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Micro-Raman study on the improvement of luminescence efficiency of GaAsN alloys

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Abstract

We have used in situ micro-Raman spectroscopy to clarify the mechanism of the luminescence efficiency improvement of GaAsN alloys by laser irradiation. Raman peak intensity of GaAs-like longitudinal optical (LO) mode phonon was observed to increase with the laser irradiation time. With increasing laser power density, the Raman intensity of GaAs-like LO mode phonon was found to increase more rapidly and to be saturated in a shorter time. Changes in the Raman intensity can be expressed by the same equation used for the luminescence efficiency improvement. Time constants of changes in the Raman intensity were almost in agreement with those of the luminescence efficiency improvement. This indicates that the increase in Raman intensity of GaAs-like LO phonon is closely related to the luminescence efficiency improvement.

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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 luminescence efficiency becomes significantly low. 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 laser irradiation at low temperature improves the radiative efficiency of GaAsN alloys and that the improvement is irreversible [3]. In the present paper, we have used in situ micro-Raman spectroscopy to investigate the relation between the changes in the luminescence efficiency and structural changes in GaAsN alloys.

2. Experimental procedure

The samples used in this study were GaAsN alloys grown on GaAs (0 0 1) 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. To investigate the mechanism of the luminescence efficiency improvement by laser irradiation, we have carried out in situ micro-Raman scattering measurements for GaAsN alloys 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. Laser irradiation with a power density of 24–220 kW/cm^2 was intermittently performed to improve the luminescence efficiency of GaAsN alloys. Although the laser power density was considerably high, the increase in temperature is estimated to be at most several K, based on the calculation of heat conduction. Therefore, the heating effect by the laser

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irradiation can be ignored under the conditions used in this study. Raman measurements were performed between the laser irradiation at the laser-irradiated spot using weak probe laser light with a power density of 16.4 kW/cm^2 to reduce the improvement effect due to laser irradiation.

3. Results and discussion

Fig. 1 shows a typical Raman spectrum obtained from GaAsN alloys at 4.2 K. The nitrogen concentration in this sample is 0.74%. As can be seen in this figure, GaAs-like longitudinal optical (LO) mode phonon, transverse optical (TO) mode phonon, and nitrogen local vibration mode (LVM) peaks are observed at 293, 269, and 470 cm^{-1}, respectively. The peak intensity of GaAs-like LO mode phonon slightly increased after the strong laser irradiation. Since the intensity of the nitrogen LVM peak was small as shown in this figure, we could not obtain any clear results concerning the nitrogen LVM in this study.

Fig. 2 shows the relative Raman intensity of GaAs-like LO mode phonon of GaAsN alloys as a function of the laser irradiation time. The Raman intensity was observed to rapidly increase with the laser irradiation time at the early stage and to be saturated afterwards for all the samples used in this study. The temporal changes in the Raman intensity can be roughly expressed by the following equation fitted for the improvement in the luminescence efficiency by laser irradiation [3]:

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

as shown by solid curves in this figure. The time constant τ ranged from 3 to 10 s. The changes tend to become larger by increasing nitrogen concentration. This is probably because the density of nonradiative recombination centers is higher for GaAsN alloys with higher N concentrations [5].

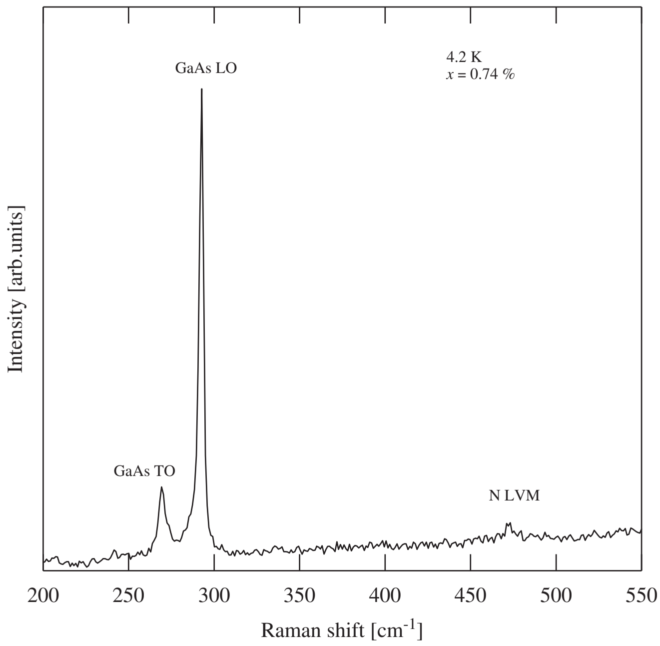

Fig. 1. Raman spectrum of a GaAs$_{1-x}$N$_x$ ($x = 0.74\%$) alloy measured at 4.2 K.

