MRS SOC. VOL. 378 (1995)

TIME RESOLVED PHOTOLUMINESCENCE SPECTROSCOPY ON GaN EPITAXIAL LAYERS

B. K. Meyer, D. Volm, C. Wetzel[#], L. Eckey[a], J.-Ch. Holst[a], P. Maxim[a], R. Heitz[a], A. Hoffmann[a], I. Broser[a], E. N. Mokhov[b], P. G. Baranov[b], C. Qiu[c] and J.I. Pankove[c]

Technische Universität München, Physik-Department E16, 85747 Garching, Germany
[a]Technische Universität Berlin, Institut für Festkörperphysik, 10623 Berlin, Germany
[b]Ioffe Physico Technical Institut, 194021 St. Petersburg, Russia
[c]Astralux, Boulder, CO, USA

ABSTRACT

Free and bound exciton luminescences as well as donor-acceptor pair recombination of GaN epitaxial layers on 6H-SiC and sapphire substrates were investigated using time integrated and time resolved photoluminescence measurements at low temperatures. Lifetimes are determined for the donor bound exciton at 3.4722eV and for two acceptor bound excitons with energies of 3.4672eV and 3.459eV. Luminescences between 3.29eV and 3.37eV are identified as due to excitons deeply bound to centers located near the substrate-epilayer interface.

INTRODUCTION

Recent success in growth technology that allowed to produce p- type GaN[1], and the realisation of the first blue light emitting diodes[2] have revived widespread interest in this material. For further progress towards a GaN based blue or ultraviolet (UV) optoelectronic device a thorough understanding of the recombination mechanisms and the role of impurity related transitions is necessary. The formation of excitons, their capture by shallow impurities and defects, and the subsequent radiative decay is one of the most efficient recombination mechanisms in direct semiconductors. For GaN, investigations on the recombination dynamics have been restricted to donor-acceptor-pair (DAP) transitions[3] and deeper luminescences[4]. The excitonic range of GaN is new ground regarding dynamical studies. In addition, the assignment of blue and UV luminescences of GaN to specific recombination processes has been tentative in some cases, as will be seen below. Here, luminescence transients can often give a fingerprint of the processes involved, thus allowing an identification of their nature.

EXPERIMENTAL

GaN epilayers were grown on 6H-SiC (0001) substrates using a modification of the sublimation sandwich method described earlier[5]. The samples prepared for this study have an epilayer thickness of 50 µm, exhibit n-conductivity and an electron mobility between 30 and 80cm^2/Vs. They are nominally undoped[6]. The GaN layers on sapphire were grown by the metal organic chemical vapor deposition (MOCVD) technique at temperatures around 1030 °C. The source gases were ammonia and Tri-Ethyl-Gallium. Further details can be found in ref.7. All layers were n-type with free carrier concentrations ranging from high 10^{17} cm^{-3} to 10^{19} cm^{-3} as determined by room temperature Hall effect measurements.

For time integrated and time resolved photoluminescence measurements the samples were excited by 5ps 100 kW/cm^2 laser pulses at 3.75eV from a frequency doubled dye laser which is pumped by a modelocked and frequency doubled Nd:YAG laser. The photoluminescence signal was analysed in a 0.35m subtractive double spectrometer and detected by a MCP photomultiplier. For time resolved measurements a single photon counting setup was used with a 50 ps FWHM response to the laser pulse. Employing convolution techniques the overall time resolution is enhanced to 15 ps. Some time integrated experiments were performed using the 325 nm line of a HeCd laser for excitation.

EXPERIMENTAL RESULTS AND DISCUSSION

In low temperature PL a number of near gap emissions is generally observed. They may be roughly classified into three groups as due to free and shallow bound exciton transitions between 3.45 eV and 3.48 eV (see Fig.1.a), deeply bound exciton transitions between 3.31 eV and 3.37 eV (see Fig. 1.c and d) and donor-acceptor-pair (D-A) recombination at 3.27 eV (see Fig. 1.b). The donor acceptor pair band at 3.27eV which is followed by four clearly discernible phonon replica was first identified by Dingle and Illegems[8] using time resolved luminescence spectroscopy. The acceptor could be Mg due to a memory effect in the reactor. However, this D-A pair band is also typical for undoped GaN in the absence of memory effects, and is thought to involve residual Carbon acting as a shallow acceptor.

