

Zero-phonon lines of nitrogen-cluster states in $\text{GaN}_x\text{As}_{1-x}$: H identified by time-resolved photoluminescence

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The incorporation of only a few percentage of nitrogen atoms into a III–V host material, e.g., GaAs or GaP, leads to dramatic changes in the electronic and optical properties of these compounds [1]. These materials show a very strong band gap bowing with increasing nitrogen concentration [2, 3]. Post-growth annealing of these dilute nitrides induces a noticeable blue-shift of the band-gap [1], while post-growth hydrogenation effectively passivates the incorporated nitrogen atoms due to the formation of various N–H complexes [4, 5].

Both post-growth effects have been studied intensively [1]. Numerous experimental results have shown that the nitrogen-induced disorder leads to the formation of various localized states related to isolated N atoms, NN-pair states, and nitrogen-clusters (NC) even in the very dilute regime (nitrogen concentrations lower than 0.3%) [6, 7]. The modification of the electronic properties, e.g., the electron

effective mass and the gyromagnetic factor of electrons [8, 9], by these localized states cannot be explained in the framework of k-p models taking into account only the interaction between the host conduction-band (CB) and the localized state of a single nitrogen atom [10, 11]. The theoretical description of the band-formation process in dilute nitrides must be modified to include various N cluster states [12, 13].

In former photoluminescence (PL) experiments the various optical transitions corresponding to different NC states were often attributed to LO-phonon replicas [6, 14]. In this article, we use time-resolved photoluminescence (TRPL) measurements to clarify that actually only zero-phonon lines are observed in our PL spectra.

Two $\text{GaN}_x\text{As}_{1-x}$ epitaxial layers of 0.5 μm thickness grown by metal-organic vapor-phase epitaxy are studied. The effective nitrogen concentration x_{eff} is determined by the free exciton recombination energy (see Ref. [8]) to be 0.049% and 0.111%, respectively. The sample containing $x = 0.111\%$ of nitrogen is irradiated by a low-energy ion gun with different hydrogen doses ($3.5 \cdot 10^{18}$ – $5 \cdot 10^{18}$ ions/cm²) at 300 °C. This reduces the effective nitrogen concentration x_{eff} of the hydrogenated samples to about 0.083% and 0.002%, respectively [15, 16]. The samples are mounted onto a cold finger of a helium cryostat. A 100 fs Ti/Sapphire laser centered at 760 nm with a repetition rate of 80 MHz is used for optical excitation. The emitted light is collected in a backscattering geometry and is dispersed by a spectrometer with a spectral resolution of 0.5 nm. TRPL measurements are performed at low excitation densities ($\rho_{\text{exc}} \sim 8 \text{ W/cm}^2$) and low temperatures ($T \leq 70 \text{ K}$) since only at these experimental conditions the emission of various NC states are clearly resolved. The time resolution of the cooled S1 streak camera in these experiments is 15 ps.

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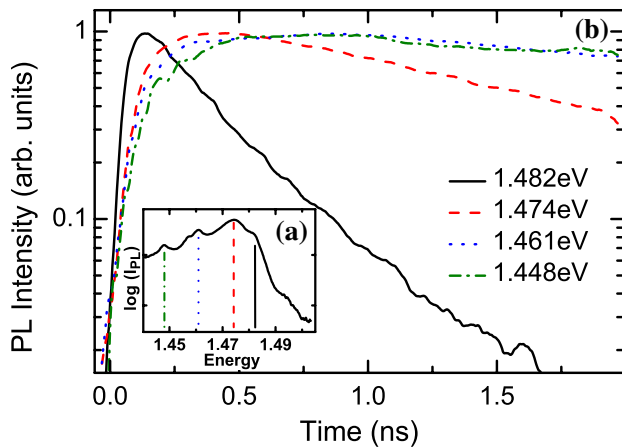


Fig. 1 Time-resolved PL for different detection energies marked by lines in the inset showing the time-integrated PL spectrum ($x_{\text{eff}} \sim 0.111\%$, $T = 10 \text{ K}$, $\rho_{\text{exc}} \sim 8 \text{ W/cm}^2$)

The inset in Fig. 1 shows the time-integrated PL of the 0.111% sample for low temperature ($T = 10 \text{ K}$) and very low excitation density ($\rho_{\text{exc}} \sim 8 \text{ W/cm}^2$).^{1,2} Optical transitions of interest are marked by vertical lines: the free band-to-band transition (FBB) at 1.482 eV (solid, black line), the free-electron to neutral-carbon acceptor transition (e,C) at 1.474 eV (dashed, red line), and two transitions related to NC states at 1.461 and 1.448 eV (dotted, blue line and dash-dotted, green line, respectively). The (e,C) transition has been identified by magneto-PL measurements [9], whereas the FBB transition can clearly be identified on the basis of PL spectra taken shortly after the optical excitation (see Fig. 2).

