On the nature of the 3.41 eV luminescence in hexagonal GaN

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Abstract

We studied the recombination at about 3.410 eV in nominally undoped GaN and highly oxygen-doped GaN by photoluminescence (PL) and cathodoluminescence (CL). For this line we find an upper limit for the thermal activation energy of $E_A \leqslant 21 \pm 3$ meV. In time-resolved PL, lifetimes of 300–480 ps are observed indicating excitonic recombination. The defect giving rise to this emission can be created by Ar^+ ion implantation. In conclusion, the 3.410 eV luminescence is attributed to excitons bound to structural defects in hexagonal GaN. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In low-temperature photoluminescence (PL) of GaN a recombination band at about 3.41 eV is often observed. Based on intentional O doping by water injection during growth or post-growth O implantation it has been tentatively assigned by Chung and Gershenzon to a free to bound transition (D^0h) involving an oxygen donor level [1]. PL of GaN dominated by the 3.41 eV luminescence was also observed by Grandjean et al. [2] during a nitridation study of sapphire where after nitridation, 600 Å of GaN were grown. Recently, Shreter and Rebane attributed the 364 nm (3.404 eV) PL-system in their GaN samples to the formation of bound excitons on c-axis screw dislocations. They also observed an additional fine structure and a PL line 7 meV higher in energy which they assigned to the excitons bound to charged dislocations [3]. Previously, one was able to distinguish four different lines within the 3.41 eV

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band at 3.407, 3.412, 3.419 and 3.424 eV, named L1–L4, for strain-free GaN [4].

In this paper we will show that the L2 and L3 lines coincide with the lines reported by Shreter and Rebane taking into account residual strain in their layers. Time-resolved PL gives evidence that the L2 line can be attributed to the recombination of bound excitons. It is concluded that this recombination occurs at structural defects which can be intentionally created by Ar^+ ion implantaion.

2. Experimental procedure

GaN films grown on Al_2O_3 and 6H-SiC by high-temperature vapor-phase epitaxy (HTVPE) [5] exhibiting the 3.41 eV luminescence were selected. In addition, GaN films grown on Al_2O_3 by low-pressure chemical vapor deposition (LPCVD) with n-type carrier concentrations up to 5×10^{19} cm^{-3} were chosen [6], where by a comparison of SIMS results and Hall-effect measurements evidence for oxygen as the main n-type dopant was found. Steady-state PL was performed in an optical cryostat. The luminescence was excited with the 325 nm line of a He–Cd laser. The emitted light was dispersed by a 0.25 m monochromator and detected by a UV-sensitive photomultiplier. Time-resolved PL was done with a Nd : YAG pumped dye laser emitting at 3.75 eV. The signal was analysed in a 0.35 m subtractive double spectrometer and detected by a MCP photomultiplier; for details see Ref. [7]. Low-temperature cathodoluminescence (CL) was performed in a modified SEM equipped with a CL wavelength image option (see Ref. [8]).

3. Results and discussion

Typical PL spectra of the HTVPE samples are shown in Fig. 1. The luminescence is dominated by the donor bound exciton at 3.472 eV, known as I_2 and the 3.41 eV band coinciding with the L2 line reported earlier [4]. At lower energies contributions of donor–acceptor pair transitions (DAP) can be seen.

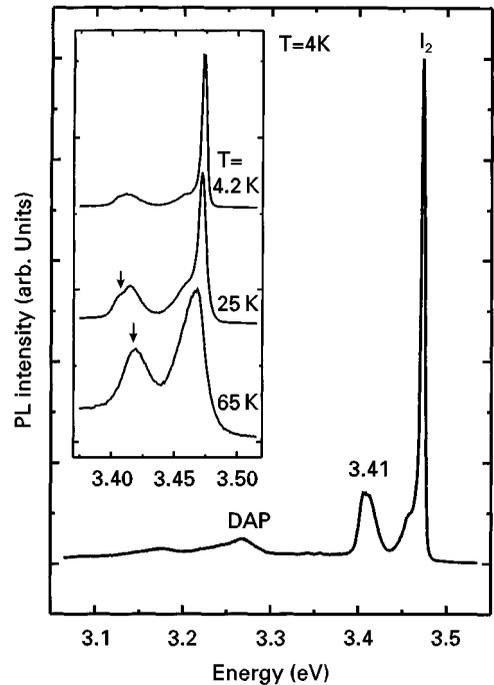In temperature-dependent PL measurements it appears at first sight that the 3.41 eV line shifts to

