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Photoluminescence in wurtzite GaN containing carbon

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ABSTRACT

We studied photoluminescence (PL) from a set of GaN layers grown on sapphire substrates by metalorganic chemical vapor deposition with the concentration of carbon varied by the growth conditions. One of the remarkable features in these samples is the extremely low intensity of the shallow donor-acceptor pair band. Analysis of the PL data gives the shallow acceptor concentration of less than 10^{14} cm^{-3} in most of the C-doped GaN layers. This result shows that C does not form a shallow acceptor, C_N, in appreciable concentrations in wurtzite GaN. As for the YL band, there is no clear correlation between its intensity and the degree of C-doping. The question of identification of the deep acceptor responsible for the YL band in undoped and C-doped GaN still remains to be solved.

INTRODUCTION

While carbon in cubic GaN introduces a shallow acceptor level that is responsible for *p*-type conductivity [1], its role in wurtzite GaN is not well established [2]. Some researchers expect that C introduces a shallow acceptor that may be responsible for the ultraviolet luminescence (UVL) band, also known as the shallow donor-acceptor pair (DAP) band, in unintentionally doped or Si-doped GaN [3,4]. First-principle calculations also predict [5] that C_N is a shallow acceptor with low formation energy in wurtzite *n*-type GaN, especially when Ga-rich conditions of growth are employed, and therefore it may be responsible for the UVL band in GaN. There are many reports that C-doping greatly enhances the yellow luminescence (YL) band (a broad band peaking at about 2.2 eV in the majority of GaN samples) and presumably is involved in the defect responsible for this band [2]. However, the fact that there is no clear correlation between the concentration of C and the intensity of the YL band was also noted [6]. Armitage *et al.* [7] suggested that C-related defects cause the YL band in C-doped GaN while a gallium vacancy is responsible for the YL band in undoped GaN. On the other hand, first-principles calculations of Wright [5] show that the YL band is unlikely caused by a carbon-related defect.

In this work, we studied photoluminescence (PL) from a set of GaN layers grown on sapphire substrate by metalorganic chemical vapor deposition (MOCVD) with concentration of carbon varied by the growth conditions. Our results suggest that concentration of C_N, assumed to be a shallow acceptor in wurtzite GaN [5], is very low. We observed a strong YL band but could not find a correlation between its intensity and concentration of C.

EXPERIMENTAL DETAILS

A set of six GaN layers on *c*-plane sapphire substrates was prepared by EMCORE Corporation and studied by several research groups within the Wood-Witt Initiative “Defects in GaN”. The layers were grown by MOCVD method and contained different amounts of carbon impurity controlled by growth conditions such as growth pressure and growth rate [6,8]. Concentration of carbon has been estimated by the Secondary Ion Mass-Spectrometry (SIMS), and the electrical properties have been evaluated from the Hall effect and electrical conductivity measurements, the results are presented in Table I [9,10].

Table I. Characteristics of GaN samples

Sample #	[C] from SIMS *) (cm^{-3})	Electrical resistivity
EM1256	$(2\text{-}5)\times10^{16}$	Low-ρ
EM0234	Nonuniform **)	High-ρ
EM7053	$(7\text{-}14)\times10^{16}$	High-ρ
EM6881	$(5\text{-}8)\times10^{16}$	SI
EM7169	$\sim1\times10^{17}$	SI
EM7049	$(1.5\text{-}2)\times10^{17}$	SI

*) The data for the depth of 0.1–0.3 μm from the sample surface.
**) Varied from 10^{16} to 3×10^{17} cm^{-3} in different areas of the wafer.

Total concentration of oxygen and silicon, which may create shallow donors in GaN [2], did not exceed ~10^{17} cm^{-3} in all the samples. In the sample EM1256, the electrical resistivity at room temperature was low enough to find the concentration of free electrons, *n*, and estimate the concentrations of the shallow donors and all the acceptors. These values are approximately 2×10^{16}, 6×10^{16}, and 4×10^{16} cm^{-3}, respectively [10]. In semi-insulating (SI) samples, the room-temperature resistivity exceeded 10^8 Ω·cm; therefore, the concentration of free carriers in these samples is apparently below ~10^9 cm^{-3}.

