Multiphoton photoluminescence from GaN with tunable picosecond pulses

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UV photoluminescence (PL) from GaN thin films was observed by multiphoton excitation. The two-photon PL excitation spectrum near the band gap agrees with the theoretical two-photon-absorption spectrum. The pump-intensity dependence and the PL excitation spectrum in the infrared indicate the existence of midgap defect states around 1 eV above the valence band. This is confirmed by the PL excitation spectrum obtained with a two-color, two-photon excitation process.
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Recently there has been a great deal of interest in the study of wide-band-gap semiconductors, because of their potential applications to electronics and optoelectronics.[1] Among them, GaN particularly has attracted much attention for being the most promising material for construction of blue lasers and blue luminescent devices. The wurtzite GaN crystal has a direct band gap of 3.4 eV at room temperature. Excitations above the band gap usually give rise to a luminescence with two characteristic spectral peaks: one at ~3.35 eV is identified as the band-edge emission, and the other at ~2.3 eV has been assigned to transitions from shallow donor to deep midgap states.[2–4] While linear optical properties of GaN have been studied extensively,[1,5] the reported nonlinear optical measurements are mainly on its second- and third-order nonlinear susceptibilities.[6]

In this paper, we describe our recent experiments on multiphoton-excited luminescence from GaN. With sufficiently intense picosecond pump pulses, even a five-photon-excited luminescence process could be readily observed. The excitation spectrum of the two-photon-excited luminescence reflects directly the two-photon absorption spectrum of GaN for the valence-conduction interband transition if no intermediate resonances are involved. In a measurement with two tunable input beams, however, the two-photon excitation actually exhibited an intermediate resonance at ~1 eV. This provides direct evidence of the existence of midgap states responsible for the yellow luminescence at 2.3 eV.

The GaN sample used in our experiment was grown on the basal plane of a sapphire substrate by the metal-organic chemical-vapor deposition method. A buffer layer (500 Å) of AlN was first deposited on sapphire at 400 °C, and then the wurzite GaN layer was grown on AlN at 1100 °C. The source materials were trimethylaluminum (TMA), trimethylgallium (TMG), and NH_3. The flow rates were 88 μmol/min for TMA, 44 μmol/min for TMG, and 10 L/min for NH_3. The polycrystalline GaN layer was 3.4 μm thick, with an n-type carrier concentration in the low 10^{17} cm^{-3} presumably due to Si impurities and N vacancies.

Our PL experiment was carried out using a high-energy, widely tunable optical parametric generator-amplifier system pumped by the third harmonic of a picosecond-pulsed Nd:YAG (yttrium aluminum garnet) laser.[7] The output wavelength of the system was tunable from 0.4 to 9 μm with a pulse energy up to 300 μJ/pulse, and a pulse duration of about 15 ps. This beam was weakly focused on the room-temperature sample along the optic (hexagonal c) axis with a maximum intensity of 0.5 GW/cm^2 to assure absence of laser damage. Photoluminescence (PL) from the sample was collected and sent through a monochromator to be spectrally analyzed, and finally detected by a photomultiplier and a gated integrator.

The solid curve in Fig. 1 is the PL spectrum of our GaN sample obtained by weak, one-photon excitation at 3.5 eV using the third-harmonic output of the picosecond-pulsed Nd:YAG laser. Similar to those reported in the literature, it consists of a near-band-edge emission peak at 3.35 eV with a shoulder at 3.4 eV (transition from conduction-band-shallow-donor states to valence-band states) and a weak broad yellow luminescence peak centered around 2.3 eV.[2–4] The full width at half maxima of this band-edge emission was 17 nm (150 meV). To see whether multiphoton excitation induces the same luminescence, we also present in Fig. 1 the PL spectra of the band-edge peak obtained with several different pump frequencies. The different curves in Fig. 1 are normalized to the same peak height. They do appear nearly the same, although the peak widths of the multiphoton-

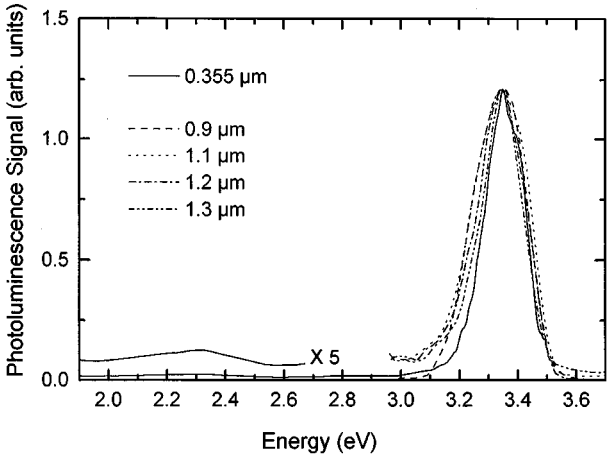

FIG. 1. Photoluminescence spectra of GaN. Solid line is for the above-bandgap (at 3.5 eV) excitation; all the other lines are for multiphoton excitations at different pump wavelengths.

