity versus deposition time as measured for samples grown in NH_3 are shown in Fig. 2.3 Both increasing the temperature of growth and the pressure of the reactive atmosphere increases the growth rate. The values

obtained for growth rate for the films we are presenting in the thesis are summarized in Table 2.1: a comparison with typical values for other growth techniques is proposed. Reading the growth rate column it can be seen that PLD is a competing technique with MBE and MOCVD (to be noted that the growth rate in the CVD techniques can be significantly increased, as the work of Maruska et al. [14] testifies), having in addition the advantage of working at relatively low substrate-temperature.

GROWTH TECHNIQUE	GROWTH ATMOSPHERE	TEMPERATURE SUBSTRATE [°C]	GROWTH RATE [nm/min]	TYPICAL THICKNESS [nm]	REFERENCES
PLD	NH_3 (≈10^{-1} mbar)	600	≈15	≈300	[12]
PLD	NH_3 (≈10^{-1} mbar)	700	≈30	≈300	[12]
PLD	NH_3 (≈10^{-3} mbar)	700	≈5	≈300	[13]
PLD	UHV	700	≈0.11	≈50	[7]
PLD	N_2	700	≈0.22	≈50	[7]
CVD	NH_3	925	≈500	≈5×10^3→20×10^3	[14]
MBE	N_2/NH_3	750/900	≈1/5	≈5×10^3	[15]
PEMPE	ATOMIC N	650→825	≈10	≈500	[21]
HVPE	NH_3 DILUTED IN N_2	1050→1070	≈100→500	≈10×10^3→30×10^3	[17]
MOCVD	CRACKED NITROGEN SOURCES	1000→1080	≈10→100	≈1×10^3	[16]
MOCVD	MAIN FLOW TRIMETHYLGALLIUM (TMG)+ NH_3+H_2 WITH A SUBFLOW OF N_2+ H_2	1000→1030	≈50	≈5×10^3	[18,19,20]

Table 2.1 Growth rate and growth conditions for the films grown by PLD, compared with results obtained by other techniques. PLD is pulsed laser deposition, CVD is chemical vapour deposition, MBE is molecular beam epitaxy, PEMBE is plasma-enhanced molecular beam epitaxy, HVPE is hydride vapour phase epitaxy and MOCVD is metalorganic chemical vapour deposition. All the films are grown on sapphire.

By solving the Fresnel equations, and taking into account also the surface roughness, related to reflection from the growing thin film of GaN, and

fitting the experimental curves, we extracted values for surface roughness of 20.2 nm, 30.3 nm and 41.5 nm respectively for temperatures: T=600°C, T=500°C and T=400°C (see Fig. 2.4). These values are in good agreement with data extracted from a statistical analysis of the cross sectional lines of the AFM's micrographs [6].

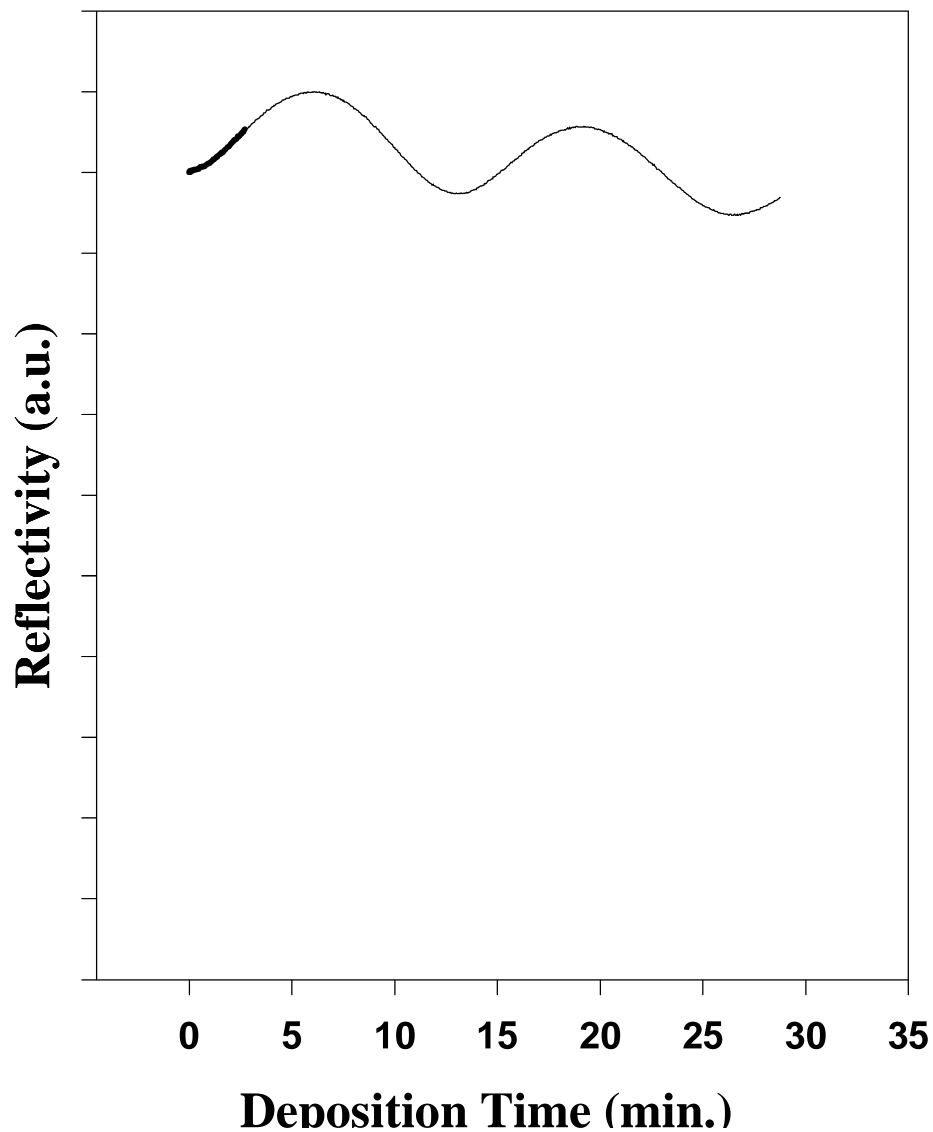


Fig. 2.3 In-situ optical reflectivity, shown in real time, indicating the increase in growth rate as both the temperature and pressure are increased [6,7,8].

Fig. 2.4 shows the reflectivity versus thickness of the sample; this latter quantity was estimated from absorption measurements.

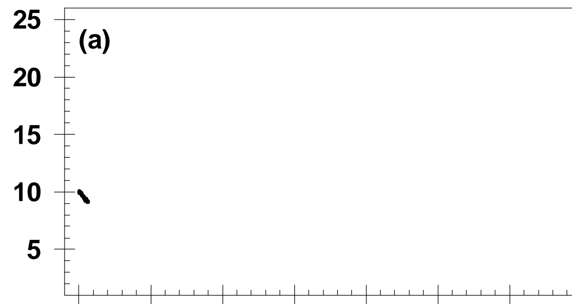


Fig. 2.4 Reflectivity curves versus thickness of the film. The grey lines are a fit based on the solution of Fresnel equations.

The situation for films grown in N_2 was different for the same range of substrate temperature (T>500 °C); in fact the growth is very slow and no structures in the reflectivity versus time traces on a time scale of 2 hours is

observed. This could be related to the low reactivity of ablated GaN with N_2 and perhaps could be solved using an ionised or atomic source of nitrogen.

One of the setbacks of the growth in ammonia was the lack of blue-UV luminescence from the samples, as will be shown in detail in Chapter 4.

To solve this problem and with the aim of reproducing the results of R.D. Vispute (free-exciton emission at 77 K [13]) we tried growing the GaN in ammonia, at a lower pressure, of 2×10^{-3} mbar in a background pressure of

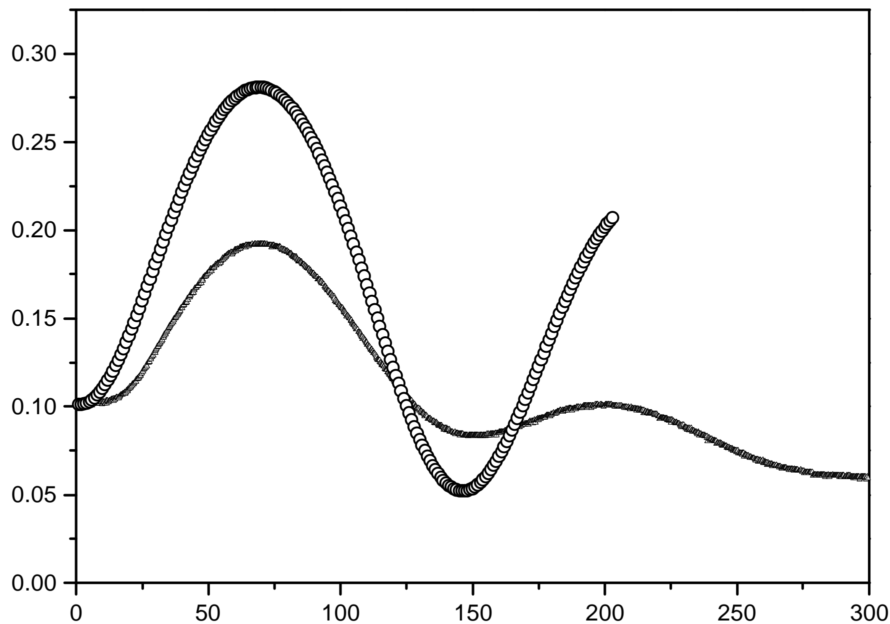


Fig. 2.5 Reflectivity curves for the film grown in ammonia at a pressure of 2×10^{-3} mbar. Triangles are the measured reflectivity. Open circles are a simulation of the reflectivity in the ideal situation of no absorption at 670 nm (the laser wavelength) and average superficial roughness of 20 nm. The full line is a fit that, solving the Fresnel equations associated with the reflection of the laser on the growing GaN layer, takes into account both the absorption of the film and the superficial roughness.

1×10^{-6} mbar. This value is two orders of magnitude less than those previously used [1,6].

The reflectivity trace for a film grown under these conditions is shown in Fig. 2.5. The damping of the reflectivity versus thickness shows that the film is absorbing at 670 nm. The drop of the trace is caused by sample roughness.

The fit based on the solution of the Fresnel equations of the reflection of light (670 nm) at the surface of the growing film, gives a complex refractive index $n = 2.22 + i \cdot 0.44$ and an average superficial roughness of about 44 nm. The real part of the refractive index is quite low (the expected value is 2.36), but the obtained fit is not in excellent agreement with the experimental data. This fact could be due to the rough estimation we gave of the thickness of this sample, which was estimated from the simulated curve with ideal values for the refractive index and for the absorption coefficient at 670 nm. It that should be more precisely measured, as was done for all the other samples presented in the thesis, via absorption measurements or via ellipsometry. Anyway the information we extracted from the data presented in Fig. 2.5 is the quality (transparency and superficial quality) of the films has to be improved, and this could be achieved optimizing the growth conditions in the low ammonia pressure regime ($\approx10^{-3}$ mbar).

2.3 Results and conclusions

Pulsed laser deposition of GaN thin films, in UHV, ammonia and nitrogen atmospheres, was successfully demonstrated. A representative set of parameters for growing in NH_3, N_2 and UHV in optimized and um-optimized is presented in Table 2.2. This samples were produced and optimized both during this work and in previous work by Dr. Duncan Cole [6].

Ion probe signals for optimized growth conditions were also presented and it is found that the growth of good quality films is achieved when the ablated ions are partially backscattered by the reactive atmosphere with the ion signal showing the typical shape explained in the framework of the "shock wave" model.

Successful growth of GaN at 2×10^{-3} mbar of ammonia was demonstrated. The quality of these films has to be optimized.

growth atm.	partial pressure (mbar)	laser fluence (J cm^{-2})	temp. of substrate (° C)	color	Lum.	wavelength (nm)	energy gap (eV)	resistivity at RT (Ω cm)	x-ray rocking FWHM (arcmin)	Ref.