Steady-state PL was excited with a He-Cd laser (325 nm), dispersed by a 1200 rules/mm grating in a 0.3 m monochromator and detected by a cooled photomultiplier tube. A closed-cycle optical cryostat was used for temperatures between 10 and 320 K.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of six GaN samples measured at 10 K and very low excitation intensities. At 10 K, a strong PL peak was observed at 3.480-3.484 eV, having the full width at half maximum (FWHM) of 6 -12 meV in different samples. This peak was assigned to the annihilation of an exciton bound to a neutral shallow donor (the DBE peak). With increasing temperature this peak quenched and, at about 30 K, gave way to the free exciton line, shifted by ~6 meV to higher energies. In all the samples, a relatively strong YL band was observed with the maximum at 2.2 eV (Fig. 1). The UVL band was observed only in one sample (EM0234) at 10 K. In the sample EM1256, the UVL band could be detected at temperatures close to 100 K (Fig. 2), when the exciton emission substantially quenched while the quenching of the UVL band started above 100 K.

In two samples (EM7053 and EM7049) an unstable blue luminescence (BL2) band with the maximum at 3.0 eV was observed. The characteristic feature of the BL2 band, sometimes observed in high-resistivity GaN layers grown by MOCVD method [2,11], is bleaching under UV exposure with concurrent enhancement of the YL band. Previously we proposed that the BL2 band is related to some native defect which disintegrates at low temperatures under UV illumination (recombination-enhanced defect reaction) [12]. In Fig. 1, the spectra for the samples EM7053 and EM7049 are shown before such UV exposure. As a result of the exposure with the

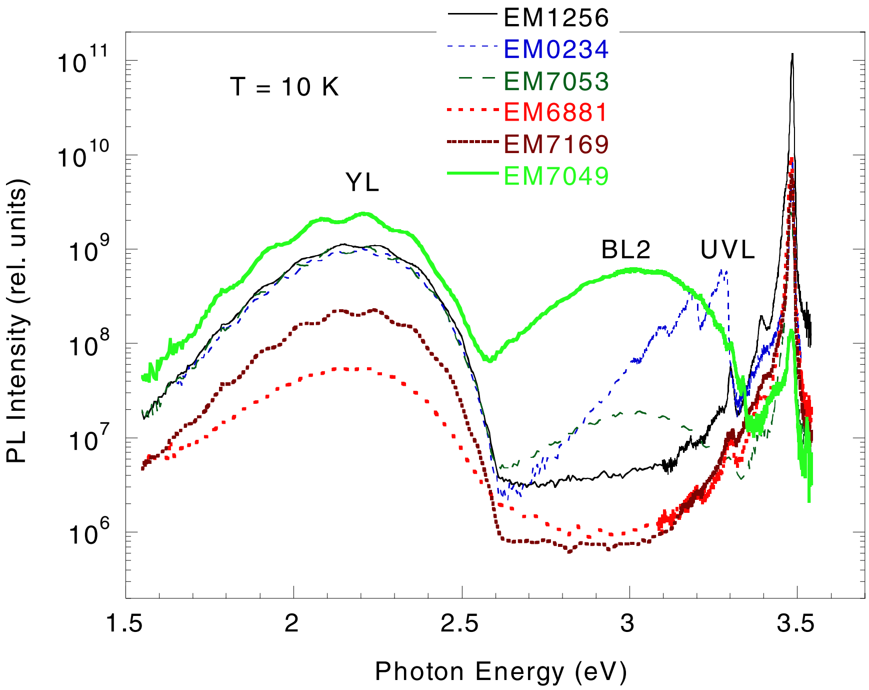

Figure 1. Low-temperature PL spectra of GaN layers containing different concentration of carbon. Excitation power density is 0.01-0.1 mW/cm^2.

power density of 300 mW/cm^2 at 325 nm during 3 hours, the intensity of the BL2 band decreased 4 times and that of the YL band increased by a factor of 1.8 in sample EM7049.

