Selective excitation and thermal quenching of the yellow luminescence of GaN

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We report the observation of narrower structures in the yellow luminescence of bulk and thin-film *n*-type GaN, using the technique of selective excitation. These fine structures exhibit thermal quenching associated with an activated behavior. We attribute these fine structures to phonons and electronic excitations of a shallow donor-deep acceptor complex, and determine its activation energy for delocalization. Our results suggest that in addition to distant donor-acceptor pairs, the yellow luminescence can also involve emission complexes of shallow donors and deep acceptors. © *1999 American Institute of Physics.* [S0003-6951(99)04347-8]

Recently, GaN and related compounds have become the subject of much interest as a result of their many applications in optical displays and optical data storage.[1] Room temperature GaN-based laser diodes[2] and light-emitting diodes[3] have become commercially available. However, many basic questions remain unanswered, such as the origin of the broadband emission centered around 2.2–2.3 eV, known as yellow luminescence (YL). Many models have been advanced to explain its origin, including transitions from shallow donor to deep acceptor,[4–9] shallow donor to deep donor,[10,11] and deep donor to shallow acceptor.[12] Even within these competing models, there are disagreements, for example whether the YL emission comes from distant donor-acceptor pairs[13] (DAPs), or from localized DAP complexes.[14]

The large linewidth (~0.5 eV) of the YL has made it difficult to discern features related to the microscopic structures of the defects involved. To overcome this difficulty, we have employed the technique of selective laser excitation to study YL in *n*-type GaN samples. This technique is a well-established method to resolve fine structures within an inhomogeneously broadened emission spectra, and has been used with many materials, including ZnSe,[15] CdSe,[16] porous Si,[17] Ge microcrystals,[18] and most recently GaInN.[19]

By using Ar^{+}-ion and tunable dye lasers, we have achieved an excitation range of 2.1–2.7 eV. We have found that several narrower peaks appear within the broad YL linewidth when the YL is excited resonantly. These selectively excited peaks also differ from the above band-gap-excited YL in their thermal behavior. They exhibit strong thermal quenching at temperatures above ~150 K. Our results are consistent with a model in which the YL contains contributions from donor-acceptor complexes.

Our experiment was performed on three GaN samples: a 2.65 μm film grown on sapphire by metalorganic chemical vapor deposition, and two bulk samples grown under high pressure. The film was heavily doped with Si. The carrier concentration from Hall-effect measurements was 5×10^{18} cm^{-3}. The bulk samples also had high carrier concentrations ($\sim 5 \times 10^{19}$ cm^{-3}), most likely due to oxygen donors. Details on their preparation have been reported elsewhere.[20] The temperature of the samples was controlled via a closed-cycle refrigerator. The photoluminescence (PL) spectra were excited by three lasers: a 50 mW HeCd laser at 3.814 eV (3.814 eV) for above the band-gap excitation studies, an Ar^{+}-ion laser with many discrete lines between 2.4 and 2.7 eV, and a Coumarin 540 dye laser with a tunable output between 2.1 and 2.35 eV. The PL signal was analyzed with a SPEX double spectrometer and detected with a cooled GaAs photomultiplier tube connected to a photon-counting system.

