Band-gap renormalization in highly excited GaN

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We have studied the band-gap renormalization in highly excited GaN thin films by means of photoluminescence (PL) spectral measurements from 6 to 300 K. The renormalized band-gap energy is determined from the low-energy edge of the broad PL band due to the high-density electron and hole ($e-h$) plasmas. The reduction of the band-gap energy depends on the density of $e-h$ plasmas, but is independent of temperature. The renormalized band-gap energy is calculated using two theoretical models. Our results suggest that the $e-h$ pair correlation plays an essential role in highly excited GaN. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1650552]

In the last decade, blue GaN-based laser diodes and light-emitting diodes have been developed, and these innovations have had large impacts on fundamental research as well as on industrial applications.[1] A great deal of effort has been devoted to clarifying the optical properties of highly excited GaN and III-nitride compounds for the understanding of the stimulated emission mechanism and for the design of lasers with high efficiencies.[2–5] However, much information about the optical phenomena associated with high carrier concentrations is still unclear.

In highly excited semiconductors, the band-gap shrinkage is observed because of the many-body effects in highly dense electron–hole ($e-h$) systems.[6–8] Exchange and correlation energies renormalize the band-gap energy of highly excited semiconductors. The magnitude of the renormalized band gap in narrow-gap semiconductors, such as Si, Ge, and GaAs, is well explained by a universal formula of the Vashishta and Kalia (VK) model.[8] On the other hand, in wide-gap II–VI compound semiconductors with large exciton-binding energies, there are large discrepancies between the experimental observations and the theoretical VK calculations.[9] In some wide-gap semiconductors with an extremely large exciton-binding energy (e.g., ZnO and CuCl), the $e-h$ pair correlation or excitonic effects play an essential role in the band-gap renormalization.[10] Furthermore, it is pointed out that the effect of the LO-phonon coupling becomes important in wide band-gap semiconductors.[11,12] The nature of the band-gap renormalization is unclear in wide band-gap semiconductors.

The determination of the band-gap energy of highly excited GaN is important for the understanding of many-body effects in wide band-gap semiconductors and the development of the optimized III-nitrides optoelectronic devices. The exciton-binding energy E_b and the exciton Bohr radius a_B of an A exciton of GaN are ~25 meV and ~3 nm, respectively,[13,14] and the exciton-binding energy of GaN is between those of GaAs and ZnO. In this work, we have measured photoluminescence (PL) spectra under intense femtosecond laser excitation at 6–300 K and determined the renormalized band-gap energy from the broad PL due to the $e-h$ plasmas (EHPs). From the comparison between the experimental and theoretical results in GaN, the effects of the $e-h$ pair correlation and the strong electron–LO–phonon coupling will be discussed.

All samples in this work were fabricated by a metalorganic chemical vapor deposition method. These samples were grown on 5 μm GaN epitaxial layers with the 25 nm buffer layers on sapphire *c*-plane (0001) substrates. Femtosecond laser pluses (wavelength: 333 nm; pulse width: 130 fs; repetition rate: 1 kHz) were used as an excitation source. The PL spectra were measured at 6–300 K using a liquid-nitrogen-cooled charge-coupled device with a 50 cm single monochromator. The excitation spot size was precisely determined using a knife-edge method. In addition, the value of 6×10^4 cm^{-1} is used as the absorption coefficient of GaN at 333 nm and at 6 K, where in Refs. 15–18 different values have been experimentally reported for the absorption coefficient (2.6×10^4–1×10^5 cm^{-1}). In our experiments, the excitation laser energy density was varied from ~1 nJ cm^{-2} to ~1.4 mJ cm^{-2} that corresponds to the carrier density from ~7.9×10^{13} to ~1.1×10^{20} cm^{-3}, where the reflectivity is ~0.2.[14] The A-exciton energy under cw Xe-lamp excitation was determined from the photoreflectance (PR) measurements at various temperatures. For PR measurements, the reflectance signals were modulated under a 325 nm He–Cd laser chopped at 210 Hz and detected by a Si photodiode with a lock-in amplifier.

Figure 1(a) shows the PL and PR spectra of GaN thin films at 6 K, where the $e-h$ pair density (n_{e-h}) is 1.1×10^{20} cm^{-3}. The PR spectrum shows that free *A*-4 (E_{XA}) and *B*-exciton energies (E_{XB}) of our samples are 3.493 and 3.502 eV at 6 K, respectively. Under intense laser excitation, PL bands appear at low energy below the free *A* exciton, as shown in Fig. 1(a). It is concluded that the sharp PL band at 3.486 eV and the broad PL band at 3.474 eV are the biexciton emission (*M* line) and the *P* line, respectively, because the binding energy of biexciton is 5.7 meV,[19,20] and the P_2-line energy is given by $E_{XA}-(3/4)\,E_b$.[21] In addition, we have found a broad PL band near 3.40 eV.

