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Screening of excitons in GaN crystals

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Abstract. A study was made of the screening of excitons in a GaN sample, which was simultaneously excited with a HeCd laser and an Ar^+ ion laser. The Ar^+ ion laser excites carriers in a two step process, involving an impurity or defect. A comparison with transport measurements shows that the photoluminescence is probably emitted from a higher-quality portion of the sample than that which conducts the current.

The effects of free-carrier screening on excitons have been reported in both bulk materials, such as Ge [1, 2] and GaSe [3], and quantum-well structures [4, 5]. In this paper, we report screening effects on excitons in GaN. Our experimental method involves two lasers: a HeCd laser at 325 nm which excites free electrons and holes, and an Ar^+ ion laser at 514.5 nm, which excites electrons from valence band to an intermediate level in the band and then from the intermediate level to the conduction band. In the recombination process free exciton transitions, bound exciton transitions, free to bound transitions and bound to bound transitions are observed. The increased number of free electrons excited by the Ar^+ ion laser will effectively screen the shallow levels; in particular, we are focusing on the donor-bound-exciton (DBE) levels. Screening results in a decrease in the binding energy and thus a decrease in the intensity of the DBE transition. As the excitons are screened from the donors, the DBE decay route is eliminated as one of the decay processes by which excitons are dissipated. The screened free excitons may then decay without further attachments (free exciton decay), or they may bind to other centres such as acceptors (acceptor bound excitons—ABEs) where the binding energy of the exciton to the acceptor is greater than that to the donor, or they may decay non-radiatively. Our experiment shows that as the DBE intensity decreases, the free-exciton intensity as well as the ABE intensity increases. We find that approximately 50% of the integrated decrease in intensity of the DBE is accounted for by increases in the free-exciton emission intensity and ABE emission intensity.

The GaN layer used in this study was grown at 1050 °C by hydride vapour phase epitaxy to a thickness of 60 μm [6]. The substrate was a 2 inch wafer of (0001) Al_2O_3 (sapphire), and the PL sample was a 2 mm × 8 mm piece cut from near the centre of the wafer. Temperature-dependent (80–400 K) Hall-effect measurements of the mobility and electron concentration were performed on an adjacent 7 mm × 7 mm piece, and the data, after being corrected for a degenerate n-type interface layer [7] by using a two-layer Hall model [8], were fitted by a solution of the Boltzmann and charge-balance equations. The results are as follows: $N_D = 1.2 \times 10^{17}$ cm^{-3}, $E_D = 17$ meV and $N_A = 3 \times 10^{16}$ cm^{-3}, where the symbols have their usual meanings. For comparison with other samples, we note that the 300 K mobility was 950 cm^2 V^{-1} s^{-1}, and the peak mobility 2535 cm^2 V^{-1} s^{-1} (occurring at 120 K).

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The PL was excited with a HeCd laser and, for some experiments, simultaneously with an Ar^+ ion laser. The measurements were made at 2 K with the sample immersed in liquid He. The spectra were analysed with a high-resolution, 4 m spectrometer equipped with an RCAC31034A photomultiplier tube for detection.

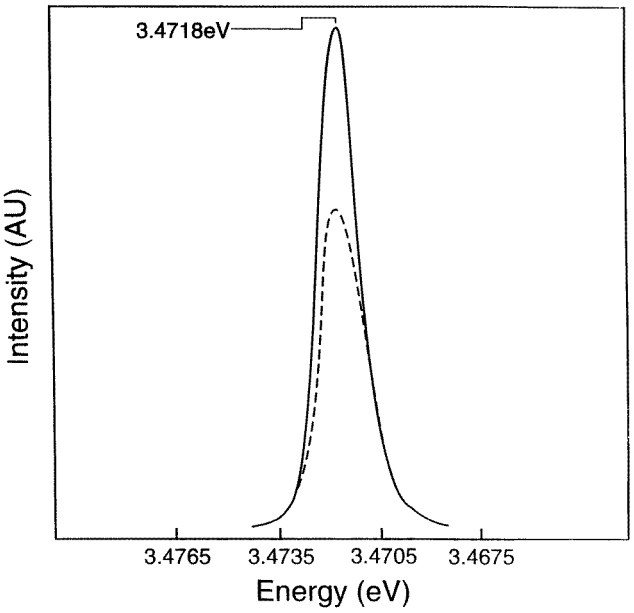

Figure 1. PL spectra from a high quality GaN sample: ——, excited with a HeCd laser: - - - -, simultaneously excited with a HeCd laser and an Ar^+ ion laser.

