Photoluminescence from exciton-exciton scattering in a $GaAs_{1-x}N_x$ thin film

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We have investigated photoluminescence (PL) properties under high-density-excitation conditions at 10 K in a $GaAs_{1-x}N_x$ thin film ($x=0.008$) with a narrow band-gap energy of 1.34 eV. A PL band was observed with a threshold-like nature, and its intensity was found to exhibit quadratic dependence on the excitation power. At the threshold excitation power, the PL-peak energy is lower than the energy of the fundamental exciton by the magnitude of the exciton binding energy that is ~4 meV. The results described above indicate that the PL band originates from exciton-exciton scattering, the so-called P emission, which is typically observed in wide-gap semiconductors with large exciton binding energies. Furthermore, we have confirmed the existence of optical gain in the energy region of the P band using a variable-stripe-length method. © *2010 American Institute of Physics*. [doi:10.1063/1.3309695]

For the past three decades, the inelastic scattering of excitons has attracted attention as a key process leading to stimulated emission.[1] In the inelastic scattering process of two $n=1$ excitons, where n denotes the quantum number of the hydrogenic exciton series, one is scattered into a higher-energy exciton state with $n\geq 2$, while the other is scattered into a photon-like state, the energy of which is lower than that of the $n=1$ exciton state by the magnitude of the energy difference between the $n=1$ and $n\geq 2$ states. The exciton-exciton scattering process causes the so-called P emission. It should be noted that the P emission has been typically observed in wide-gap III-V, II-VI, and I-VII semiconductors such as GaN,[2,3] lightly alloyed $In_xGa_{1-x}N$,[4] CdS,[5] ZnO,[6,7] and CuI (Ref. 8) because of the large exciton binding energies leading to the high stability of excitonic systems. On the other hand, narrow-gap semiconductors with small exciton binding energies have been excluded from the investigation of exciton-exciton scattering.

In this letter, we report on the clear evidence for the occurrence of the P emission in a thin film of a dilute nitride semiconductor of $GaAs_{1-x}N_x$ with $x=0.008$ under high-density-excitation conditions. The physical properties of $GaAs_{1-x}N_x$ exhibit specific behaviors. The incorporation of only a few percent of nitrogen leads to a drastic negative shift in the band-gap energy and produces localization states of carriers and excitons.[9] In this study, we observed a photoluminescence (PL) band peculiar to the high-density-excitation condition. The PL band appears with a threshold-like nature, and its intensity exhibits a quadratic dependence on the excitation power. The energy of the PL band is lower than the fundamental exciton energy by the magnitude of the exciton binding energy. These PL properties are consistent with the characteristics of the P emission. In addition, we confirmed the existence of optical gain in the energy region of the P emission using a variable-stripe-length (VSL) method.

The sample used in this study is a thin film of $GaAs_{1-x}N_x$ with $x=0.008$ and a thickness of 500 nm grown on a (001) GaAs substrate by metal-organic vapor phase epitaxy (MOVPE): See Ref. 10 for the details of the MOVPE growth. For PL measurements, the excitation source was the second-harmonic-generation light (532 nm) of a pulsed yttrium-aluminum-garnet laser with a pulse width of 1 ns and a repetition rate of 10 kHz, and the emitted light was analyzed with a cooled charge-coupled device attached to a single monochromator with a spectral resolution of 0.2 nm. In addition, photoreflectance (PR) spectroscopy was performed in order to determine the fundamental exciton energy. For PR measurements, the probe light was produced by combining a halogen lamp and a single monochromator with a resolution of 0.3 nm, and the pump light was the 514.5 nm line of an Ar^+ laser. The PR signal was detected with a conventional lock-in technique. All optical measurements were performed at 10 K.

Figure 1 shows the PR spectrum and excitation-power dependence of PL spectra in the $GaAs_{1-x}N_x$ thin film with $x=0.008$, where the intensity of each PL spectrum is normalized by the maximum intensity. In the PR spectrum, the open circles indicate the experimental spectrum, and the solid curve depicts the result of the line-shape analysis based on a third derivative functional form[11] that is a conventional analysis model. The high-energy and low-energy PR signals can be attributed to the heavy-hole (HH) and light-hole (LH) excitons, respectively, because it is well known that the oscillator-strength ratio of the HH exciton to the LH exciton is 3:1. The arrows labeled E_{HH} and E_{LH} indicate the energies of the HH and LH excitons that were estimated from the line-shape analysis; $E_{HH}=1.352$ eV and $E_{LH}=1.341$ eV. From the lattice constants of cubic GaN (0.4531 nm) and GaAs (0.5653 nm),[12] it is considered that the $GaAs_{1-x}N_x$ layer on the GaAs substrate has a biaxial (in-plane) strain of $\varepsilon=+0.16\%$ under the pseudomorphic growth condition. The biaxial strain lifts the degeneracy of the HH and LH excitons. On the basis of the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory,[13,14] the strain-induced energy shifts of the HH and LH band-gap energies, $\delta E_{g,HH}$ and $\delta E_{g,LH}$, are given by