In order to discuss the origin of the broad PL band, PL

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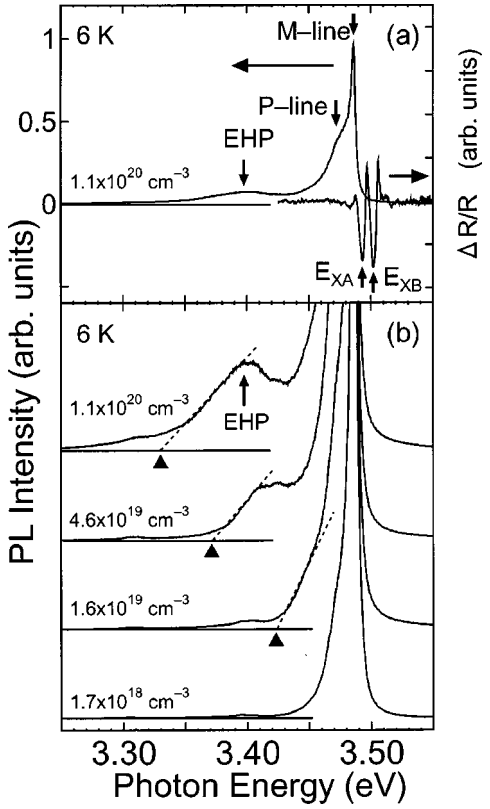

FIG. 1. (a) PL spectrum of highly excited GaN at $n_{e-h}\sim 1.1\times 10^{20}$ cm^{-3} at 6 K. Three different PL bands (M line, P line, and EHP) are shown. The PR spectrum of GaN at 6 K is also shown. The exciton energies, E_{XA} and E_{XB}, are determined from the PR spectrum. (b) Low-energy tail of the broad PL band at different n_{e-h} in GaN at 6 K. The triangles show the estimated renormalized band gap of highly excited GaN.

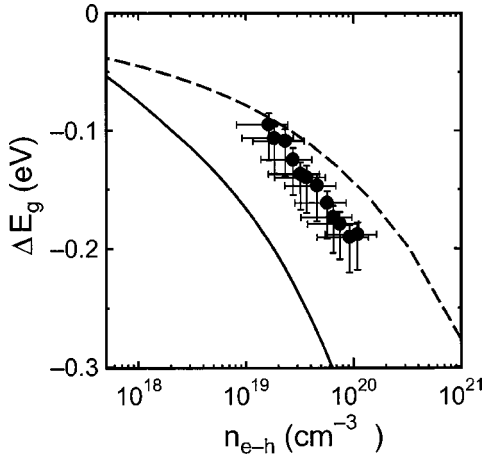

FIG. 2. Shrinkage of the band gap as a function of n_{e-h} in GaN at 6 K. The broken and solid lines are numerical calculations for GaN based on Refs. 8 and 10, respectively.

spectra in the low energy region at different carrier densities are shown in Fig. 1(b). Below $n_{e-h}\sim 1.7\times 10^{18}$ cm^{-3}, the broad band is not clearly observed in our experimental conditions. For n_{e-h} above 1.6×10^{19} cm^{-3}, the broad PL band appears below the P line, and its peak position shifts toward the lower energy with increasing n_{e-h}. The Mott density for GaN (Ref. 7) is roughly estimated by $\sim(\frac{4}{3}\pi a_B^3)^{-1}=\sim 1\times 10^{19}$ cm^{-3}. Therefore, the broad PL band observed under high excitation is due to the EHPs. The renormalized band-gap energy can be determined from the low-energy edge of the broad PL band due to the EHPs. In Fig. 1(b), the broken line is a straight line along the lower energy tail of the PL band from EHPs. The crossing point between the broken line and the base line [closed triangles in Fig. 1(b)] gives the experimentally determined renormalized band-edge $\tilde{E}_g$.

Figure 2 shows the band-gap shrinkage ($\Delta E_g=\tilde{E}_g-E_g$) of GaN at 6 K as a function of n_{e-h}. The closed circles with error bars are experimental data. The solid line is given by the numerical calculation of the self-energy of the $e-h$ pair Green function given in Ref. 22, where the $e-h$ pair correlation is taken into account. On the other hand, the broken line is given by the VK theory where the $e-h$ correlation is neglected. In both calculations, we only need two parameters: E_b and a_B. We find that the magnitude of the ΔE_g determined from the experiment is between the solid and broken lines. In narrow band-gap semiconductors with large exciton Bohr radius, such as Si, Ge, and GaAs, the band-gap shrinkage is known to be well described by the VK theory, whereas for wide band-gap II–VI semiconductors the considerable deviation between experimental data and the VK theory has been reported in Ref. 9. On the other hand, on the order of 10^{19} cm^{-3}, the n_{e-h} dependence of ΔE_g in the solid line is larger than that in the broken line. The n_{e-h} dependence of ΔE_g in the solid line is consistent with the experimental observation. In addition, it is believed that the estimated carrier density in this work is overestimated, because we assume that the created carrier density is equal to the incident photon density. Further experiments are needed for the evaluation of the carrier density. It is pointed out that in GaN the Coulomb effect is important in optical gains at high carrier densities.[3] Therefore, it is believed that the $e-h$ pair correlation plays an essential role in highly excited GaN.