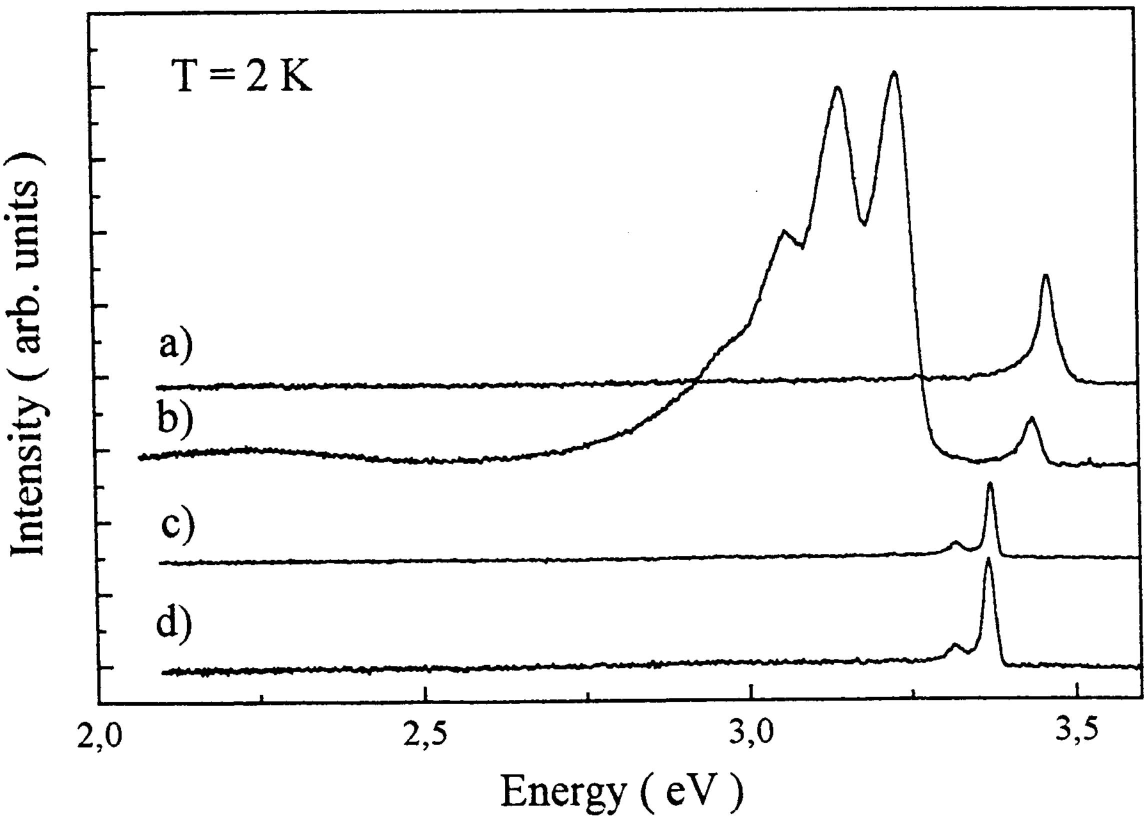

Fig. 1: Photoluminecence spectra for GaN epitaxial layers on sapphire substrates grown by MOCVD. The samples had free carrier densities of $5x10^{17}$ (a), $9x10^{17}$ (b), $2x10^{19}$ (c) and $7x10^{19}$ cm^{-3} (d) as determined by room temperature Hall effect.

We determined the carrier density by an analysis of the D-A pair transients (see Fig. 2) following the theory of Thomas et al.[9] and obtained a concentration of $1x10^{18}$ cm^{-3}. The parameters which enter are the Bohr radius of the donor $r_D=13.5x10^{-10}$ m, and the constant $W_{max}=1.3x10^8$.

When the carrier density is in the range of 10^{19} cm^{-3} the shallow bound exciton lines disappear and only the deeply bound exciton lines are seen (see Fig. 1.c,d).