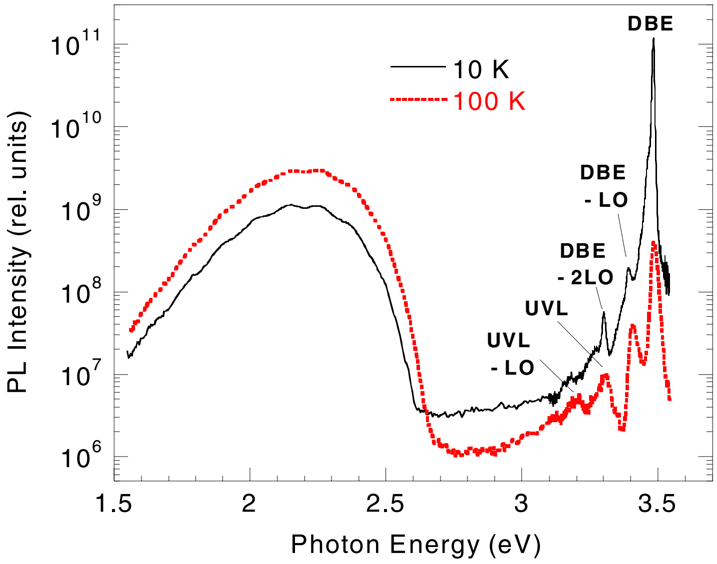

Figure 2. PL spectrum of the sample EM1256 at 10 and 100 K. Excitation power density is 0.1 mW/cm^2. The UVL band can be seen at 100 K with the zero-phonon line at 3.3 eV. The intensity of the YL band increased at 100 K due to holes released from the quenching of the exciton band.

With increasing excitation intensity at 10 K, the YL and UVL bands partially saturated in the excitation power density (P_{exc}) range of 0.01-300 mW/cm^2, while the BL2 band increased nearly linearly, and the exciton emission intensity increased slightly superlinearly with P_{exc} in this range. Figure 3 shows PL spectra for the sample EM0234 at selected P_{exc}. The zero-phonon line of the UVL band in this sample consisted of two peaks: at 3.27 and 3.29 eV at low excitation intensities. With increasing P_{exc} from 0.01 to 300 mW/cm^2 the 3.27 eV peak shifted to higher energies and merged with the 3.29 eV peak.

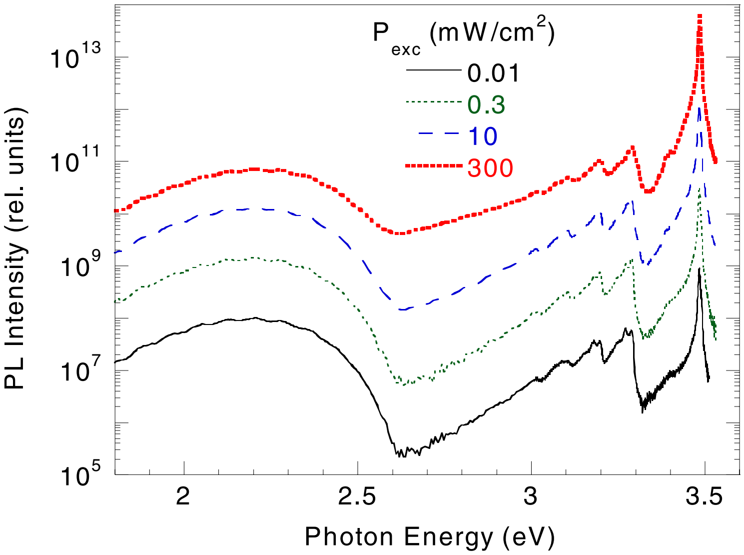

Figure 3. PL spectrum of the sample EM0234 at 10 K measured at different excitation power densities.

Table II presents the values of quantum efficiency (QE) for different recombination channels in the studied samples as determined by comparison of the integrated PL intensity for a particular band with the PL intensity obtained from a calibrated standard sample in the same experimental conditions [13,14].

Table II. Quantum efficiency of different PL bands in GaN samples

Sample \ Band	YL (2.2 eV)	BL2 (3.0 eV)	UVL (3.3 eV)	Exciton
EM1256	2.5→ 0.04% *)	< 0.005% **)	0.01%→ <0.01%	3.4→ 9%
EM0234	2.2→ 0.05%	< 0.01%	0.35→ 0.035%	0.47→ 1.2%
EM7053	2.2→ 0.1%	0.04%	< 0.001%	0.12→ 0.3%
EM6881	0.15→ 0.01%	<0.002%	< 0.001%	0.4→ 0.8%
EM7169	0.6→ 0.03%	< 0.002%	<0.001%	0.3→ 0.6%
EM7049	5→ 0.55%	1.4→ 1.2%	<0.005%	0.03→ 0.6%

*) The arrow indicates variation of QE with increasing P_{exc} from 0.01 to 300 mW/cm^2.
**) The values with the "less" sign give the upper limit for the band not observed in the spectra.