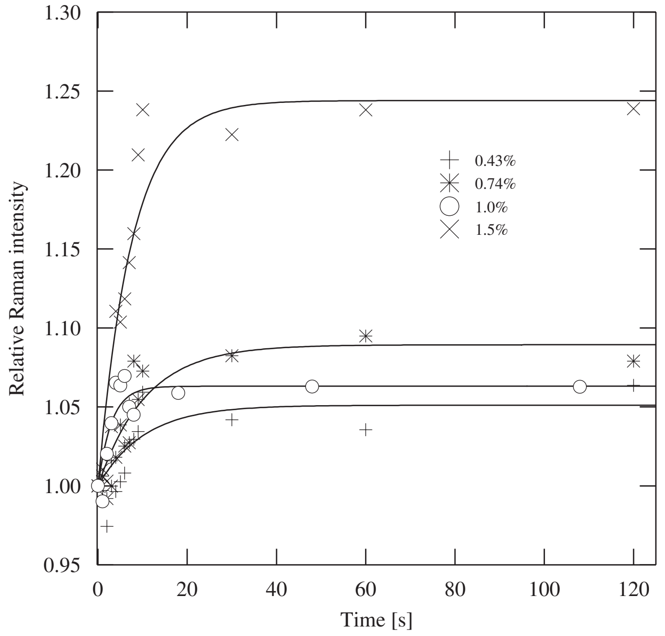

Fig. 2. Relative Raman intensity of GaAs-like LO mode phonon of GaAsN alloys as a function of the laser irradiation time.

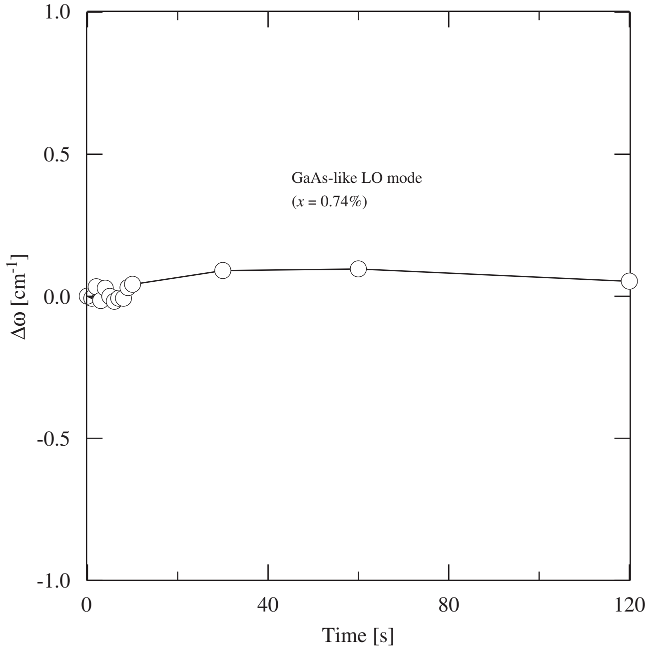

Fig. 3. Relative changes in the Raman peak position of GaAs-like LO mode phonon of GaAsN alloy ($x = 0.74\%$).

Fig. 3 shows relative changes in the Raman peak position of GaAs-like LO mode phonon of GaAs$_{1-x}$N$_x$ ($x = 0.74\%$) alloy. As shown in this figure, the Raman peak position change is hardly observed. Also for other samples, the Raman peak position changed little. This indicates that the average strain in GaAsN alloys or the average bond length between Ga and As atoms changes little by the laser irradiation. In other words, the nitrogen concentration in the laser-irradiated region remains the same, and long-range diffusion of nitrogen atoms out of the laser-irradiated region does not occur. This is consistent with the fact that the luminescence peak wavelength was not changed before and after the strong laser irradiation [3].

Fig. 4 shows the excitation power density dependence of the temporal change in the Raman intensity of GaAs-like LO mode phonon of $GaAs_{1-x}N_x$ ($x = 0.74\%$). With increasing excitation power density, the Raman intensity is found to increase more rapidly and to be saturated in a shorter time. This tendency is similarly seen in the improvement in the luminescence efficiency by laser irradiation [5]. Fig. 5 shows the excitation power dependence of the time constant of changes in Raman intensity of the GaAs-like LO mode phonon peak due to laser irradiation. Since the time constants τ of changes in the Raman intensity are estimated to be 5–60 s, the structural changes detected by Raman measurements cannot be explained by long-range inter-diffusion, as discussed before. Time constants of the luminescence efficiency improvement due to laser irradiation are also shown in Fig. 5. Time constants of changes in the Raman intensity are rather in agreement with those of the luminescence efficiency improvement, suggesting that the increase in the Raman intensity of GaAs-like LO mode phonon is directly related to the luminescence efficiency improvement. Taking into account the fact that the improvement in luminescence efficiency results from the decrease in nonradiative recombination centers, the increase in GaAs-like LO mode phonon peak intensity indicates that the structural defects such as vacancies, interstitials, or some kind of complexes that disturb the propagation of phonons and work as nonradiative recombination centers are reduced by laser irradiation.