$$\delta E_{g,HH} = \delta E_H - \delta E_T/2, \tag{1a}$$

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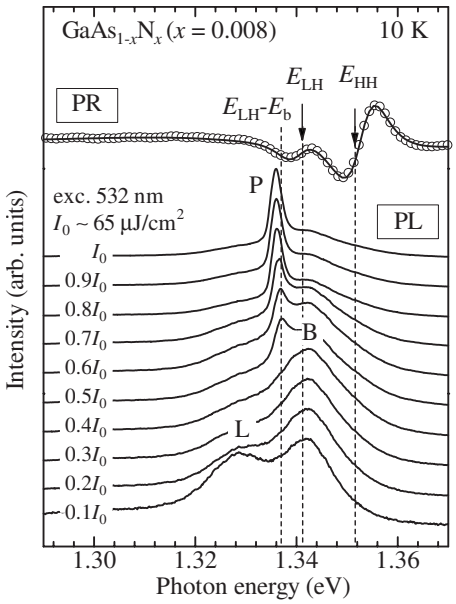

FIG. 1. PR spectrum and PL spectra at various excitation powers in the $GaAs_{1-x}N_x$ thin film with $x=0.008$ at 10 K, where the intensity of each PL spectrum is normalized by the maximum intensity. In the PR spectrum, the open circles indicate the experimental spectrum, and the solid curve depicts the results of the line-shape analysis based on a third derivative functional form. The arrows indicate the energies of the LH and HH excitons (E_{LH} and E_{HH}) estimated from the line-shape analysis of the PR spectrum. E_b denotes the exciton binding energy.

$$\delta E_{g,LH} = \delta E_H + \delta E_T/2 - (\delta E_T)^2/(2\Delta_0), \tag{1b}$$

$$\delta E_H = 2a[\ (C_{11} - C_{12})/C_{11})]\varepsilon, \quad \delta E_T = 2b[(C_{11} + 2C_{12})/C_{11}]\varepsilon, \tag{1c}$$

where the parameters of a and b are the hydrostatic- and tetragonal-deformation potentials, respectively, C_{ij} is the elastic stiffness constant, and Δ_0 is the spin-orbit splitting energy. For $GaAs_{1-x}N_x$, the values of the parameters used in the present calculation are linearly interpolated from those of GaAs and GaN.[15] The calculation with Eqs. (1a) and (1b) suggests that the LH-band-gap energy is lower than the HH-band-gap energy by the magnitude of 12 meV. The experimental HH-LH splitting energy is 11 meV. Thus, the analysis of the strain effect is reasonable.

Three PL bands labeled L, B, and P are observed in the PL spectra of Fig. 1. In the lowest excitation power of $0.1I_0$, the broad PL band labeled L observed on the low-energy side of the LH exciton is remarkable. The L-PL intensity drastically decreases with increasing excitation power, reflecting the saturation of localized states by photogenerated carriers. Thus, the L band is attributed to the localized exciton. The localized states originate from considerable disorders of the band-edge states caused by the incorporation of nitrogen.[9,16] The PL band labeled B is attributed to the LH exciton because its peak energy agrees with E_{LH}.

