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Ultrafast decay of photoluminescence from high-density excitons in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals: Diffusive propagation of exciton-polaritons

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We report on the ultrafast decay dynamics of photoluminescence (PL) in highly excited $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals under exciton resonant excitation at low temperatures. When the excitation intensity is increased, the P-band emission appears due to exciton-exciton inelastic scattering processes. The PL intensity of the P band decays rapidly, with a much shorter decay time than the radiative recombination time of the excitons. We show that the ultrafast PL decay dynamics can be understood as due to the disorder-induced diffusive propagation of photonlike exciton-polaritons in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals.

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Random potential fluctuations in mixed crystals or alloy disorders, strongly affect the optical spectra and photoluminescence (PL) dynamics of excitons. In semiconductor mixed crystals, the localization of excitons¹⁻³ and biexcitons⁴⁻⁸ occurs in random-potential fluctuations induced by compositional fluctuations in mixed crystals. In GaN-based wide-gap semiconductors, the many-body effects of excitons and exciton-photon interactions play essential roles in the optical responses due to their large exciton binding energies and oscillator strengths. Because their optical properties can be controlled by changes in their compositional fraction, GaN-based mixed crystals make excellent samples for studying the exciton-exciton and exciton-photon interactions in random potentials.

In highly photoexcited GaN-based semiconductors, PL due to exciton-exciton inelastic scattering (P-band emission) appears,⁹⁻¹¹ where one exciton is scattered into an exciton-like polariton state and the other into a photonlike (lower) polariton state with energy and momentum conserved.¹² P-band emission is closely related to exciton-polariton formation in semiconductor solids, but thus far, the dynamics of P-band decay has been unclear. Moreover, exciton-polariton formation is related to slow light propagation in semiconductors. The control of light propagation has been widely studied in a variety of semiconductors.¹³⁻²⁰ In disordered materials, multiple photon scattering leads to light diffusion, and light propagation is in connection with weak localization and coherent backscattering of light.²¹⁻²⁴ In GaN crystals, bound exciton states due to inevitable impurities cause multiple photon scattering.¹³ In mixed crystals, on the other hand, material properties and potential fluctuations can be controlled by changing their composition fraction. In disordered potentials in mixed crystals, the composition-dependent localization of excitons and biexcitons would affect significantly the exciton-polariton propagation, and cause unique optical responses, different from those of binary and elemental semiconductors. Understanding alloy disorder effects on P-band emission and exciton-polariton propagation processes in GaN-based mixed crystals is thus very important from both a fundamental physics viewpoint and for optical device applications in the blue spectral region.

In this Brief Report, we report ultrafast PL decay due to diffusive exciton-polariton propagation in highly excited $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals. Subpicosecond time-resolved PL spectra reveal that the P-band emission appears due to exciton-exciton inelastic scattering under high-density exciton resonant excitation, and that the decay time of the P-band emission is much shorter than the radiative recombination time of the excitons. We show that the ultrafast decay of P-band PL is explained by the *diffusive* propagation of photonlike exciton-polaritons in mixed crystals.

The samples were $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial films. Following the deposition of 1- μm -thick GaN buffer layers, 1- μm -thick $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial layers were grown on (0001) sapphire substrates using a metalorganic chemical vapor deposition technique.²⁵ $\text{Al}_x\text{Ga}_{1-x}\text{N}$ epitaxial layers with Al concentrations of $x=0.038$, 0.057, and 0.077 were used in this study. Wavelength-tunable femtosecond laser pulses, obtained from an optical parametric amplifier system based on a regenerative amplified Ti:sapphire laser, were used as the excitation source. The pulse duration and repetition rate were ~ 150 fs and 1 kHz, respectively. The sample temperature was kept at 7 K, and the typical laser spot size on the samples was ~ 100 μm . An optical Kerr gate method in a 1-mm-thick quartz cell with toluene as the Kerr medium was used for the time-resolved PL spectral measurements, with a time resolution of 0.7 ps. The PL spectra were measured as a function of delay time using a liquid-nitrogen-cooled charge-coupled device with a 50 cm single monochromator. Under weak excitations intensity (~ 0.01 mJ/cm^2), $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples showed two PL peaks: localized exciton and biexciton emissions.⁴ Here, we measured PL spectra under intense excitation condition (higher than 0.5 mJ/cm^2) to study exciton-exciton scattering emission. Because of the thick GaN buffer layer, we used the backscattering configuration for PL measurements.

