Dynamics of bound-exciton luminescences from epitaxial GaN

L. Eckey,[a)] J.-Ch. Holst, P. Maxim, R. Heitz, A. Hoffmann, and I. Broser
Technische Universität Berlin, Institut für Festkörperphysik, 10623 Berlin, Germany

B. K. Meyer and C. Wetzel
Technische Universität München, Physik-Department E16, 87547 Garching, Germany

E. N. Mokhov and P. G. Baranov
Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia

(Received 19 June 1995; accepted for publication 29 October 1995)

Free- and bound-exciton luminescences of GaN epitaxial layers grown by a sublimation technique on 6H-SiC substrates were investigated using time-integrated and time-resolved photoluminescence measurements at low temperatures. Lifetimes were determined for the donor-bound exciton at 3.4722 eV and for two acceptor-bound excitons with energies of 3.4672 eV and 3.459 eV. On the basis of our results we obtain an upper limit of the free-exciton oscillator strength of 0.0046 for GaN. Luminescences between 3.29 eV and 3.37 eV are identified as due to excitons deeply bound to centers located near the substrate-epilayer interface. Free excitons are captured by these centers within 20 ps. © *1996 American Institute of Physics.* [S0003-6951(96)04102-3]

Recent success in growth technology that allowed to produce *p*-type GaN[1] and the realization of the first GaN based high-power blue light-emitting diodes[2] have revived a widespread interest in this material. For further progress toward a blue or ultraviolet (UV) laser diode a thorough understanding of the recombination mechanisms and the influence of impurities and defects on the quantum efficiency is necessary. For instance, the capture of excitons by deep centers such as localized states at defects can drastically reduce the radiative output near the band gap, which of course is detrimental for device performance. Investigations on the recombination dynamics have been limited to donor-acceptor-pair (DAP) transitions[3] and deeper luminescences.[4] We therefore used time-integrated and time-resolved photoluminescence (PL) and investigated the rise and decay processes of free- and bound-exciton luminescences in GaN epitaxial layers to learn about relaxation and recombination dynamics in the near-gap region.[5]

GaN epilayers were grown on 6H-SiC (0001) substrates using a modification of the sublimation sandwich method described earlier.[6] The samples prepared for this study have an epilayer thickness of 50 μm, exhibit *n*-conductivity and a room temperature electron mobility between 30 and 80 cm^2/Vs.[7] They are nominally undoped. For time-integrated and time-resolved low-temperature ($T=1.8$ K) photoluminescence measurements the samples were excited by 5 ps 100 kW/cm^2 laser pulses at 3.75 eV. The photoluminescence signal was analyzed in a 0.35 m subtractive double spectrometer and detected by a microchannel plate photomultiplier. The overall time resolution is 15 ps.

The low temperature PL may be roughly classified into three groups as due to free- and shallow-bound-exciton transitions between 3.45 eV and 3.48 eV, deeply-bound-exciton transitions between 3.29 eV and 3.37 eV, and donor-acceptor-pair (DAP) recombination at 3.27 eV. Fig. 1 gives spectra of two samples A and B. In sample A we observed all three groups of near-band gap luminescences. In sample B only the deeply bound excitons appear. We determined the carrier density of sample A by an analysis of the DAP transient following the theory of Thomas *et al.*[8] and obtained a concentration of $1\times10^{18}\ cm^{-3}$. The carrier density of sample B is in the range of $10^{19}\ cm^{-3}$ judging from the disappearance of the shallow-bound-exciton lines.

For sample A the dominant peak is observed at 3.4722 ± 0.0010 eV with a FWHM of 5 meV [Fig. 1 (a)]. Emission from GaN at 3.47 eV is commonly ascribed to the recombination of an exciton bound to a shallow neutral donor and therefore referred to as I_2.[3] Three minor structures are detected on the high-energy and low-energy shoulders of I_2 at 3.4805 eV (FE), 3.4672 eV (I_1'), and 3.459 eV (I_1), respectively, as shown in the inset of Fig. 1(a). The 3.4805 eV emission is due to the free-exciton (FE) corresponding very well to FE recombination energies reported so far.[3] In agree-