In Fig. 1, the sharp PL band labeled P suddenly appears at the excitation power of $0.5I_0$ on the low-energy side of the LH exciton. The energy of the P-PL band (E_P) at the threshold excitation power is lower than E_{LH} by the magnitude of the exciton binding energy (E_b) that is 4 meV; $E_P=E_{LH}-E_b$. Here, we assume that the exciton binding energy of $GaAs_{0.992}N_{0.008}$ is equal to that of GaAs because the alloy composition is very small. Figure 2 shows the spectrally integrated P-PL intensity as a function of excitation power. To evaluate the P-PL intensity, we fitted the spectral shape with three Gaussian functions corresponding to the L, B, and P bands. The inset in Fig. 2 shows an example of the spectral shape analysis using three Gaussian functions (dashed curves) at the excitation power of ~65 $\mu J/cm^2$. The combination of the three Gaussian functions, which is indicted by the solid curve, sufficiently explains the experimental spectral shape. The P-PL intensity (I_P) increases superlinearly with an increase in excitation power (I_{exc}). The fitted result of the excitation-power dependence is $I_P \propto I_{exc}^2$. In the exciton-exciton scattering process, the excitation-power dependence of the P-PL intensity is expected to be a quadratic law because a collision of two excitons is essential. The energy of the P band is given by[6]

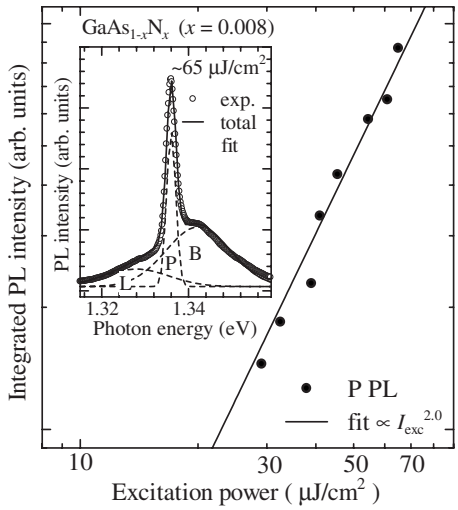

FIG. 2. Spectrally integrated P-PL intensity (I_P) as a function of excitation power (I_{exc}) at 10 K. The solid line indicates the fitted result of the excitation-power dependence, $I_P \propto I_{exc}^2$. The inset shows an example of the spectral shape analysis using three Gaussian functions (dashed curves) at the excitation power of ~65 $\mu J/cm^2$. The open circles indicate the experimental spectral shape, and the solid curve depicts the combination of the three Gaussian functions.

$$E_P = E_{n=1} - (E_{n\geq 2} - E_{n=1}) - 3\delta k_B T_{eff}, \tag{2}$$

where $E_{n=1}$ and $E_{n\geq 2}$ are the energies of the $n=1$ exciton (the initial state of the scattering process) and the $n\geq 2$ exciton, respectively, δ is a positive constant smaller than 1, and T_{eff} is the effective temperature of the excitonic system. The effective temperature usually increases with an increase in excitation power, which leads to a low-energy shift of the P band as shown in Fig. 1. The properties of the P band described above conclusively indicate that the P band originates from the exciton-exciton scattering process.

It should be noted that the P emission clearly observed in the narrow-gap semiconductor of $GaAs_xN_{1-x}$ with the small exciton binding energy. There have been no reports on the P emission in GaAs, so that the appearance of the P emission is peculiar to $GaAs_{1-x}N_x$. Here, we briefly discuss why the P emission is observed in $GaAs_{1-x}N_x$. The results obtained using near-field scanning optical microscopy of $GaAs_{1-x}N_x$ thin films demonstrate the formation of alloy-potential domains with a typical size of the order of submicrometer.[10] Thus, it is expected that the potential domains for localization are filled under high-density-excitation conditions, and then act as collision centers for free excitons, resulting in an

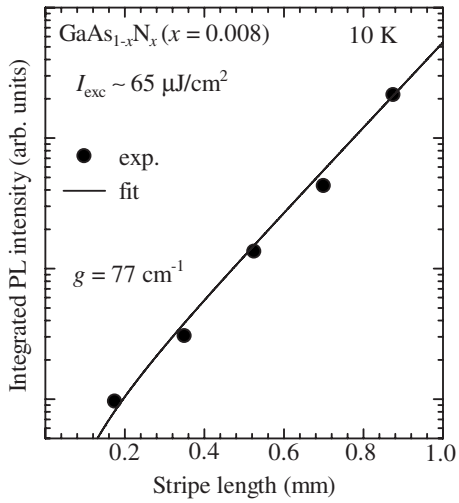

FIG. 3. Stripe-length dependence of the spectrally integrated P-PL intensity detected from the sample edge in the $GaAs_{1-x}N_x$ thin film with $x=0.008$ at 10 K, where the excitation power is $\sim 65\ \mu J/cm^2$. The solid curve indicates the fitted result using Eq. (3).

enhancement of the efficiency of exciton-exciton scattering. This seems to be the origin of the appearance of the P emission, which was also confirmed in lightly alloyed $In_xGa_{1-x}N$.[4]