Note that QE for all the PL bands except for the exciton band in the sample EM7049 was independent of P_{exc} below 0.01 mW/cm^2, meaning that none of the recombination channels were saturated with photogenerated holes at such low excitation power. In these conditions, concentrations of acceptors responsible for the defect-related PL bands could be established by the method developed in [13-15] if the time-resolved PL is studied at different temperatures and the dependence of PL intensity on excitation intensity is studied in detail. The results of such detailed studies will be published elsewhere. In this work we only make a rough estimate of relative concentrations of the shallow acceptor responsible for the UVL band, N_{UVL}, and the deep acceptor responsible for the YL band, N_{YL}. Taking the hole capture coefficients for these acceptors as $C_{UVL} = 1\times10^{-6}$ and $C_{YL} = 3\times10^{-7}$ cm^{3}s^{-1}, respectively [2], and using the following expression [13]

$$\frac{N_{UVL}}{N_{YL}} = \frac{I_{UVL}}{I_{YL}} \frac{C_{YL}}{C_{UVL}} , \qquad (1)$$

where I_{UVL} and I_{YL} are the integrated PL intensities of the UVL and YL bands measured at 10 K at $P_{exc} \leq 0.01$ mW/cm^2, we obtain that the N_{UVL}/N_{YL} ratio is 0.0013 and 0.06 in the samples EM1256 and EM0234, respectively, less than 0.002 in EM6881, and less than 0.001 in the rest samples. The concentration of the deep acceptor responsible for the YL band in these samples is presently unknown. However, it is known that the total concentration of all acceptors is 4×10^{16} cm^{-3} in the sample EM1256 and should not exceed ~10^{17} cm^{-3} in other samples, even with the assumption that all carbon atoms formed acceptors (see Table I). Therefore, the concentration of the shallow acceptors in all the samples, except for EM0234, is less than 10^{14} cm^{-3}. Note that the concentration of the deep acceptors responsible for the YL band may be much less than the assumed above value of ~10^{17} cm^{-3}. So, in undoped GaN the deep acceptors with the concentration of (2-7)$\times10^{15}$ cm^{-3} were responsible for the YL band with QE of 2-11% [13]. In this case the concentration of the shallow acceptor should be reduced in the same proportion. The fact that in GaN layers with high a concentration of carbon (of the order of 10^{17} cm^{-3}) the concentration of the shallow acceptor is much less than 10^{14} cm^{-3} is very surprising. Indeed, the theory predicts that C prefers to occupy an N site in wurtzite GaN and acts as a shallow acceptor [5].

The identification of the YL band in C-doped and undoped GaN is another puzzle. Similar to earlier reports [6], we observed no clear correlation between the concentration of C in GaN and the intensity of the YL band. Although the QE of the YL band is high in the studied samples, its typical values in undoped GaN layers are about the same or even higher [13]. Comprehensive research should be carried out on a set of GaN samples in the future, including estimates of the concentration of the deep acceptors responsible for the YL band from PL studies, concentrations of various impurities by SIMS method, and concentrations of vacancy-related defects from positron annihilation spectroscopy [16].

CONCLUSIONS

We studied photoluminescence in a set of six GaN layers grown by MOCVD method on sapphire substrates and containing different concentrations of carbon controlled by growth conditions. Most of the samples demonstrated a strong yellow luminescence band caused by unknown deep acceptor and the absence of the UVL band related to the recombination via the shallow acceptor. From the estimates of the quantum efficiency of different recombination channels, the concentration of the shallow acceptor has been estimated as much less than 10^{14} cm^{-3} in most of the studied samples. This fact allows us to conclude that formation of the shallow acceptor C_N is very unlikely in wurtzite GaN. No clear correlation between the concentration of C and efficiency of the defect-related PL bands could be established. The unstable blue band with the maximum at 3.0 eV was observed in two samples with relatively high concentration of C. The identity of the defects responsible for PL bands in C-doped GaN remains unsolved.

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