The PL spectra are dominated by the DBE transition, shown as the solid curve in figure 1. The full width at half maximum for this transition is 2.0 meV, representative of good quality material. The sample was excited with a HeCd laser at an excitation intensity of approximately 40 W cm^{-2}. When simultaneously excited with an Ar^+ ion laser, having an exciting intensity of approximately 15 kW cm^{-2}, the DBE intensity is reduced, as shown by the dashed curve in figure 1. The DBE intensity is further reduced as the exciting intensity of the Ar^+ ion laser is increased. The Ar^+ ion laser excites electrons from the valence band to an intermediate level in the gap region and subsequently from the intermediate level to the conduction band. The increased electron population will screen the impurity potentials, which lowers the binding energies, resulting in fewer DBEs. A reduction in the number of DBE transitions would be expected to result in an increase in the number of free exciton transitions as well as an increase in the number of localized free excitons at centres having larger binding energies, such as neutral acceptor centres. It is also likely that some of the lost DBE transitions will decay through non-radiative processes. In n-type samples, such as the one being investigated, it would be expected that the neutral ABE emission would be much weaker than the DBE emission, since in thermal equilibrium the acceptors would all be ionized. The neutral acceptors would then be created only by the exciting source.

In figure 2 (solid curve) the ABE emission is highlighted by adjusting the sensitivity setting of the detector so that the DBE emission intensity is off scale. Two ABE peaks are observed at 3.4545 eV and 3.4490 eV. The ABE emission was reported by Andrianov *et al* [9] to occur in the energy range 3.45–3.46 eV. ABE emission was also reported by Dingle

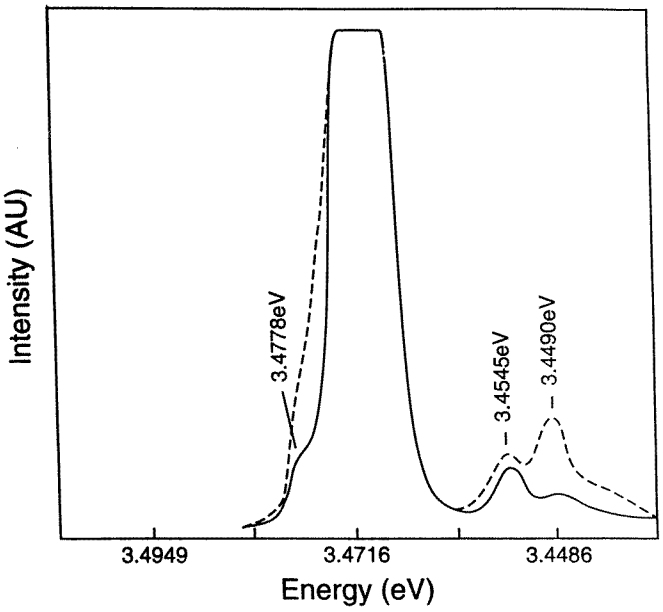

Figure 2. Expanded PL spectra from figure 1: ——, excited with a HeCd laser; - - - -, simultaneously excited with a HeCd laser and an Ar^+ ion laser.

et al [10] and Ilegems *et al* [11, 12] at 3.455 eV. Since there is a large energy spread in the acceptor binding energies for the different chemical acceptors in GaN [13], a similar but smaller spread (following the Haynes rule [14]) in the ABE energies would also be expected. The binding energy of the exciton to a neutral donor is approximately 6 meV as reported in [1]. Good agreement with this energy is observed in the present sample, where the energy of the free exciton associated with the A-band is shown in figure 2 at 3.4778 eV. From the free-exciton energy and the ABE emission energy at 3.4545 eV, the binding energy of the exciton to this acceptor is 23.3 meV. Comparing this binding energy with that of the DBE, it is clear that the DBE will be screened at lower excitation intensities than the ABE.

The solid curve in figure 2 was obtained by exciting the sample with the HeCd laser. Exciting simultaneously with the HeCd laser and the Ar^+ ion laser, the dashed curve was obtained. Here an increase in the free-exciton emission intensity as well as the ABE intensity was observed. In the presence of screening, the number of DBE transitions decreases because fewer excitons are being bound to donors. Integrating the two curves in figure 1 and taking the difference, the decrease in DBE intensity is obtained. Likewise integrating the two curves in figure 2 and taking the difference gives the total intensity gain due to the increase in free-exciton emission intensity and the ABE emission intensity. Approximately half of the decrease in intensity of the DBE emission is accounted for by the increase in the intensity of the free-exciton emission and the ABE emission. The remainder may decay through non-radiative processes.