References

[1] J. I. Pankove and J. E. Berkeyheiser, Proc. IEEE **60**, (1972) 1456. S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, Appl. Phys. Lett. **67**, (1995), 1868. J. I. Pankove, J. Lumin., **7**, (1973) 114. F. P. Kesamanly, Sov. Phys. Semicon. **8**, (1974) 147. J. I. Pankove, S. Bloom and G. Harbecke, RCA Rev. **36**, (1975) 163. T. Strite, Comp. Semicon. Jan./Feb. 1996, 56. S. Nakamura, Adv. Mater. **8**, (1996) 689. S. Nakamura, J. Cryst. Growth, **170**, (1997) 11. S. Nakamura, IEEE J. Sel. Top. In Quant. El., **3**, (1997) 435. S. Nakamura, Physics World Feb. 1998, 31. H. P. Maruska, D. A. Stevenson and J. I. Pankove, Appl. Phys. Lett. **22**, (1973) 303. H. P. Maruska and D. A. Stevenson, Solid-State Electron. **17**, (1974) 1171. J. I. Pankove, E. A. Miller and J. E. Berkeyheiser, RCA Rev. **32**, (1971) 383. J. I. Pankove and E. R. Levin, J. Appl. Phys. **46**, (1975) 1647.

[2] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, Jpn, J. Appl. Phys. **34**, (1995), L979. J. Lang, Y. Laurent, M. Maunaye and R. Marchand, Prog. Cryst. Growth Charact. **2**, (1979) 207. J. I. Pankove, Mat. Res. Soc. Symp. Proc. **97** (1987) 409; **162**, (1990) 515. R. F. Davis, Proc. IEEE **79**, (1991) 702. R. F. Davis, Z. Sitar, B. E. Williams, H. S. Kong, H. J. Kim, J. W. Palmour, J. A. Edmond, J. Ryu, J. T. Glass and C. H. Carter Jr., Mat. Sci. Eng. **B1**, (1988) 77. S. Nakamura, MRS Bull. Feb. 1997, 29. S. Nakamura, III-Vs Review, **9**, (1996) 22. A. N. Vasilishchev, L. N. Mikhailov, V. G. Sidorov, M. D. Shagalov and Yu. K. Shalabutov, Sov. Phys. Semicon. **9**, (1976) 1189. A Shintani and S.

Minagawa, J. Electrochem. Soc. **123**, (1976) 1725. Y. Ohki, Y Toyoda, H. Kobayashi and

I. Akasaki, Inst. Phys. Conf. Ser. **63**, (1982) 479. G. Jacob, R. Madar and J. Hallais, Mater. Res. Bull. **11**, (1976) 445.

[3] S. Strite and H. Morcoç, J. Vac. Sci. Technol. **B10**, 1992, 1237. H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Inst. Phys. Conf Ser. **106**, (1989) 725. H. Amano and I. Akasaki, Oyo Buturi **60**, (1991) 163 [in Japanese]. G. Jacob, M. Boulou and M. Furtado, J. Cryst. Growth **42**, (1977) 136. G. Jacob, M. Boulou and D. Bois, J. Lumin. **17**, (1978) 263.

[4] S. Nakamura, Mat. Sci. & Eng. **B43**, 1997, 258.

[5] R. Wood et al., Phys. Rev. Lett. **79**, 1997, 1571.

[6] D. Cole, Ph.D. thesis, Trinity College, University of Dublin (1998), *Chapter 4.* M. Cazzanelli, D. Cole, J. Versluijs, J.F. Donegan and J.G. Lunney, to be published on Mat. Sci. & Eng.B (1999).

[7] D. Cole, J.G. Lunney, F.P. Logue, J.F. Donegan, J.M.D. Coey, Mater. Sci. Eng. **B48**, (1997) 239.

[8] M. Cazzanelli, D. Cole and J.G. Lunney, Europhysics Conference Abstracts, **22H**, (1998) 464..

[9] R. Jordan, Ph.D. thesis, Trinity College, University of Dublin (1997), *Chapter 3.*

[10] J. F. McGilp, Progress in Surf. Sci, **49**, (1995), 1.

[11] K. Ploog, Angew. Chemie, **27**, (1988) 593.

[12] D. Cole, J.G. Lunney, Mater. Sci. Eng., **B50**, (1997), 20.

[13] M. Cazzanelli and J. G. Lunney, *unpublished.* R.D. Vispute, *private communication.*

[14] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett., **15**, (1969), 327.

[15] Philippe Vermaut , P. Ruterana, G. Nouet, A. Salvador, H. Morkoç, MRS Internet J. Nitride Semicond. Res., **1**, (1996), 42. Markus Kamp , M. Mayer, A. Pelzmann, K. J. Ebeling, MRS Internet J. Nitride Semicond. Res., **2**, (1997), 26.

[16] B. Beaumont, M. Vaille, P. Lorenzini, Pierre Gibart , T. Boufaden, B. el Jani, MRS Internet J. Nitride Semicond. Res., **1**, (1996), 17.

[17] Raj Singh , Richard J. Barrett, John J. Gomes, Ferdynand P. Dabkowski , T.D. Moustakas, MRS Internet J. Nitride Semicond. Res., **3**, (1998), 13. Yu.V. Melnik, K.V. Vassilevski, I.P. Nikitina, A.I. Babanin, V. Yu. Davydov, V.A. Dmitriev, MRS Internet J. Nitride Semicond. Res., **2**, (1997), 39.

[18] S. Nakamura, Jpn. J. Appl. Phys., **30**, (1991), L1705. I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu, and N. Sawaki, J. Cryst. Growth, **98**, (1989) 209. S. Yoshida, S. Misawa and S. Gonda, Appl. Phys. Lett., **42**, (1983) 427. . S. Yoshida, S. Misawa and S. Gonda, J. Vac. Sci. & Technol. **B1**, (1983) 250.

[19] S. Nakamura, Jpn. J. Appl. Phys., **30**, (1991), 1620. H. Amano, N. Sawaki, I. Akasaki and Y. Toyoda, Appl. Phys. Lett., **48**, (1986) 353. H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Jpn. J. Appl. Phys., **28**, (1989) L2112. H. Amano, T Asahi and I. Akasaki, Jpn. J. Appl. Phys., **29**, (1990) L205.

[20] S. Nakamura, Jpn. J. Appl. Phys., **31**, (1992), 2883. H. Amano, I Akasaki, K. Hiramatsu and N. Koide, Thin Sol. Films, **163**, (1988) 415.

[21] H. Angerer, O. Ambacher, R. Dimitrov, Th. Metzger, W. Rieger, M. Stutzmann, MRS Internet J. Nitride Semicond. Res., **1**, (1996), 15.

[22] T. N. Hansen, J. Schou and J. G. Lunney, Europhys. Lett., **40**, (1997) 441.

[23] D. W. Koopman, Phys. Fluids, **14**, (1971) 1707. F. F. Chen in *Plasma Diagnostic Techniques*, Ed. By R. H. Huddleston and S. L. Leonard, Academic Press, New York, 1994.

[24] T. N. Hansen, J. Schou and J. G. Lunney, to be published in Appl. Surf. Sci. (1999).

[25] T. P. Hughes, *Plasmas and Laser Light,* Adam Hilger 1975.

[26] P. E. Dyer, A. Issa, P. H. Key, Appl. Phys. Lett., **57**, (1990) 186.

[27] A. Gupta, B. Braren, K. G. Casey, B. W. Hussey, R. Kelly, Appl. Phys. Lett., **59**, (1991) 1302.

[28] D. B. Geohegan, Appl. Phys. Lett., **60**, (1992) 2732.

[29] W. K. A. Kumuduni, Y. Nakayama, Y. Nakata, T. Okada, M. Maeda, J. Appl. Phys. **74**, (1993) 7510.

[30] A. V. Bulgakov, N. M. Bulgakova, J. Phys. D: Appl. Phys. **31**, (1998) 693.

[31] P. E. Dyer, J. Sidhu, J. Appl. Phys. **64**, (1988) 4657..

[32] J. L. Bobin, Y. A. Durand, Ph. P. Langer, G. Tonon, J. Appl. Phys. **39**, (1968) 4184.

[33] R. B. Hall, J. Appl. Phys. **40**, (1969) 1941.

Chapter 3

Structural and electrical properties of the films

3.1 Characterisation of the films

Atomic force micrographs of the top surface of the samples were taken. The surface roughness was then estimated. The AFM micrographs were then compared with SEM images of the GaN films.

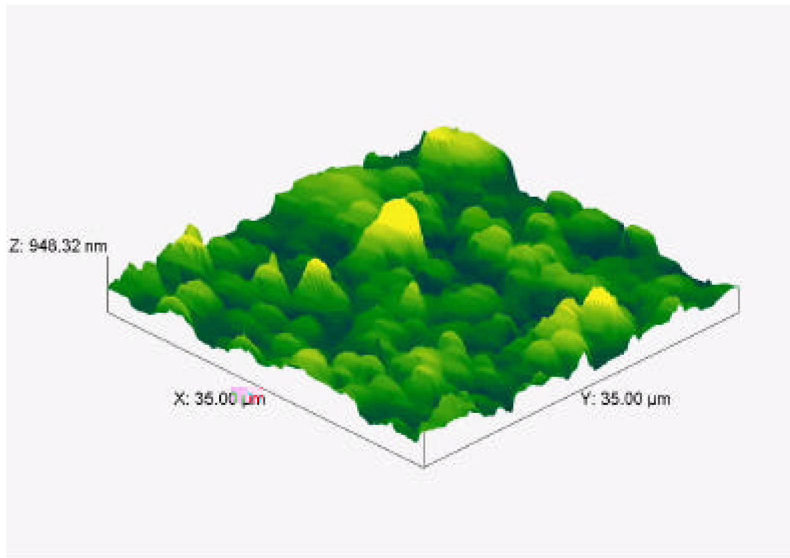
$\theta/2\theta$ scans will not be presented for all the GaN samples since the the XRD spectra of all the samples are very close to the data presented in Fig. 3.4, which is then representative of the overall XRD behaviour of the produced PLD-GaN. The films were characterised after their growth via x-ray diffraction in the normal $\theta/2\theta$ mode in order to establish the crystalline structure of the films. In all the films studied in this thesis the structure obtained was the hexagonal one (wurtzite).

$\theta/2\theta$ x-ray diffraction, indicating that the growth occurred along the (0001) direction, showed the (0002) reflection. We measured the x-ray rocking curve (ω-scan) of this reflection in order to better establish the crystalline quality of the films, investigating the extent of misorientation of the crystal planes around the Bragg position $\boldsymbol{q}_B$ of the (0002) reflection.

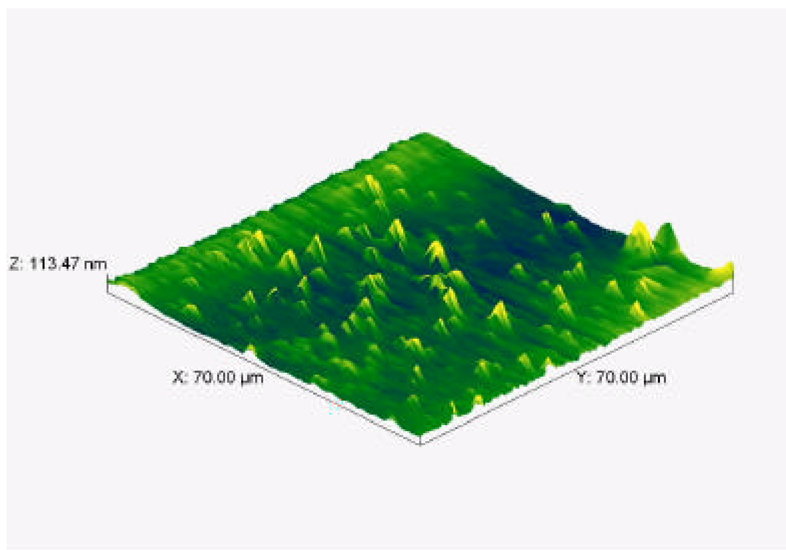
The electrical properties of the films were also measured in the four-contact Van der Pauw configuration, and the values for resistivity (ρ), Hall mobility (μ_H) and doping level (n/p) established.

3.2 Atomic force microscopy and SEM

The surface morphology of the films was studied by AFM, using a commercial microscope [1].



(a) NH_3



(b) UHV

Fig 3.1 (a),(b) Atomic force micrographs for GaN films grown in ammonia (a), UHV (b).