Finally, we discuss the existence of optical gain originating from the exciton-exciton scattering process. In order to measure the optical gain, we used the VSL method.[17] A rectangular beam of the excitation light with variable lengths was focused on the surface of the sample near the edge, and the PL that passed through the stripe region was then detected from the sample edge. If the optical gain is present in the stripe region, the PL intensity is expected to show the dependence on the stripe length L as[17]

$$I(\hbar\omega) = I_s(\hbar\omega)\{\exp[g(\hbar\omega)L] - 1\}/g(\hbar\omega), \quad (3)$$

where $I_s(\hbar\omega)$ and $g(\hbar\omega)$ are the spontaneous emission intensity and net optical gain, respectively. The net optical gain is $g(\hbar\omega)=g'(\hbar\omega)-\kappa(\hbar\omega)$, where $g'(\hbar\omega)$ is the optical gain due to stimulated emission, and $\kappa(\hbar\omega)$ is the optical loss. Figure 3 shows the stripe-length dependence of the spectrally integrated P-PL intensity in the $GaAs_{1-x}N_x$ thin film with $x=0.008$, where the excitation power is $\sim 65\ \mu J/cm^2$. The solid curve indicates the fitted result using Eq. (3). The net optical gain is evaluated to be 77 cm^{-1}. Thus, we clearly confirm the presence of the optical gain in the energy region of the P-PL band.

In conclusion, we have found that the P-PL band originating from exciton-exciton scattering is observed in the thin film of the narrow-gap semiconductor of $GaAs_{1-x}N_x$ with $x=0.008$. The P-PL band appears with a threshold-like behavior under high-density-excitation conditions, and its energy is lower than that of the fundamental exciton (LH exciton) by the magnitude of the exciton binding energy. The excitation-power dependence of the spectrally integrated P-PL intensity obeys the quadratic law. The results described above demonstrate the occurrence of the P emission. The presence of the optical gain of the P-PL band is confirmed by the VSL method. As there have been no reports on the P emission in GaAs, the appearance of the P emission is peculiar to $GaAs_{1-x}N_x$.

The sample of the $GaAs_{1-x}N_x$ thin film was provided by Sumitomo Electric Industries.

[1]For a review, see C. Klingshirn and H. Haug, Phys. Rep. **70**, 315 (1981).
[2]S. Bidnyk, T. J. Schmidt, B. D. Little, and J. J. Song, Appl. Phys. Lett. **74**, 1 (1999).
[3]K. Kazlauskas, G. Tamulaitis, A. Zukauskas, T. Suski, P. Perlin, M. Leszczynski, P. Prystawko, and I. Grzegory, Phys. Rev. B **69**, 245316 (2004).
[4]M. Nakayama, R. Kitano, M. Ando, and T. Uemura, Appl. Phys. Lett. **87**, 092106 (2005).
[5]K. Bohnert, G. Schmieder, and C. Klingshirn, Phys. Status Solidi B **98**, 175 (1980).
[6]C. Klingshirn, Phys. Status Solidi B **71**, 547 (1975).
[7]Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
[8]I. Tanaka and M. Nakayama, J. Appl. Phys. **92**, 3511 (2002).
[9]I. A. Buyanova, W. M. Chen, G. Pozina, J. P. Bergman, B. Monemar, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **75**, 501 (1999).
[10]M. Takahashi, A. Moto, S. Tanaka, T. Tanabe, S. Takagishi, K. Karatani, M. Nakayama, K. Matsuda, and T. Saiki, J. Cryst. Growth **221**, 461 (2000).
[11]D. E. Aspnes, Surf. Sci. **37**, 418 (1973).
[12]O. Madelung, *Semiconductors; Data Handbook* 3rd ed. (Springer, Berlin, 2004) pp. 103, 117.
[13]M. Chandrasekhar and F. H. Pollak, Phys. Rev. B **15**, 2127 (1977).
[14]M. Nakayama, T. Doguchi, and H. Nishimura, J. Appl. Phys. **72**, 2372 (1992).
[15]I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).
[16]M. Nakayama, Y. Iguchi, K. Nomura, J. Hashimoto, T. Yamada, and S. Takagishi, J. Lumin. **122-123**, 753 (2007).
[17]K. L. Shaklee, R. F. Leheny, and R. E. Nahory, Phys. Rev. Lett. **26**, 888 (1971).