Figure 1 shows time-resolved PL spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x=0.038$) under excitation intensities of (a) 0.5, (b) 3.5, and (c) 10 mJ/cm^2 . The excitation photon energy was set to the free exciton energy ($E_0=3.58$ eV). At an excitation intensity of 0.5 mJ/cm^2 , a broad PL band (M band) appears at around 3.57 eV. This PL band is due to biexciton luminescence be-

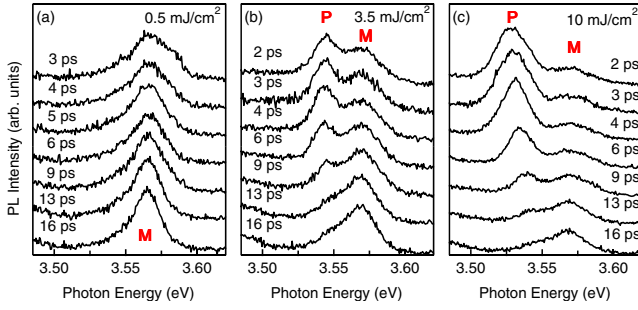


FIG. 1. (Color online) Time-resolved PL spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x=0.038$) under excitation intensities of (a) 0.5 mJ/cm^2 , (b) 3.5 mJ/cm^2 , and (c) 10 mJ/cm^2 . Biexciton (M) and P-band (P) luminescence appear in spectra.

cause the asymmetric spectral shape of M band obeys inverse Maxwell-Boltzmann distributions and the PL intensity increases superlinearly with excitation intensity.⁴ As the excitation intensity is increased to 3.5 mJ/cm^2 , an additional PL band, labeled P appears at around 3.54 eV , as shown in Fig. 1(b). The P-band PL intensity increases superlinearly with the excitation intensity (power-law index of ~ 1.5). The power dependence of this PL band is similar to that of exciton-exciton scattering (P-band) emission reported in GaN by Hvam *et al.*⁹ In highly excited GaN crystals, the P-band emission shows nonlinear power dependence because of two exciton collision processes. In addition, the P band appears at low energies below the biexciton M-band PL.¹⁰ Then, we conclude that the nonlinear PL line in Fig. 1 appears due to the P-band emission of exciton-exciton inelastic scattering in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ crystals.

In the P-band emission process (inelastic scattering between two excitons), one exciton is scattered into an excited excitonlike polariton state, and the other into the photonlike (lower) polariton state, conserving energy and momentum. In our experiments, with increasing excitation intensity, the P-band peak at short delay times gradually shifts to lower energies, and the spectral shape broadens. The P-band intensity reaches a maximum after a few picosecond time delay. At the excitation intensity of 10 mJ/cm^2 , the P-band peak at 2 ps delay appears at 3.528 eV and P-band emission dominates biexciton emission. These experimental features can be clearly explained by the exciton-exciton scattering processes. In fact, the spectral shape of the P-band emission cannot be fitted well by the e-h plasma emission shape.²⁶ Under intense laser excitation, nonradiative Auger recombination causes a decrease in the exciton density and an increase in effective electron temperature. The increase in effective electron temperature causes the production of exciton-polaritons located at lower energies via exciton-exciton scattering, thereby causing a redshift of the P-band emission. The exciton-polariton escape time (PL decay time) becomes faster at lower energy (photonlike polaritons), leading to the PL peak shift to higher energy with delay time.¹² The increase in electron temperature also causes the biexciton to dissociate into two excitons because the biexciton binding energy is small [less than 10 meV (Ref. 5)]. The P-band intensity disappears within a 10 ps delay time, with the lower energy side of the P-band emission decaying more rapidly. The dynamical as-

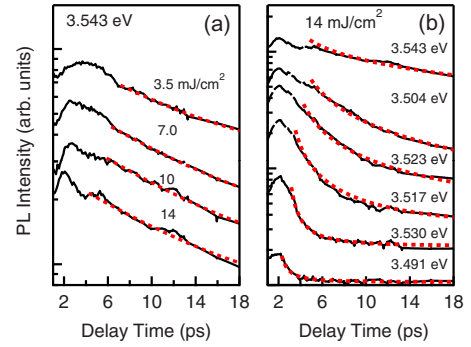


FIG. 2. (Color online) (a) Excitation intensity dependence of the temporal evolution of P-band intensity at 3.543 eV . A single exponential decay curve (8.3 ps time constant) is shown by broken lines. (b) PL energy dependence of the temporal evolution of P-band intensity at 14 mJ/cm^2 . The broken lines show fitting results using Eq. (4).

pect of the P-band emission can be explained by the propagation of a photonlike exciton-polariton produced by exciton-exciton inelastic scattering processes, as discussed below.