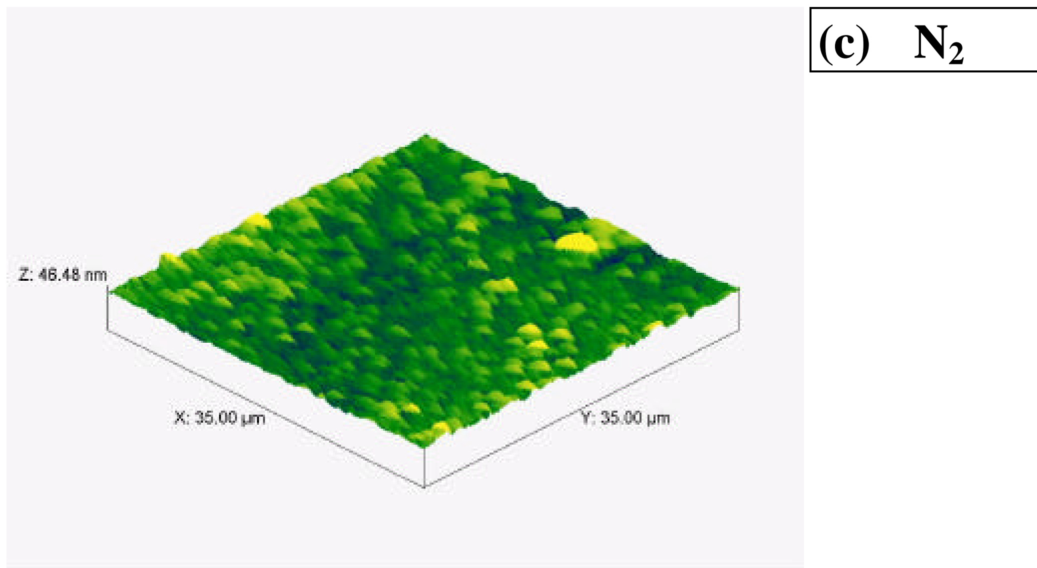


Fig 3.1 (c) Atomic force micrographies for GaN films grown in N_2.

The surface morphology obtained from atomic force microscopy of three films grown respectively in N_2, NH_3 and UHV are presented in Fig. 3.1 (a), (b), (c).

The figure shows the beneficial effect on the surface quality (a critical parameter for the performance of GaN based LEDs) of the insertion of an N_2 reactive atmosphere into the chamber during the deposition [2]. It has to be noted that the thicknesses of the three films are different: 260 nm for NH_3, 70 nm for UHV samples and 43 nm for the N_2 sample. The thicknesses were measured via variable-wavelength optical ellipsometry [3].

Scanning electron microscopy (SEM) was also used to characterize the films, and the micrographs for the films grown in ammonia and in nitrogen are presented in Fig. 3.2. This data also confirm the positive effect on the surface quality when nitrogen is used instead of ammonia.

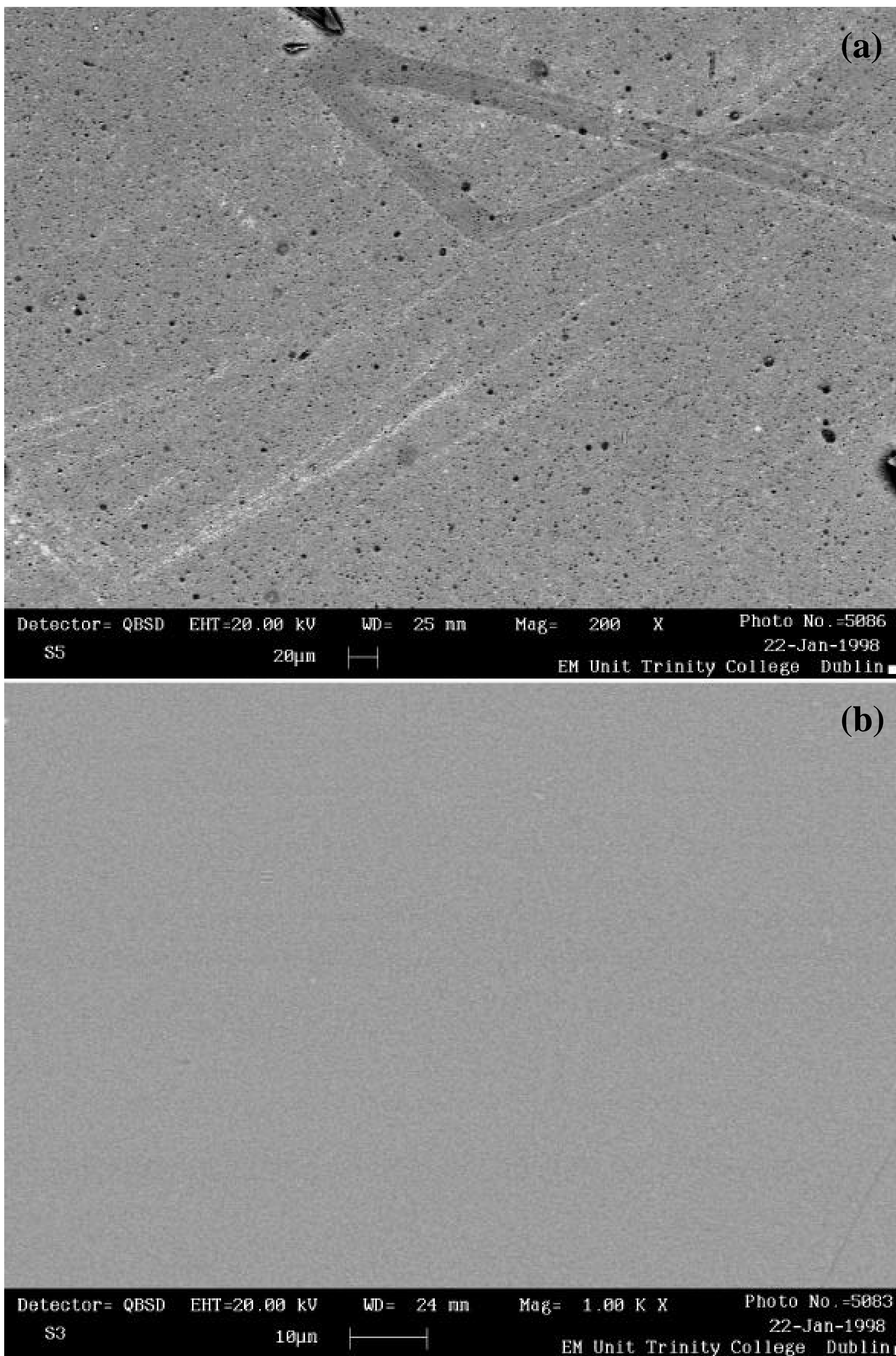


Fig. 3.2 SEM photographs for the films grown in ammonia (a) and in nitrogen (b).

AFM on the samples grown in ammonia at low pressure shows that the surface roughness is of the order of hundreds of nanometers (and so much worse than that of films grown in 0.2 mbar of ammonia, which was of the order of few tens of nanometers). Another indication that these samples, although very promising, have to be optimized.

3.3 X-ray diffraction

A pictorial view of the crystal structure of the wurtzitic GaN is presented in Fig. 3.3. As mentioned in the introductory paragraph of this chapter, not all the θ/2θ x-ray diffraction data will be presented. Fig. 3.4 shows a typical XRD curve for the wurtzite GaN films.

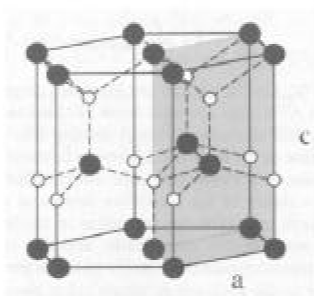


Fig. 3.3 The wurtzite GaN structure: atoms of one species are dark grey, those of the other species are white, the unit cell is shaded.

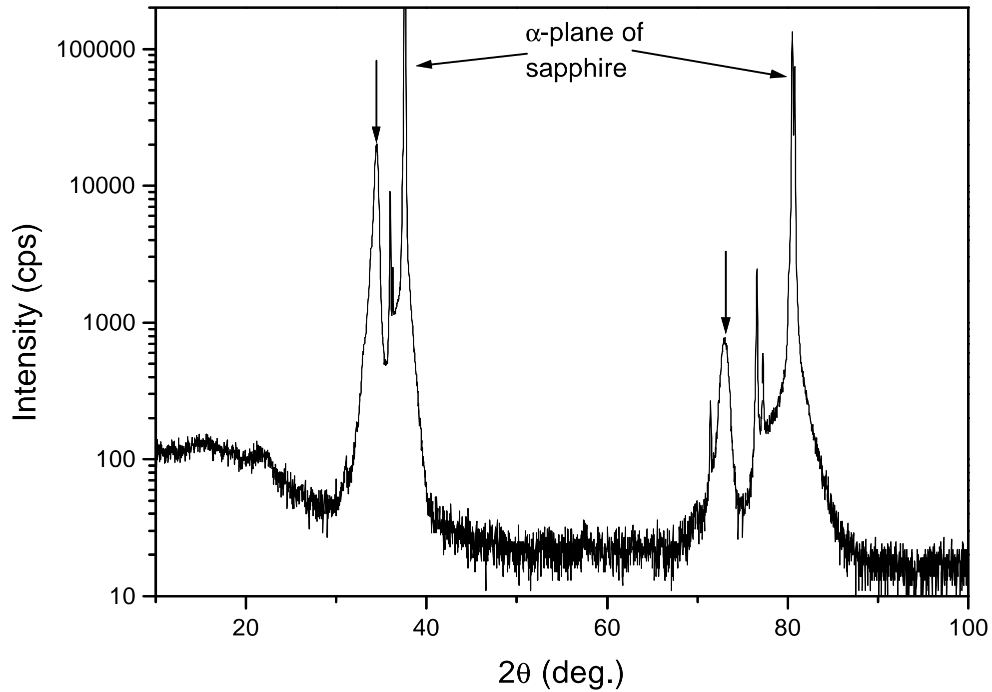


Fig. 3.4 Typical XRD in the θ/2θ configuration for a wurtzite PLD GaN sample. The reflection at 2θ=34.5 ° is due to the (0002) planes of wurtzite GaN. Vertical arrows indicates the x-ray diffraction from (0002) planes of GaN. The two most intense peaks are the reflection from the sapphire substrate. The weak peaks close to the sapphire diffraction are due to W (tungsten) contamination at the cathode.

Attention will be concentrated on the x-ray rocking curves (ω scans) of the (0002) reflection for the samples grown in different atmospheres.

Fig. 3.5 shows a comparison between the ω scans of the three samples. The double texture which is clearly seen in the UHV sample is much reduced in the NH_3 sample and is smallest in the N_2 sample.The origin of this feature is not clear. It was previously observed in pulsed laser deposited II-VI materials [4] and attributed to the presence of a

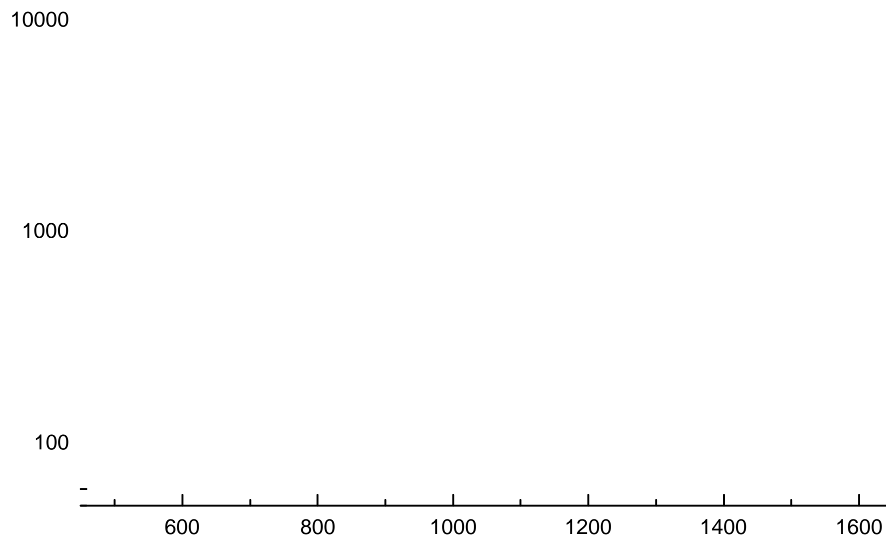


Fig. 3.5 X-ray rocking curves of the (0002) reflection from the wurtzite GaN. Triangles represent the sample grown in ammonia; squares the sample grown in nitrogen and circles the sample grown in UHV. The resolution of the diffractometer in this configuration is 16 arcmin. Note that the full width at half maximum (FWHM) reported in the legend of the figure are convoluted with the instrumental response of the diffractometer. Deconvoluted values are much narrower.

very poor crystalline region at the interface film/substrate; in other words it was attributed to the presence in the wurtzite film of residual sections of cubic GaN and this presence reflects a major misorientation of the planes around the (0002) reflection from the wurtzite GaN [5].