Figure 1 depicts the energy dependent TRPL transients for the specific energies shown in the inset. Rise times are discussed first. The FBB transition exhibits the fastest rise time, as expected, followed by the (e,C) transition, which exhibits a slightly slower increase in the PL intensity shortly after optical excitation. The NC related transitions on the low-energy side of the spectrum have the slowest rise times because of carrier relaxation from delocalized, higher energy states into highly localized cluster states. Finally, the rise-time of the NC transition at 1.448 eV is slightly longer than that of the transition at 1.461 eV, thus indicating some carrier relaxation from high- to low-energy NC states.

The dependence of decay times on energy is similar to that shown by the rise times. The FBB transition shows the fastest decay time ($\sim 0.3 \text{ ns}$) due to the large optical matrix element of the band–band recombination and the fast

¹ In this case, time-integrated PL means the integration of the time-resolved PL signal over the first 2 ns.

² On the high-energy side of the spectrum a signature can clearly be seen at 1.493 eV. This signal is attributed to the carbon-related (e,C) transition in the GaAs buffer layer.

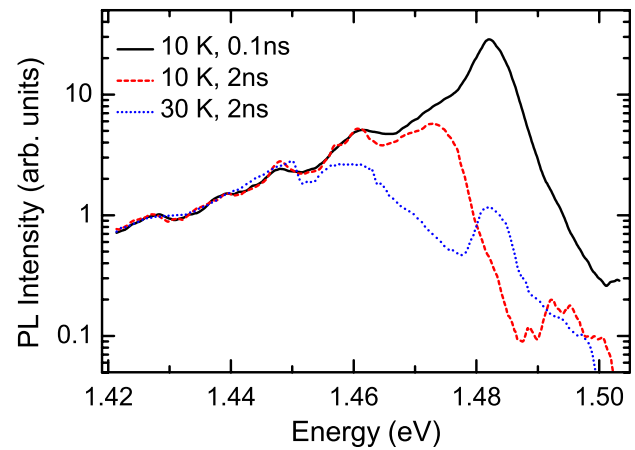


Fig. 2 Emission spectra at different temperatures and detection times after optical excitation: $T = 10 \text{ K}/t_{\text{det}} \sim 0.1 \text{ ns}$ (solid), $T = 10 \text{ K}/t_{\text{det}} \sim 2 \text{ ns}$ (dashed), and $T = 30 \text{ K}/t_{\text{det}} \sim 2 \text{ ns}$ (dotted). The spectra are normalized to the PL intensity at $E = 1.428 \text{ eV}$ ($x_{\text{eff}} \sim 0.111\%$, $\rho_{\text{exc}} \sim 8 \text{ W/cm}^2$)

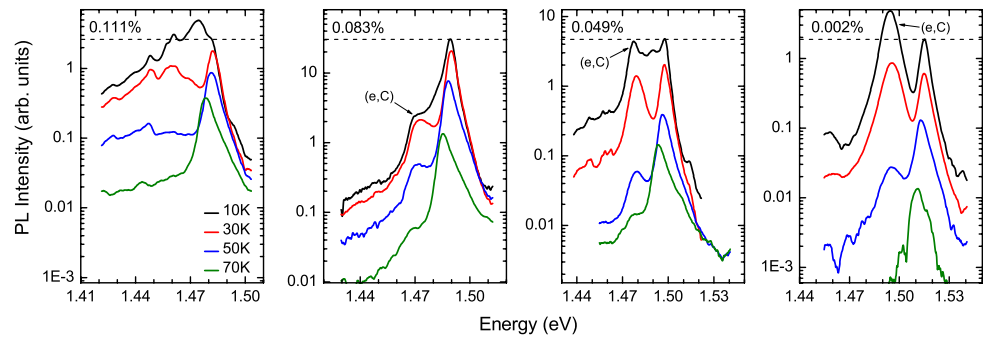
relaxation of electrons into localized states. The decay time is much longer ($\sim 1.5 \text{ ns}$) for the (e,C) transition, because of hole localization in the carbon-acceptor states. The longest decay time ($>4 \text{ ns}$) is that of the NC related transitions due to carrier relaxation into localized NC states.

