Analysis of the Carbon-Related "Blue" Luminescence in GaN

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ABSTRACT

The properties of a broad 2.86 eV photoluminescence band in carbon-doped GaN were studied as a function of C-doping level, temperature, and excitation density. The results are consistent with a C_{Ga}-C_N deep donor-deep acceptor recombination mechanism as proposed by Seager *et al*. For GaN:C grown by molecular-beam epitaxy (MBE) the 2.86 eV band is observed in Si co-doped layers exhibiting high n-type conductivity as well as in semi-insulating material. For low excitation density (4 W/cm^2) the 2.86 eV band intensity decreases as a function of cw-laser exposure time over a period of many minutes. The transient behavior is consistent with a model based on carrier diffusion and charge trapping-induced Coulomb barriers. The temperature dependence of the blue luminescence below 150 K was different for carbon-contaminated GaN grown by metalorganic vapor phase epitaxy (MOVPE) compared to C-doped MBE GaN.

I. INTRODUCTION

Understanding the properties of carbon in GaN is important given the carbon contamination in metalorganic vapor phase epitaxy (MOVPE) growth processes and also the intentional application of C-doping for growth of semi-insulating GaN in molecular-beam epitaxy (MBE).[1] Recently several groups have reported a "blue" luminescence band associated with carbon incorporation,[2-5] and progress has been made toward understanding the recombination mechanism.[6] However, while the C_{Ga}-C_N donor-acceptor pair recombination hypothesis presented in ref. 3 is consistent with theoretical calculations, possible alternative explanations (invoking, for example, the shift of the Fermi level toward the middle of the gap which occurs with carbon doping) have not yet been ruled out. Further characterization of samples grown by different methods and with varying doping concentrations is necessary for complete understanding of the "blue" band emission mechanism. Additionally, at low temperature the "blue" band often exhibits transient behavior as a function of exposure time to the excitation laser[6-10] and the reason for this behavior is still a matter of some debate.

In the present study the temperature and excitation dependence of the "blue" luminescence are characterized in both MBE and MOVPE GaN:C layers towards clarifying the recombination mechanism and defect origin. MBE-grown samples of varying carbon and silicon doping concentrations including both semi-insulating and n-type material are investigated. The transient behavior of the deep level luminescence bands at low temperature is also studied for different values of the laser excitation density.

II. EXPERIMENTS

All but one of the GaN:C layers investigated were grown by plasma-assisted MBE in Ga-rich conditions on MOVPE GaN/sapphire templates, using CCl_4 or CS_2 vapor as the doping source. In samples doped only with carbon semi-insulating characteristics were obtained, while layers co-doped with high concentrations of both carbon and silicon showed high n-type conductivity. Details of the MBE growth and material characterization have been published elsewhere.[11] The sample set also included a semi-insulating MOVPE GaN layer supplied by Emcore (Somerset, NJ). This sample was prepared by a conventional low-pressure MOVPE process and exhibited a carbon concentration of 3×10^{17} cm^{-3}.

Photoluminescence (PL) was excited by a HeCd laser at 325 nm with power densities varied in the range 2-200 W/cm^2 using neutral density filters. Light emitted by the sample was diffracted by a double-grating monochromator and detected with a multi-alkali photo-multiplier using the standard lock-in technique. The temperature was varied from 12-400 K using a closed-cycle helium cryostat. The data were corrected for the wavelength dependence of the sensitivity of the optical system. Unless otherwise specified all PL data reported are for the *steady-state* condition after continuous exposure to the HeCd laser.

III. RESULTS

A. Variation of the photoluminescence spectra with carbon concentration and measurement temperature

Figure 1 shows PL spectra at 12 K for several MBE GaN samples of varying carbon concentrations. Room-temperature measurements for the same sample set are shown in Fig. 2. Before coming to the "blue" luminescence (BL), we first point out several general features of Figs. 1 and 2. The band-edge luminescence absolute intensity dramatically decreases as the carbon concentration increases. Another important difference is that while the low-carbon concentration reference sample ([C] = 5×10^{16} cm^{-3}) exhibits strong shallow donor-acceptor pair (DAP) luminescence (~3.27 eV and phonon replicas), this emission is surprisingly weak in GaN:C samples. Moreover, as has been discussed in ref. 11 the reference sample of low acceptor concentration exhibits a strong acceptor-bound exciton peak, while GaN:C samples of higher acceptor concentration show only donor or free-exciton peaks. One also notes that the ~2.2 eV "yellow" band (YL) is observed in all samples, but is especially strong in some carbon-doped layers. Our findings concerning YL in GaN:C have been reported previously.[12] Additional deep-level luminescence of unknown origin peaking near ~2.5 eV also appears strongly in layers of lower carbon concentration, overlapping the YL on its high energy side and the BL on its low energy side. This ~2.5 eV emission is strongest in nominally undoped reference material and is not related to carbon.

All carbon-doped layers exhibit a broad and strong BL peaking at ~2.86 eV. The absolute intensity of the BL is highest in moderately C-doped layers, which show better overall optical quality compared to more heavily doped layers. Within the precision that a peak position can be determined for such a broad luminescence feature (± 10 meV), the

BL peaks at the same energy in all MBE GaN:C samples irrespective of doping level. The BL band shape is asymmetric due to convolution on its low energy side with the above mentioned ~2.5 eV emission and/or the YL. This makes it difficult to estimate a value for the BL band width even in one sample, let alone compare different samples. We tentatively suggest a full-width at half maximum of 300 meV for the BL, but the uncertainty in this estimate may be as large as 100 meV.