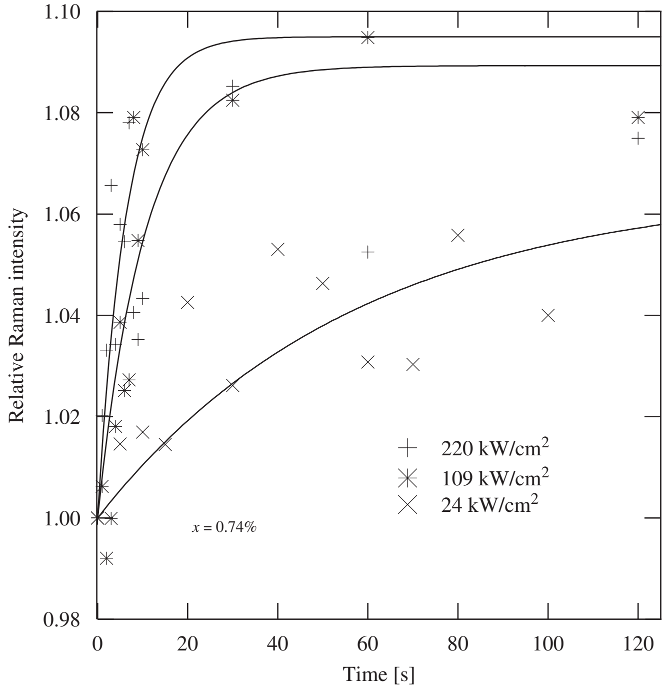

Fig. 4. Excitation power density dependence of temporal changes in the Raman intensity of GaAs-like LO mode phonon of GaAsN.

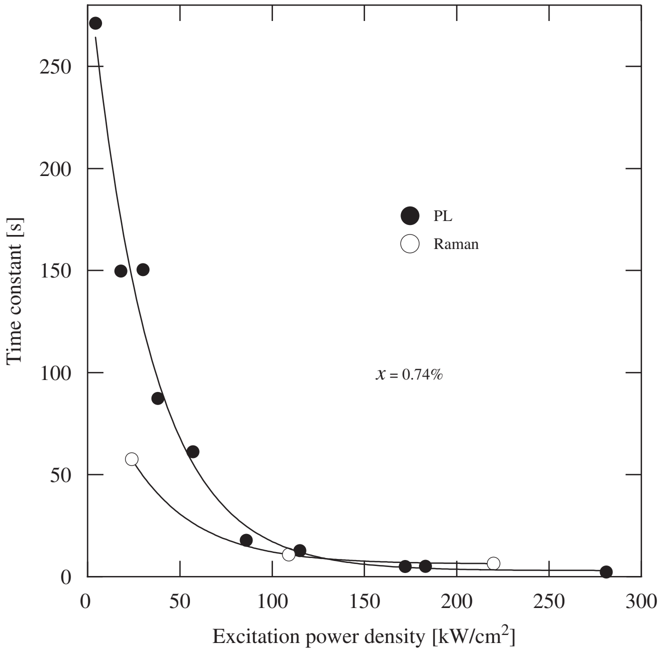

Fig. 5. Excitation power dependence of time constant of changes in the Raman intensity of GaAs-like LO mode phonon due to laser irradiation. Excitation power dependence of time constant of the luminescence efficiency improvement is also plotted.

4. Conclusions

We used in situ micro-Raman spectroscopy to clarify the mechanism of the luminescence efficiency improvement of GaAsN alloys by laser irradiation. The Raman intensity of GaAs LO mode phonon was found to increase more rapidly and to be saturated in a shorter time with the laser irradiation time. Changes in the Raman intensity were expressed by the same equation used for the luminescence efficiency improvement, and the time constants of changes in the Raman intensity were in agreement with those of the luminescence efficiency improvement. Therefore, the increase in the Raman intensity of GaAs-like LO mode phonon is closely related to the luminescence efficiency improvement, and indicates that the structural defects disturbing the phonon propagation are eliminated by laser irradiation. Since this phenomenon is in a time scale of several seconds, the structural changes correspond not to long-range inter-diffusion but to local structural changes leading to the elimination of nonradiative recombination centers.

Acknowledgments

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