Fig. 1. Low-temperature PL spectra of HTVPE-grown GaN. The I_2 line as well as the 3.41 eV band appear. At lower energies additional donor–acceptor pair transitions (DAP) with their respective phonon replicas are visible. The inset displays the evolution of the 3.41 eV band with temperature. The low-energy part (L2) quenches and the high-energy part (L3) becomes dominant.

higher energies (10 K < T < 50 K) by approx. 7–8 meV (L3 line [4]) whereas from T > 70 K it more or less follows the band gap decrease in energy. This would support the attribution to a D^0h type recombination as drawn by Chung and Gershenzon [1]. However, a closer look to the line shape reveals a superposition of two lines with the low-energy part quenching more rapidly (inset Fig. 1). This is in qualitative agreement with the findings of Shreter et al. [3]. Shreter and Rebane assigned a PL peak at 364 nm (3.404 eV) to an exciton bound on a c-axis screw dislocation [3]. However their I_2 line position is at 357.6 nm (3.465 eV), indicating residual strain in their films (I_2 bulk value 3.472 eV). It is known from PL under hydrostatic pressure that the 3.41 eV band behaves like a shallow defect and moves with the band gap [9]. Taking this into account the 3.404 eV

luminescence observed by Shreter and Rebane is identical to the our L2 line in strain-free GaN. In addition, the L3 line corresponds to their recombination 7 meV higher in energy. In the HTVPE sample, we find a thermal activation energy of $E_A = 21 \pm 3$ meV for the high-energy part from temperature-dependent PL. This serves as an upper activation energy value for the L2 line.

Typical luminescence transients taken of I_2 and 3.41 eV band are shown in Fig. 2. The measurements are represented by dotted curves, full lines are the pertaining fits. Lifetimes obtained for GaN/6H-SiC amount to 90–120 ps for the I_2 line and 355–480 ps for the 3.41 eV band. For GaN films on Al_2O_3 the lifetimes are shorter, 30–50 ps for I_2 and 300–380 ps for 3.41 eV, most likely due to lower quality of GaN/Al_2O_3 films grown by HTVPE [5]. In Fig. 3 the lifetimes of both transitions together with lifetimes of bound excitons from Ref. [7] are plotted versus $E_B^{3/2}$. E_B denotes the localization energy of donor (I_2) and acceptor (I_1, I_1') bound excitons from Ref. [7] and the activation energy obtained for the 3.41 eV luminescence, respectively. The plot gives evidence that according to the theory of Rashba and Gurgenishvili [10], the 3.410 eV line can be interpreted as bound exciton.
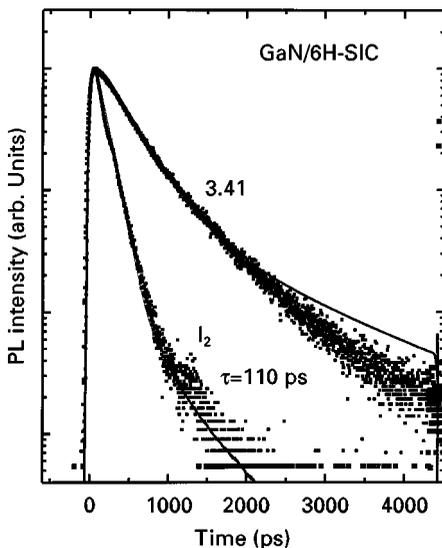