The presence of BL in the nominally undoped low-carbon reference sample can be certainly ruled out considering both the low temperature and room temperature data. The BL is not seen in any MBE GaN samples without carbon doping, but appears in all C-doped layers, even n-type conducting material co-doped with Si and C as shown in Fig. 3. In low-temperature PL measurements of co-doped samples with [Si] in the mid-10^{18} cm^{-3} and [C] in the low 10^{19} cm^{-3}, shallow DAP emission appears strongly and the BL is relatively weak. However with thermal ionization of the Si donors the shallow DAP emission vanishes, and the BL intensity becomes nearly equal to the band-edge intensity at room temperature.

The absolute intensity of the BL decreases as the C-doping level exceeds 2×10^{18} cm^{-3}, but this does not necessarily imply a decrease in the concentration of the defects responsible as will be discussed in section IV.A below. Figure 4 shows the intensity of the BL at 12 K as a function of the carbon doping level, expressed in units normalized to the sum of the donor-bound and free exciton peak intensities. The BL intensity relative to the band edge emission increases monotonically with carbon concentration.

The deep-level emission spectra as a function of temperature from 12-295 K for two representative MBE GaN:C samples are shown in Figs. 5 and 6. Figure 5 shows the result for a moderately C-doped (4×10^{18} cm^{-3}) layer of fairly good optical quality, while the spectra of a more heavily doped layer (2×10^{19} cm^{-3}) are given in Fig. 6. There is no discernable change in the BL peak position from 12-295 K for either MBE GaN:C sample. Rather complicated behavior of the deep level emission intensity is evident in Fig. 5 with the YL having its highest intensity at 12 K and then decreasing in intensity between 12 K and 125 K (while the BL becomes slightly stronger). Above 125 K the YL intensity then starts to increase as the BL thermal quenching begins. On the other hand, in Fig. 6 the intensities of both the YL and BL decrease monotonically with increasing sample temperature, though the decrease in the BL becomes more pronounced above 125 K.

The change in BL/YL intensity below 125 K in Fig. 5 is interpreted as a decrease in the radiative efficiency of the YL band. A similar decrease in the YL intensity in the range 10-100 K was reported in n-type GaN by Zhang and Kuech,[13] who proposed ionization of shallow donors as the reason for the reduction in YL efficiency (assuming a DAP-type transition). Regardless of the origin of this effect, the differences between Figs. 5 and 6 can be attributed to the differences in the overall optical quality between the two layers. For the less heavily doped sample, carriers made available by a decrease in the radiative efficiency of the YL from 12-125 K instead recombine radiatively at BL-related defects, and the opposite process occurs during quenching of the BL above 125 K. However, in the heavily doped layer a decrease in the radiative efficiency of one PL channel does not lead to an increase in intensity of the other channel since the additional carriers are simply lost to non-radiative recombination. If one assumes the PL intensity is limited by the capture of holes,[14] then evidently a common acceptor is not involved in

both the YL and BL; if so then Fig. 6 would show the same competitive behavior between YL and BL as Fig. 5, which is not the case.

Figure 7 shows an Arrhenius plot of the integrated intensity of the BL in the range 12-400 K for a representative MBE GaN:C sample. The activation energy for quenching of the BL is ~150 meV. The intensity falls below the detection limit at temperatures above 400 K even in the layers with the strongest BL. The thermal quenching behavior of the BL in MBE material does not depend on the C-doping level it and appears similar to the behavior reported previously for MOVPE GaN:C.[6]

All data discussed so far pertain to MBE grown GaN:C samples. In *room-temperature* luminescence measurements of semi-insulating GaN:C grown by MOVPE the BL is nearly identical to that in the MBE samples. However at *low temperatures* (<150 K) the peak position of the BL is significantly different in the MOVPE material. The MOVPE GaN sample shows a strong variation in BL peak position with temperature, as shown in Fig. 8. A red shift of ~0.15 eV occurs as the temperature is increased from 13 to ~150 K. The low-temperature BL peak position in Fig. 8 (3.0 eV) is the same as that reported by Seager *et al.*[6] for MOVPE GaN:C of comparable carbon concentration (low 10^{17} cm^{-3} range). It should be pointed out the carbon concentration of the MOVPE sample is an order of magnitude lower than the *least* heavily doped layer in the MBE sample set. Thus the differences in the PL are not necessarily caused by differences in the growth techniques, and might instead be related to the carbon concentration.

B. Transient luminescence behavior as a function of exposure time to the excitation laser

There have been several reports of transient properties of deep level luminescence bands in GaN.[6-10] Specifically, in low temperature measurements the "blue" band intensity decreases with increasing exposure time to the excitation laser, accompanied by an increase in YL intensity (the latter increases only in the initial stages of the experiment). Warming the sample to room temperature in vacuum restores the original luminescence properties.

For the present GaN:C samples, transient low-temperature luminescence behavior was observed when the measurements were performed at a relatively *low* excitation density (4 W/cm^2) as shown for a representative sample in Fig. 9. On the other hand, for *high* excitation densities (20 W/cm^2 and above) no transient behavior was observed, as shown in Fig. 10. We considered the possibility that at high excitation power the transition to the steady-state condition might occur so quickly that the transient behavior cannot be measured. However, additional experiments described below established that this is certainly not the case.

Figure 11 shows two luminescence spectra taken from the same sample in identical conditions aside from the initial "pre-exposure" to the laser at high power. The first spectrum (dashed line) was measured directly at 50 K and 4 W/cm^2 with no previous exposure to the laser beam. After the sample was stored at room temperature in vacuum overnight, the second spectrum (solid line) was collected. For this spectrum the sample was cooled to 50 K and then exposed to the laser beam at 20 W/cm^2 for 30 min immediately prior to collecting PL data at 4 W/cm^2. The two spectra in Fig. 11 are

identical, and the same transient behavior is observed at 4 W/cm^2 regardless of pre-exposure at 20 W/cm^2. This proves that there is no transient behavior at all in the cw-PL spectra during laser exposure at 20 W/cm^2.