To clarify the decay dynamics of the photonlike exciton-polariton, we studied the temporal evolution of the P-band intensity. Figure 2(a) shows the temporal evolution of the P-band intensity at 3.543 eV with different excitation intensities. The decay time is almost independent of the excitation intensity. The excitation intensity dependence of the PL decay time suggests that the PL decay dynamics is a linear process. Figure 2(b) shows the temporal evolution of the PL intensity at different photon energies. The excitation intensity was 14 mJ/cm^2 . Although the rise times of the PL intensity are almost independent of the PL energy, the decay time decreases with the PL energy. The decay time of the P-band emission is significantly dependent on the emission energy. The typical decay time of the P band (less than 10 ps) is much shorter than the exciton radiative recombination time of a GaN-based wide-gap semiconductor.²⁷

The decay times of the PL intensity are extracted by fits of Fig. 2(b) using a single-exponential function. The single-exponential decay times are plotted as a function of the PL energy in Fig. 3(a) (solid circles). In bulk crystals, the group velocity of photonlike exciton-polaritons on the lower energy branch is faster than that in the polariton-bottleneck region. Thus, the PL decay time is determined not by the exciton radiative recombination time but by the propagation time of the exciton-polariton. The group velocity of the exciton-polaritons is described as,²⁸

$$v_g(E) = \frac{\partial \omega}{\partial k} = c \frac{\sqrt{\varepsilon_b + \frac{f}{1 - E^2/E_{ex}^2}}}{\varepsilon_b + \frac{f}{(1 - E^2/E_{ex}^2)^2}}, \quad (1)$$

where E_{ex} , f , ε_b , and c are the exciton resonant energy, oscillator strength, background dielectric constant, and speed of light in vacuum, respectively. The energy-dependent propagation velocity of the exciton-polariton plays an essen-

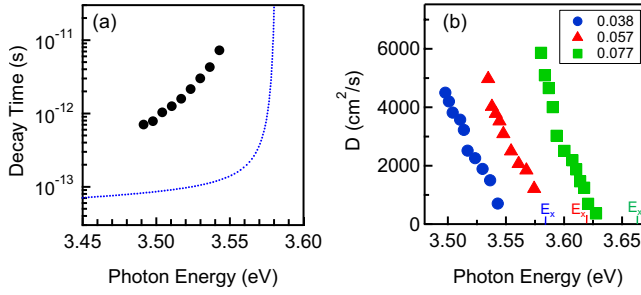


FIG. 3. (Color online) (a) The PL decay time (solid circles) and calculated decay time based on the *ballistic* propagation model (dotted curve) as a function of photon energy. (b) The energy dependent diffusion coefficients of the P-band emission with different Al compositions x (circles, squares, and triangles for $x=0.038$, 0.057, and 0.077, respectively). The labels E_x show the exciton energies of three samples.

tial role in the PL decay dynamics of the P band. Due to the exciton-exciton scattering process, “photonlike” exciton-polaritons are distributed along a photonlike polariton branch. Once photonlike exciton-polaritons are created, they propagate in the sample. Until exciton-polaritons are scattered by phonons, excitons, impurities, and so on, the propagation of exciton-polaritons in the sample is considered as a ballistic propagation. According to the ballistic propagation model,²⁸ we estimated the escape time of exciton-polaritons from the sample surface with the group velocity represented by Eq. (1), assuming the initial spatial profile of the exciton-polariton: $n(z)|_{t=0}=n_0 \exp(-\alpha z)$, where $\alpha=8.7 \times 10^4 \text{ cm}^{-1}$ is the absorption coefficient at the excitation wavelength^{29,30} and z is direction perpendicular to the sample surface. In $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals, however, the ballistic exciton-polariton escape time is calculated to be one or two orders of magnitude shorter than the experimental decay times of P-band emission. This is shown in Fig. 3(a), where we use a background dielectric constant $\epsilon_b=9.3$ and oscillator strength $f=0.002$ for A excitons in GaN crystals.³¹ It is reasonable that the ballistic propagation would be strongly inhibited due to disorder potentials in the mixed crystals. We conclude that the ballistic propagation of exciton-polaritons gives no simple and natural explanation of this ultrafast light decay.