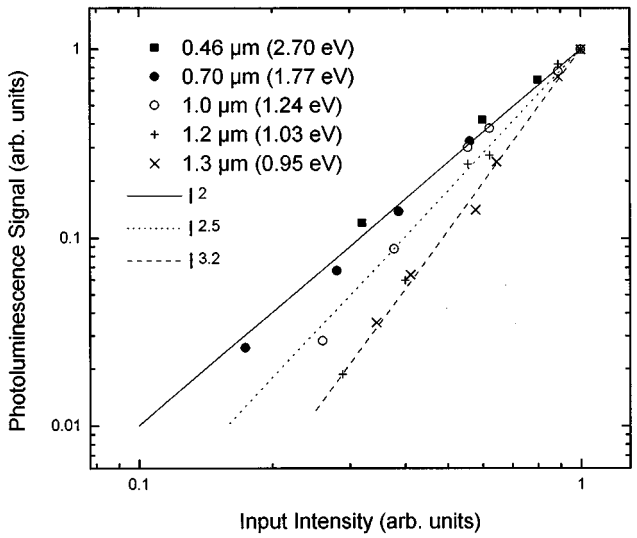

FIG. 2. Intensity dependence of PL with different excitation wavelength. Solid line: I^2. Dotted line: $I^{2.5}$. Dashed line: $I^{3.2}$.

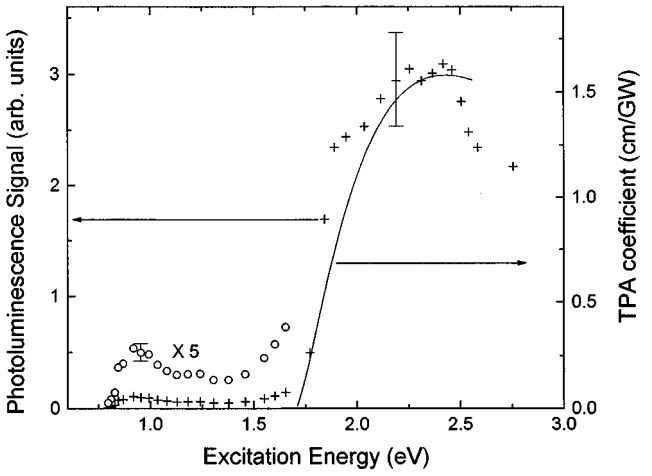

FIG. 3. Photoluminescence excitation (PLE) spectrum of GaN obtained with the pump intensity fixed at 0.3 GW/cm^2. The solid line is a theoretical curve describing two-photon absorption in GaN near the band gap using the parabolic band approximation.

excited PL seem to be somewhat broader mainly because of the poorer monochromator resolution used in the measurement.

We have studied the pump intensity dependence of the multiphoton-excited PL at various pump wavelengths. Figure 2 describes the results of a few selected cases. Here PL was collected through a monochromator set at 370 nm, with a 20-nm passing bandwidth. For pump wavelengths between 0.4 and 0.7 μm (corresponding to 3.1 and 1.77 eV), an I^2 dependence was observed, where I is the pump intensity. This indicates that the excitation was a direct two-photon process as one would expect from the relation $\hbar\omega_p < E_g < 2\hbar\omega_p$, with ω_p being the pump frequency and E_g the band gap. As the pump wavelength increased from 0.75 to 1.1 μm (1.65 to 1.13 eV), the observed pump intensity dependence changed gradually from I^2 to I^3, while the expected dependence from a direct multiphoton-excited PL should be I^3. For a pump wavelength between 1.1 and 1.7 μm (1.13 and 0.73 eV), I^n with $n \geq 4$ is expected for direct excitation, but $I^{3.2}$ was observed. The deviation can be explained if the multiphoton excitation process involves saturable intermediate resonances. This appears to be the case in GaN, as we shall discuss below.