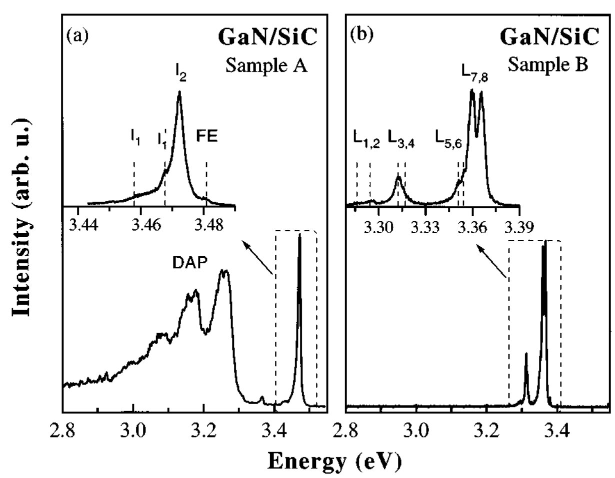

FIG. 1. Low-temperature photoluminescence spectra of two GaN/SiC epilayers A and B exhibiting carrier densities of $1\times10^{18}\ cm^{-3}$ (A) and about $10^{19}\ cm^{-3}$ (B).

[a)]Electronic mail: ludger@marie.physik.tu-berlin.de

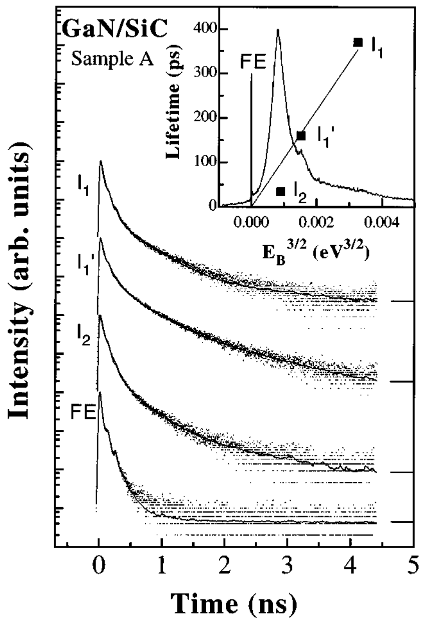

FIG. 2. Low-temperature photoluminescence transients taken in the range of free- and shallow-bound excitons of sample A. Dotted curves represent the measurements, full lines the pertaining fits. In the inset the lifetime of the observed bound excitons and the PL spectrum (dashed) are plotted vs $E_B^{3/2}$.

ment with Monemar and Lagerstedt,[9] we ascribe the emissions I_1 and I_1' to the recombination of excitons bound to two different neutral acceptors. The second prominent feature of sample A is the DAP band at 3.27 eV which is followed by four clearly discernible phonon replica, first identified by Dingle *et al.*[8] Weaker structures appear in sample A around 3.37 eV and on the high-energy shoulder of the DAP band, at 3.31 eV.

Luminescence transients taken in the range of the shallow-bound-exciton lines of sample A are shown in Fig. 2. The measurements are represented by dotted curves. The labels refer to the luminescence spectrum of Fig. 1(a). 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 Fig. 2. ‘‘Bumps’’ in the transients are caused by the system response and are therefore also reproduced in the fits. For the dominating I_2 and the lower-energy emissions I_1' and I_1 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 be determined unambiguously. 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 $\tau=20\pm5$ ps is obtained, very close to our limit of time resolution.

In the inset of Fig. 2 the lifetimes of the bound excitons are plotted versus $E_B^{3/2}$ along with a linear fit and the luminescence spectrum. E_B denotes the localization energy of the exciton at the impurity. The observed proportionality is expected for bound excitons according to the theory of Rashba and Gurgenishvili.[10] Since the overlap between the initial-state and final-state wave functions is larger for a donor-bound exciton than for an acceptor-bound exciton with the same localization energy the oscillator strength of the donor-bound excitons increases resulting in a shorter lifetime. This accounts for the apparent ‘‘deviation’’ of the donor exciton lifetime from the linear fit and has been observed in other materials as well.[11,12] From the slope of the linear fit the important, yet unknown parameter of the free-exciton oscillator strength can be evaluated (for the method cf., e.g., Ref. 13). It amounts to 0.0046 ± 0.0005, a value that has to be considered an upper limit due to the neglection of the contribution of nonradiative decay channels to the observed lifetimes. However, from the agreement of the trend of the lifetimes with the theory of Rashba and Gurgenishvili the radiative decay is seen to dominate. If a nonradiative Auger process would dominate the recombination the lifetimes should follow the fourth power of the binding energy.[15] The calculated value of the free-exciton oscillator strength is in the range of those reported for other direct wide-gap semiconductors such as ZnSe and ZnO.[13,14]

