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Photoluminescence dynamics of GaN under intense band-to-band and exciton resonant excitation

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We have studied the dynamics of highly dense exciton and electron-hole (*e-h*) systems in GaN by means of optical Kerr-gate time-resolved photoluminescence (PL) spectral measurements. In high-density *e-h* pairs above the Mott density, the broad electron-hole plasma emission appears at first, and then the narrow PL due to the biexciton and the inelastic exciton-exciton scattering is observed. When the pump light resonantly excites the *A* excitons, highly dense *e-h* systems with low effective temperatures are formed, and unique PL bands are observed. These PL peaks can be explained by a picture that the *A* excitons are scattered into the *A*, *B*, and *C* bands.

Recently, the development of wavelength-tunable femtosecond laser systems and remarkable progress in semiconductor crystal growth have enabled us to study intrinsic optical processes and dynamics in wide-gap semiconductors. GaN and III-nitride compounds are key materials for fundamental semiconductor physics and also for blue and ultraviolet optoelectronic devices.[1] Because of the large exciton binding energy, highly excited GaN provides us an excellent stage for the study of the excitonic many-body effects in semiconductors. With an increase of the excitation laser intensity, the exciton density exceeds the Mott transition density, and the exciton state turns to the electron-hole plasma (EHP) state.[2] In highly excited GaN, the band-gap shrinkage and the broad EHP emission are observed because of the many-body effects in dense electron-hole (*e-h*) systems.[3–6] It is pointed out that in wide-gap GaN the *e-h* pair correlation effect play an essential role in optical gains and electronic processes.[6–8] However, the dynamical behaviors of highly dense excitons and *e-h* systems in GaN are not clear.

Time-resolved photoluminescence (PL) spectral measurements are one of the most useful methods for understanding the dynamics of highly dense excitons and *e-h* systems. In GaN thin films, the PL dynamics have been studied only under the band-to-band excitation.[3–6] Under the band-to-band excitation, the photogenerated *e-h* systems are "hot" because of large excess energy. On the other hand, the exciton resonant excitation produces "cold" *e-h* systems with low effective carrier temperatures.[9,10] The low-temperature and high-density *e-h* systems provide essential information on the collective effects and excitonic processes in highly excited semiconductors.[9–12] In this work, we report the PL dynamics of highly excited GaN at low temperatures, and the dynamical behaviors of highly dense excitons and *e-h* systems are discussed through the comparison of time-resolved PL spectra between the band-to-band and the *A*-exciton resonant excitations. Under the exciton resonant excitation, unique exciton-related PL bands are clearly observed, and the origin of the PL bands is discussed.

The samples used in this work were fabricated by the metal organic chemical vapor deposition (MOCVD) method. The thickness of the GaN epitaxial layer was 5 μm, grown on a sapphire *c*-plane substrate with a 25-nm GaN buffer layer. We determined that the transition energies of *A*, *B*, and *C* excitons in our samples are 3.493, 3.502, and 3.516 eV, respectively, by means of photoreflectance measurements at 6 K.[6]

Wavelength-tunable femtosecond laser pulses were obtained from an optical parametric amplifier system based on a regenerative amplified mode-locked Ti:sapphire laser. The pulse duration and the repetition rate were ~150 fs and 1 kHz, respectively. For time-resolved PL spectral measurements, an optical Kerr gate method was used with toluene as a Kerr medium in a quartz cell having 1-mm thickness. The time resolution was about 0.7 ps. The excitation photon energies for the band-to-band and the *A*-exciton resonant excitations were tuned to 3.723 and 3.493 eV, respectively. The PL spectra were measured as a function of the delay time, using a liquid-nitrogen-cooled charge-coupled device (CCD) with a 50-cm single monochromator. The sample temperature was kept at 6 K.

Figure 1 shows time-resolved PL spectra of GaN thin films under the band-to-band excitation (3.723 eV) at different excitation intensities: (a) 8, (b) 130, and (c) 380 μJ/cm². Under weak excitation of 8 μJ/cm², a PL band appears at ~3.486 eV. Similar PL bands appear under higher excitation intensities at several tens of picoseconds or more as shown in Figs. 1(b) and 1(c). The spectral shape of these PL bands can be fitted by an inverse-Boltzmann function,[13] which is char-
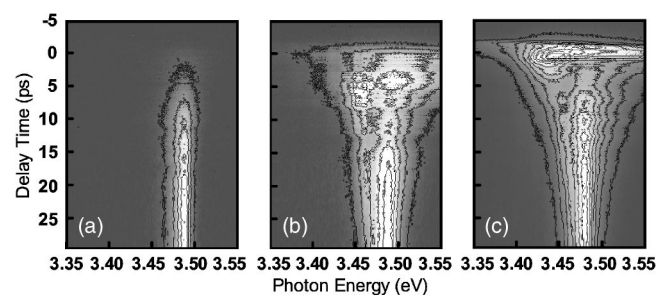

