Strongly localized excitons in gallium nitride

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We report on strong excitonic luminescence in wurtzite GaN at 3.309 and 3.365 eV (T=6 K). These lines lie well below the band gap and are found commonly in layers grown by different techniques and on different substrates. From detailed photoluminescence investigations we find small thermal activation energies and a very weak electron–phonon coupling. The photoluminescence behavior under hydrostatic pressure is indicative of strongly localized defects. These findings are similar to observations of excitons localized at extended defects such as dislocations in II–VI compounds. © 1995 American Institute of Physics. [S0003-6951(95)01343-X]

The recent surge of interest in gallium nitride and its alloys InGaN and AlGaN is driven by the successful implementation of bright blue and blue-green light emitting diodes.1–4 However, the successful development of advanced optoelectronic devices such as laser diodes will likely require a better understanding of the defect formation and recombination processes in GaN. Here we report on the observation and characterization of excitonic luminescence transitions in wurtzite GaN about 150 meV below the fundamental electronic band gap. Results of photoluminescence (PL) measurements, performed at various temperatures and large hydrostatic pressures, will be used to characterize the nature of these strong luminescence transitions at 3.309 and 3.365 eV.

Wurtzite GaN epilayers were grown by a high temperature vapor phase technique.5,6 A 60 μm thick layer was grown onto a c-plane 6H–SiC substrate. Another sample approximately 1 μm thick was grown by electron cyclotron resonance enhanced molecular beam epitaxy (ECR-MBE) onto a c-plane sapphire.7,8 The PL of the ECR-MBE films strongly depends on the microwave power in the ECR discharge. Especially films at low microwave power show strong PL at 3.47 eV, which can be attributed to donor bound excitons. As the microwave power increases the band-edge luminescence weakens and the spectrum is dominated by transitions within the gap. As we are interested in an analysis of these transitions, a sample grown under high microwave power is studied here. All samples are unintentionally n type with a net carrier concentration in the low 1017 cm–3.

PL was excited using the 325 nm line of a 20 mW HeCd laser. Luminescence was dispersed by a 0.85 m double monochromator and detected by an UV-sensitive photomultiplier. The sample was mounted in a variable temperature cryostat operating from 4.2 to 300 K. Hydrostatic pressure was applied by means of a diamond anvil cell using nitrogen as the pressure medium. Pressure was measured using standard ruby R1 fluorescence.

Low temperature PL of both GaN samples is presented in Fig. 1. Unlike typical GaN PL spectra, the luminescence here is clearly dominated by two narrow lines significantly below the band gap [3.50 eV (Ref. 9)] at 3.365 eV (I3) and 3.309 eV (I4). They become especially pronounced when focusing onto the GaN-substrate interface region of the 60 μm film. In these selected samples there is no indication of shallow donor bound excitons (I2) typically observed at 3.472 eV.6 On the other hand there is only a very weak contribution in the range of donor–acceptor transitions below 3.1 eV (see inset). Similar lines have been observed in samples grown by other techniques including metalorganic vapor phase epitaxy.10–12 In all these studies the line positions are identical to within experimental error and the intensity ratio of I3 to I4 is constant.

Lines similar to I3 in wurtzite GaN have been reported in the literature before.13–16 They have been tentatively attributed to phonon replica of shallow bound excitons13–16 or...
localized defect levels like the nitrogen vacancy (I3). I4 has been reported once and was attributed to an unspecified donor–acceptor transition. No further investigations have been reported which would clarify their origin. In all those reports, these lines were partly obscured by other contributions that did not allow for a further characterization. On the other hand, similar features were reported recently in apparently cubic GaN grown on GaAs. These lines at 3.366 and 3.310 eV were interpreted in terms of shallow bound excitons in the cubic phase of GaN. In our material, however, no cubic phases could be observed by either x-ray diffraction or by optical absorption. The wurtzite phase is known to be the thermodynamically more stable phase under standard conditions of growth, and cubic GaN has only been reported on cubic substrates like GaAs and Si. In this material however one always finds a significant fraction of wurtzite phases. Incorporation of cubic phases in wurtzite material has been reported as well and cannot be completely excluded here.

![Figure 2](image1.png)

**FIG. 2.** Temperature dependence of the I3 and I4 lines. Comb markers indicate a phonon replica obvious at higher temperature. In the inset intensities are compared to the behavior of the I2 line.

The dominance of the I3 and I4 peaks in these samples enabled us to study their dependence on temperature and hydrostatic pressure. As there are no other peaks at higher energies, the interpretation that I3 and I4 are phonon replicas of higher energy transitions can be ruled out. The narrow linewidths of 11.5 meV (I3) and 9 meV (I4) indicate an excitonic nature. This is further supported by the very short decay times below 10 ns as has been observed in time resolved PL.