Emission lines in the range between 3.31 eV and 3.37 eV are observed in both samples A and B, cf. Figs. 1(a) and 1(b). In the latter they appear much stronger, and the missing DAP luminescence allows us to detect two weaker structures around 3.29 eV. We labeled all discernible lines L_1 through L_8 with increasing energy. As can be seen in the inset of Fig. 1(b) the dominating 3.36 eV emission of sample B mainly consists of two peaks, L_8 at 3.366 eV, and L_7 at 3.360 eV, with linewidths of about 4 meV. In addition, we resolve two weak structures L_6 and L_5 at 3.354 eV and 3.350 eV, respectively. At 3.311 eV we see the second prominent deeply-bound-exciton line L_3. Its asymmetric lineshape on the high-energy side is most likely caused by another weak line L_4 around 3.32 eV. Two further weak lines L_1 and L_2 are resolved at 3.286 eV and 3.296 eV. Several authors have reported luminescences from GaN in the range between 3.31 eV and 3.37 eV. The first to observe lines L_7 and L_8 were Pankove *et al.*, who observed this doublet on the tail of a 150 meV broad near-gap luminescence.[16] L_3 at 3.311 eV was first reported by Dai *et al.* along with L_7 and L_8, and ascribed to a DAP recombination.[17] Recently, Hong *et al.* [18] presented PL spectra of *cubic* epitaxial layers of GaN on (100) GaAs substrates corresponding well to the results of Dai *et al.* and to our spectrum of *hexagonal* GaN [Fig. 1(b)]. The authors tentatively assigned the higher-energy lines around 3.36 eV to shallow bound excitons and L_3 to the DAP recombination of cubic GaN, based on the room temperature band gap of cubic (c-) GaN ranging between 3.25 eV[19] and 3.30 eV.[20] We performed time-resolved measurements to obtain additional information about the nature of these luminescences. In Fig. 3 photoluminescence transients are shown taken at different spectral positions in this range.

All of these transients exhibit a rise time constant of 20 ±5 ps and are dominated by one exponential decay. The lifetimes observed range between 45 ps for L_7 and 650 ps for L_3. For L_3 we observe an additional, weaker rise process

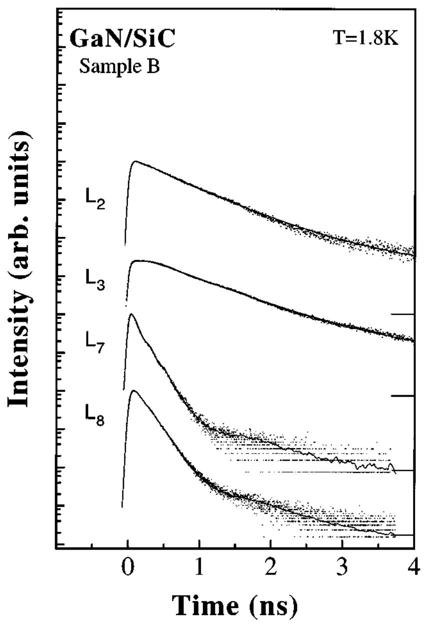

FIG. 3. Low-temperature photoluminescence transients taken in the range of deeply bound excitons of sample B. Dotted curves represent the measurements, full lines the pertaining fits.

which is governed by a time constant of 110±10 ps, corresponding exactly to the decay time of line L_8. In view of the intensity ratio of these two lines it seems very unlikely that both emissions are from different excited states of one single center. Therefore, the rise process of L_3 cannot be ascribed to a relaxation process within one center. Instead, we ascribe it to an energy transfer from the center causing the emission L_8 to that responsible for L_3. The 20 ps rise time observed in all transients of Fig. 3 is explained by the capture of free-excitons by the centers involved. The complete picture of the relaxation and recombination dynamics concluded from Fig. 3 is given in Fig. 4. The predominantly monoexponential decay of line L_3 excludes an interpretation of this emission as due to DAP recombination in hexagonal or cubic GaN, as given by Dai *et al.*[17] and Hong.[18] Its nature is therefore subject to discussion like that of the other luminescences in the range between 3.29 eV and 3.37 eV. The assignment of these lines to shallow bound excitons in small cubic phases, following Hong *et al.*, in otherwise hexagonal material seems attractive. The lower energy gap of c-GaN would lead to an excitonic binding energy of only a few meV for the higher energy lines $L_{7,8}$ rendering them shallow bound excitons of c-GaN. This in turn would be able to account for the short lifetimes observed, in terms of a high oscillator strength as discussed above. A closer look at the lifetimes (cf. Fig. 4) reveals, however, that they vary rather erratically as a function of binding energy in contrast to our observations on shallow bound excitons in hexagonal GaN presented above. It is not plausible that the dynamics of shallow bound excitons in cubic GaN should follow different laws than those in hexagonal GaN. We therefore propose a different interpretation: Lines L_1 through L_8 are due to excitons deeply bound to centers located in structurally disturbed regions of GaN such as, in particular, the substrate-epilayer interface range.