Figure 3 displays the photoluminescence excitation (PLE) spectrum taken with the pump intensity fixed at 0.3 GW/cm^2. In this measurement, PL was again collected through a monochromator set at 370 nm with a 20-nm bandwidth. The most notable feature in the PLE spectrum is the sudden drop when the pump photon energy $\hbar\omega_p$ decreases below $E_g/2 \sim 1.7$ eV as the two-photon excitation changes over to three-photon excitation. We expect that in the range of $\hbar\omega_p < E_g < 2\hbar\omega_p$, the PLE spectrum essentially reflects the two-photon absorption spectrum, assuming that the luminescence efficiency is independent of the excitation. For $2\hbar\omega_p \sim E_g$, from the two-band parabolic approximation we have the following expression for the two-photon absorption (TPA) coefficient for a direct-gap semiconductor;[8]

$$\beta(\omega_p) = K_{pb}\frac{\sqrt{E_p}}{n(\omega_p)^2 E_g^3}\frac{(2x-1)^{3/2}}{(2x)^5} \quad \text{for } x \geq \tfrac{1}{2}$$

$$= 0 \quad \text{for } x < \tfrac{1}{2} \qquad (1)$$

where $K_{pb} = 1940$ cm/GW(eV)$^{5/2}$ is the material independent parameter, $E_p = 2/m|\langle s|p_i|x_i\rangle|^2 = 18$ eV for GaN ($|s\rangle$ and $|x_i\rangle$ are the wave functions of conduction and valence bands, respectively, and p_i is the momentum operator), $n(\omega_p)$ is the index of refraction at ω_p, and $x = \hbar\omega_p/E_g$. The solid curve in Fig. 3 is calculated from Eq. (1) to compare with the observed PLE in the $\hbar\omega_p \geq E_g/2$ region and the fit appears quite satisfactory. The estimated two-photon absorption coefficient for GaN at 2 eV is ~ 1 cm/GW. Given a sample thickness of 3.4 μm as in our case and a laser intensity of 0.3 GW/cm^2, the two-photon absorption is only $\sim 10^{-4}$. This makes a quantitative measurement of two-photon absorption difficult, but, via PLE, the two-photon absorption spectrum can be obtained fairly easily.

For $\hbar\omega_p$ below 1.7 eV, we need at least three photons to excite the electrons above the band gap and, accordingly, PLE decreases by more than an order of magnitude, as shown in Fig. 3. We would expect another drop in PLE as $\hbar\omega_p$ decreases below $E_g/3 = 1.13$ eV, since one more photon is needed to excite the electrons across the band gap. However, the observed PLE actually increases and exhibits a peak at ~ 0.95 eV. After the peak, the PLE decreases rapidly as expected. This suggests that there is an intermediate resonance at ~ 0.95 eV in the multiphoton excitation process. We can actually relate it to the midgap impurity or defect states involved in the emission of yellow luminescence at 2.3 eV often seen from GaN samples.[2–4] Hofmann *et al.*[3] and Perlin *et al.*[4] have investigated the origin of this omnipresent yellow luminescence, and concluded that it is due to transitions from the shallow donor to the deep midgap states. These midgap states should be about 1 eV above the valence-band maximum. Therefore in the multiphoton excitation of photoluminescence, we can expect a resonance enhancement at ~ 1 eV due to transitions from the valence band to these

midgap states. Pump saturation at this resonant step would then make the overall multiphoton excitation process at ~ 1 eV appear to have a pump intensity dependence of $\sim I^3$, as shown in Fig. 2.

To further confirm the existence of these midgap states, we employed a two-photon, two-color excitation scheme instead of the above-mentioned multiphoton excitation scheme. The optical parametric generator-amplifier system we used simultaneously generated two tunable coherent beams of frequencies ω_1 and ω_2, but the sum frequency $\omega_1+\omega_2$ was fixed at 3.5 eV (corresponding to a wavelength of 355 nm), which is slightly above the band gap of GaN. With both ω_1 and ω_2 beams impinging on the sample, the two-photon excited PL was easily observed. Tuning of ω_1 and ω_2 with $\omega_1+\omega_2$ fixed allowed us to scan over possible intermediate resonances without changing the final level of excitation. Indeed, as shown in Fig. 4, the PLE spectrum as a function of ω_1 exhibits a resonance peak at ~ 1 eV. In the experiment, the intensities of the ω_1 and ω_2 beams were about 0.07 and 0.3 GW/cm^2, respectively. With the ω_1 beam alone, the PL was hardly detectable. With the ω_2 beam alone, the PL was less than one-third of the peak value shown in Fig. 4, and no resonant features could be detected throughout the tuning range. The result of Fig. 4 provides direct evidence of the existence of the midgap states at ~ 1 eV above the valence band. The resonant peak width of 145 meV is also comparable with the width of the 2.3-eV yellow luminescence.