The time dependence of the integrated intensity of the blue band shown in Fig. 9 can be well fit by an exponential decay with a time constant of 16 min. This time constant is of the same order of magnitude as reported in previous investigations of metastable "blue" luminescence, but the quenching is less pronounced. The steady-state integrated intensity of the BL in MBE GaN:C is still about 20% of the initial value, whereas nearly complete quenching was reported in refs. 6 and 7. Also the absence of any transient effects at high excitation power levels in the present samples is in disagreement with the behavior reported by Kim *et al.*[8] They observed bleaching of the blue band for an excitation density as high as 97 W/cm^2. These differences will be discussed in section IV.D below.

C. Variation of the deep level luminescence with excitation density

Figure 12 shows the excitation density dependence of the deep level luminescence spectrum (at steady state) for a heavily C-doped layer measured at 12 K. The YL is saturated at a lower excitation density than the BL. The same qualitative trend with excitation power for the intensities of the main luminescence channels is observed for all C-doping levels in the range 1×10^{18}-5×10^{19} cm^{-3}. The same trend is also observed in room-temperature measurements.

Within a precision of ±10 meV, no change in the BL peak position was detected when the excitation power density was varied from 2-200 W/cm^2. Less heavily doped layers also did not exhibit any peak shift of the BL with excitation power (data not shown here). While a peak shift is often observed for DAP transitions, the lack of shift is not necessarily an argument against a DAP origin of the BL, as will be discussed further in section IV.B below.

IV. DISCUSSION

A. Link between the 2.86 eV emission band and carbon defects

Considering the results shown in the previous section, one concludes that the 2.86 eV emission band in MBE GaN is directly related to recombination at defects introduced by carbon doping. This conclusion is based on the following observations:
1) Samples without intentional carbon doping ([C] < 10^{17} cm^{-3}) show no BL (Figs. 1 and 2).
2) Carbon doped samples ([C] > 10^{18} cm^{-3}) always show BL (Figs. 1 and 2).
3) The BL intensity relative to the band-edge intensity increases monotonically with increasing [C] (Fig. 4).
4) Carbon and silicon co-doped samples exhibiting high n-type conductivity confirmed by Hall effect (n ~1×10^{18} cm^{-3}) have strong BL at room temperature (Fig. 3).

The normalized data of Fig. 4 suggests that increased non-radiative recombination at higher carbon concentrations might be the main reason for the decrease in absolute BL intensity in more heavily C-doped layers (Figs. 1 and 2). However, normalization to the band edge (as in Fig. 4) introduces a complication in that the BL and band edge emission channels may be affected to different degrees by the presence of non-radiative centers. Therefore no definite statement can be made about the concentration of BL centers as a function of C-doping level based on Fig. 4. The data of Fig. 2 do in fact imply a decrease in the radiative efficiency of the BL as the C-doping exceeds 8×10^{18} cm^{-3}, since the band-edge and YL intensity diminish only slightly in more heavily doped layers while the BL becomes markedly weaker.

In any case it is clear that BL only appears in MBE GaN when C-doping is introduced, and the presence of this emission is unrelated to the Fermi level position; it is seen in both semi-insulating and strongly n-type samples doped with carbon. In ref. 3 it was found that BL only appeared in semi-insulating MOVPE GaN layers where carbon was the majority impurity, and this was attributed to the Fermi level dependence of the formation energy of the defect responsible for BL (assigned to C_{Ga}, which has an unfavorable formation energy in n-type conditions). The above interpretation is not inconsistent with our observation of BL in n-type MBE GaN:C. In contrast to MOVPE, MBE growth occurs far from equilibrium and energetically unfavorable defects can be incorporated in significant concentrations, especially for heavy doping.

The reduction in overall luminescence efficiency as the carbon concentration increases above 10^{18} cm^{-3} can be attributed to an increasing density of non-radiative centers associated with heavy carbon doping. Among the semi-insulating GaN:C layers the free carrier concentration is not a significant factor affecting the PL efficiency, as samples with higher electrical resistivity also exhibited higher PL efficiency.[11] The introduction of additional structural defects with carbon doping cannot be ruled out completely, but there was no degradation in x-ray rocking curves or surface morphology for doping levels up to the low 10^{19} cm^{-3}.[11] Thus in addition to the optically active BL and YL[12] defects, carbon probably also introduces non-radiative point defects or complexes at high doping levels.

B. Defect model for the carbon-related blue luminescence

Seager *et al.*[3] proposed a mechanism for the carbon-related BL involving DAP recombination between C_{Ga} deep donors and C_N acceptors. In considering whether our data are consistent with this model, we first consider the most common experimental method used to confirm the the DAP origin of a luminescence feature, i.e. the peak shift to higher energy with increasing excitation density. In the present samples no shift is observed, but this does not mean that the BL is *not* a DAP transition since in some circumstances no peak shift is observed for such transitions. For example, when the impurity concentrations are low enough that appreciable numbers of close pairs do not exist in the sample, a DAP peak shift is not observed. At first the statement above may seem irrelevant to the present work, since the layers studied here have carbon concentrations as high as 3×10^{19} cm^{-3}. However there is good reason to believe that the optically active carbon concentration in MBE GaN:C in general, and the concentration of defects involved in BL in particular, is much lower than that measured by SIMS.