3.4 Electrical characterisation

We investigated the electrical properties of the films using the Van der Pauw method. The resistivity (**r**), doping level (*n/p*) and Hall mobility ($\boldsymbol{m}_H$) were studied in the temperature range from 77 to 300 K (0.013 to 0.0033 K^{-1}). In the Van der Pauw configuration the sample consists of a square with a contact in each of the corners. Actually any shape is permissible, although this will lead to complications in the data analysis. Suppose the contacts are numbered 1,2,3,4 consecutively around the periphery of the square sample, and V_{ijkl} means the voltage read between i and j, when the current flows between k and l. In this case the electrical parameters may be expressed by

$$\boldsymbol{r} = \frac{\boldsymbol{p}\, t}{\ln 2}\frac{1}{4}\left(\frac{V_{12}}{I_{43}} + \frac{V_{23}}{I_{14}} + \frac{V_{34}}{I_{21}} + \frac{V_{41}}{I_{32}}\right)\Omega \cdot cm \qquad (a)$$

$$\boldsymbol{m}_H = \frac{10^8}{B}\frac{\ln 2}{\boldsymbol{p}}\frac{2\left(V_{1324} + V_{2413}\right)}{V_{1243} + V_{2314} + V_{3421} + V_{4132}}\frac{cm^2}{V \cdot s} \qquad (b)$$

$$n/p = 6.25 \times 10^{10}\frac{B}{t}\frac{1}{2}\left(\frac{I_{24}}{V_{13}} + \frac{I_{13}}{V_{24}}\right)cm^{-3} \qquad (c)$$

Where t is the thickness of the film, B is the magnetic field, and the units are in C.G.S.

Fig. 3.6(a) shows the doping of the different films. The first remarkable feature is that the films grown in different atmospheres have different background doping level, n-type in the case of ammonia-grown, and p-type in the other two. The p-type doping of the film grown in N_2 is similar to the results of Feiler et al. [2]

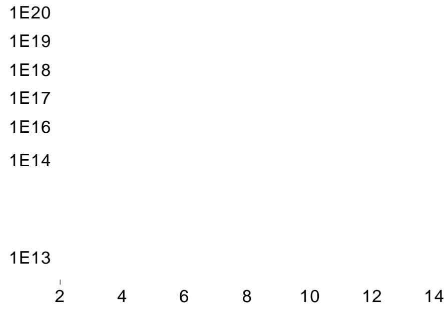


Fig. 3.6(a) The doping level for the three samples. (b) The Hall mobility of the film and (c) the resistivity. The T^{-1} range spans from 0.003 to 0.013 K^{-1}.

The values of doping in the three films are very different: they vary from values ≥ 10^{18} cm^{-3} for the UHV p-type conducting film to 10^{13} cm^{-3} for the N_2-grown film. The difference in the type of doping between the films and the very low value of doping in the N_2 grown film, suggests the presence in the films of autocompensation effects generated both by donor and acceptor centers in the films. The atmosphere dependent doping is clearly interesting for the development of n/p junction lasers.

The Hall mobility (top right inset Fig. 3.6(b)) shows only a small variation versus temperature. Low mobility values were obtained in the nitrogen and UHV films while the ammonia grown films show a much

higher Hall mobility. This is an indication of the high density of defects in our samples. The 77 K (≅0.013 K^{-1}) Hall mobility of the ammonia film has a very high value of around 3000 $cm^2\ V^{-1}\ s^{-1}$, but this film shows the poorest luminescent properties [6].

The resistivity (Fig. 3.4(c)) is low for both the films grown in ammonia and UHV and reaches a value of around 800 Ω cm in the N_2 sample. It is very important to note that the contacts used weren't optimized, but were made by simply connecting a metallic wire to the GaN film via a thin silver paint droplet. An optimization of the contact resistance, that is known to be critical for a more quantitative and precise measurement of electrical properties of epitaxial films, is planned for the near future, employing Indium contacts at the GaN/contact interface, in order also to increase the level of reproducibility of the results.

3.4 Comparison with other techniques and conclusions

The literature on the structural and electrical properties of GaN is very extensive. An efficient way to compare the result obtained in this work with the results obtained on GaN grown by other techniques is to summarize the results in a table and then to draw a comparison of the data. This information is presented in Table 3.1.

Superficial roughness has a value that is higher than what is typically obtained by other groups with PLD [2], [7-9] and this fact indicates that this a direction in which improvements can be achieved; looking at the value for

superficial roughness obtained by Nakamura [13], [22,23], which is two times the value obtained in this work, one can be optimistic about the weak influence of this parameter on the performance of a possible device based on PLD-GaN.

The full width at half maximum (FWHM) of the x-ray rocking (that is a reasonable figure of merit for the crystalline quality of the material) that we obtained in the N_2 growth is worse than what was obtained with the other growth techniques, and in particular from the values obtained by Nakamura [13]. The values we presented for the sample presented in the table and produced in this work are not deconvoluted from the instrumental response of the diffractometer. The deconvoluted values should then be much narrower. I think that this is one of the direction for future investigation on PLD- grown GaN in Trinity.

The values for the resistivity are comparable to the available data of the literature for the other growth techniques. A value that is quite low (relatively to literature) is that one of the UHV sample and further study should be devoted to clarifying this behaviour.

The values of Hall mobility fit very well with all the reported literature data, while material grown in NH_3 shows a very high mobility comparable to MBE grown GaN [30]. This high value is very interesting because an electroluminescent device would work at lower voltage. Also this point needs to be well assessed, trying to repeat the measurement on statistics of samples grown in the same atmosphere (NH_3) and with optimized contact/GaN film interface.

Another interesting point is that regarding the doping level. First of all it has to be noted that the proposed doping level refers to an unintentional doping, and for this reason an uncontrolled parameter, that needs then to related to the growth conditions to be understood and controlled. We found that the growth in ammonia leads to a n-type background doping level that is comparable to what is reported in literature by Ilegems and Montgomery [25] while the p-type doping found for the N_2 and UHV growth is much more unusual. It seems that this may be a feature of the PLD technique, infact it is in agreement, also for the values, with the report of Feiler et. al. [2].

In summary, pulsed laser deposition revealed itself as a technique producing an average quality material (from the structural and electrical point of view) in respect to the other growth techniques reported in the literature[2], [7-23] used to produce GaN.

In addition it has interesting peculiarities, like the p-type doping at very high dopant concentrations (> 10^{18} cm^{-3}), which could be linked with the nitrogen stoichiometry of the films, and which could have application in the development of PLD-GaN based p/n junctions, or the very high Hall mobility of films grown in NH_3 under optimized conditions.

Growth techn.	Growth atmosphere	ρ at RT (Ω cm)	μH at RT (cm^2 V^{-1} s^{-1})	n/p at RT (cm^{-3})	Hex/Cub	FWHM Rock. Curve (arcmin)	Superf rough. (nm)	Ref.	Demonst LED or LD

References

[1] D. Cole, Ph.D. thesis, Trinity College, University of Dublin (1998), *Chapter 4.*

[2] D. Feiler, R. S. Williams, A. A. Talin, H. Yoon, M.S. Goorsky, J. of Cryst. Growth **171** (1997) 12.

[3] The measurements were performed with Prof. McGilp on a SOPRA ellipsometer, in the Physics Department in Trinity College Dublin.

[4] H. Masterson, Ph.D. thesis, Trinity College, University of Dublin (1994).

[5] N. Herres, H. Obloh, K.-H. Bachem, K. Helming, submitted to Mat. Sci. & Eng.

[6] M. Cazzanelli, D. Cole and J.G. Lunney, submitted to ESCAMPIG '98.

[7] R. D. Vispute, V. Talyansky, R. P. Sharma, s. Choopun, M. Downes, T. Venkatesan, Y. X. Li, L. G. Salamanca-Riba, A. A. Iliadis, K. A. Jones, J. McGarrity, Appl. Surf. Sci. **127-129**, (1998) 431.

[8] G. S. Sudhir, H. Fujii, W. S. Wong, C. Kisielowski, N. Newman, C. Dieker, Z. Liliental-Weber, M. D. Rubin, E. R. Weber, Appl. Surf. Sci . **127-129**, (1998) 471.

[9] R. Leuchtner, , W. Brock and L. Hristakos, Mat. Res. Soc. Symp. Proc. **395**, (1996) 343.

[10] M. Cazzanelli, D. Cole, J. Versluijs, J.F. Donegan and J.G. Lunney, to be published on Mat. Sci. & Eng.B (1999).

[11] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett. **15**, (1969) 327.

[12] J. I. Pankove, J. Lumin. **7**, (1973) 114.

[13] S. Nakamura, Jpn. J. Appl. Phys. **30**, (1991) L1705.

[14] Markus Kamp , M. Mayer, A. Pelzmann, K. J. Ebeling, MRS Internet J. Nitride Semicond. Res. 2, (1997) 26.

[15] M. J. Paisley, Z. Sitar, J. B. Posthill and R. F. Davis, J. Vac. Sci. Tech. **A7**, (1989) 701.

[16] H.Angerer, O. Ambacher, R. Dimitrov, Th. Metzger, W. Rieger, M. Stutzmann, MRS Internet J. Nitride Semicond. Res. 1, (1996) 15.

[17] J. Kozlowski, R. Paszkiewicz, R. Korbutowicz, M. Panek, B. Paszkiewicz, M. Tlaczala, MRS Internet J. Nitride Semicond. Res. 3, (1998) 27.

[18] B. Beaumont, M. Vaille, P. Lorenzini, Pierre Gibart , T. Boufaden, B. el Jani, MRS Internet J. Nitride Semicond. Res. 1, (1996) 17.

[19] T Detchprohm, T Kuroda, K Hiramatsu, N Sawaki, H Goto, Inst. Phys. Conf. Ser. 142, (1996) 859-862.

[20] Yu.V. Melnik, K.V. Vassilevski, I.P. Nikitina, A.I. Babanin, V. Yu. Davydov, V.A. Dmitriev, MRS Internet J. Nitride Semicond. Res. 2, (1997) 39.

[21] Raj Singh , Richard J. Barrett, John J. Gomes, Ferdynand P. Dabkowski , T.D. Moustakas, MRS Internet J. Nitride Semicond. Res. 3, (1998) 13.

[22] S. Nakamura, Jpn. J. Appl. Phys. **30**, (1991) 1348.

[23] S. Nakamura, IEEE Journ. Sel. Top, Quant. Electr. **3**, (1997) 435. S. Nakamura, MRS Bull. **12**, (1997) 30. S. Nakamura, Mat. Sci. Eng. **B43**, 81997) 258.

[24] S. Nakamura, T. Mukai and M. Senoh, Appl. Phys. Lett. **64**, (1994) 1687.

[25] M. Ilegems and H. C. Montgomery, J. Phys. Chem. Solids **34**, (1973) 885.

[26] Z. Yang, L. K. Li, and W. Wang, Appl. Phys. Lett. **67**, (1995) 1686. J. W. Orton and C. T. Foxon, Proc. 1997 Int. Meeting of the Electrochemical society (Paris), (1997) 124. S. H. Cho, U. Tanaka, K. Hata, T. Maruyama and K. Akimoto, Jpn. J. appl. Phys. **35**, (1996) L644.

[27] M. Ilegems, J. Cryst. Growth **13/14**, (1972) 360.

[28] J. w. Yang, J. N. Kuznia, Q. C. Chen, M. Asif Kahn, T. George, M. De Graef and S. Mahajan, Appl. Phys. Lett. **67**, (1995) 3759. To be noted that the material was grown on GaAs (111)A.

[29] U. Strauss, H. Tews, H. Riechert, r. Averback, M. Scheinle, B. Jobst, D. Volm, T. Streibl, B. K. Meyer and W. Ruhle, MRS Internet J. Nitride semicon. Rec. **1**, (1997) 44. To be noted that the material was grown on the c-plane of sapphire.

[30] M. Rubin, N. Newman, J. S. Chan, T. C. Fu and J. T. Ross, Appl. Phys. Lett. **64**, (1994) 64.

Chapter 4

Luminescence of the films

4.1 Introduction

The luminescent properties of GaN thin films grown by pulsed laser deposition have been studied to understand the nature of the luminescent centres and the recombination dynamics. The films were grown on heated sapphire substrates using KrF excimer laser ablation of GaN in a reactive atmosphere of nitrogen. At low temperatures the continuous wave (CW) blue luminescence of the samples shows two sharp lines attributed to excitonic recombination at extended defects. The luminescence peaks are centred at 3.360 eV and 3.305 eV at low temperature. An analysis of the temperature dependence of photoluminescence lifetimes assesses the relative contributions of radiative and non-radiative recombination in the centres responsible for these emissions. The measurement of room temperature nanosecond radiative lifetimes for these lines supports the excitonic nature of the luminescence.