These PL peaks could be detected for sample temperatures up to about 140 K and the variation of the peak intensity of I3 and I4 is given in the inset of Fig. 2. Above 40 K we observe a strong luminescence quenching corresponding to an activation energy of 27 and 14 meV for I3 and I4, respectively. This is surprising when considering the large energy shift of 140 and 190 meV with respect to the band gap. For comparison the temperature dependence of the I2 lines at 3.47 eV from another GaN/6H–SiC sample presented recently is also shown in Fig. 2. For these shallow bound excitons, an activation energy of 7.6 meV is found. Both values are clearly distinct from values typical for donor–acceptor transitions where activation energies range from 160 to 250 meV. The smallest activation energy reported so far for a transition involving an acceptor is around 135 meV. The very small activation energy ties the resemblance of I3 and I4 lines to shallow bound excitons rather than donor–acceptor transitions.

In addition more spectral features show up in the vicinity of these lines at higher temperatures (Fig. 2). While I3 and I4 decrease with temperature, two series of phonon replica, indicated by comb labels, become obvious at higher temperatures. The intensity ratio of the phonon replica with respect to the zero phonon line is another characteristic feature for the transition involved, because it is a measure of the electron-phonon coupling in the defect system. In the low temperature limit the ratio is given by a Poisson distribution and is measured by means of the Huang–Rhys factor. In GaN typical values of S for donor–acceptor transitions are in the range of 1 to 2 (see spectrum in Ref. 6). Here we only find very small factors of S=0.05 (I3) and S<0.035 (I4), which corresponds to very weak electron–phonon coupling. These values are comparable to those found for shallow bound excitons and together with a small activation energy support an interpretation of excitonic transitions strongly decoupled from the actual band edge.

Further information on the nature of the defects involved can be obtained by an application of hydrostatic pressure. Hydrogenic states are built of the wave functions of the nearest band extrema only and their levels follow the shift of the band gap upon hydrostatic pressure. In contrast, strongly localized defects are described by wave functions from the full Brillouin zone and are only weakly influenced by the band edges that form the band gap. PL spectra from samples under hydrostatic pressure are shown in Fig. 3. Within the range of interest the low temperature spectra up to 4.4 GPa are presented. With the exception of some minor changes in the line shape of I3 and indications of a line splitting, that need further investigation, no significant shift in the line position is observable. This is in striking agreement with previous reports on cubic substrates like GaAs and Si.

![Figure 3](image2.png)

**FIG. 3.** Hydrostatic pressure dependence of the I3 PL line. While at pressures of 4.4 GPa the band gap increases by 190 meV, I3 does not shift significantly.


draw an arrow here pointing to the diagram and write: **Significant shift in the line position is observable.**
contrast to both shallow bound excitons and donor–acceptor transitions.\textsuperscript{27} Being hydrogenic states they typically follow the increasing band gap at a slope of 44 meV/GPa in GaN\textsuperscript{27} equivalent to an overall shift of 190 meV at 4.4 GPa. A similar shift has been observed for transitions within the cubic phase of GaN.\textsuperscript{28} This automatically rules out any explanation of shallow excitons within the cubic phases of GaN.\textsuperscript{19}

In summary we find strong excitonic luminescence with very narrow lines, a rather small thermal activation energy and a very weak electron–phonon coupling. This indicates that I3 and I4 are excitonic transitions despite their large localization energy with respect to the band gap. Under hydrostatic pressure this system behaves like a very strongly localized defect system independent from the pressure dependence of the band gap. The observation of I3 and I4 and their constant ratio of intensities seems to be independent of the growth technique and of the substrate used. They are especially pronounced in the regions close to the substrate. Impurity effects therefore are very unlikely and structural defects have to be considered. These characteristics of I3 and I4 are very similar to an observation of strongly localized defects in wurtzite GaN.\textsuperscript{29} These excitons appear 210 and 245 meV below the band gap and always show up as a pair. Despite their large localization energy, they exhibit only a very weak electron phonon coupling. They show a strong correlation with high densities of dislocations within the interface region of the ZnTe films and the GaAs substrates. These dislocations originate in the strong lattice mismatch of the epitaxial layer and the substrate (8%). In GaN extended defects have been reported at densities of 10\textsuperscript{9} cm\textsuperscript{-2} and higher.\textsuperscript{30} Considering the large lattice mismatch between GaN and sapphire (14%) and the still significant one between GaN and 6H–SiC (3.5%), it appears very likely that extended defects like misfit dislocations localize excitons in GaN in a similar way as is observed for the ZnTe/GaAs system.

In conclusion we have investigated excitonic luminescence lines in wurtzite GaN far below the band gap. From application of large hydrostatic pressure we find that these lines behave like those originating from strongly localized defects. From strong similarities with lines observed in ZnTe we attribute those lines to excitons localized at extended defects.

Note added in proof. The lines at 3.36 eV and 3.31 eV have also been observed\textsuperscript{4} with stained copper excited by a He–Cd laser.

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