In disordered mixed crystals where an electromagnetic wave is strongly scattered, the exciton-polariton dynamics is dominated by diffusive propagation process rather than ballistic propagation process. To understand the mechanism of the ultrafast light decay more quantitatively, we analyze the decay dynamics of the P-band emission using a diffusive propagation model of exciton-polaritons.

For the spatiotemporal evolution of exciton-polaritons, $n(z, t)$ at the PL energy E , coordinate z , and time t , we use the diffusion equation of exciton-polaritons,

$$\frac{\partial n(z, t)}{\partial t} = D(E) \frac{\partial^2 n(z, t)}{\partial z^2}, \quad (2)$$

where the emission-energy-dependent $D(E)$ is a diffusion coefficient. We used an exponential function with an absorption coefficient of $\alpha=8.7 \times 10^4 \text{ cm}^{-1}$ as the initial spatial profile

of the exciton-polariton: $n(z)|_{t=0}=n_0 \exp(-\alpha z)$. In addition, the boundary condition of the exciton-polariton density at the sample surface $n(z, t)|_{z=0}=0$ for $t>0$ is used to account for the fact that the exciton-polaritons at the sample surface rapidly escape to free space and become light. The spatiotemporal evolution of the exciton-polariton density is described as,³²

$$n(z, t) = \frac{1}{2\sqrt{\pi Dt}} \int_0^\infty n_0(z') \left\{ \exp\left[-\frac{(z-z')^2}{4Dt}\right] - \exp\left[-\frac{(z+z')^2}{4Dt}\right] \right\} dz'. \quad (3)$$

Therefore, the PL intensity dynamics of exciton-polariton $I(t)$ is proportional to the time derivative of the density,

$$I(t) \propto -\frac{\partial}{\partial t} \int_0^\infty n(z, t) dz = D \left. \frac{\partial n(z, t)}{\partial z} \right|_{z=0} = -D\alpha \operatorname{erfc}(\sqrt{Dt}\alpha) \exp(Dt\alpha^2) + \sqrt{\frac{D}{\pi t}}. \quad (4)$$

We extract the diffusion coefficients from the fits of the decay profiles in Fig. 2(b) using Eq. (4). Here, we focus on the decay profiles at large delay times for the fitting procedure because we neglect the PL rise time in the calculation in Eq. (4). The fitting results are plotted in Fig. 2(b) as the broken curves, where we consider the long-decay components due to the M-band emission and the background signals as constant for the fitting procedure. The obtained diffusion coefficients in mixed crystals with different Al composition ($x=0.038$, 0.057, and 0.077) are summarized as a function of the emission energy in Fig. 3(b). The diffusion coefficient of exciton-polaritons depends on the observed PL energy, becoming larger for lower photon energies. Increase in the diffusion constant means a reduction in the exciton-polariton multiple scattering rate, i.e., reduction in light-matter interactions. This is related to the photonlike character of exciton-polaritons at lower photon energies. In mixed crystals, the density of localized states below the band edge increases with alloy disorders, and disordered potentials cause exciton localization. In fact, the energy interval between the exciton energy E_x and the photon energy for a small value of D (e.g., $D=1500 \text{ cm}^2/\text{s}$) increases with Al composition x (48 meV for $x=0.038$, 56 meV for $x=0.057$, and 58 meV for $x=0.077$). These experimental results show that alloy disorders in mixed crystals enhance the multiple scattering of exciton-polaritons at low energy below the exciton energy E_x . These results clearly show that the decay dynamics of P-band emission in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals is dominated by the diffusive propagation of exciton-polaritons.

We measured the time-resolved P-band PL in GaN epitaxial layer with 2.6 μm layer thickness. Even in GaN crystals, a diffusive component is observed in the PL experiment. However, the diffusion coefficients of GaN crystals are much larger than those of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ mixed crystals (i.e., at 40

meV below E_x , diffusion coefficients are ~ 2300 cm²/s for GaN and ~ 1260 cm²/s for Al_{0.038}Ga_{0.962}N). Although exciton-polariton scatterings due to alloy disorders are absent in GaN crystals, exciton-exciton inelastic scattering causes diffusive exciton-polariton propagation. Our findings indicate that the disordered potentials in mixed crystals could cause the slow diffusive exciton-polariton propagation.

In conclusion, we reported the decay dynamics of P-band emission in Al_xGa_{1-x}N mixed crystals. The ultrafast PL decay dynamics is well explained by the diffusive propagation

of the exciton-polariton formed by exciton-exciton scattering under high-density excitation. The diffusive propagation of the exciton-polariton is attributed to alloy disorders in Al_xGa_{1-x}N mixed crystals.

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