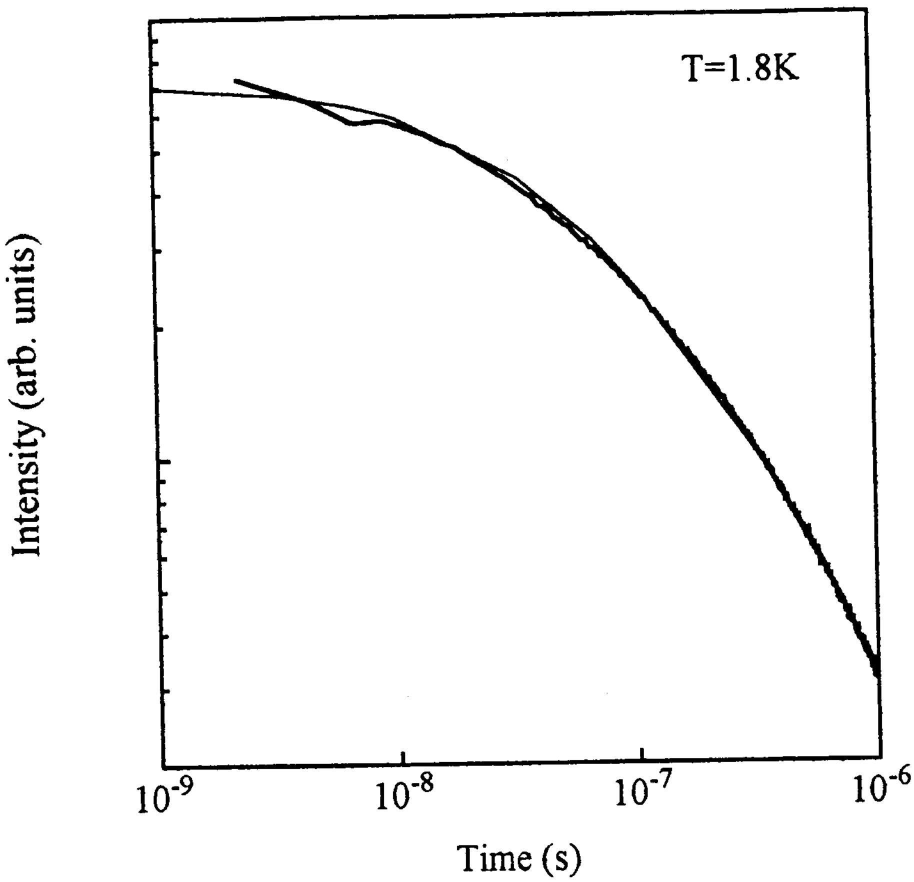

Fig. 2: Transient of the donor-acceptor pair luminescence in GaN. The drawn line is fit to the experimental data, for details see text.

For the GaN on SiC layers on the shallow and deeply bound excitons additional fine structure could be resolved. They are shown in Figs.3 and 4. In the first sample the dominant peak (2) is observed at 3.4722 eV with a FWHM of 5 meV (Fig. 3). Emission from GaN at 3.47eV is commonly ascribed to the recombination of an exciton bound to a shallow neutral donor and referred to as I_2. Three minor structures are detected on the high and low energy shoulders of I_2 at 3.4805eV (FE), 3.4672eV (I_1'), and 3.459eV (I_1). The 3.4805 eV emision is due to the free exciton (FE) corresponding very well to FE recombination energies reported so far[3]. From data presented below and in agreement with Monemar and Lagerstedt[10] we ascribe the emissions (3) and (4) to the recombination of excitons bound to two different neutral acceptors and therefore label them I_1' and I_1. Luminescence transients taken in the range of the shallow bound exciton lines of sample A are shown in the inset of Fig. 3. The measurements are

represented by dotted curves. The labeling numbers correspond to the detection energies of the respective transients, referring to the luminescence spectrum of Fig. 3.
The partial overlap of the recombination lines and the spectral window of 3 meV during these time resolved measurements require a careful analysis of the transients. It was carried out using the convolution of the system response to the laser pulse with three independent exponential decays of different amplitudes. The obtained fits are represented by solid lines in the inset of Fig. 3. For the dominating I_2 (2) and the lower energy emissions I_1' (3) and I_1 (4) an unchanging set of time constants was obtained. Since the respective amplitudes of the three fitted exponential decays vary with the detection position the lifetimes of the bound excitons can unambiguously determined. They amount to 34±5 ps for I_2, 160±15 ps for I_1 and 370±40 ps for I_1'. For the free exciton a lifetime of 15 ps is obtained.

