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What determines the emission peak energy of the blue luminescence in highly Mg-doped *p*-GaN?

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We report a study of the 2.8 eV blue luminescence (BL) in heavily Mg-doped *p*-GaN via resonant excitation with a tunable blue dye laser. The dependence of the BL on the excitation photon energy (E_{ex}) is unlike that of the yellow luminescence found in *n*-type GaN. An Urbach-type band tail, with Urbach parameter of 33 meV is observed in the vicinity of the BL energy. We propose that the peak energy of the BL marks the transition from localized states to delocalized states within this band tail.
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GaN is a wide-band-gap III–V semiconductor with applications such as light emitting diodes and laser diodes.[1] One challenge in the fabrication of GaN diodes has been the achievement of a high concentration of holes. The acceptors of highly doped *p*-type GaN are often compensated.[2,3] Accompanying this compensation is the appearance of a broad blue luminescence (BL) centered around 2.8 eV.[4] The origin of the BL has remained controversial. Most groups working on this problem agree that the BL involves a donor–acceptor pair (DAP) transition.[3–9] However, the donors and the acceptors are assumed to be shallow in some models and deep in others. Some models emphasize the importance of potential fluctuations caused by ionized impurities.[10,11] So far there has been no satisfactory explanation as to what determines the peak energy of this emission. In this letter we report a study of the BL via resonant excitation with a tunable laser. We found that the dependence of the BL on the excitation photon energy (E_{ex}) is quite unlike that of the yellow luminescence (YL) found in *n*-type GaN.[12] First, the BL intensity increases *exponentially* as a function of E_{ex} indicating the existence of an Urbach tail in the absorption edge of *p*-GaN. The emission peak energy (E_{em}) depends on E_{ex} like Raman scattering (RS) for $E_{ex}<2.8$ eV but changes to a behavior more like photoluminescence (PL) for $E_{ex}>2.8$ eV. To explain these results we propose that emission peak energy of the BL represents the energy where the photoexcited carrier lifetime changes from being dominated by relaxation to being dominated by radiative recombination. The peak of the BL is an analog of the ''bottleneck'' in the decay of exciton polaritons.[13]

Our experiment was performed with a Stilbene 420 dye laser pumped by an UV Ar^+-ion laser. The ''normal'' BL (i.e., BL excited by above-band-gap photons) from our GaN sample was excited by a HeCd laser at 3.814 eV. The sample was maintained at 12 K by a closed-cycle helium refrigerator. The BL signal was analyzed with a SPEX double spectrometer and detected with a cooled GaAs photomultiplier tube. The sample was grown via metalorganic chemical vapor deposition (MOCVD) on a sapphire substrate. It was annealed at 750 °C for ~4 min after growth and has a room temperature carrier concentration of $p=2\times10^{17}\,\mathrm{cm}^{-3}$, which is well below the Mg concentration ($>10^{19}\,\mathrm{cm}^{-3}$) introduced during growth.

In Fig. 1 we compare the ''normal'' BL spectrum of our sample (which is similar to those reported in the literature) with selectively excited spectra. Small oscillations are noticeable in all spectra as a result of Fabry–Perot interference occurring in the GaN film. The selectively excited BL exhibited little reduction in width when compared to the ''normal'' BL. The selectively excited BL showed a shift in E_{em} with E_{ex}. A plot of $E_{em}-E_{ex}$ vs E_{ex} is shown in Fig. 2. We find this dependence to be separable into two regimes: (1) For $E_{ex}<\sim2.8$ eV, the energy $E_{ex}-E_{em}$ was approximately constant, as in RS, and ~180 meV (±10 meV). (2) For $E_{ex}>\sim2.8$ eV, E_{em} varied *linearly* with E_{ex}, as is typical in PL. However the slope of $E_{em}-E_{ex}$ vs E_{ex} is -0.43 (±0.05), rather than -1 for normal PL (where E_{em} would be a constant). To highlight the unusual nature of BL (shown by a dashed line for $E_{ex}>2.8$ eV), in Fig. 2 we have indicated the dependence of normal PL and RS by dotted and solid lines, respectively. Another unusual feature of the selectively excited BL is the *exponential* dependence of its intensity (I_{BL}) on E_{ex}: $I_{BL}\sim\exp(E_{ex}/E_0)$, where $E_0=33$ meV(±5 meV) as shown in the inset of Fig. 2. This behavior is reminiscent of