FIG. 1. Time-resolved PL spectra of GaN thin films at 6 K under the band-to-band excitation (3.723 eV). Excitation densities are (a) 8, (b) 130, and (c) 380 μJ/cm².
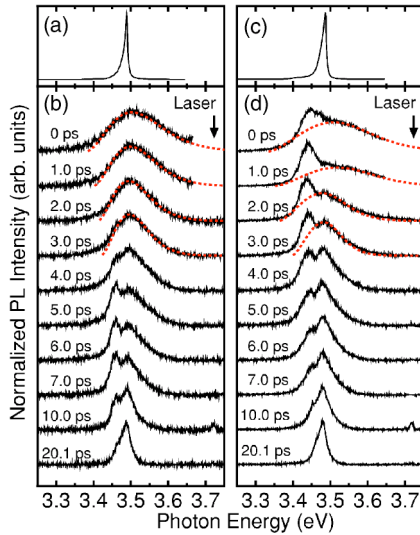
FIG. 2. (Color online) Temporal changes of the PL spectra of GaN thin films under the band-to-band excitation (3.723 eV). The excitation densities are (a,b) 130 and (c,d) 380 μJ/cm^2. Time-integrated PL spectra are shown in (a) and (c). The broken curves are fitting using a non-k-conservation model.
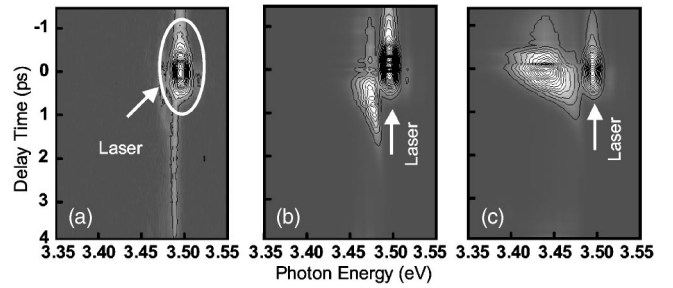

FIG. 3. Time-resolved PL spectra of GaN thin films at 6 K under the A-exciton resonant excitation (3.493 eV). Excitation densities are (a) 7, (b) 110, and (c) 330 μJ/cm^2.

acteristic for the spectral shape of the biexciton emission. In addition, the energy difference between the 3.486-eV PL peak and the 3.493-eV A-exciton peak is consistent with the biexciton binding energy of $\sim$6 meV.[14,15] Therefore, it is concluded that this PL band is due to the biexciton emission (so-called M line). Because the exciton density is still high in the observed time region, a PL band due to the A exciton was not observed.

Under high excitation intensities above 100 μJ/cm^2, the broad PL band appears just after the laser excitation, as shown in Figs. 1(b) and 1(c). The peak energy of the broad emission shifts towards lower energy with an increase of the excitation intensity. It is considered that the broad emission is attributed to the EHPs. The M-line emission appears around 3.486 eV at >5 ps. The appearance of the M line suggests that the e-h pair density rapidly decreases below the Mott density, and the exciton dynamics determines the PL properties. The EHP signal disappears rather fast ($\sim$4 ps). The average lengths of the diffusion for electrons and holes at $t=4$(ps) are $(Dt)^{1/2}=100$ and 45 nm, respectively, where D is the diffusion coefficients, which are 25 and 5 cm^2/s for electrons and holes for GaN, respectively.[16] Since the penetration depth at 3.723 eV is about 100 nm, the decrease of electron-hole density by the diffusion is by a factor of $1/2$, and it is not negligible small. Consequently, the carrier diffusion process as well as radiative and nonradiative recombination of EHP causes the rapid disappearance of the EHP emission.