It has already been noted above that the overall PL efficiency of GaN:C decreases with doping level above 2×10^{18} cm^{-3}, and the efficiency of the BL in particular decreases relative to other luminescence channels (including the band-edge) above 8×10^{18} cm^{-3}. These results imply that some fraction of carbon incorporates as non-radiative centers (not BL centers) even at moderate doping levels, and the absolute concentration of BL-related centers decreases for the highest doping levels. In addition to these observations, several arguments were presented in ref. 11 supporting the hypothesis that the active dopant concentration is much lower than the carbon concentration measured by SIMS. One such argument was the precipitation of graphite in heavily doped GaN layers, as was also found in an independent study.[15] Thus we argue that while the BL is directly related to carbon defects, only a fraction of the total carbon incorporated participates in BL transitions, and this fraction becomes smaller at higher doping levels. Therefore even in layers with a high SIMS carbon concentration, it is plausible that the concentrations of donors and acceptors participating in the BL are low enough to make it difficult to observe the effects of Coulomb interactions in the DAP transitions.

Aside from the excitation density dependence, several other experiment results from the previous section can be used to test the deep DAP model for the BL mechanism. The very large difference between the BL thermal ionization energy (Fig. 7) and optical emission energy (~150 meV vs. ~600 meV) strongly supports the deep DAP model. In principle the energy difference could be also attributed to recombination involving a single deep level which undergoes a very large lattice relaxation upon ionization. However there is no reason to suppose that such a hypothetical defect exists, and assigning the BL to a single deep level leaves us without a satisfactory explanation for certain surprising PL characteristics of MBE GaN:C.

As seen from Fig. 1 and data given in ref. 11, nominally undoped n-type reference samples grown by MBE exhibit strong shallow DAP and acceptor-bound exciton peaks. But surprisingly, when the material is doped with carbon the former luminescence weakens dramatically and the latter disappears completely, even though the concentration of acceptors is clearly *higher* in GaN:C than in the reference material. We cannot satisfactorily explain this unexpected behavior under the assumption of a single deep level model for the BL. On the other hand, it is easily understood when the C_N-C_{Ga} deep DAP model is applied. In this model the shallow DAP emission weakens and the acceptor-bound exciton peaks vanish because the deep DAP transition (i.e. the BL) dominates the recombination of holes trapped on C_N shallow acceptors in C-doped GaN.

The measured thermal activation energy for quenching of the BL (Fig. 7) cannot be clearly assigned to an acceptor or donor ionization process. It can however be argued that the thermal ionization energy of the deep donor in the transition is *at least* 150 meV. If the donor and acceptor have comparable ionization energies, the quenching process should be controlled by the species of lower concentration. Therefore if the donor thermal ionization energy were less than 150 meV, a smaller value would be measured in the luminescence quenching experiment (since C-donors are the minority species).

The optical ionization energy of C_N is believed to be ~230 meV[16] which then requires the energy of the BL deep donor to be about 400 meV. This energy is in fair agreement with the level predicted for C_{Ga}, which is the most likely candidate for the BL-related deep donor as shown by Seager *et al.*[3] Nitrogen vacancy-related defects could possibly be considered as alternative candidates for the BL-related donors, as they have

been proposed to explain the "blue" PL band in heavily-Mg doped GaN[17-19], and the experimentally determined optical ionization energy is close to 400 meV. However incorporation of V_N defects is energetically unfavorable except in p-type conditions[20]; significant concentrations would certainly not be expected in n-type conducting layers exhibiting BL (Fig. 3). In fact thermally stimulated current spectroscopy investigations of MBE GaN:C showed that traps believed to be related to V_N were actually *eliminated* with increased carbon doping.[21] At least in the MBE GaN samples, there is no plausible candidate for the BL deep donor other than C_{Ga}.

C. Temperature dependence of the blue band peak position in MBE and MOVPE GaN

The differences in the temperature dependence of the peak position of the BL between MBE and MOVPE GaN:C (Figs. 5 and 6 vs. Fig. 7) are interesting. The variation with temperature of the BL peak position in MOVPE GaN:C (and the lack of any variation in MBE GaN:C) can be best explained if two recombination processes of different emission energy contribute to the BL in MOVPE material, while a single processes is dominant in MBE samples. Under this assumption, in MOVPE material the lower energy emission process (involving deeper defects) contributes more strongly to the luminescence at higher temperatures, accounting for the red-shift of the BL peak. A red-shift related to preferential thermal ionization of close pairs[22] within a single DAP mechanism is not a plausible explanation for the behavior of the MOVPE GaN layer, since no other signs of Coulomb interactions among the DAPs (e.g. a peak shift with excitation power) were observed.

The defect origin of the additional emission process contributing to the "blue" band in MOVPE GaN:C at low temperatures is unknown. In ref. 3 blue luminescence was not observed at all in *n-type* MOVPE GaN, so the additional recombination process probably involves defects with formation energies that become favorable and/or transition final states that become empty when the Fermi level shifts away from the conduction band toward the middle of the gap. At this time further speculation on the nature of this defect would not be productive. Since we do not have an MBE sample of comparably low C-doping level as the MOVPE GaN (3×10^{17} cm^{-3}), we cannot be sure if the difference in BL characteristics is related to the growth processes (MBE vs. MOVPE) or simply the large difference in carbon concentration.