There is a long interest in GaN as a material for the fabrication of blue and UV light emitters [1-9]. This interest was renewed after the recent demonstration of laser emission at room temperature from GaN [10]. However the physical mechanisms leading to efficient light emission from this material are not well understood. The energy gap (at 1.6 K) is 3.503 eV for bulk material and the principal emission peak in the luminescence

spectrum at 1.6 K is observed at 3.477 eV [11]. There are also reports of strong luminescence lines well below the band gap, for thin films grown on different substrates [1,3,7,22-23]. At 6 K these lines are at 3.365 eV (I_3) and 3.309 eV (I_4). Previous studies attributed I_3 to a LO (longitudinal optical) phonon replica of shallow bound excitons [4] or to the neutral donor of the nitrogen vacancy [7].

I_4 was previously attributed to a donor-acceptor pair transition [7]. In the work of Wetzel et al. [1] the excitonic nature of these recombinations was proposed mainly on the basis of the relatively low activation energy (I_3, 27 meV and I_4, 14 meV) of these lines in contrast to the much higher values expected for donor-acceptor transitions [24,25]. The behaviour of these transitions under hydrostatic pressure also suggested that they were due to recombination of excitons localized at extended defects [1].

In this chapter we present continuous wave (CW) and time resolved (TR) photoluminescence (PL) [26] studies of GaN grown on sapphire by PLD. The emission of PLD GaN is dominated by I_3 and I_4 emissions. Our interest was focussed on the physical origin and luminescence dynamics of these lines [12].

4.2 Experimental results

The samples we studied were grown in ammonia and in nitrogen, and the attention was focussed on the samples grown in nitrogen, which showed a strong blue-UV emission. The most representative one was a 43 nm thick GaN layer grown on $(11\overline{2}0)$ sapphire substrate by laser ablation of a sintered

GaN target in a N_2 atmosphere. The structural characterization has been presented in Chapter 3 and elsewhere [8], [9]. For continuous wave photoluminescence (CW-PL) measurements, we used the 325 nm line of an He-Cd laser with a power of 0.1 W cm^{-2}. The luminescence was recorded with 0.1 nm spectral resolution. These measurements were done at the Department of Physics and Applied Physics of the University of Strathclyde, by the group of Dr. K. P. O'Donnell.

The time resolved photoluminescence (TR-PL) measurements were done using a frequency doubled mode-locked Ti:sapphire laser operating at 356 nm, with a repetition rate tunable from 82 MHz to single shot and with a pulse duration of 1.5 ps [27]. A schematic diagram of the apparatus [28] and the experiment is given in Fig.4.1. The time-averaged excitation power was 90 μW at 82 MHz, which results in a peak power of ≈10 W cm^{-2}. The luminescence was dispersed by a 0.25 m grating monochromator (CHROMEX) and detected by a streak-camera operating in photon counting mode [29]. The temporal resolution was less than 15 ps. The time resolved measurements were done in the Physics Department of the University of Trento in collaboration with Claudio Vinegoni in the Optical Spectroscopy Group of Dipartimento di Fisica. The CW-PL and TR-PL measurements were performed at room temperature (RT) and at lower temperatures in the range (12-300 K), using helium cryostats. For the absorption measurements at room temperature in the visible range a double-beam spectrophotometer with a tungsten lamp was employed.

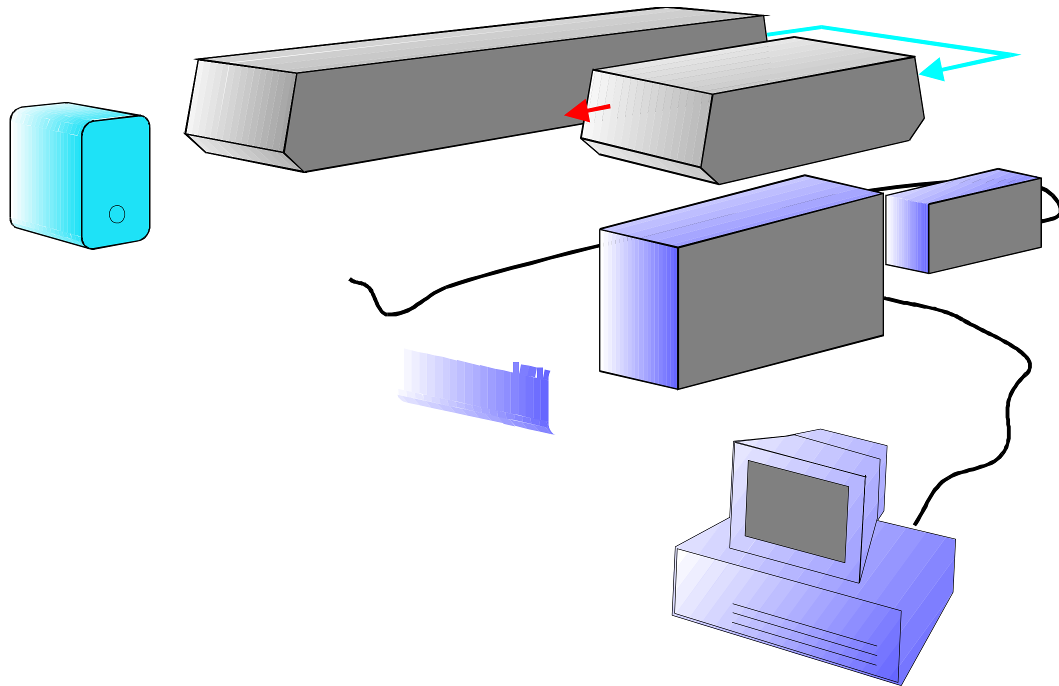


Fig.4.1 Time resolved photoluminescence apparatus employed for the lifetimes measurements. (1) is the calculator which acquires the data and controls the experiment. (2) is the delay unit which triggers the pulses to the streak camera (3). (4) is the monochromator. (5) is the sample holder/cryostat. (6) is the power meter to control/monitor the incident power during the experiment. (7) is the fast photodiode connected to the delay unit to give the trigger pulse. (8) is the autocorrelator to monitor and to optimize the pulse shape at the exit of the laser source (9)+(10)+(11). (9) is the pump laser, consisting of a 15 W multiline argon ion laser. (10) is a mode locked, 3 W Ti:Al_2O_3 laser operating in the picosecond configuration. (11) is the pulse picker to control the repetition rate of the pulse train and the second harmonic generator.

An absorption spectrum was taken in order to determine the band gap energy of the GaN film (at 300 K). Fig.4.2 plots the square of the absorbance (α^2) versus energy.

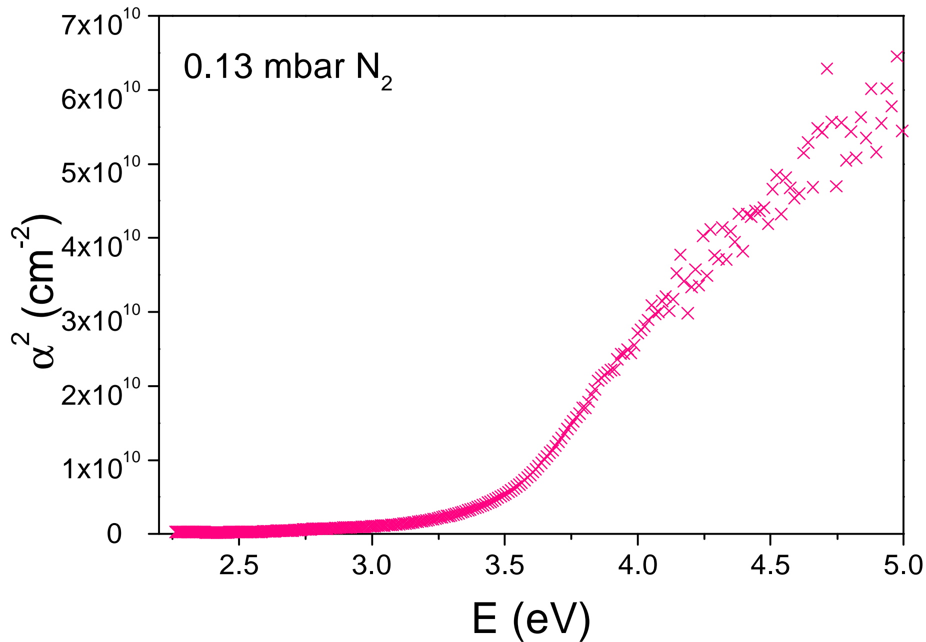


Fig. 4.2 Absorption spectrum at 300 K for a sample grown by PLD in 0.13 mbar of N_2 at a deposition temperature of 720 °C using a laser fluence of 2.8 J cm^{-2}.

We found that the film is transparent in the visible spectrum, and the energy gap is at 3.4 eV. This value is very close to the values of CVD, MOCVD and MBE-grown GaN [10,19,20], . The samples grown in ammonia and in UHV were also measured, and the absorption spectra show lower values of energy gap (see Table 2.2) and also a decrease of the absorption coefficient α at a fixed energy, with an accentuation of this effect in the UHV sample. It has to be noted that these two samples, which show lower absorption at fixed energy, show also the poorer photoluminescence (PL) properties, suggesting then that in order to have efficient PL emission, they the absorption properties of the samples have to be improved. Further details are described in detail elsewhere [13].

4.2.1 Continuous wave photoluminescence

Fig. 4.3 shows the 12 K PL spectrum of the GaN sample (is the sample grown in N_2 at 0.2 mbar and 700 ° C) in the energy range below the band gap, which is situated at 3.5 eV [11]. The spectrum is dominated by two narrow lines at 3.360 eV and 3.306 eV, labelled I_3 and I_4 respectively, following the notation of ref. [3]. The spectrum also displays a smaller peak at 3.23 eV. The luminescence of the film is also compared with that of the precursor material (dotted line).

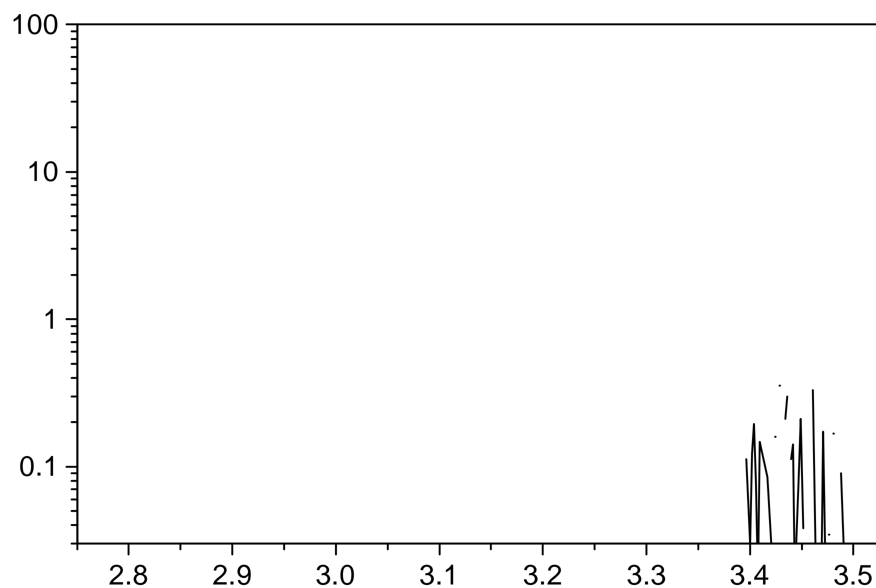


Fig. 4.3 CW-PL of the precursor powder (dots) and of the PLD GaN film (full line) at 12 K and in logarithmic scale.

The comparison between the low temperature (12 K) CW-PL spectra of the starting powder targets and the PLD epitaxial GaN film shows a striking

difference between the two. The powder shows a broad luminescence band in the region 2.7 to 3.5 eV with weakly resolved features at 3.409, 3.265 and 3.185 eV. In contrast, the film shows two narrow lines at 3.360 eV and 3.306 eV which we attribute to I_3 and I_4 lines observed previously [1,3,7,22-23].

Fig. 4.4 shows an overview of the temperature-dependent behaviour of the CW-PL of the PLD GaN film; the spectrum evolves from single broad blue-band in the temperature range 300 K to 200 K to a spectrum showing three well resolved lines below 200 K. In addition to I_3 and I_4 a third weaker peak centered at about 3.23 eV also appears below 200 K. Also noticeable is the doublet nature of I_3 in the temperature range from 125 K to 75 K. Further investigation to clarify the physical origin of the doublet structure of I_3 is necessary.