Figure 2 shows temporal changes of the PL spectra at 6 K under the band-to-band excitation: The excitation densities are (a, b) 130 and (c, d) 380 μJ/cm^2. The time-integrated PL spectra are shown in Figs. 2(a) and 2(c). It is known that the spectral shape of spontaneous EHP emission can be described by the non-k-conservation model, where the k-selection rule for optical transitions is assumed to be bro-

ken in highly dense e-h systems.[17,18] In this calculation, the spectral shape of the EHPs is determined by the renormalized band-gap energy $(\widetilde{E_g})$, the e-h pair density $(n_{e\text{-}h})$, and the effective electron temperature (T_e). The experimental data at short delay times within 3 ps can be fitted very well by this model, shown by the broken curves in Figs. 2(b) and 2(d).[19] When the excitation density is 380 μJ/cm^2, $n_{e\text{-}h}$ estimated from the above-mentioned spectral shape calculation is 4×10^{19} cm^{-3} at 0 ps. We also calculated it using absorption coefficient $(6\times10^4$ cm$^{-1})^6$ and reflectivity (20%).[20] The calculated value is 3.1×10^{19} cm^{-3}, which is almost the same as that we estimated from the spectral shape calculation. These results indicate that the broad emission is attributed to the spontaneous emission of EHPs. In addition, in Fig. 2(d), the narrow PL band is superimposed on the broad EHP emission within $\sim$3 ps. This is due to the stimulated emission of EHPs, because the peak energy of the narrow superimposed PL band agrees with that of the optical gain spectrum.[21]

In Fig. 2(b), at the delay time between 5 and 10 ps, a peak appears below the M-line emission energy. It is believed that this emission is due to the exciton-exciton scattering (so-called P line) emission,[22] whose details will be discussed later. Under the band-to-band excitation, time-resolved PL studies show that the EHP emission appears just after the laser excitation and sequentially the exciton-related PL bands appear with delay time. However, the band-to-band excitation produces high-temperature e-h systems. The thermal broadening due to high electron temperatures leads to ambiguous discussions. Rather, we can clearly observe the change of the EHP state to the exciton state and the exciton-related PL in low-temperature e-h systems formed by the A-exciton resonant excitation.

Figure 3 shows the time-resolved PL spectra under the A-exciton resonant excitation (3.493 eV) at (a) 7, (b) 110, and (c) 330 μJ/cm^2. Under the A-exciton resonant excitation, the scattering of the laser light appears around 0 ps delay time. In Fig. 3(a), the M line at 3.486 eV appears at the delay time of about 2 ps. With an increase of the excitation density, at around 0 ps delay time the broad PL band due to the EHPs appears at $\sim$3.45 eV, and the peak energy slightly shifts to the higher energy with delay time.

Figure 4 shows temporal changes of the PL spectra under the A-exciton resonant excitation at 330 μJ/cm^2. The integrated PL spectrum is shown in Fig. 4(a). With an increase of the delay time, the broad emission due to the EHPs continu-
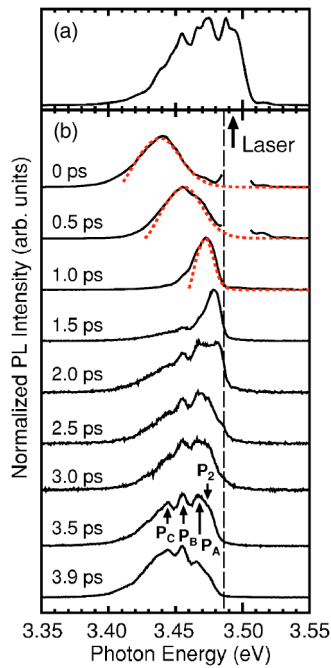
FIG. 4. (Color online) Temporal changes of PL spectra of GaN thin films under the A-exciton resonant excitation (3.493 eV). The excitation density is 330 μJ/cm^2. Time-integrated PL spectra are shown in (a). The broken curves are fitting using a non-k-conservation model.

ously shifts to the M-line peak energy, where the M-line energy is indicated by the dashed line in the figure. The broken curves are calculated spectra using the non-k-conservation model.[17,18] There is a good agreement between the experimentally observed and theoretically calculated PL spectra. Surprisingly, the spectral shape of the PL band drastically changes after ~2 ps, i.e., a few new PL peaks appear below the M-line energy. Three PL peaks appear at 3.468, 3.456, and 3.445 eV, and these are indicated by P_A, P_B, and P_C, respectively. In addition, we also observed a shoulder at higher energy of P_A line, which is denoted by P_2. Since the EHP emission disappears at ~3.5 ps, n_{e-h} decreases below the critical density of the exciton Mott transition.