In conclusion, we have observed band-edge photoluminescence from GaN with multiphoton excitation using tunable picosecond pump pulses. The PL was easily detectable even with a moderate pump intensity. The pump intensity dependence of the PL becomes more nonlinear as the pump wavelength is increased as expected. The PLE spectrum of single-color, two-photon excitation near the band gap agrees qualitatively with the theoretical two-photon absorption spectrum. The PLE spectrum of four-photon excitation shows a resonant peak at ~ 1 eV. This peak arises from an intermediate resonance due to transitions from the valence band to the midgap defect states. The same resonant transitions are also observed in the two-color, two-photon-excited PLE spectrum.

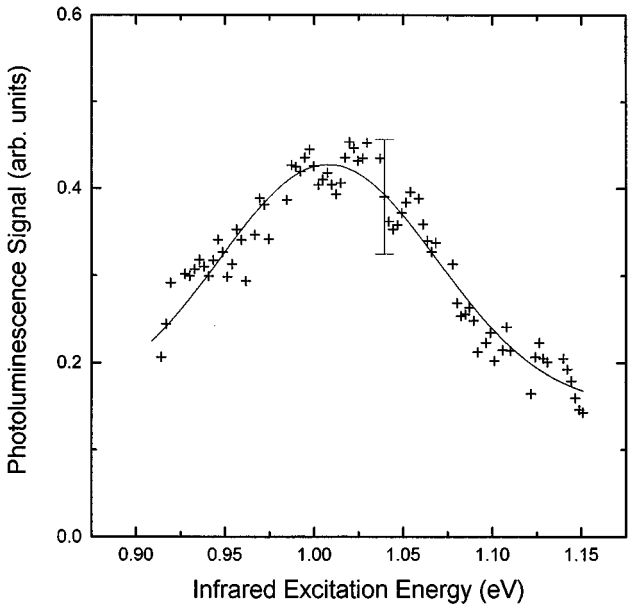

FIG. 4. Photoluminescence excitation spectrum of GaN with two-photon, two-color excitations. Sum of the two photon energies is fixed at 3.5 eV (355 nm), and only the infrared photon energy ($\hbar\omega_1$) is shown as a variable in the plot. The solid line is a Gaussian fit to the data with the peak position 1.0 eV, and a peak width of 145 meV.

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[1] See, for example, S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992); H. Morkoc *et al.*, J. Appl. Phys. **76**, 1363 (1994).

[2] T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2395 (1980).

[3] D. M. Hofmann *et al.*, Phys. Rev. B **52**, 16 702 (1995).

[4] P. Perlin *et al.*, Phys. Rev. Lett. **75**, 296 (1995); T. Suski *et al.*, Appl. Phys. Lett. **67**, 2188 (1995).

[5] J. I. Pankove, H. P. Maruska, and J. E. Berkeyheiser, Appl. Phys. Lett. **17**, 197 (1970); S. Logothetidis, J. Petalas, M. Cardona, and T. D. Moustakas, Phys. Rev. B **50**, 18 017 (1994); W. R. L. Lambrecht, B. Segall, J. Rife, W. R. Hunter, and D. K. Wickenden, *ibid.*, **51**, 13 516 (1995).

[6] J. Miragliotta, D. K. Wickenden, T. J. Kistenmacher, and W. A. Bryden, J. Opt. Soc. Am. B **10**, 1447 (1993); J. Miragliotta and D. K. Wickenden, Phys. Rev. B **50**, 14 960 (1994); **53**, 1388 (1996).

[7] J. Y. Zhang, J. Y. Huang, Y. R. Shen, and C. Chen, J. Opt. Soc. Am. B **10**, 1758 (1993).

[8] C. C. Lee and H. Y. Fan, Phys. Rev. B **9**, 3502 (1974); B. S. Wherrett, J. Opt. Soc. Am. B **1**, 67 (1984); E. W. Van Stryland *et al.*, Opt. Eng. (Bellingham) **24**, 613 (1985); D. C. Hutchings and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 2065 (1992); J. A. Bolger *et al.*, Opt. Commun. **97**, 203 (1993).