D. Origin of the deep level luminescence transient behavior as a function of exposure time to the excitation laser

The data of Fig. 9 rule out trapping-enhanced recombination via the YL channel as a possible explanation for the metastable deep-level luminescence (since the YL as well as the BL decreases throughout the measurement). On the other hand, the metastable luminescence can be explained by a model that invokes Coulomb fields associated with non-uniformly distributed intrinsic charge-trapping centers (e.g. dislocations) which block diffusion of carriers to the point defects responsible for BL, as proposed in ref. 6. The intrinsic charge traps are assumed to be shallow enough that they can be emptied by

warming the sample to room temperature, explaining the BL recovery. Using such a model the transient behavior of the BL in the present samples can be understood.

The carbon concentration in our intentionally C-doped GaN (10^{18}-10^{19} cm^{-3}) is much higher than in the material studied in previous reports. The weaker BL bleaching effect at low excitation density in more heavily C-doped material is to be expected, since the average distance carriers must diffuse will decrease when the doping concentration increases. The absence of any metastable behavior in GaN:C measured at high laser power is understood less easily, since the result of Fig. 11 implies that intense excitation *prevents* build-up of charge to form Coulomb barriers. A possible explanation for this phenomenon is that the photo-carrier density at high excitation power is sufficient to screen the attractive potential of the intrinsic charge-trapping centers, such that carriers do not diffuse toward them and instead recombine via other defects within the sample. We cannot be certain whether the above explanation is correct because the number of unknowns in the material is too large to attempt a calculation of the steady state photo-carrier density at 20 W/cm^2 excitation density. Nevertheless, screening of the charge trapping centers is the most likely explanation for the observed phenomenon.

The fact that Kim *et al.*[8] observed transients in the BL even for an excitation density as high as 97 W/cm^2 is not inconsistent with the above interpretation. The minimum excitation density needed to screen the intrinsic charge trapping centers should vary significantly from sample to sample. This would be determined by factors such as the average effective spacing between the intrinsic charge trapping defects and the carrier lifetimes. It should be noted that the photo-carriers responsible for screening the trapping centers need not be of the same type as the photo-carriers limiting the luminescence intensity. Indeed, MBE GaN:C layers show quite strong photoconductivity[21] despite their comparatively low PL efficiency. Dislocations would seem to be likely candidates for the intrinsic charge trapping centers, but this hypothesis cannot be tested with the present sample set since all the layers have approximately the same dislocation density.

Some authors[7,8,9] have hypothesized that the transient behavior of the BL originates from actual metastable point defects rather than the carrier diffusion and charge trapping processes discussed above. The fact that transient effects are observed in the present samples only for low excitation density is a compelling argument against this hypothesis. The effects of photo-carrier capture barriers or photo-induced point defect reactions would be apparent for any excitation density, whereas Fig. 11 shows that 30 min exposure at 20 W/cm^2 does not affect any change in the material at all. Furthermore, photoconductivity experiments showed no evidence of metastable point defects in the present samples.[21]

While we are confident that the charge trapping model applies for semi-insulating GaN:C, we do not suggest that this model is valid for all GaN samples exhibiting so-called blue luminescence. For example the authors of ref. 9 state that the nominally undoped sample they studied was n-type (not semi-insulating), and in such a sample one would not expect to observe the carbon-related BL in the first place. The "blue" luminescence studied in ref. 9 may have a completely different defect mechanism and hence its transient behavior may also have a different explanation. Some "blue" luminescence bands that appear in nominally undoped n-type GaN have been discussed in refs. 23-25.

V. CONCLUSIONS

A broad band peaked at ~2.86 eV appears in the luminescence spectrum of MBE GaN doped with carbon above 1×10^{18} cm^{-3}, both in semi-insulating and n-type material. This band is directly caused by carbon defects and is not an indirect result of carbon incorporation. The peak position does not shift with measurement temperature or excitation power. The 2.86 eV band saturates at higher excitation power than the yellow band. A thermal quenching energy of ~150 meV was determined for the 2.86 eV band.

The luminescence properties of MBE GaN:C can be successfully explained using the C_{Ga} deep donor-C_N acceptor model proposed previously[3] for the carbon-related 2.86 eV band. The "blue" luminescence efficiency decreases relative to other luminescence channels for doping levels above 8×10^{18} cm^{-3} and it was argued that the concentrations of electrically active C_{Ga} and C_N defects in highly C-doped GaN are much lower than the carbon concentration measured by SIMS. This can account for the lack of any peak shifts related to Coulomb interactions.

The 2.86 eV band in MBE GaN:C shows transient behavior when measured at lower excitation density, but not when measured at higher excitation density. The transient behavior is apparently unrelated to metastable point defects, but can be understood using a model that invokes carrier diffusion and charge-trapping induced Coulomb barriers to explain the transients in luminescence intensity.

The luminescence spectrum of semi-insulating MOVPE GaN:C also shows a "blue" band which is virtually identical to that of moderately C-doped MBE GaN for measurement temperatures above ~150 K. However, as the temperature decreases below 150 K the band peak position gradually shifts to 3.0 eV in the MOVPE material. This difference suggests that two emission processes contribute to the "blue" band in MOVPE GaN, and only one of them (the process dominating at high temperature) is definitely related to carbon.

The carbon-related mechanism discussed in this work is only one of several recombination processes that cause so-called blue luminescence in GaN. The "blue" band observed in nominally undoped semi-insulating MOVPE GaN and intentionally C-doped GaN can safely be attributed to carbon, but caution should be exercised when interpreting the "blue" luminescence in other types of GaN samples. The carbon-related band can be clearly distinguished from other types of "blue" luminescence[17-19, 23-25] by its different behavior in variable temperature and variable excitation density measurements.