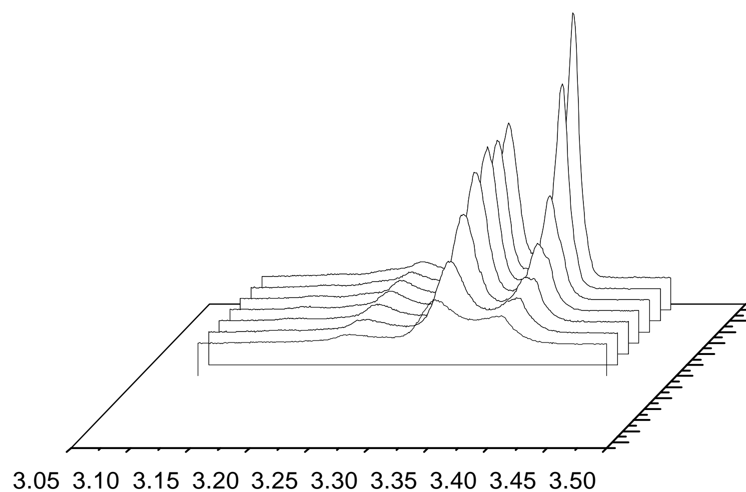


Fig. 4.4 CW-PL spectra of GaN films as a function of temperature in the range between 12 and 300 K. The spectra have been shifted for clarity.

Fig. 4.5 shows the temperature variation of the relative quantum efficiencies (η defined as the ratio $\frac{I(T)}{I(T=0\,K)}$) of I_3 and I_4 relative to the total low temperature emission intensity integrated in the region 3.1 eV to 3.45 eV. This quantity is clearly an upper bound to the quantum efficiency of the sample, since:

- even at low temperature there may be some non-radiative recombination competing with the radiative
- there may be other emissions outside the integration region

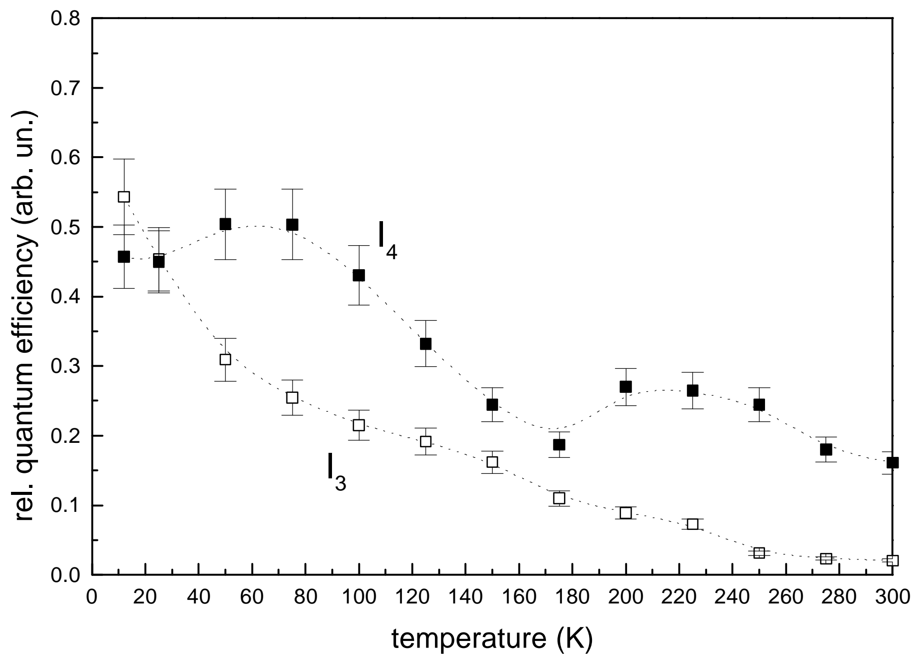


Fig. 4.5 Temperature dependence of the relative quantum efficiency of I_3 (open squares) and I_4 (full squares). The dotted lines are guides for the eye.

It is clear that in the range 200 K to 25 K, the quantum efficiency for I_3 is lower than for I_4. This data will be used in the next section in the extraction of radiative and non-radiative contribution to the measured luminescence lifetime. The temperature dependence of both curves shows the typical decrease of the integrated intensity with increasing temperature. This fact is due to the thermal dissociation of the excitons responsible for these emissions. With increasing temperature, the excitons start to dissociate into free carriers [14] and the exciton emission intensity decreases consequently.

The temperature dependence of the integrated emission intensity of the I_3 and I_4 lines is shown in Fig. 4.6.

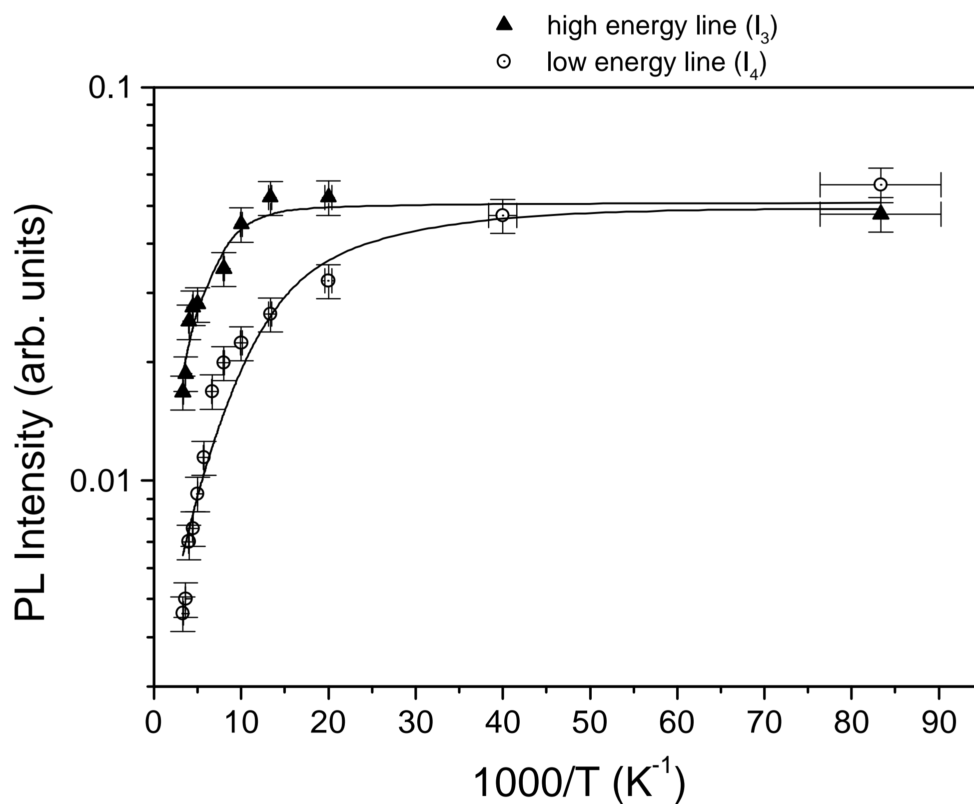


Fig. 4.6 Arrhenius plot of the integrated intensity of the I_3 and I_4 peaks. The lines are least square fits, with a thermal activated quenching mechanism (see text).

For temperatures > 65 K there is a strong decrease of the intensity of I_3 peak, while for the I_4 peak the decrease in intensity starts at about 125 K.

In order to obtain an estimate of the thermal activation energy of I_3 and I_4 peaks, we fitted the temperature dependence of the photoluminescence intensity to the simple model of Ashkinadze et al. [15]:

$$I_T(T) = \frac{I_0}{1 + C(T) \cdot e^{-\frac{E}{k_B T}}} \qquad (1)$$

where $I_T(T)$ is the PL intensity as a function of temperature, I_0 the PL intensity at T=0 K and E is the activation energy, $C(T)$ for high enough temperature [16] is given by:

$$C(T) = \frac{\tau_{rad}(T)}{\tau_{non-rad}(T)} \qquad (2)$$

An estimate of the temperature-dependent C parameter for each excitonic peak was extracted from the data and used in (1). A fit of the experimental data for both the I_3 and I_4 peaks is shown in Fig. 4.6. A good fit is obtained ($\chi^2<0.1$) which yelds activation energies of 27 meV for the I_4 peak and 14 meV for the I_3 peak. These small activation energies and the small energy shifts of I_3 and I_4 with temperature (Fig. 4.7) support the attribution of these lines to excitonic recombination on extended defects, in agreement with Wetzel et al. [1]. In fact as the temperature rises from 7 to 225 K the red shift of I_3 and I_4 is

27 meV and 17 meV respectively, while the energy gap shifts by 72 meV [11] (see Fig. 4.7).

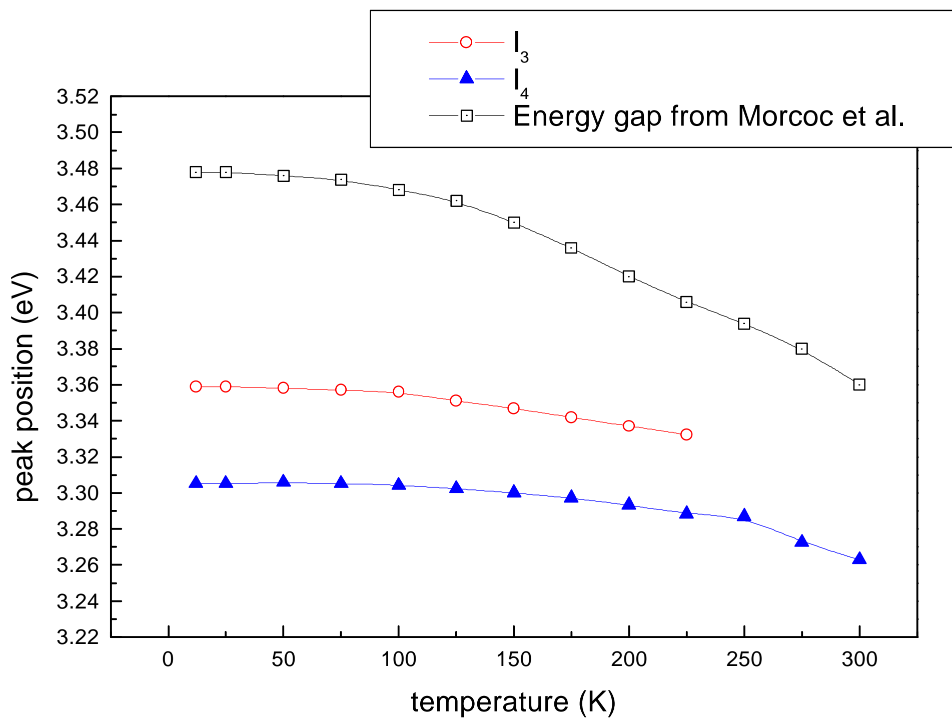


Fig. 4.7 Temperature dependence of the peak position. Open squares are data from the literature [11] for the energy gap (E_g) position. Open circles give the spectral position of I_3. Full triangles represent I_4.

The behaviour of the PL emission linewidth versus temperature (Fig. 4.8) [19], shows that the lines are quite broad even at low temperature, and the linewidths depend only weakly on temperature. An analysis

analogous to that one reported in ref. [17] was attempted, that takes into account the exciton-LO phonon scattering via Frölich interaction, but we found that the energy of the phonon that should be involved in the well known formula [18]

$$\Gamma_h = \frac{\Gamma_{ph}}{e^{\frac{h\nu_{LO}}{k_B T}} - 1} \qquad (3)$$

is lower than the 92 meV value of the LO-phonon of GaN. This picture then is not sufficient to explain the linewidth broadening mechanism of PLD GaN. The breadth of the x-ray rocking curves (see Fig. 3.5), and the AFMs micrographs (see Figg, 3.1(c)) indicate a relatively high level of disorder in the material that could result in strong of inhomogeneous broadening of the photoluminescence lines. An additional theoretical effort should be spent in order take account of this effect and give a better description of the data presented in Fig. 4.8.