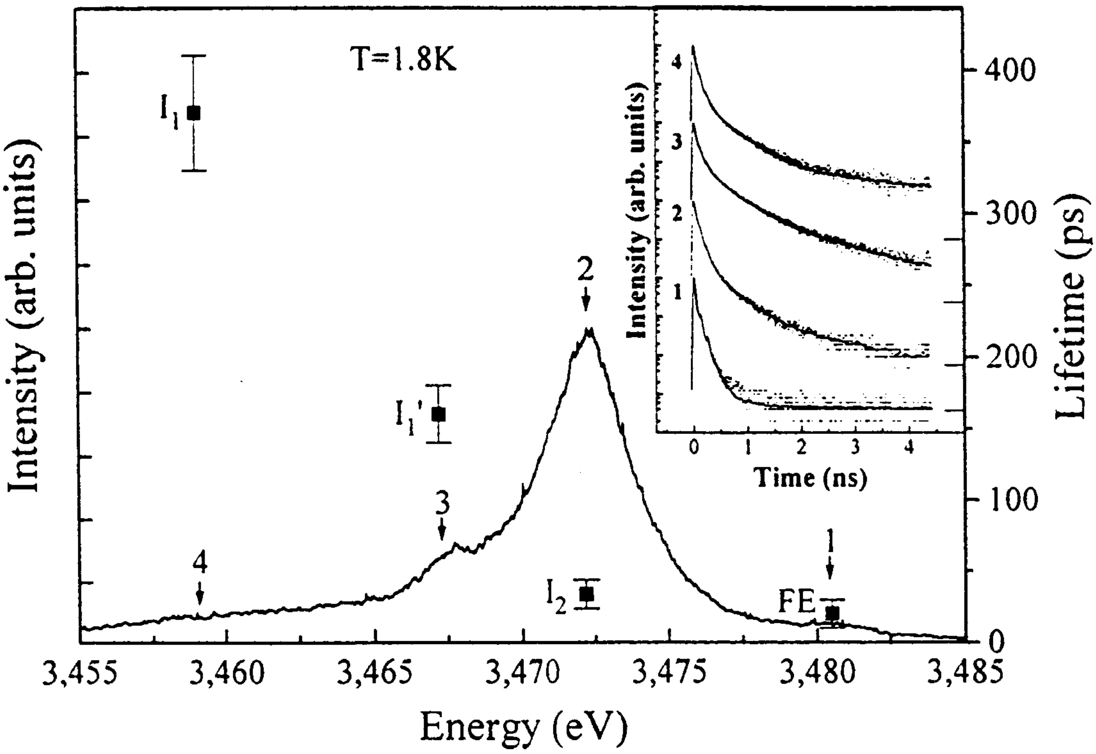

Fig. 3: Luminescence spectrum of GaN on SiC showing free and shallow donor bound exciton recombinations. At the transition energies marked with the numbers 1 to 4 luminescence transients were recorded (see inset); the dotted curves represent the measurements, full lines the pertaining fit.

These assignments of observed luminescence decay constants to the lifetimes of the shallow bound excitons are plausible also by a qualitative comparison of the four tansients which are plotted on a logarithmic scale in Fig. 3. The short free exciton decay in transient (1) as well as the lifetime of 34 ps of the donor bound exciton observed in transients (2), (3) and (4) govern the decay for about the first 400 ps. As mentioned above, the time constant of the I_2 line is observed in all of these three transients because of the spectral overlap of the luminescence lines. Between 400 ps and about 2.5 ns on the time axis the line with the 160 ps time constant is dominating, most prominently at position (3), which is the I_1' transition energy. This justifies the assignment of the 160 ps time constant to the I_1' recombination. The 370 ps time constant becomes most obvious after about 3 ns in transient (4). It is therefore identified as the lifetime of the I_1' complex.