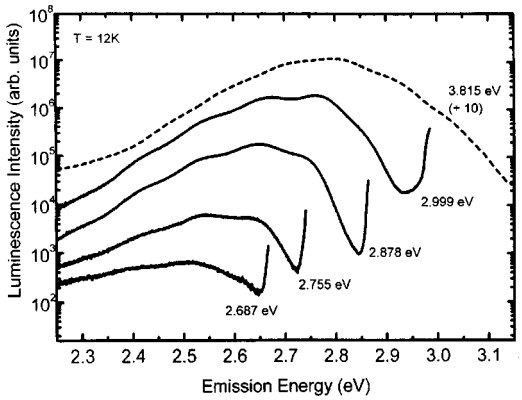

FIG. 1. ''Normal'' BL (dashed curve) excited at 3.815 eV energy, compared to representative selectively excited BL (solid curves) excited at various photon energies, on a $\log_{10}$ scale. The excitation energy is shown next to each spectrum. In all cases the sample temperature was 12 K.

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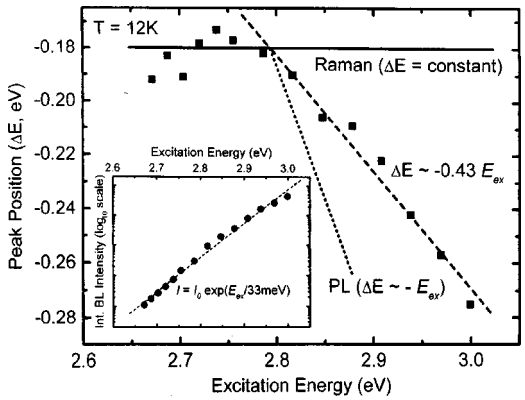

FIG. 2. Peak positions of selectively excited BL (shown as $E_{em}-E_{ex}$) plotted as a function of excitation energy E_{ex}. The dashed line is a linear fit to data for $E_{ex}>2.8$ eV. The dotted and solid lines represent the usual dependence on E_{ex} expected for normal PL and RS, respectively. The inset shows the integrated intensity of the selectively excited BL peaks plotted as a function of E_{ex}, on a $\log_{10}$ scale. The solid line is a linear least-squares fit of the data with the expression: $I_{BL}\sim\exp(E_{ex}/E_0)$ with $E_0=33$ meV. The sample temperature was 12 K.

Urbach tails in the absorption edges of highly disordered materials.

The exponential dependence of $I_{BL}(E_{ex})$ can be understood if we assume that I_{BL} is proportional to the absorption coefficient of the GaN sample at E_{ex}. Observation of Urbach tails has previously been reported by Qiu *et al.* in both *n*- and *p*-type GaN using photoconductivity spectroscopy.[14] They determined Urbach parameters (E_0) of 180–280 meV in both types of GaN samples. In an unintentionally doped *n*-type sample they observed an additional Urbach tail nearer the band gap with Urbach parameter of ~50 meV. They suggested that both tails existed in all samples, with the narrower tail near the band edges being mainly due to potential fluctuations introduced by dopants, and the broader one, which extended well below 2 eV, tentatively attributed to ''defect states.'' Thus our measured value of E_0 is quite consistent with the Urbach parameter attributed to potential fluctuations by Qiu *et al.*

The exponential and continuous density of states indicated by the band tail in highly doped *p*-type GaN makes it difficult to understand what determines the BL peak energy. Figure 2 suggests that *the 2.8 eV peak energy of the BL is the energy where the BL undergoes a transformation from RS to PL* (we will address the deviation of the slope from −1 in the PL regime later). We note that the RS behavior of the BL is similar to that of the YL and can be understood by assuming that the selectively excited DAP states recombine without energy relaxation. In addition, the Raman shift ($E_{ex}-E_{em}$) of ~180 meV is approximately equal to the energy of two longitudinal optical (LO) phonons in GaN. The absence of spectral narrowing when the BL is selectively excited suggested that the BL is *homogeneously* broadened by strong coupling between the LO phonons and the DAP involved in the recombination. This result is in good agreement with the conclusion of Kaufmann *et al.*[15] who independently deduced (from their analysis of the BL line shape) a Frank–Condon shift of 180 meV. It is generally assumed that PL, unlike RS, involves energy relaxation of the photoexcited electrons and holes before radiative recombination. The fact that the BL changes from RS to behaving like PL for $E_{ex}>2.8$ eV therefore indicates that DAP excited above this energy can relax to lower energy states.