Since the low-energy NC transitions have both rise and decay times longer than those of the emission from the CB, they cannot be attributed to phonon replicas of invisible zero-phonon transitions energetically degenerate with the CB band. Hence, the analyzed NC transitions are zero-phonon lines.

The comparison between PL spectra taken at $T = 10 \text{ K}$ in the 0.111% sample and shown in Fig. 2 for different delay times after optical excitation confirm the energy dependence found for the decay times. Immediately after optical excitation the PL is dominated by the FBB transition. Two ns after excitation, the FBB transition is barely visible in the PL spectrum, whereas the (e,C) peak-intensity is only slightly reduced and the NC features are almost unchanged (see footnote 2). This PL dependence on delay time is accounted for, once more, by the difference in the degree of localization between the CB and the strongly localized defect states as well as by the carrier relaxation towards lower energies.

The dotted, blue line depicts the PL spectrum corresponding to $T = 30 \text{ K}$ and $t_{\text{det}} \sim 2 \text{ ns}$. The (e,C) band and the NC feature at 1.461 eV strongly decrease in intensity, the FBB signal partially recovers, whereas the intensity of the NC transitions at energies lower than 1.45 eV does not change sizably. These findings can be explained by the strongly energy dependent activation of carriers out of the localized states into the conduction-band. The strong reduction in the intensity of the 1.461 eV PL band further

Fig. 3 Time-integrated PL spectra for different temperatures ($T = 10, 30, 50,$ and 70 K) and for as-grown and hydrogenated samples with $x_{\text{eff}} \sim 0.111\%$, 0.083% , 0.049% , and 0.002% . The carbon-acceptor transitions (e,C) are marked by arrows. The dashed lines are explained in the text ($\rho_{\text{exc}} \sim 8 \text{ W/cm}^2$)



proves that this transition is a zero-phonon line of a NC state in the band gap.

Finally, the time-integrated PL spectra taken at different temperatures ($T = 10\text{--}70$ K) for all four as-grown and hydrogenated samples ($x_{\text{eff}} \sim 0.111\%$, 0.083% , 0.049% , and 0.002%) are compared in the four panels of Fig. 3. The scale of the ordinate axis is the same for all graphs, while the PL spectra of each sample have been arbitrarily vertically shifted in order to align the FBB transition intensity at $T = 10$ K of the four samples (see dashed lines).

The data of the 0.111% -sample, already shown in Fig. 2, are depicted on the left-hand side of Fig. 3. The intensity of the (e,C) and 1.461 eV NC transition clearly quenches with temperature, while the intensity of the 1.448 and 1.428 eV NC transition is sizable up to $T = 70$ K. Therefore, the 1.428 eV NC transition cannot be the LO-phonon replica of the 1.461 eV NC transition. A further increase in temperature results in the well-known Varshni-like red shift of the PL features and in an overall reduction in the PL intensity because of an increase in the nonradiative recombination rate.

By decreasing the effective nitrogen concentration, e.g., by hydrogenating the sample with increasing H doses, the FBB transition at $T = 10$ K shifts to higher energy together with the CB edge. In turn, the FBB transition thermally quenches at a faster rate due to an increasing competition between nonradiative recombination and localization. In fact, the density of localized states below the CB edge, as well as the degree of localization at the CB edge (as estimated from its fractional Γ -character, see Refs. [8, 9]) decrease with decreasing effective nitrogen concentration. Therefore, thermally activated carriers can recombine nonradiatively at higher recombination rates.

The temperature-dependent PL spectra of the 0.049% -sample provide additional evidence of the zero-phonon character of the NC transitions. At $T = 10$ K, two distinct features are clearly observed at 1.483 and 1.490 eV. These features vanish at $T = 30$ K, whereas NC transitions are still observed at lower energies. Therefore, all NC transitions in the PL spectra of our TRPL measurements can be accounted for by zero-phonon lines of states at energy lower than the CB minimum.