The above-band-gap-excited PL showed band-edge emission around 3.4–3.5 eV, as well as a strong YL peak centered around 2.25 eV. When the samples are excited by photons with energy below the band gap, the YL intensity decreases considerably and its line shape also changes significantly. The insets of Figs. 1(a) and 1(b) show, respec-
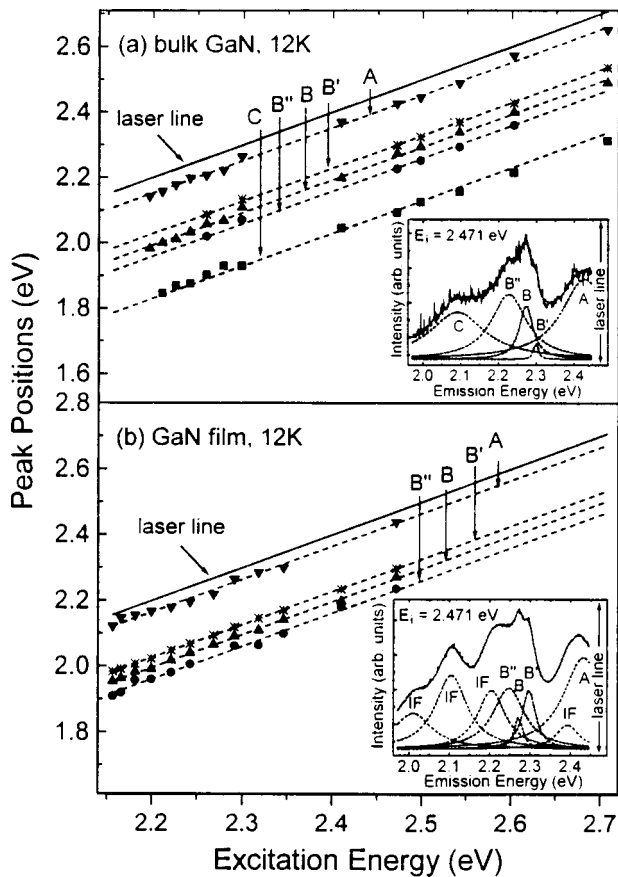
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FIG. 1. Summary of the emission peak energies observed in the 12 K (PL) spectra of (a) a bulk GaN sample and (b) a GaN film, when excited between 2.2 and 2.7 eV. Inset: examples of typical below band-gap PL spectra in both bulk and thin film GaN (excited at 2.471 eV). The broken curves represent a deconvolution of the experimental (solid curve) spectrum into a sum of Lorentzians. The peaks labeled ''IF'' in the inset of (b) are caused by interference fringes and are not plotted in the peak energy summary.
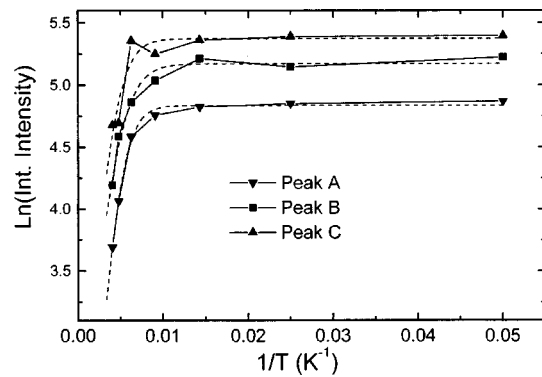

FIG. 2. Arrhenius plot of the temperature dependence of the PL intensity of peaks A, B, and C in the second bulk sample, with fit (dashed curves).

tively, the PL of a bulk and thin film sample for a typical below the band-gap excitation (2.471 eV in both cases), at 12 K. Several peaks are now observable instead of one broadband. By deconvoluting the PL spectra into a sum of Lorentzians, we have extracted the positions of several peaks which contribute to the PL. These peaks (labeled as A, B′, B, B″, and C), are shown as the broken curves in the insets of Fig. 1. The second bulk sample displays similar results, except the finer structures in peak B are not resolved. The deconvolution process in the thin film sample is complicated by the presence of interference fringes [labeled as IF in Fig. 1(b) inset]. We have been able to distinguish these fringes from the YL peaks by noting that the IF peak energies *do not* change with excitation photon energy, E_i, while the YL peak energies *vary linearly* with E_i. The dependence of peaks A, B, on E_i etc., is plotted in Fig. 1(a), for the bulk GaN sample, and Fig. 1(b), for the film. The similarities in these results for GaN samples grown by two completely different methods is a strong indication that similar defects are involved in their emission.

Note that the fine structures' energies, E_{YL}, ''follow'' the excitation photon energy E_i, so that $E_i - E_{YL}$ = constant. The values of $E_i - E_{YL}$ for peaks A, B′, B, B″, and C in Fig. 1(a) are, respectively, 40, 170, 200, 240, and 370 meV (± 10 meV). The energies determined from both

Figs. 1(a) and 1(b) agree within experimental uncertainties. In the second bulk sample (not shown), peak A has a slightly larger energy separation, 50 ± 10 meV.

Peaks A, B, and C in the bulk samples show strong thermal quenching effects as shown by the Arrhenius plot in Fig. 2. Similar effects are more difficult to observe in the thin film sample because of the sensitivity of the interference fringes to temperature change. In addition to thermal quenching, all the peaks exhibit broadening so that the fine structures are difficult to discern at room temperature. Note that these results contrast with published above-the-gap excitation of the YL, which displays little dependence on temperature.[13,21] The data can be fit with the formula: $I = I_0/1 + \alpha e^{(-E^*/k_B T)}$, with three adjustable parameters: I_0, α, and E^* (a thermal activation energy). The fitted E^*s for peaks A, B, and C, are respectively 67, 65, and 73 meV (± 10 meV).