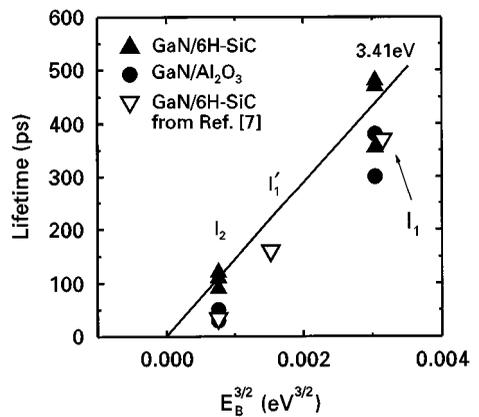Fig. 3. The lifetimes of the bound excitons (I_2, I_1, and I_1') from Ref. [7] and of I_2 and 3.41 eV of this work are plotted vs. $E_B^{3/2}$ according to the theory of Rashba and Gurgenishvili [10].

Fig. 2. Low-temperature PL transients taken in the range of I_2 and the 3.41 eV band are displayed.
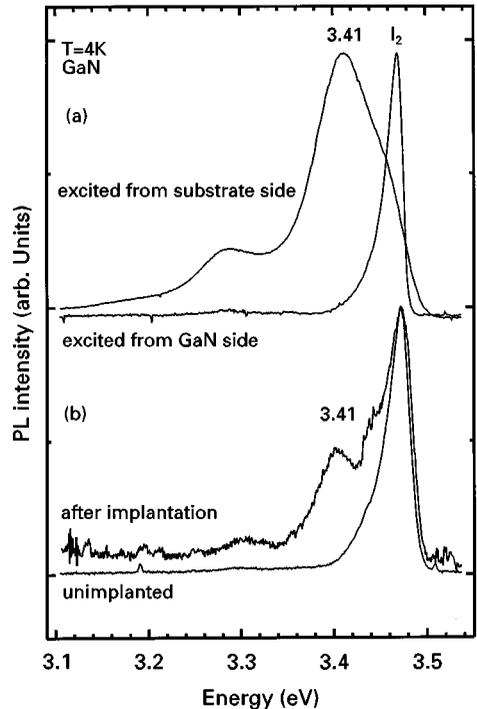

Fig. 4. Low-temperature PL spectra of LPCVD-grown GaN are displayed. (a) By excitation from the GaN side only the I_2 line is observed, whereas the 3.41 eV band appears and dominates when the interface region is probed by excitation from the substrate side. (b) Before and after implantion with 180 keV Ar^+ ions with a dose of 5×10^{13} cm^{-2}. Both spectra are normalized to the I_2 line. The ion damage leads to a significant emission of the 3.41 eV band.

The question arises what kind of defect or impurity gives rise to the bound excition recombination. The tentative assignment of oxygen impurities involved [1] cannot be supported. In PL of highly oxygen-doped LPCVD GaN samples only the I_2 line is present. However, by exciting the same sample from the backside a strong contribution of the 3.41 eV band can be observed indicating its presence near the Al_2O_3–GaN interface where the structural quality is much lower (Fig. 4a). This is in line with the fact that in most cases the 3.41 eV band is found in GaN samples of lower structural quality [2,4,5].

Furthermore, we were able to create the 3.41 eV luminescence by ion implantation. To exclude doping effects Ar^+ ions were used. The samples were implanted with 180 keV Ar ions at doses of 5×10^{13} to $1 \times 10^{14} \, cm^{-2}$ and subsequently annealed for 15 s at 1150°C in nitrogen ambient (further details are given in Ref. [11]). In Fig. 4b, PL spectra of an unimplanted and annealed and an implanted and annealed GaN samples are compared. The implanted sample clearly exhibits an additional luminescence around 3.41 eV. Similar changes in PL have been observed by ECR and RF plasma-assisted MBE growth where the bias voltage and therefore the portion of energetic ions was varied. For higher ion damage an increase of the 3.41 eV luminescence was observed [12]. These findings indicate that the 3.41 eV luminescence is not related to a particular impurity but to structural defects in GaN.