Since 2.8 eV is also the energy of the BL emission peak, one can understand this seeming coincidence with the following model. Let us assume that there is a strong increase with energy in the rate of carriers hopping between impurities (a relaxation rate) in the Urbach tail. This is reasonable since carriers with higher energy are expected to have higher probability of hopping into lower energy states. The recombination rate due to tunneling between donors and acceptors should also strongly increase with energy, since the higher energy photons are emitted by spatially closer DAPs. However, if we assume that these two rates differ in their dependence on energy, then it is possible that the relaxation rate can be lower than the recombination rate at low energies but becomes higher at a well-defined energy, E_C. Under this assumption, the emission should behave like RS for $E_{em}<E_C$ since photoexcited carriers recombine before relaxation. For $E_{em}>E_C$ carriers have time to relax before recombination and therefore the emission should behave more like PL. Furthermore, the emission will peak at E_C for $E_{em}>E_C$ since carriers will tend to relax towards to E_C.

We note that this model bears similarity to the exciton-polariton ''bottleneck.''[13] Although the density of states of exciton polariton are known to be continuous, the polariton emission shows usually one to two peaks whose energies do not necessarily coincide with the exciton energy. It was pointed out by Toyozawa that the polariton emission would peak at energies where the exciton-polariton lifetime was maximum (the bottleneck).[16] Since the dependence of recombination rate on carrier energy within a DAP transition model is exponential,[17] our model is plausible only if the dispersion in the relaxation time of carriers is even greater. Strong dispersion in the hopping time of carriers has been reported in amorphous and glassy semiconductors in the vicinity of a ''mobility edge.'' The corresponding energy separation between the mobility edges for electrons and holes is known as the ''mobility gap.'' We, therefore, suggest that the peak energy of ~2.8 eV for the BL is determined similarly by the energy of a ''mobility gap'' in the band tails which gives rise to a bottleneck in the relaxation. In principle, this bottleneck in GaN could be observed by energy dependent time-resolved photoluminescence (TRPL). For emission with $E_{em}<2.8$ eV, the decay time will be dominated by slow radiative recombination of localized carriers. For $E_{em}>2.8$ eV, the carriers are delocalized and their decay time becomes very fast as a result of relaxation into lower energy states. *Energy-resolved* TRPL studies have not been reported for the BL in GaN. It was, however, mentioned in a recent TRPL study of the BL that the decay time ''is more strongly energy position dependent than the yellow luminescence.''[18]

Finally, in our model we will explain the observed relationship of $E_{em}-E_{ex}$ approximately $-0.43\,E_{ex}$ which seems to suggest that the carriers do not relax all the way down to the bottleneck as proposed above. We first note that several groups have reported blueshifts in the DAP emission with increasing *excitation intensity* I_{ex}. For example, Kuskovsky *et al.*, found a nearly *linear* dependence of the DAP emission peak position on $\log_{10}I_{ex}$ in heavily *n*-doped ZnSe.[19] Similar

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dependence has been reported for the BL by Reshchikov *et al.*,[5] and by Kaufmann *et al.*[6] whose data indicate values of $dE_{em}/d(\log_{10}I_{ex})$ of ~57 and 82 meV per intensity decade, respectively. From similar measurements on our GaN sample using above band gap excitation we obtained $dE_{em}/d(\log_{10}I_{ex})=72\pm8$ meV. Kuskovsky *et al.* explained their results via a model in which photoexcited carriers screened the potential fluctuations introduced by dopants and therefore produced a blueshift in E_{em} with carrier density N. We can explain why $E_{em}-E_{ex}$ approximately $-0.43\ E_{ex}$ if we assume that N is proportional to $\exp(E_{ex}/E_0)$ as a result of the Urbach tail in the below-band-gap absorption. Combining this assumption with a linear dependence of E_{em} on $\log_{10}N$ then implies a *linear* dependence of E_{em} on E_{ex}, rather than a E_{em} which is independent of E_{ex} as in normal PL. In fact from the -0.43 slope (from the peak position dependence) combined with the measured E_0 (from the intensity dependence), we calculate that $dE_{em}/d(\log_{10}N)$ ~43 meV. This value is smaller than the directly measured value of $dE_{em}/d(\log_{10}I_{ex})=72$ meV, which may possibly be explained by noting that in the E_{em} vs I_{ex} experiment carriers are excited by above-band-gap photons while in the E_{em} vs E_{ex} experiment the carriers are excited by below-band-gap photons. The more energetic carriers in the former experiment should be more effective in screening the potential fluctuations and produce a larger value for $dE_{em}/d(\log_{10}N)$.

In conclusion, we have interpreted the results of our experiment on selectively excited BL in highly Mg-doped GaN within a model of DAP recombination which includes two features: (1) a large potential fluctuation due charged donors and acceptors which gives rise to an Urbach tail and a blueshift of the emission energy with photoexcited carrier density; and (2) a sharp transition from localized states to delocalized states occurring within the Urbach tail at the BL peak energy of 2.8 eV.

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