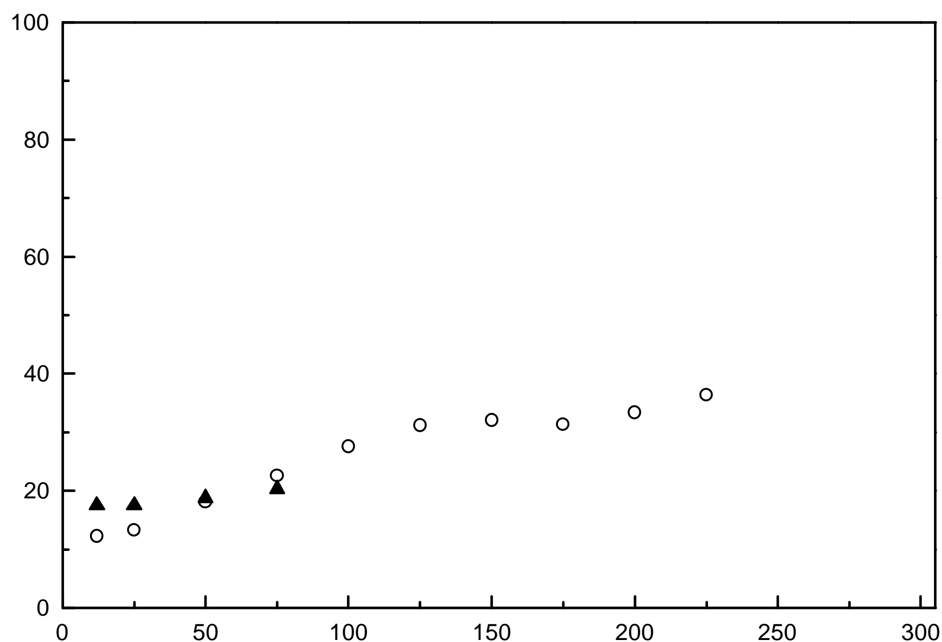


Fig. 4.8 Full width at half maximum (FWHM) for the I_3 (open circle) and I_4 (full triangles). The open squares represent the total FWHM of the emission where it was not possible to deconvolve the single contribution of I_3 and I_4. Dashed line is a guide for the eyes.

4.2.2 Time resolved photoluminescence

TR-PL was studied both on the N_2 and NH_3 grown samples and the temperature dependent lifetimes (t_{lum}) of I_3 and I_4 are shown in Fig. 4.9. The lifetime increases with temperature, as was observed before for the decay time of the free exciton in GaN [14].

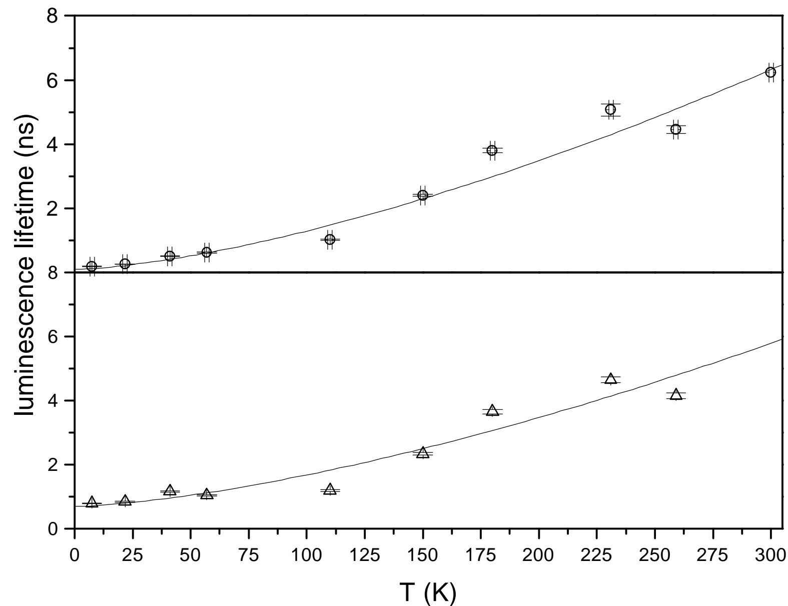


Fig. 4.9 Top inset shows the measured lifetime (t_{lum}) for I_3. Bottom inset shows the measured lifetime for I_4. Full lines are guides for the eye.

From the combination of the relative quantum efficiency (Fig. 4.5) with the luminescence lifetimes (Fig. 4.9) it is possible to make an estimate of the radiative (t_{rad}) and non radiative ($t_{non-rad}$) lifetimes of the sample.

The radiative (t_{rad}) and non radiative ($t_{non-rad}$) lifetimes are related to the luminescence lifetime and quantum efficiency (*h(T)*) by the equations:

$$\boldsymbol{t}_{rad}(T) = \frac{\boldsymbol{t}_{lum}}{\boldsymbol{h}(T)}$$
$$\boldsymbol{t}_{non-rad}(T) = \frac{\boldsymbol{t}_{lum}}{1-\boldsymbol{h}(T)} \qquad (4,5)$$

The extracted radiative and non-radiative lifetimes for I_3 and I_4 are shown in Fig. 4.10 in the temperature range 7-200 K. Both lifetimes increase with temperature; for the I_4 emission the qualitative behavior of luminescence lifetime, radiative and non-radiative lifetimes is similar to that of the I_3 emission, suggesting that the two lines have a similar physical origin. Both $\boldsymbol{t}_{lum}$ and $\boldsymbol{t}_{rad}$ are rather different for I_3 and I_4, though values of $\boldsymbol{t}_{non-rad}$ are quite similar.

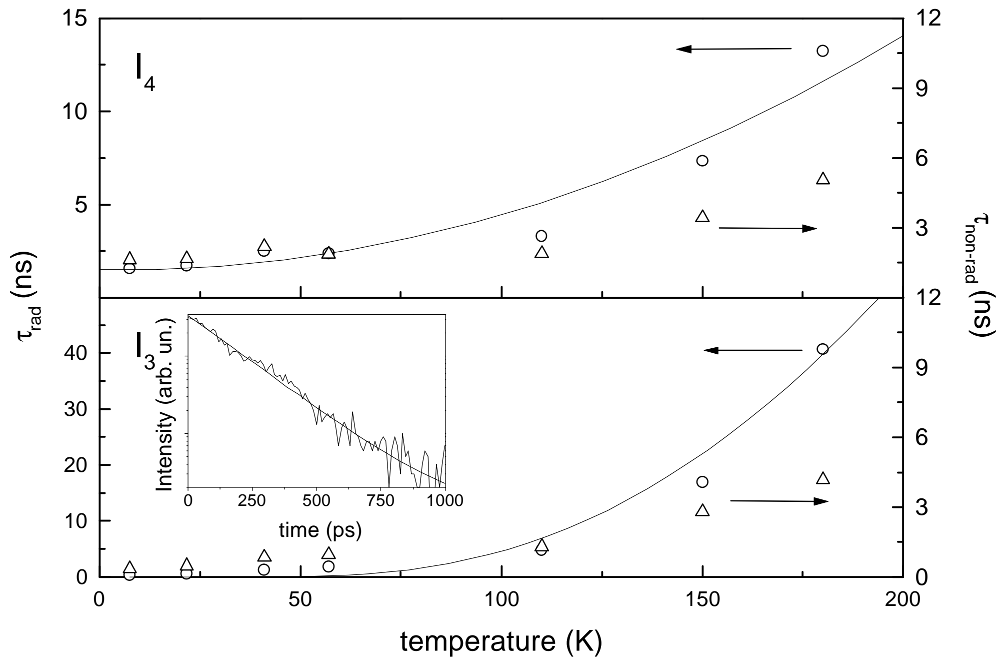


Fig. 4.10 Temperature dependence of radiative ($\boldsymbol{t}_{rad}$) and non radiative ($\boldsymbol{t}_{non-rad}$) lifetimes of PLD GaN. The full line is a guide for the eye. Lower inset is a typical luminescence decay where the full line is an exponential fit.

The increase of luminescence lifetime with increasing temperature can be related to the thermal delocalization of excitons from extended defects. With increasing temperature, excitons that at low temperature are strongly localized at dislocations, start to delocalize and the radiative lifetime value increases to a value of few nanoseconds. Further evidence of localisation/delocalisation of excitons in PLD-GaN might be obtained by studying the absorption spectrum of thicker films. The radiative and non-radiative lifetimes plotted in Fig. 4.10, show that at high temperature the principal recombination channel is non-radiative, and that the radiative lifetime increases monotonically with increasing temperature. Equations (4,5) were only applied in the temperature range 7-200 K, because at higher temperature the lines evolve into a single broad band, and the individual contribution of the I_3 and I_4 lines to the $t_{rad}(T)$ and $t_{non-rad}(T)$ cannot be easily resolved. The radiative and non-radiative lifetimes were measured at a fixed average incident intensity of ≈1 W cm^{-2}; by increasing the incident intensity it should be possible to saturate the non-radiative trapping centers and to give a more precise estimation of the radiative and non-radiative recombination rates.

TR-PL was measured also on samples grown in higher pressure ammonia. The results were less interesting, and will be presented only for completeness.

The ammonia samples show only a weak broad yellow band in luminescence at room temperature with a lifetime of a few μs(see top inset of Fig. 4.11).

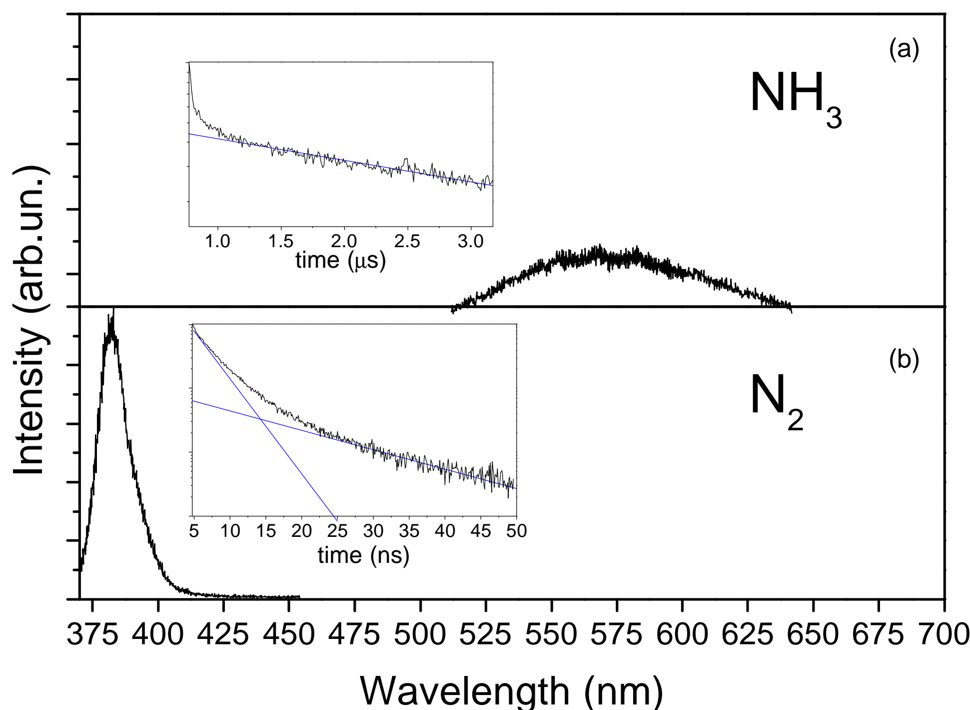


Fig. 4.11 Time-resolved photoluminescence at 300 K for films grown in N_2 (bottom layer), and in NH_3 (top layer).

The temperature dynamics of the luminescence lifetime (t_{lum}) was also analyzed. The results are shown in Fig. 4.12. What can be said is that the situation is completely different from the samples grown in nitrogen and that the lifetime is almost constant over the wide temperature range investigated. This can be related to the fact that the recombination responsible for the weak yellow emission, that characterize the ammonia samples, is related to the presence of deep traps which, having a lower recombination probability, show a long recombination lifetime. The weak dependence on temperature reflects the fact that this emission is dominated by non-radiative processes.

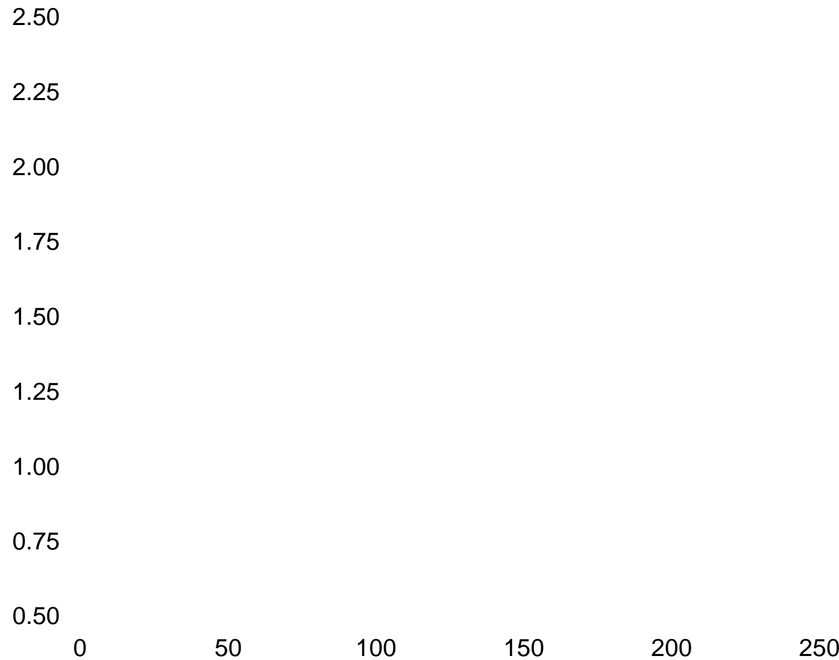


Fig. 4.12 Luminescence lifetime versus temperature, for the sample grown in ammonia.

