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Photo-induced improvement of radiative efficiency and structural changes in GaAsN alloys

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We have investigated the excitation power density and nitrogen concentration dependence of the changes in the radiative efficiency of GaAsN alloys to examine the mechanism of the photo-induced improvement of radiative efficiency. With increasing excitation power density, the radiative efficiency increased more rapidly. The measure of the improvement $I_{\mathrm{after}}/I_{\mathrm{before}}$ superlinearly increased with increasing nitrogen concentration x up to ~1%. This suggests that the nonradiative recombination centers eliminated by photoexcitation are not defects formed by a single nitrogen atom but complexes formed by gathering of several nitrogen atoms. Micro Raman study revealed that the GaAs-like LO mode phonon peak intensity increased with photoexcitation time in a similar way to the increase in the radiative efficiency. Considering that this phenomenon is in a time scale of several seconds, the photo-induced structural changes correspond not to long range inter-diffusion but to local changes in atomic configuration which lead to the decrease in the density of nonradiative recombination centers.

1 Introduction

InGaAsN is expected as a material for long-wavelength laser diodes with superior characteristics used in the optical fiber communications. Owing to its extreme immiscibility, however, it is necessary to lower the growth temperature for incorporating nitrogen atoms, and thus the radiative efficiency becomes poor. In order to improve the luminescence properties of InGaAsN, thermal annealing after the growth is often carried out [1, 2]. We previously reported the novel phenomenon that photoexcitation at low temperatures improves the radiative efficiency of GaAsN alloys and that the improvement is irreversible [3]. In the present paper, we have investigated the excitation power density and nitrogen concentration dependence of the changes in the radiative efficiency of GaAsN alloys to examine the mechanism of the photo-induced improvement. Photo-induced structural changes have been also studied using micro Raman scattering spectroscopy.

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2 Experimental

The samples used in this study were GaAsN alloys grown on GaAs (001) substrates by low-pressure metalorganic vapor phase epitaxy [4]. Trimethylgallium, arsine, and 1,1-dimethylhydrazine were used as the Ga, As, and N sources, respectively. The nitrogen concentration in GaAsN alloys was determined using X-ray diffraction. Micro photoluminescence (PL) measurements were performed using a diode-pumped solid state laser ($\lambda = 532$ nm) focused to ~1 μm in diameter as the excitation source at 4.2 K. The excitation power density was changed from 10 to 6×10^5 W/cm^2. The PL was detected with a 30-cm monochromator and an intensified charge coupled device camera. In order to investigate the photo-induced structural changes, we have also carried out micro Raman scattering measurements at 4.2 K. The 632.8 nm line of a He-Ne laser was used as the light source. An intensified charge-coupled device camera was used as the detector.

3 Results and discussion

Figure 1 illustrates the improvement of PL intensity of GaAsN alloy by photoexcitation. Both the PL spectra shown in this figure were measured from GaAs$_{1-x}$N$_x$ ($x = 0.74\%$) at 4.2 K under the same excitation conditions. Dashed and solid curves correspond to the PL spectra measured before and after the photoexcitation with a high power density of 64 kW/cm^2 at 4.2 K, respectively. The PL intensity after photoexcitation is approximately 5 times as strong as that before. It should be noted that no distinct PL peak shift was observed, although the post-growth annealing often results in the PL peak shift to higher energies as well as the improved PL intensity [1, 2].

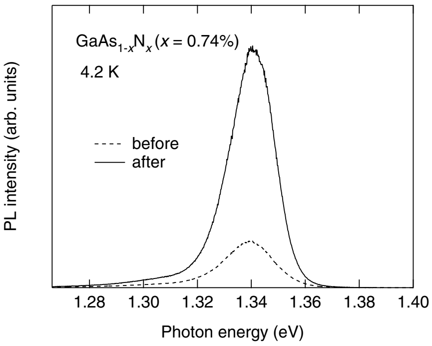

Fig. 1 PL spectra of GaAs$_{1-x}$N$_x$ ($x = 0.74\%$) alloy measured before (dashed curve) and after (solid curve) high-power density photoexcitation.

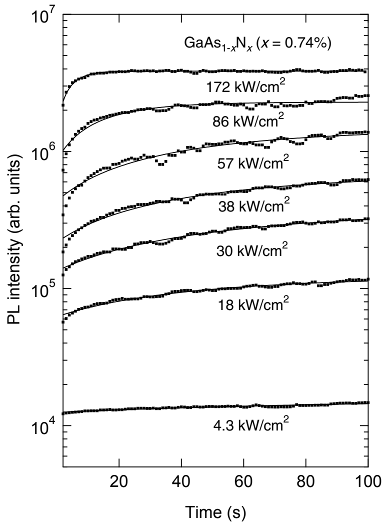

Fig. 2 Excitation power density dependence of the PL intensity. With increasing excitation power density, the PL intensity increases more rapidly.

Figure 2 shows the excitation power density dependence of the temporal change of the PL integrated intensity. With increasing excitation power density, the PL intensity is found to increase more rapidly and to be saturated in a shorter time. Solid curves shown in this figure were obtained from fit to the experimental data using the following expression:

$$I(t) = I(0)\exp\left(-\frac{t}{\tau}\right) + I(\infty)\left\{1-\exp\left(-\frac{t}{\tau}\right)\right\}. \tag{1}$$

These fits can explain well the temporal changes of the PL intensity except at the early stage of photoexcitation, and the estimated time constants τ ranged from 2 to 270 s for various excitation power density. Since excitons are localized in (In)GaAsN alloys at low temperature [2, 5], PL efficiency is expected to be strongly correlated with the density of nonradiative centers. Thus, exponential change of the PL intensity suggests that the density of nonradiative recombination centers exponentially decreases with the photoexcitation time. In other words, the rate equation for the nonradiative recombination center density n is expressed as $dn/dt = -n/\tau$. Figure 3 shows the excitation power dependence of the time constant of the photo-induced improvement. The time constant τ is found to almost inversely proportional to the excitation power density, i.e., $1/\tau \propto P$.