It is noted that the deeper acceptor exhibits a greater increase in intensity than the shallower acceptor. The charge cloud, created by the increase in electrons excited by the Ar^+ ion laser, will screen both donors and acceptors. The deeper the centre the less screening it will experience, which would account for the deeper acceptor showing a greater

increase in intensity than the shallower acceptor.

Free-carrier screening will modify a spherical Coulomb potential $\varphi \sim e/4\pi \in r$ by adding a multiplicative factor, $\exp(-r/r_D)$, where r is the distance from the centre of the charge, and r_D, the Debye length, is given by [15]

$$r_D = \left(\in kT/e^2 n_{eff} \right)^{1/2} \tag{1}$$

where $n_{eff} = n + (n + N_A)[1 - (n + N_A)/N_D]$. The major part of the hydrogenic charge cloud will be at the Bohr radius, $a_B = 0.529\epsilon/m^* \simeq 22.4$ Å, since $m^* \simeq 0.22$ [16] and $\epsilon \simeq 9.3$ [17]. Thus, significant screening will occur in *pure* material when $a_B \simeq r_D$, or at $n_{eff} = 2 \times 10^{16}$ cm^{-3}, since $T = 2$ K, in this case. If a hole in GaN has about four times the mass of an electron, then about 16 times as many electrons would be required to screen an acceptor. At $T = 2$ K, n should be very small so $n_{eff} = N_A(1 - N_A/N_D) \simeq 2.4 \times 10^{16}$ cm^{-3}. Thus, further screening of donors by the Ar^+ ion laser would require a steady-state free-electron concentration of at least 10^{16} cm^{-3}, which seems reasonable, since the Ar laser should have sufficient intensity by the two-step process. Creation of additional carriers due to thermal heating of the sample by the Ar laser would be minimal. The sample is immersed in liquid He, and there is no shift in the emission energy or broadening of the emission line that would reflect a change in sample temperature.

It is interesting to look at the dark (without laser excitation) screening another way, in terms of wave function overlap. A common empirical relationship used to describe donor screening is

$$E_D = E_{D0} - \alpha N_D^{1/3} \tag{2}$$

where $E_{D0} \simeq 13.6 m^*/\epsilon^2 \simeq 35$ meV. Measured values of α include 2.2×10^{-5} meV cm for n-type GaAs and 3.5×10^{-5} meV cm for n-type Si [18]. Meyer *et al* [19] have suggested that $\alpha \simeq 2.1 \times 10^{-5}$ meV cm for n-type GaN; if so, then for $N_D = 1.2 \times 10^{17}$ cm^{-3}, we would expect $E_D \simeq 25$ meV. Note, however, that our calculation of E_{D0} (35 meV) may be too high, since another measured value of ϵ is 10.4 [20]. This latter value of ϵ leads to $E_{D0} = 28$ meV, which would make $E_D = 18$ meV. Thus, our Hall-measured value, $E_D = 17$ meV, is reasonable.

The measured 6 meV binding energy of the exciton to the screened donor determines a Haynes fraction of about $6/17 \simeq 0.35$, which is much larger than that normally observed. A possible reason is that our PL measurements are representative of better parts of the sample than those which conduct the current. If the material producing the PL has an average donor concentration much less than N_D, then $E_D \simeq E_{D0}$, and the Haynes fraction would be $6/35 \simeq 0.2$, a more reasonable number than 0.35. (In Si, the Haynes fraction is 0.1, and in GaAs it is 0.2.) Note that such a discrepancy between Hall and PL data in inhomogeneous material has been observed many times in the past. In the present case, the inhomogeneity is perhaps caused by dislocations, which can produce regions of good material (surrounding the dislocations) by a gettering process.

Another explanation for the difference in the Haynes fraction observed from electrical measurements compared with that observed from optical measurements may be that the screening of the donor electron is reduced by the presence of an exciton bound to the donor. Then the exciton would 'see' an unscreened donor and would be more tightly bound than would have been expected. These questions must await further experimentation and theory.

In conclusion, the screening of donor-bound excitons is clearly observed in GaN samples when a second laser is employed to increase the carrier concentration. More of the excitons then become bound to acceptors which are deeper, or they remain free. The electrons

bound to donor cores are also screened, with binding energies decreasing from 32 ± 4 meV (low-doping case) to about 17 meV (present sample). The application of the Haynes rule to the donor-bound excitons in the dark suggests that the donors which bind excitons are relatively unscreened.

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