Emission lines in the range between 3.31 eV and 3.37 eV are observed in many samples. In one sample - again with carrier densities around 10^{19} cm^{-3} - they appeared much stronger. The missing D-A recombination allowed to detect two weaker structures around 3.29 eV. We labeled all discernable lines L1 through L8 with increasing energy.

As can be seen in Fig. 4 the dominating 3.36eV emssion mainly consists of two peaks, L8 at 3.366 eV, and L7 at 3.360 eV, with line widths of about 4 meV. In addition, we resolve two weak structures L5 and L6 3.350 eV and 3.354 eV, respectively. At 3.311eV we see the second prominent deeply bound exciton line L3. Its asymmetric lineshape on the high energy side is most likely caused by another weak line L4 around 3.32 eV. Two further weak lines L1 and L2 are resolved at 3.286 eV and 3.296 eV.

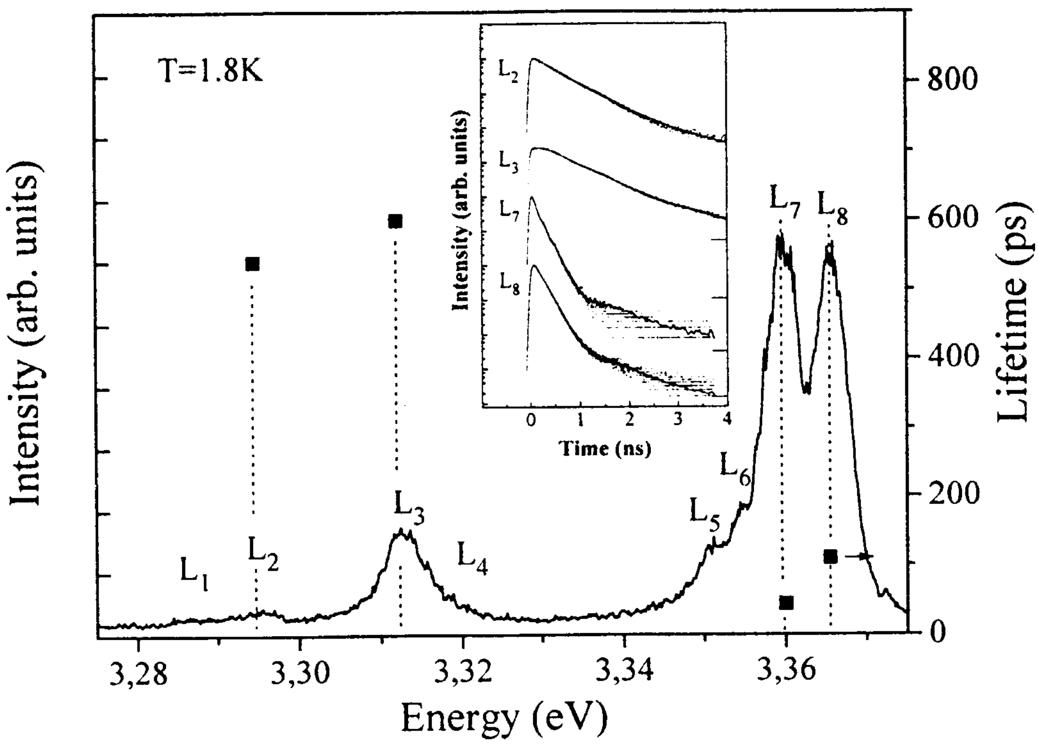

Fig. 4: Luminescence spectrum of GaN on SiC showing deeply bound exciton recombinations. At the transition energies marked with the numbers L1 to L8 luminescence transients were recorded, four of them are shown in the inset; the dotted curves represent the measurements, full lines the pertaining fit.