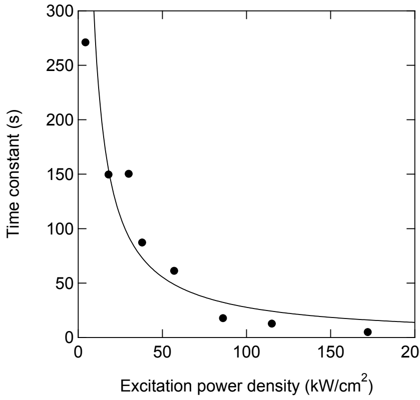

Fig. 3 Excitation power dependence of the time constant of the photo-induced improvement. The time constant is found to almost inversely proportional to the excitation power density.

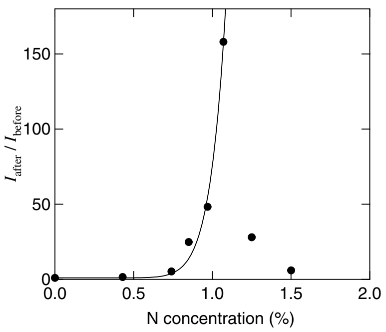

Fig. 4 Nitrogen concentration dependence of the measure of the improvement, I_{after}/I_{before}, which superlinearly increases with increasing nitrogen concentration up to ~1%. When the nitrogen concentration exceeds ~1%, the PL intensity ratio I_{after}/I_{before} decreases.

We also studied the nitrogen concentration dependence of the improvement in the radiative efficiency of GaAsN alloys. Figure 4 shows the nitrogen concentration dependence of the PL intensity ratio I_{after}/I_{before} between before and after high-power density photoexcitation. The measure of the improvement I_{after}/I_{before} was found to superlinearly increase with increasing nitrogen concentration x up to ~1%. Considering that $(I_{after}$ - $I_{before})/I_{before}$ is approximately proportional to the nonradiative recombination center density in as-grown samples $n(0)$, $n(0)$ is superlinearly dependent on the nitrogen concentration. This suggests that the nonradiative recombination centers repaired by photoexcitation are not defects formed by a single nitrogen atom but complexes formed by gathering of several nitrogen atoms. When the nitrogen concentration ex-

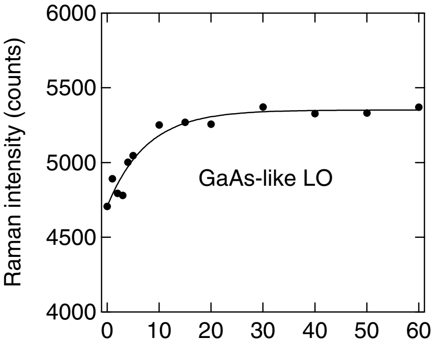

Fig. 5 Raman intensity of GaAs-like LO mode phonon as a function of photoexcitation time.

ceeded ~1%, the measure of the improvement $I_{\text{after}}/I_{\text{before}}$ rather decreased. This decrease may be due to the influence of structural defects which cannot be repaired by photoexcitation, for example, misfit dislocations in GaAsN alloys.

In order to examine the photo-induced structural changes, we have used micro Raman scattering spectroscopy. Laser irradiation with a power density of ~100 kW/cm^2 was intermittently performed at 4.2 K. Micro Raman scattering measurements were carried out between the photoexcitations at the laser-irradiated position using a weak laser light to avoid the photoexcitation effect. Figure 5 shows the Raman intensity of GaAs-like LO mode phonon as a function of photoexcitation time. The GaAs-like LO mode phonon peak intensity is found to rapidly increase with time at the early stage and to be saturated in a while. This temporal change can also be fitted by Eq. (1), as shown by a solid curve in this figure. The time constant τ is estimated to be 7.5 s. The increase in the Raman intensity of GaAs-like LO mode phonon indicates structural defects which disturb the propagation of the phonon are eliminated by photoexcitation. Although not shown here, it was also observed the nitrogen local vibration mode at ~470 cm^{-1} intricately changed with time in terms of the peak intensity and position. Since this phenomenon is in a time scale of several seconds, the photo-induced structural changes correspond not to long range interdiffusion but to local changes in atomic configuration which lead to the decrease in the density of nonradiative recombination centers.

4 Conclusions

We investigated the excitation power density and nitrogen concentration dependence of the changes in the radiative efficiency of GaAsN alloys to examine the mechanism of the photo-induced improvement of radiative efficiency. With increasing excitation power density, the PL intensity increased more rapidly. The time constant τ of the increase in the PL intensity ranged from 2 to 270 s, and the product of the time constant τ and photoexcitation power density was found to be nearly constant. The measure of the improvement $I_{\text{after}}/I_{\text{before}}$ superlinearly increased with increasing nitrogen concentration x up to ~1%. This suggests that the nonradiative recombination centers repaired by photoexcitation are complexes formed by gathering of several nitrogen atoms. When the nitrogen concentration exceeded ~1%, the measure of the improvement $I_{\text{after}}/I_{\text{before}}$ rather decreased. This decrease may be due to structural defects which cannot be repaired by photoexcitation, for example, misfit dislocations. Micro Raman spectroscopy revealed that the GaAs-like LO mode phonon peak intensity increased with photoexcitation time in a similar way to the increase in the PL intensity. This phenomenon in a time scale of several seconds indicates that the photo-induced structural changes correspond to local changes in atomic configuration which lead to the decrease in the density of nonradiative recombination centers.

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