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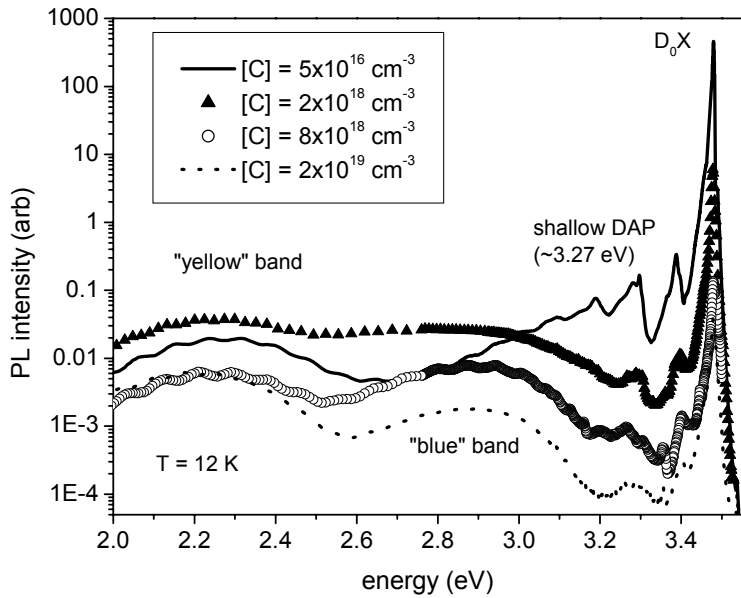25. M.A. Reshchikov, P. Visconti, and H. Morkoç, Appl. Phys. Lett. **78,** 177 (2001).

Figure 1. PL spectra for a series of MBE GaN layers of varying carbon concentration, measured at 12 K and excitation density 20 W/cm^2. The intensity is expressed in the same arbitrary units for all samples.
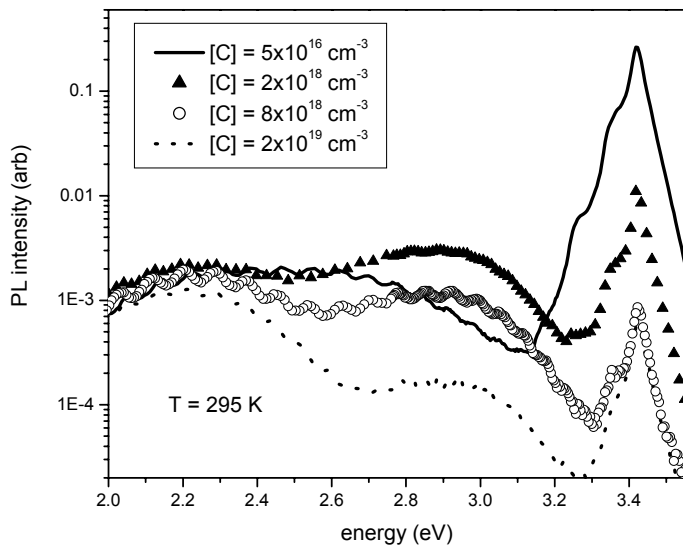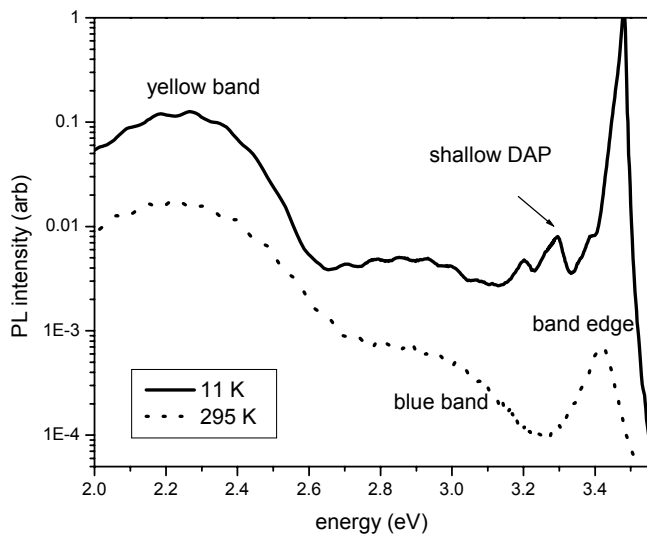

Figure 2. PL spectra for a series of MBE GaN layers of varying carbon concentration, measured at 295 K and excitation density 20 W/cm^2. The intensity is expressed in the same arbitrary units for all samples.