In summary, we have reported on TRPL measurements of as-grown and hydrogenated $\text{GaN}_x\text{As}_{1-x}:\text{H}$ samples taken for different detection energies and temperatures in samples with different effective nitrogen concentrations $x_{\text{eff}} \sim 0.002\text{--}0.111\%$. All the transitions attributed to NC states are accounted for by zero-phonon lines.

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References

- Buyanova IA, Chen WM (2004) Physics and applications of dilute nitrides. In: Manasreh MO (series ed) Optoelectronic properties of semiconductors and superlattices. Taylor and Francis, New York, and references therein
- Weyers M, Sato M, Ando H (1992) Jpn J Appl Phys 31:L853. doi:10.1143/JJAP.31.L853
- Wei S-H, Zunger A (1996) Phys Rev Lett 76:664. doi:10.1103/PhysRevLett.76.664
- Polimeni A, Baldassarri Höger von Högersthal G, Bissiri M, Capizzi M, Fischer M, Reinhardt M, Forchel A (2001) Phys Rev B 63:201304. doi:10.1103/PhysRevB.63.201304
- Fowler WB, Martin KR, Washer K, Stavola M (2005) Phys Rev 72:035208. doi:10.1103/PhysRevC.72.035208; Du M-H, Limpitjumnong S, Zhang SB (2005) Phys Rev B 72:073202. doi:10.1103/PhysRevB.72.073202
- Liu X, Pistol ME, Samuelson L, Schwetlick S, Seifert W (1990) Appl Phys Lett 56:1451. doi:10.1063/1.102495
- Klar PJ, Gruning H, Gungerich M, Heimbrodt W, Koch J, Torunski T, Stolz W, Polimeni A, Capizzi M (2003) Phys Rev B 67:121206. doi:10.1103/PhysRevB.67.121206
- Masia F, Pettinari G, Polimeni A, Felici M, Miriametro A, Capizzi M, Lindsay A, Healy SB, O’Reilly EP, Christofoli A, Bais G, Piccin M, Rubini S, Martelli F, Franciosi A, Klar PJ, Volz K, Stolz W (2006) Phys Rev B 73:073201. doi:10.1103/PhysRevB.73.073201
- Pettinari G, Masia F, Polimeni A, Felici M, Frova A, Capizzi M, Lindsay A, O’Reilly EP, Klar PJ, Stolz W, Bais G, Piccin M, Rubini S, Martelli F, Franciosi A (2006) Phys Rev B 74:245202. doi:10.1103/PhysRevB.74.245202

10. Shan W, Walukiewicz W, Ager III JW, Haller EE, Geisz JF, Friedman DJ, Olson JM, Kurtz SR (1999) Phys Rev Lett 82:1221. doi:[10.1103/PhysRevLett.82.1221](https://doi.org/10.1103/PhysRevLett.82.1221)
11. Wu J, Shan W, Walukiewicz W, Yu KM, Ager III JW, Haller EE, Xin HP, Tu CW (2001) Phys Rev B 64:085320. doi:[10.1103/PhysRevB.64.085320](https://doi.org/10.1103/PhysRevB.64.085320)
12. Kent PRC, Zunger A (2001) Phys Rev Lett 86:2613. doi:[10.1103/PhysRevLett.86.2613](https://doi.org/10.1103/PhysRevLett.86.2613)
13. Lindsay A, O'Reilly EP (2004) Phys Rev Lett 93:196402. doi:[10.1103/PhysRevLett.93.196402](https://doi.org/10.1103/PhysRevLett.93.196402)
14. Klar PJ, Gruning H, Heimbrodt W, Koch J, Höhnsdorf F, Stolz W, Vicente PMA, Camassel J (2000) Appl Phys Lett 76:3439. doi:[10.1063/1.126671](https://doi.org/10.1063/1.126671)
15. Polimeni A, Baldassarri Höger von Högersthal G, Masia F, Frova A, Capizzi M, Sanna S, Fiorentini V, Klar PJ, Stolz W (2004) Phys Rev B 69:041201. doi:[10.1103/PhysRevB.69.041201](https://doi.org/10.1103/PhysRevB.69.041201)
16. Felici M, Trotta R, Masia F, Polimeni A, Miriametro A, Capizzi M, Klar PJ, Stolz W (2006) Phys Rev B 74:085203. doi:[10.1103/PhysRevB.74.085203](https://doi.org/10.1103/PhysRevB.74.085203)