In extremely weak excitation condition, the PL band due to the bound exciton was observed. Since the density of the impurities is finite, the number of the bound excitons is saturated with increasing excitation density. Thus, free-exciton-related PL bands, such as free-exciton, M and P lines, emerge. In highly dense exciton states, inelastic exciton-exciton scattering processes contribute to the PL spectra. In inelastic exciton scattering processes, two $n=1$ excitons are scattered, and one of them is excited to higher energy exciton states such as $n=2,3,\ldots\infty$, while the other is scattered into a photonlike state.[2] The emission due to the photonlike state appears at lower energy of A exciton, which corresponds to the energy difference between the high-energy scattered exciton states and the $n=1$ exciton state. When the exciton is scattered into the $n=2$ A-exciton state, the P line appears at 3.474 eV, where exciton binding energy is 25 meV.[20] When the exciton is scattered into the $n=\infty$ state (i.e., the continu-
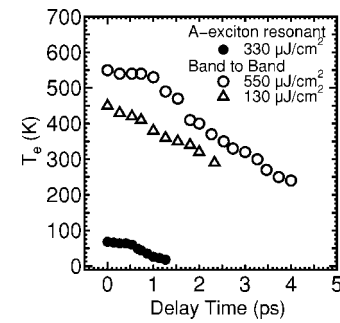

FIG. 5. Effective electron temperature (T_e) as a function of the delay time. Open circles and triangles are under the band-to-band excitation, and solid circles are under the A-exciton resonant excitation. The excitation intensity is shown in the figure.

ous A band), the P line appears at 3.467 eV. These values agree with the energies of P_2 and P_A. We denote the scattering process for the P_A-line as $2X_A \rightarrow A + P_A$, where the A-exciton state is indicated as X_A. In addition, there are two PL peaks (P_B and P_C) at the lower energy side. It is possible that the $n=1$ A exciton is scattered into the other bands such as the B and C bands. If the binding energies of the B and C excitons are almost the same as that of the A exciton, the peak energies of P lines due to the scattering into the B and C bands are 3.458 and 3.444 eV. Here the energy differences between the A and B bands and between the A and C bands are 9 and 23 meV, respectively. These values are approximately consistent with the energies of the P_B and P_C bands. Hence, it is concluded that the P_B and P_C bands originate from the P line due to the scattering of the $n=1$ A exciton into the B and C bands. These processes can be expressed as $2X_A \rightarrow B + P_B$ and $2X_A \rightarrow C + P_C$, respectively. This is a clear observation of the inelastic scatterings of excitons into different bands in GaN. These PL bands are not resolved in the time-integrated PL spectrum of Fig. 4(a). By using time-resolved PL spectroscopy they are clearly distinguished. There is no theoretical study on the inelastic A-exciton scattering processes into other bands, and it is difficult to discuss the selection rules in highly dense exciton systems at present. This point is under discussion in this field.[8]

From the fitting of spontaneous EHPs emission spectra shown by the broken curves in Figs. 2(b), 2(d), and 4(b), effective electron temperature T_e can be obtained. Figure 5 shows T_e as a function of the delay time. The open circles and triangles show the T_e at the excitation intensity of 550 and 130 μJ/cm^2 under the band-to-band excitation. The solid circles show the T_e at 330 μJ/cm^2 under the A-exciton resonant excitation. Under the band-to-band excitation, T_e rises to ~500 K just after the laser excitation. On the other hand, T_e is only ~70 K under the A-exciton resonant excitation, and is much lower than that under the band-to-band excitation, because the excess energy of the excitation photon is small in the case of the resonant excitation. Moreover, under the A-exciton resonant excitation, the increase of the lattice temperature is smaller, and T_e becomes ~20 K after ~1.5 ps, as shown in Fig. 5. When we estimated the P-line energy after ~3.5 ps in Fig. 4, we assumed that the T_e was 6 K. From Fig. 5, it is considered that this assumption is reasonable. Here, we should note that the exciton binding en-

ergy is 25 meV, which means that exciton is stable below ~ 290 K.[23] The temperature T_e is well below it even at 0 ps under the resonant excitation. Therefore, highly dense and cold excitons were created under the resonant excitation, and PL lines, P_B and P_C, were able to be observed. In the band-to-band excitation, however, the thermal broadening due to the high T_e hinders the fine structures in the PL spectra.

In conclusion, we have studied the PL dynamics of highly dense e-h and exciton systems near the Mott density under the band-to-band and the A-exciton resonant excitations in GaN. Under the band-to-band excitation, the effective electron temperature is high, and broad electron-hole plasma and exciton-related emissions were observed. Under the A-exciton resonant excitation, the emissions due to inelastic scattering of the $n=1$ A exciton into the A, B, and C bands appeared after several picoseconds. The detailed optical processes in highly excited GaN were revealed by time-resolved PL spectra of cold e-h systems formed by the A-exciton resonant excitation.

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