In trying to explain our data we find these three features noteworthy: (1) given the high donor concentrations in our samples (above the Mott critical density), the electrons should be free and one might wonder why the YL exhibits any narrowing; (2) the selectively excited peaks still have a rather large amount of broadening (presumably homogeneous, ~ 0.1 eV); and (3) the temperature dependence of the YL depends on if it is excited resonantly.

Spectral narrowing of DAP emission has been observed in ZnSe[15] and CdSe[16] by exciting donors and acceptors within a narrow range of spatial separation. However, in degenerate *n*-type samples, such as the GaN used in our study, the electrons are free and therefore can recombine with all photoexcited holes localized at the acceptors. As a result, the emission process would not necessarily involve the same donor as in the absorption process, and there would be no sharpening of the YL when selectively excited. However, some theories[6,22] and experiments[14,23] have suggested that the YL of GaN originates from *complexes*, or clusters, of shallow donor and deep acceptor pairs rather than from *uncorrelated* pairs. Thus, the selectively excited YL with width of ~ 0.1 eV we observe at low temperatures most likely originates from electrons and holes trapped at such DAP complexes.

The observation of peaks following the excitation line implies the existence of a continuous or quasi-continuous density of states (DOS). With DAP emission in the ZnSe and CdSe, for example, such a DOS exists due to the variations

in the spatial separation between donor and acceptor. In a DAP complex, such a DOS could arise from fluctuation in energy levels due to variations in the distance or arrangement between the donor and acceptor, or from variations in the surroundings. Neugebauer and Van de Walle,[6] for instance, note that the inhomogeneous broadening of such defect complexes may be large since defect levels can be broadened and shifted when the complexes are located near extended defects. The remaining homogeneous broadening of ~0.1 eV we observe has to be attributed to a strong electron-phonon interaction which is often present in such localized complexes. Although electron-phonon interaction has been used to explain the entire low temperature linewidth of YL,[13] our results suggest that only ~0.1 eV out of a total width of ~0.5 eV is due to electron-phonon interaction.

To explain the different temperature dependence between the selectively excited and above-band-gap-excited YL, we suggest that in addition to recombination between the donor-acceptor complexes, there is also recombination between distant DAPs (distant pairs). Thus, in our model, there are two separate recombination channels: DAP complexes, which would be favored by below the band-gap excitation, and distant DAPs, which would be favored when the sample is highly doped and when excited by above the band-gap excitation.[24] The distant pairs recombination is expected to be dominant in above-band-gap excitation because of the large number of photoexcited free electrons. The concentration of these free electrons is not expected to be strongly dependent on temperature. On the other hand, the electrons involved in recombination from the DAP complexes are localized, and the activation energies of around 57–73 meV probably represent the depth of traps localizing these electrons, since it is higher than the binding energy of electrons to isolated donors. At low temperatures and excited weakly by selective excitation, only electrons trapped at the DAP complexes are excited. But as temperatures increase, electrons can escape from the complexes, resulting in higher probability for nonradiative recombination and leading to the observed thermal quenching of the YL peaks. This explanation can reconcile various experiments which seem to lead to contradictory conclusions. For example, one group has observed a blue shift of the YL peak with an increase in excitation power, and has therefore concluded that the YL involves recombination of distant DAPs.[13] On the other hand, another group has reported a correlation between the strength of YL and density of extended defects, leading to the conclusion that the YL involves DAP complexes.[14] Within our model, it is possible to understand how in, certain circumstances, the DAP complex channel may become significant.

To identify the origin of peaks A, B, and C, we note that the emission may be shifted in energy from the excitation photons if (a) a phonon is emitted during the excitation or recombination process, or (b) the complex is photoexcited into a higher energy electronic state, followed by relaxation into the ground state before emission. The former process most likely accounts for the peak A. We note that substitutional Si_{Ga} and O_N donors are both lighter than the host atoms they replace, and therefore can produce localized phonons known as ''gap modes.''[25] Indeed, the energy shift

of ~40 meV for this peak lies in the gap between the acoustic and optical phonon branches in GaN,[26] and is where gap modes are expected. The peaks B and C, however, have much higher energy shifts than expected for phonon modes; therefore, we have tentatively attributed them to excited electronic states of the donor-acceptor complexes.

In conclusion, we have observed fine structures and strong thermal quenching in selectively excited YL of GaN samples. Our results suggest that in addition to distant pairs, the YL can also involve emission occurring at complexes of shallow donors and deep acceptors.

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