Figure 3. PL spectra at 12 K and 295 K for an MBE GaN layer co-doped with C (1×10^{19} cm^{-3}) and Si (5×10^{18} cm^{-3}). Room-temperature Hall effect measurements indicate a free electron concentration of 1×10^{18} cm^{-3} in the sample.
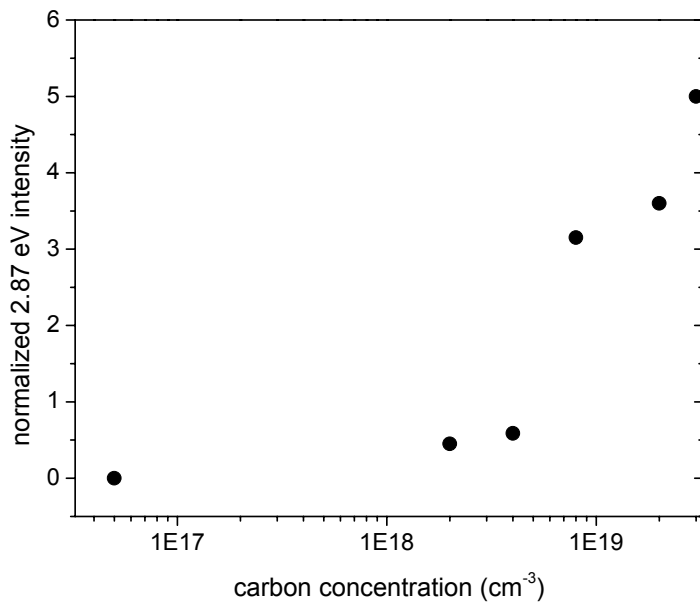
Figure 4. Intensity of the blue band at 12 K normalized to the donor-bound exciton peak intensity for MBE GaN as a function of carbon concentration. Excitation density 20 W/cm^2.
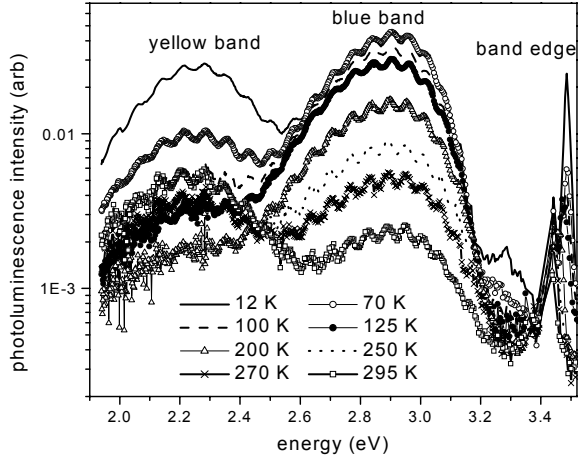
Figure 5. Temperature dependence of the deep level luminescence in MBE GaN with [C] = 4×10^{18} cm^{-3}. Excitation density 20 W/cm^{2}.
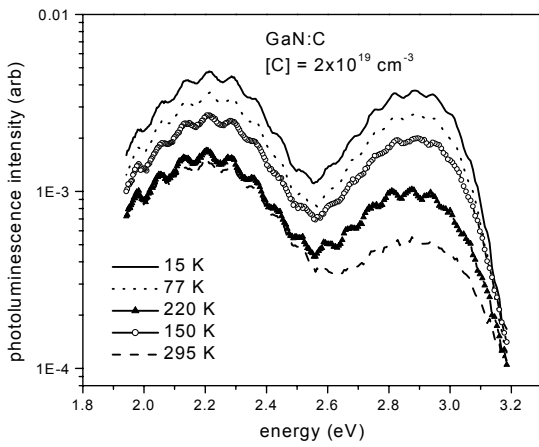
Figure 6. Temperature dependence of the deep level luminescence in MBE GaN with [C] = 2×10^{19} cm^{-3}. Excitation density 20 W/cm^{2}.
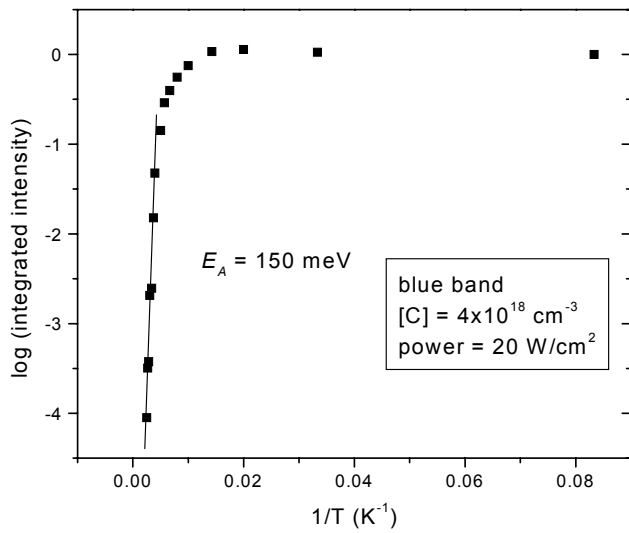
Figure 7. Arrhenius plot of the blue band luminescence intensity in MBE GaN ([C] = 4×10^{18} cm^{-3}). Excitation density 20 W/cm^2.
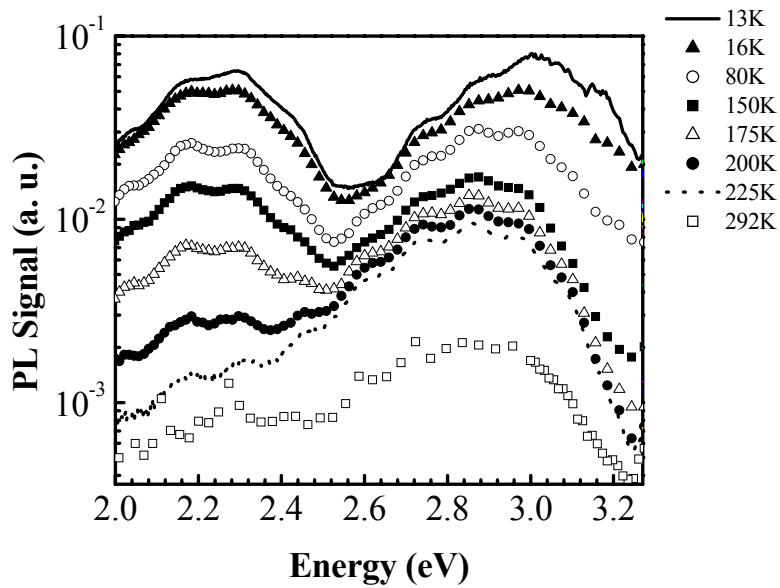