In summary, PLD gallium nitride shows a number of strong luminescence peaks from 6 K to room temperature. These peaks are well below the band gap of GaN and from comparison of CW-PL and TR-PL measurements we attribute them to recombination of excitons localized at extended defects. Additional measurements and theoretical modelling of the recombination dynamics are required in order to quantitatively understand the $t_{rad}(T)$ and $t_{non-rad}(T)$ behaviour. In this sample no direct bandgap (free exciton) emission is observed, suggesting that improvements in the growth process should be possible. However the localized exciton emission shows a radiative lifetime of the order of nanoseconds which is promising for electroluminescent device applications.

References

[1] C. Wetzel, S. Fischer, J. Krueger and E. E. Haller, R. J. Molnar and T. D. Moustakas, E. N. Mokhov and P. G. Baranov, Appl. Phys. Lett. **68** (1996) 2556. B. K. Meyer, D. Volm, C. Wetzel, L. Eckey, J.-Ch. Holst, P. Maxim, R. Hoetz, A. Hoffmann, I. Broser, E. N. Mokhov, P. G. Baranov, J. I. Pankove, Mat. Res. Soc. Symp. Proc. **Vol. 378** (1995) 521. P. Bergmann, G. Ying, B. Monemar and P. O. Holtz, J. Appl. Phys. **61**, (1987) 4589. C. H. Hong, D. Pavilidis, S. W. Brown and S. C. Rand, J. Appl. Phys. **77**, 81995) 1705. H. G. Grimmeiss and H. Koelmans, Z. Naturforschg. **14a**, (1959) 264 (in German).

[2] R. Dingle, D. D. Sell, S. E. Stokowski, P. J. Dean, and R. B. Zetterstrom, Phys. Rev B **3** (1971) 497. B. Monemar and O. Lagerstedt, J. Appl. Phys. **50**, 81979) 6480.

[3] R. Dingle, D. D. Sell, S. E. Stokowski and M. Ilegems, Phys. Rev. B **4** (1971) 1211.

[4] M. Ilegems and R. Dingle, J. Appl. Phys. **44** (1973) 4234.

[5] B. Monemar, Phys. Rev. B **10** (1974) 676.

[6] J. I. Pankove, J. of Lumin. **7** (1973) 114.

[7] R. Dai, S. Fu, J. Xie, G. Fan, G. Hu, H. Schrey and C. Klingshirn, J. Phys. C: Solid State Phys. **15** (1982) 393.

[8] P. J. Dean, Phys. Stat. Sol. (a) **81** (1984).

[9] H. G. Grimmeiss and H. Koelmans, Phys. Rev. A **14** (1959) 264.

[10] S. Nakamura, T. Mukai and M. Senoh, Appl. Phys. Lett. **64** (1994) 1687.

[11] S. Strite and H. Morkoς, J. Vac. Sci. Technol. B **10** (1992) 1237.

[12] In "Device Research Conference and Electronic Materials Conference" held in Santa Barbara, 24-28 June 1996 and in a private communication, B. J. Skromme attributed I_3 and I_4 to the "F2+" Luminescence band of sapphire and to other unidentified luminescent systems in sapphire. Care must be taken in characterizing the bare substrate on which the films are grown: from our PL studies on the substrates, we don't measure any luminescence from sapphire.

[13] D. Cole, Ph.D. thesis, Trinity College, University of Dublin (1998), *Chapter 4.*

[14] J. S. Im, A. Moritz, F. Steuber, V. Haerle, F. Scholz and A. Hangleiter, Appl. Phys. Lett. **70** (1997) 631.

[15] B. M. Ashkinadze, I. P. Kretsu, S. L. Pyshkin, S. M. Ryckin, I. D. Yarosherskii, Sov. Phys. - Sol. State **10** (12), (1969) 2921. B. M. Ashkinadze et al., Fizika and Technika Popuprov. (Sov. Phys. - Semiconductors), **3** (1969) 535.

[16] D. Kovalev, B. Averboukh, D. Volm, B. K. Meyer, H. Amano, I. Akasaki, Phys. Rev. B **54** (1996) 2518.

[17] J. P. Doran, J. F. Donegan and J. Hegarty, Sol. St. Comm., **81** (1992) 801.

[18] H. B. Bebbs and E. H. Williams, in *Semiconductors and Semimetals*, ed. By R. K. Williardson & A. C. Beer (Academic, N. Y., 1972), **Vol. 8**, pag. 291.

[19] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett., **15** (1969) 327.

[20] S. Yoshida, S. Misawa and A Itoh, Appl. Phys. Lett., **26** (1975) 461. S. Winsztal, B. Wauk, H. Majewska-Minor and T. Niemsyski, Thin Solid Films, **32**, (1976) 251. K. R. Elliott and R. W. Grant, Rockwell Project Final Report

No. MRDC41116.2FR, 1984. H. U. Bayer and W. Moench, J. Appl. Phys., **68** (1990) 586.

[21] E. McGlynn, *private communication.*

[22] R. Dingle and M. Ilegems, Sol. State Commun. **9**, (1971) 175.

[23] J. I. Pankove, J. E. Berkeyheiser, H. P. Maruska and J. Wittke, Sol. State Commun. **8**, (1970) 1051. (1970 Proc. 10th Int. conf. On Physics of Semiconductors, Cambridge, Mass, pag. 593).

[24] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer-Verlag, Heidelberg, 1996).

[25] J. I. Pankove, *Optical Processes in Semiconductors,* (Dover Editions 1975).

[26] S. Pau, Z. X. Liu and J. Kuhl, J. Ringling and H. T. Grahn, M. A. Kahn and C. J. Sun, O. ambacher and M. Stutzmann, Phys. Rev. B **57**, (1998) 7066.

[27] Proposal for “Progetto Speciale, Spettroscopia veloce”, Universita’ di Trento, 1995. *Unpublished.*

[28] M. Cazzanelli, Tesi di Laurea in Fisica, Universita’ di Trento, 1996. *Unpublished.*

[29] Operation Manual of the Streak Camera, Mod. 4094, Hamamatsu. *Unpublished.*

Chapter 5

Conclusions and suggestions for further work

In this work the production of pulsed laser deposited GaN both in N_2 and ammonia was achieved. The films were characterized structurally via atomic force microscopy, scanning electron microscopy and x-ray diffraction.

The electrical properties of the films were assessed by measuring the resistivity, the Hall mobility and the level of doping on a wide temperature range. It was found that the conduction is dominated by “defects”, in fact the measured quantities were almost independent of the temperature.

The main effort was dedicated to studying the luminescence properties of the films. We measured both the continuous wave photoluminescence as well as the time resolved photoluminescence of the films. The results of these data allowed us to attribute the emission from the nitrogen grown samples to excitonic recombination. The data for the sample grown in ammonia are less clear, but what is sure is that the emission centered in the yellow, without any emission in the blue-UV range indicates that these samples are not interesting in terms of technological applications. The microsecond lifetimes, constant on a wide temperature range, show that the luminescence is heavily affected by non-radiative recombinations.

One poor aspect of the nitrogen grown films is the thickness. The growth in nitrogen is very slow (because the reactivity of N_2 with the ablation plume is very low) and this is one of the problems that has to be solved in

order to have a growth technique competitive with more standard ones, as for example the MOCVD [1]. A way to solve this problem could be to make use of a “glow discharge” system in the chamber, which should help to “crack” the N_2 molecules making the atmosphere in the chamber more reactive [2].

Another totally different way to solve the problem, would be to optimize the growth in ammonia. In particular the decrease (of two order of magnitudes) of the pressure of ammonia in the chamber seems to be promising for the growth of high quality films.

After having found a more efficient way to produce PLD GaN films the most interesting issue would be to control the doping of the films, perhaps exploiting the atmosphere dependent (see Chapter 3) doping.

When all these problems would be solved, all the “ingredients” to produce a p/n junction [3-5] will be available.

References

[1] S. Nakamura, *The Blue Laser Diode* (Springer-Verlag, Heidelberg, 1997). S. Nakamura, Jpn. J. Appl.Phys. **30**, (1991) L1705.

[2] H.Angerer, O. Ambacher, R. Dimitrov, Th. Metzger, W. Rieger, M. Stutzmann, MRS Internet J. Nitride Semicond. Res. 1, (1996) 15.

[3] J. I. Pankove, J. Lumin. **7**,(1973) 114. J. I. Pankove, E. A. Miller and J. E. Berkeyhiser, RCA Rev. **32,** (1971) 383. J. I. Pankove and M. a. Lampert, Phsy. Rev. Lett. **33**, (1974) 331. J. I. Pankove, IEEE Trans. Electron Devices **22**, (19759 721. J. I. Pankove, Phys. Rev. Lett. **34**, (1975) 809. J. I. Pankove and E. R. Levin, J. Appl. Phys. **46**, (1975) 1647. H. Amano, K. Hiramatsu, M. Kito, N. Sawaki and I. Akasaki, J. Cryst. Growth. **93**, (1988) 79. J. I. Pankove, J. E. Berkeyheiser, H. P. Maruska and J. wittke, Sol. State Commun. **8**, (1970) 1051.

[4] S. Strite and H. Morcoc, J. Vac. Sci. Technol. **B10**, (1992) 1237. M. Lampert and P. Mark, *Current Injection in Solids* (Academic Press, New York, 1970). J. I. Pankove and P. E. Norris, RCA Rev. **33**, (1972) 377. S. Nakamura, IEEE Journ. Sel. Top. Quant. Electr. **3**, (1997) 435. J. W. Orton and C. T. Foxon, Rep. Prog. Phys. **61**, (1998), 1. I. Akasaki, H. Amano, K. Hiramatsu and N. Sawaki, Inst. Phys. Conf. Ser. **91**, (1988) 633.

[5] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer-Verlag, Heidelberg, 1996).

Appendix A

List of publications related to theM.Sc. thesis

1. *M. Cazzanelli, D. Cole, J. F. Donegan, J. G. Lunney, P. G. Middleton, K. P. O'Donnell, C. Vinegoni, L. Pavesi,. accepted for publication on Appl. Phys. Lett. (scheduled for 7th December 1998).*

2. *K P O'Donnell, P G Middleton, C Trager-Cowan, University of Strathclyde, Scotland and D Cole, M Cazzanelli, J G Lunney, Trinity College, Dublin, Ireland, "The emission spectrum of Pulsed Laser Deposited GaN and its powder precursor, accepted for publication on Mat. Sci. & Eng. B (1999)*

3. *Massimo Cazzanelli*

College, Dublin 2, Ireland. Poster presentation at Symposium L (Nitrides) of 1998 EMRS Conference

3. *Luminescent properties of GaN thin films prepared by Pulsed Laser Deposition M. Cazzanelli, D. Cole and J. G. Lunney, Trinity College, Dublin 2 Ireland. K. P. O'Donnell, P. G. Middleton, C. Trager-Cowan, University of Strathclyde, Scotland. C. Vinegoni and L. Pavesi, INFM and Dipartimento di Fisica, Universita' di Trento, Povo (TN), Italy. Poster presentation at Symposium L (Nitrides) of 1998 EMRS Conference*

4. *Luminescence of PLD GaN and its precursor powder, K P O'Donnell, P G Middleton, C Trager-Cowan, University of Strathclyde, Scotland and D Cole, M Cazzanelli, J G Lunney, Trinity College, Dublin, Ireland. Presented at CLEO/EUROPE-EQEC'98, 14-18 September 1998. Oral communication CThK2.*

5. *Pulsed laser deposition of gallium nitride, M. Cazzanelli, D.Cole, J. G. Lunney, Trinity College, Dublin, Ireland. Poster presentation at XIVth ESCAMPIG, Europhysics Conference on Atomic & Molecular Physics of Ionized Gases, 26th-29th August 1998, Malahide, Dublin, Ireland.*

AWARDS

Recipient of the Graduate Student Award for the best paper presented at Symposium L, **E-MRS** *1998, Strasbourg,16-19 June 1998.*