Figure 3(a) shows the temperature dependence of the PL spectra for $n_{e-h}=7.9\times 10^{19}$ cm^{-3}. The band-gap energies E_g for various temperatures are defined as $E_g=E_{\mathrm{XA}}+E_b$, and are shown by the triangles in Fig. 3(a), where E_{XA} at various temperatures were determined from the PR spectroscopy. In low temperatures, a sharp PL band due to the M line is observed. At temperatures above 70 K, the M line disappears and the P line predominates at the high-energy side of the spectrum. In the low-energy component of the PL spectra, we have found the emission from the EHPs. The renormalized band-gap energies are shown by the upward arrows in Fig. 3(a). In higher temperatures, the EHP emission is clearly pronounced, and the P line exhibits the thermal broadening. With an increase of temperature, the peak position of the EHP band shifts toward the lower energy. We have also found a redshift of the band-gap energy at low excitation intensities with increasing temperature, and the band-gap renormalization is almost independent of temperature.

We show in Fig. 3(b) the magnitude of ΔE_g as a function of temperature. The $e-h$ pair density is set to be $n_{e-h}\sim 7.4$–7.9×10^{19} cm^{-3}. The band-gap renormalization is almost independent of temperature between 6 and 300 K within experimental errors. Similar temperature-independency of ΔE_g is also observed for $n_{e-h}\sim 3.9\times 10^{19}$ cm^{-3}. Since GaN is a polar semiconductor, the LO–phonon coupling between carriers is strong. Therefore the difference between the carrier and the lattice temperatures is

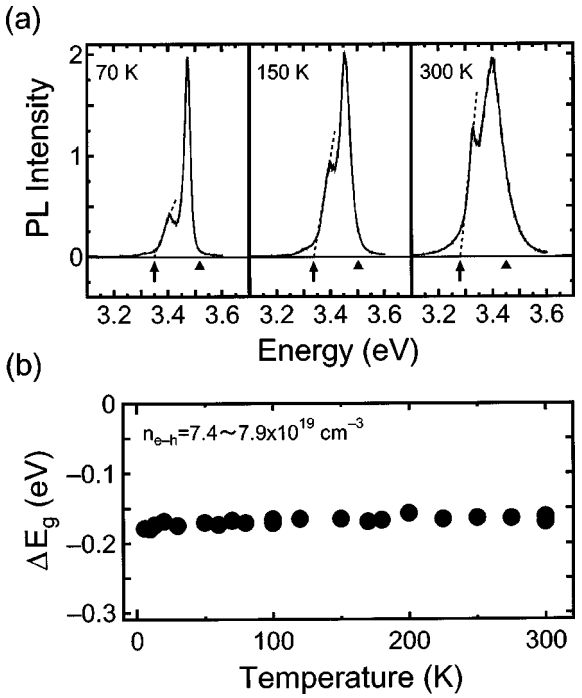

FIG. 3. (a) Temperature dependence of PL spectra at $n_{e-h}\sim 7.9\times 10^{19}$ cm^{-3}. The triangles show the band-gap energy ($E_{XA}+E_b$) determined by the PR measurements. The upward arrows show the renormalized band-gap energy. (b) Shrinkage of the band gap as a function of temperature under a certain density $n_{e-h}\sim 7.4-7.9\times 10^{19}$ cm^{-3}.

small compared to the case of more covalent semiconductors such as GaAs. In polar semiconductors such as GaN, the strong coupling between excitons and LO–phonons stabilizes the EHP state via plasma–phonon mixed states, which is similar to polaron-like states. In this case, the strong coupling between excitons and LO–phonons is known to contribute to the band-gap shrinkage.[11,12] Unfortunately, the magnitude of the band-gap reduction due to the plasma–phonon interaction cannot be calculated numerically. On the other hand, the strong exchange interaction due to the excitonic correlation effect also leads to the large band-gap shrinkage as mentioned earlier (the solid line in Fig. 2). The strong exchange interaction due to excitonic correlation is independent of temperature in high density conditions.[23] The temperature independence of the band-gap renormalization, as shown in Fig. 3(b), implies that the excitonic correlation effect plays the essential role in GaN. Further theoretical studies are needed to clarify the origin of deviation between experimental results and theoretical calculations for band-gap renormalization of GaN.

In conclusion, we have experimentally and theoretically studied the carrier-density and the temperature dependence of the band-gap renormalization of GaN. The shrinkage of the band-gap energy depends strongly on the density of EHPs, but is independent of temperature. It is pointed out that the $e-h$ pair correlation or exciton effects predominate in electronic processes in highly excited GaN.

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