Figure 8. Temperature dependence of the deep level luminescence in semi-insulating MOVPE GaN with [C] = 3×10^{17} cm^{-3}. Excitation density 20 W/cm^2.
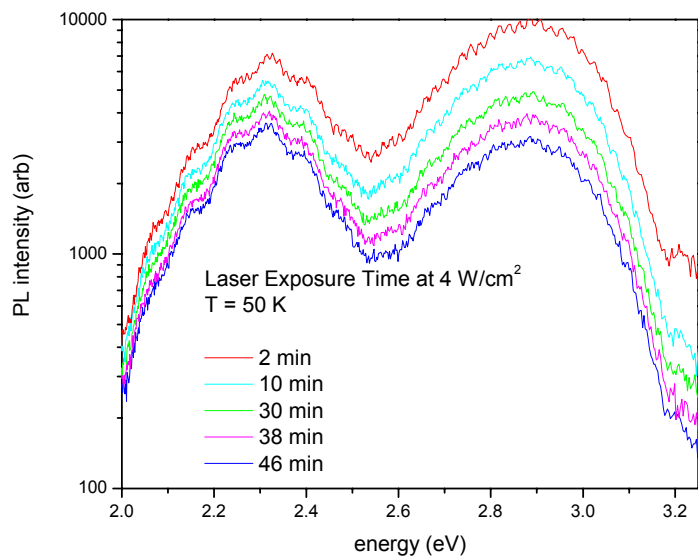
Figure 9. PL spectra as a function of exposure time to the laser for MBE GaN ([C] = 8×10^{18} cm^{-3}). Measured at 50 K and 4 W/cm^2.
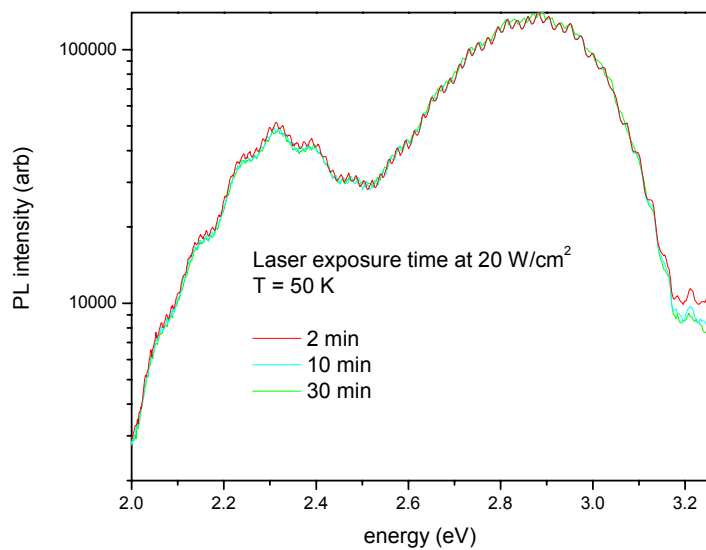

Figure 10. PL spectra as a function of exposure time to the laser for the sample of Fig. 9 measured at 50 K and 20 W/cm^2.
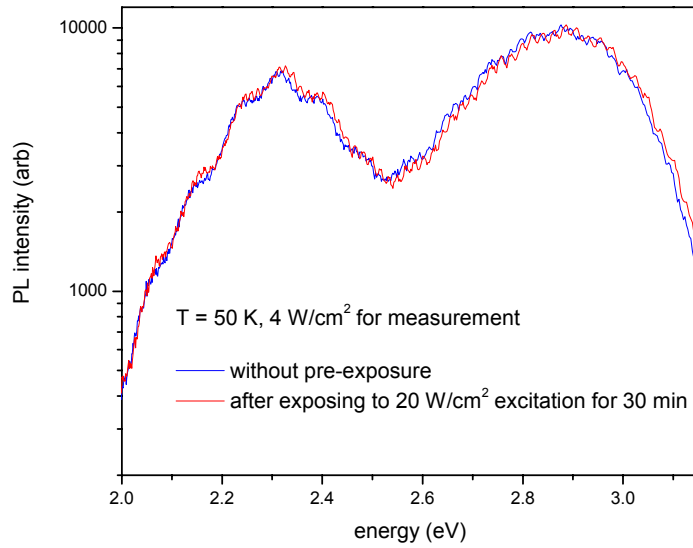
Figure 11. PL spectra for the sample of Fig. 9 measured at 50 K and 4 W/cm^2, with and without 30 min exposure to the laser at 20 W/cm^2 prior to the measurement, as described in the text.
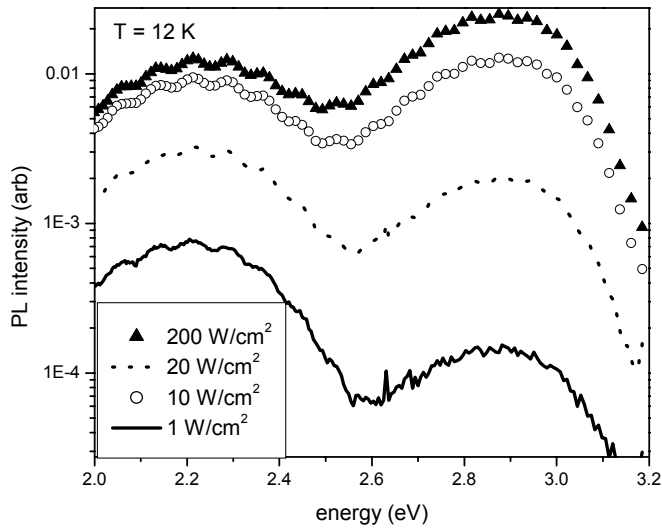

Figure 12. Excitation density dependence of the luminescence spectrum for MBE GaN:C with [C] = 2×10^{19} cm^{-3} measured at 12 K. Qualitatively similar trends with excitation density are observed for different measurement temperatures and different C-doping levels.