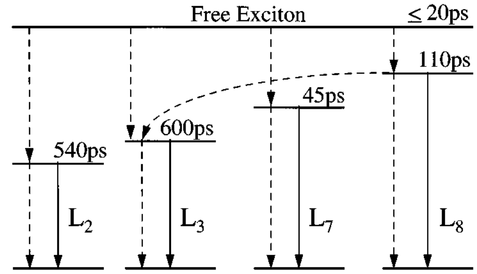

FIG. 4. Model of relaxation and recombination dynamics of deeply bound excitons in epitaxial GaN as obtained from an analysis of the transients shown in Fig. 3. Arrows with full lines denote luminescence transitions, those with dashed lines nonradiative relaxation processes.

The short lifetimes observed are caused by efficient nonradiative relaxation mechanisms. Support for this model comes from recent PL experiments in which we compared the spectra of thick GaN epitaxial layers grown on sapphire from the surface and from the interface. The deeply bound exciton lines were only visible after excitation from the substrate side, i.e., when only emission from the interface region was detected.

[1] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (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, G. Ying, B. Monemar, and P. O. Holtz, J. Appl. Phys. 61, 4589 (1987).
[5] After submission of this work two papers dealing with time-resolved measurements in the near-gap range of GaN were published: M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, A. Salvador, B. B. Sverdlov, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **66**, 3474 (1995); C. I. Harris, B. Monemar, H. Amano, I. Akasaki, *ibid.* **67**, 840 (1995).
[6] Y. A. Vodakov, E. N. Mokhov, A. D. Roenkov, and D. T. Saibekov, Krist. Tech. **14**, 729 (1979).
[7] C. Wetzel, D. Volm, B. K. Meyer, K. Pressel, S. Nilsson, E. N. Mokhov, and P. G. Baranov, Appl. Phys. Lett. **65**, 1033 (1994).
[8] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **40**, A202 (1965).
[9] B. Monemar and O. Lagerstedt, J. Appl. Phys. **50**, 6480 (1979).
[10] E. I. Rashba and G. E. Gurgenishvili, Sov. Phys. Solid State **4**, 759 (1962).
[11] G. D. Sanders and Y.-C. Chang, Phys. Rev. B **28**, 5887 (1983).
[12] R. Dingle and M. Ilegems, Solid State Commun. **9**, 175 (1971).
[13] R. Heitz, Ch. Fricke, A. Hoffmann, and I. Broser, Mater. Sci. Forum, **83–87**, 1241 (1992).
[14] G. H. Kudlek, U. W. Pohl, Ch. Fricke, R. Heitz, A. Hoffmann, J. Gutowski, and I. Broser, Physica B **185**, 325 (1993).
[15] P. J. Dean, R. A. Faulkner, S. Kimura, and M. Ilegems, Phys. Rev. B **4**, 1926 (1971).
[16] J. I. Pankove, J. E. Berkeysheiser, H. P. Maruska, and J. Wittke, Solid State Commun. **8**, 1051 (1970).
[17] R. Dai, S. Fu, J. Xie, G. Fan, G. Hu, H. Schrey, and C. Klingshirn, J. Phys. C **15**, 393 (1982).
[18] C. H. Hong, D. Pavilidis, S. W. Brown, and S. C. Rand, J. Appl. Phys. **77**, 1705 (1995).
[19] R. Powell, G. Tomasch, Y. Kim, J. Thornton, and J. Greene, Mater. Res. Soc. Symp. Proc. **162**, 525 (1990).
[20] S. Logothethidis, J. Petalas, M. Cardona, and T. D. Moustakas, Phys. Rev. B **50**, 18017 (1994).