Several authors have reported luminescences from GaN in the range between 3.31 eV and 3.37 eV, lines L7 and L8 were observed by Pankove et al.[11]. L3 at 3.311 eV was first reported by Dai et al.[12] along with L7 and L8 and tentatively ascribed to a DAP recombination. Recently, Hong et al.[13] presented PL spectra on cubic epitaxial layers of GaN corresponding to the results of Dai et al[12]. The authors ascribed the higher energy lines around 3.36 eV to bound excitons and L3 to the DAP recombination of cubic GaN. However, the understanding of the

processes in this spectral range is still in a provisional state. We performed time resolved measurements to obtain additional information about the nature of these luminescences.
In the inset of Fig. 4 photoluminescence transients are shown taken at different spectral positions in this range (see Fig. 4). The exponential decay observed in all of these transients prooves the excitonic character. In particular, the line L3 turned out to be of excitonic origin in contradiction to other interpretations[12,13]. All transients exhibit a rise time constant of 20±10 ps. This time constant corresponds to the formation of excitons and their capture by the centers causing the respective emssions. For L3 (transient (7) in Fig. 4) we observe an additional, weaker rise process which is governed by a time constant of 110±10 ps. This corresponds exactly to the lifetime measured for L8. Obviously, there is an efficient energy transfer process from the center causing the emission L8 to that responsible for L3. A single center causing both emissions cannot be outruled completely but seems very unlikely in view of the intensity ratio of these two lines. The lifetimes observed range between 45 ps for L7 and 650 ps for L3 which is very short regarding the excitonic localisation energy of about 110 to 180 meV for these lines. PL measurements by exciting the layer through the sapphire substrate showed that these luminescences are mainly localised near the interface. From the evidence collected to this point we conclude that these emssions are due to centers which are located predominantly present near the substrate-epilayer interface, e.g., at dislocations. The short lifetimes observed are primarily ascribed to efficient nonradiative processes in this structurally disturbed area.

CONCLUSION

In conclusion, we presented time resolved photoluminescence measurements of bound exciton recombinations in epitaxial GaN/SiC layers. Luminescences observed between 3.29 eV and 3.37 eV were identified as excitons deeply bound to centers located near the substrate-epilayer interface. An energy transfer process was found between the centers causing the lines at 3.366 eV and 3.311 eV.
present adress: Lawrence Berleley Lab., Berkeley, CA, USA

REFERENCES

1. H. Amano, M. Kito, K. Hiramatsu and I. Akasaki: Jpn. J. Appl. Phys. 28 , L 2112 (1989)
2. S. Nakamura, M. Senoh, and T. Mukai, Appl. Phys. Lett. 62, 2390 (1993)
3. R. Dingle, D. D. Sell, S. E. Stokowski, and M. Ilegems: Phys. Rev. B 4, 1211 (1971)
4. P. Bergmann, Gao Ying, B. Monemar, and P.O. Holtz, J. Appl. Phys. 61, 4589 (1987)
5. Y.A. Vodakov, E. N. Mokhov, A. D. Roenkov and D. T. Saibekov, Kristall und Technik 14, 729 (1979)
6. C. Wetzel, D. Volm, B.K. Meyer, K. Pressel, S.Nilsson, E.N. Mokhov and P.G. Baranov, Appl. Phys. Lett. 65, 1033 (1994)
7. C.H. Qiu, C. Hoggatt, W. Melton, W.M. Leksono and J.I. Pankove (unpublished)
8. R. Dingle and M. Ilegems, Solid State Commun. 9, 175 (1971)
9. D.G. Thomas, J.J. Hopfield, and W. M. Augustyniak, Phys. Rev. 140, A202 (1965)
10. B. Monemar and O. Lagerstedt, J. Appl. Phys. 50, 6480 (1979)
11. J. I Pankove, J. E. Berkeysheiser, H. P. Maruska, J. Wittke: Solid State Commun. 8, 1051 (1970)
12. R. Dai, S. Fu, J. Xie, G. Fan, G. Hu, H. Schrey, C. Klingshirn: J. Phys. C 15, 393 (1982)
13. C. H. Hong, D. Pavilidis. S.W. Brown, and S.C Rand, J Appl: Phys 77, 1705 (1995)