To gain more insight to the microscopic origin of the 3.41 eV band small hexagonal crystals were prepared by HTVPE for spatially resolved cathodoluminescence (CL). PL spectra of these crystals resemble Fig. 1. In Fig. 5, a SEM image of such a crystal is displayed (upper left) with the overall CL intensity plotted in the upper right figure. Below CL images are shown, were the CL intensity in
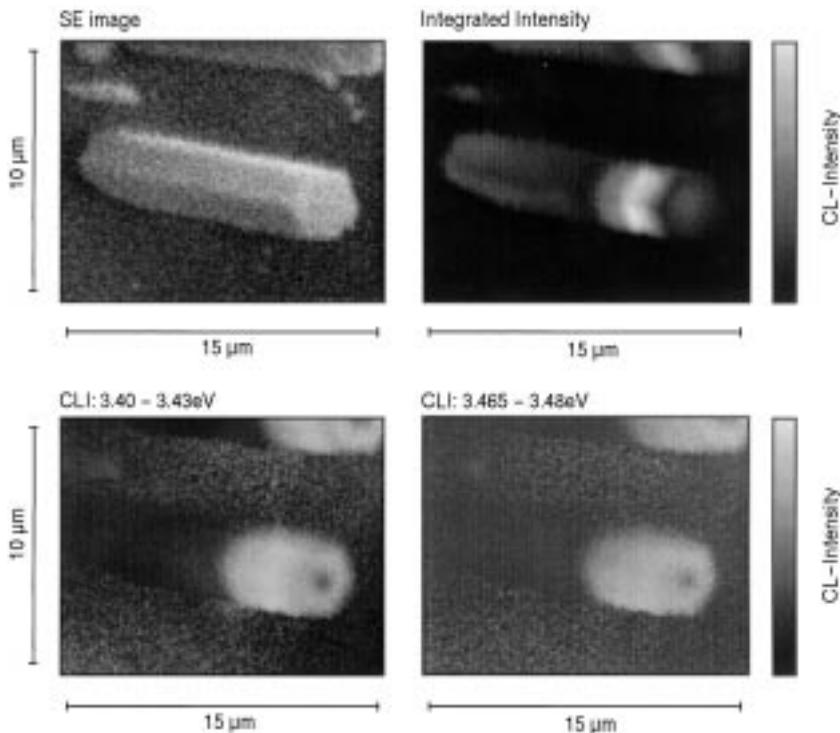

Fig. 5. SEM picture of a hegaxonal rod deposited on 6H-SiC is shown in the upper left corner. On the adjacent picture the overall intensity is plotted. On the lower two picture again the CL intensity is shown for a selected energy range. On the left side for energetic region of the 3.41 eV band and on the right side for the region of impurity bound excitons.

a specified energy range is plotted; on the lower left side for the 3.41 eV emission and on the lower right for impurity bound excitons (I_2). It can clearly be seen that both regions of highest intensity for impurity bound excitons and the 3.41 eV band coincide in contrast to Ref. [3]. It also has to be noted that the center of the hexagonal *c*-plane containing a screw dislocation network [13] is of very low intensity in both emission ranges. The peak emission of this region is around 3.20 eV.

4. Summary

We investigated the 3.41 eV ($T = 4$ K) emission band in hexagonal GaN. The 3.41 eV band is only found in GaN films or portions (interface area) of lower structural quality. Moreover, the line can be produced by causing ion damage in GaN films, e.g. by Ar^+ ion implantation. Spatial-resolved CL indicates a strong correlation between the donor bound exciton (I_2) and the L2 line whereas distinct recombination at dislocations, as proposed [3], cannot be found.

At low temperatures the emission consists of two superposed lines at 3.410 (L2) and 3.418 eV (L3). For temperatures between 10 and 50 K a shift to higher energies is found due to quenching of the L2 line and remaining of the L3 line. This emission shows an activation energy of $E_A = 21 \pm 3$ meV serving as an upper value for the activation energy of the L2 line. Time-resolved PL measurements of the L2 line reveal lifetimes in the range of 300–480 ps indicating the excitonic origin within the theory of Rashba and Gurgenishvili [10]. In summary, we attribute the 3.41 eV line to an exciton with a localization energy of $E \leqslant 21 \pm 3$ meV bound to structural defects.

Acknowledgements

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