PUBLICATION VIII

Effect of post-growth laser treatment on optical properties of Ga(In)NAs quantum wells

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Abstract:

The effects of laser irradiation on the optical properties of GaAsN and GaInNAs quantum wells are studied in detail. The laser treatment is found to affect GaAsN quantum wells quite similarly to thermal annealing. The most intense photoluminescence is obtained by utilizing both thermal and laser treatments. In quaternary GaInNAs, the effects of thermal annealing and laser treatment differ from each other. Thermal annealing of a $Ga_{0.80}In_{0.20}N_{0.02}As_{0.98}$ quantum well at 700°C for 10 minutes shifts the photoluminescence peak by 86 meV towards large photon energies and increases its integrated intensity by a factor of ten. For the same quantum well structure, the luminescence intensity increases by a factor of 2.5 due to the laser treatment, whereas the blue shift of the luminescence peak is negligible. The laser treatment effects are observed at laser irradiation intensities encountered in typical photoluminescence measurement conditions. Therefore, the effects of the laser irradiation should be taken into account when measuring the optical properties of Ga(In)NAs samples.

1 Introduction

Quaternary alloy $Ga_{1-y}In_yN_xAs_{1-x}$ is a novel material for small band gap applications on gallium arsenide [1,2]. The alloy is lattice matched to GaAs when y ≈ 3x, and only a few percent of nitrogen (x < 0.05) is needed to decrease the band gap below 1 eV. This material can be used in applications such as infrared lasers [3], multi-junction solar cells [4] and heterojunction bipolar transistors [5]. Increasing the concentration of nitrogen in GaAsN affects the band structure of the material mainly by lowering the conduction band edge. However, also the valence band edge is affected slightly, and it has been recently shown that GaAsN/GaAs material system has a type-I band alignment [6,7]. The luminescence efficiency of the as-grown GaAsN quantum well (QW) structure is small. It can be increased using post-growth thermal annealing or laser treatment [8]. There have been a lot of reports on the effects of annealing procedures [8-12], but the laser treatment procedure has not been studied extensively. The effects of these two types of treatments are known to be rather similar. The thermal annealing of whole wafers is easy, whereas the laser treatment can be focused only to a part of a wafer at a time. However, a systematic study of laser treatments may reveal new advantages. In this work, the effect of laser treatments on Ga(In)NAs QWs has been studied.

2 Experimental procedure

Ga(In)NAs layers were grown on semi-insulating GaAs (001) substrates by metal-organic vapor phase epitaxy (MOVPE) at atmospheric pressure. Trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs), and dimethylhydrazine (DMHy) were used as sources for gallium, indium, arsenic, and nitrogen, respectively. The samples consist of a 50-nm-thick GaAs buffer, a $Ga_{1-y}In_yN_xAs_{1-x}$ QW with a thickness of 5 nm, and a 50-nm-thick GaAs cap layer. The QW composition x ranged from 0 to 0.045 and y from 0 to 0.32. The growth temperature of the buffer was 650 °C. The QW and the cap layer were grown at 520–530 °C. The temperatures measured are thermocouple readings rather than surface temperatures. To study the effect of thermal annealing, pieces of samples were kept in the MOVPE reactor for 10 minutes at 700 °C in a H_2 carrier gas and excess TBAs ambient.

Photoluminescence (PL) at the temperature of 15 K was used to characterize the optical quality of the layers. The 488 nm line of an argon ion laser with an intensity of 42 W/cm^2 and a spot diameter of 30 μm was used for PL excitation. The luminescence was dispersed with a 0.55-m grating monochromator and detected by a liquid-nitrogen-cooled germanium detector. The laser treatments were performed using the same optical setup with laser intensities from 420 W/cm^2 to 38 000 W/cm^2. The GaAsN and InGaAs compositions were determined by high-resolution X-ray diffractometry using (004) reflection. The composition for GaInNAs layers were estimated by using the In content of an InGaAs layer grown in the similar growth conditions and by estimating the N content from the shift of the PL energy of the as-grown GaInNAs. The shift as a function of N content was assumed to behave in the same manner as that of the GaAsN samples.

3 Results and discussion

The as-grown $GaAs_{1-x}N_x$ QWs have a poor luminescence efficiency. If the N content x is larger than 0.03, we are not able to distinguish the luminescence from the noise. Figure 1 shows the low-temperature PL spectra of an as-grown $GaAs_{0.955}N_{0.045}$ QW before and after laser treatments. The laser treatments were performed for 1 minute with different irradiation intensities. After each exposure the PL spectrum was measured with the same excitation intensity of 42 W/cm^2. The PL efficiency of the treated samples increases gradually with increasing laser treatment intensity in the range from 420 W/cm^2 to 10 000 W/cm^2 and then saturates. The GaAs-related transitions at higher photon energies (not shown in Fig. 1) remain unchanged after the laser treatments. As the PL efficiency increases the PL peak energy also increases. This is due to a state filling effect. The low-temperature luminescence is found to originate from excitons localized in potential fluctuation at the band edges [13]. The potential fluctuation probably originates from random composition fluctuation and is enhanced due to a large band gap bowing. The low-energy tail of the PL spectrum can be used to estimate the localization potential [14], which in our QWs is typically about 16 meV. The effects of laser treatments are always irreversible. No degradation of the PL efficiency is observed even hours after the treatment. Also, the effect is local, i.e., the luminescence efficiency is increased only in the area of the laser spot. These results are in agreement with the earlier reported ones in Ref. 8.

The effects of thermal annealing and laser treatment are quite similar. Figure 2 shows the integrated PL intensity of a $GaAs_{0.968}N_{0.032}$ QW after different post-growth treatments. After annealing or laser treatment the luminescence intensity is large. The laser treated sample exhibits twice the intensity of the thermally annealed sample, which indicates that the laser treatment procedure is effective. However, the largest intensity is obtained when both treatments are implemented. These two post-growth treatments affect the GaAs-related transitions at high photon energies differently. The laser treatment has no effect on those transitions, but the thermal annealing enhances them. In general, one should be aware of these effects when performing optical measurements on arsenide-nitrides in order to avoid unintentional laser treatment.

$GaAs_{1-x}N_x$ QWs with different N content x have quite similar luminescence properties after annealing and laser treatment. Figure 3 shows the PL spectra of $GaAs_{1-x}N_x$ QWs (annealed & laser treated) with different nitrogen composition x. The full-widths at half-maximum (FWHM) of the peaks are 27–31 meV. The PL intensities are in the same order of magnitude. The least luminescence intensity is measured from the sample having the largest N content x = 0.045. Also, the low-energy tail of the PL spectrum is similar at all nitrogen levels, which shows that the compositional uniformity remains similar even though the nitrogen content is increased.

Quaternary GaInNAs is known to have an annealing behavior different from that of GaAsN [11,15]. A $Ga_{0.80}In_{0.20}N_{0.02}As_{0.98}$ QW was used to study the effects of post-growth treatments on a quaternary compound (Fig. 4). As-grown GaInNAs shows reasonable luminescence efficiency, and thus, the effect of the laser treatment is not as pronounced as in GaAsN. After the laser treatment the luminescence intensity increases by a factor of 2.5. Curiously, the blue shift of the PL peak is negligible. The thermal annealing procedure causes a 10-fold increase in the luminescence intensity and shifts the PL peak by 86 meV towards higher energies. The laser treatment has no impact on the optical properties of an annealed GaInNAs sample. This is probably due to local rearrangement of the neighboring nitrogen atoms during annealing [15]. It has been found that in as-grown GaInNAs the nitrogen atoms are mainly bonded to four neighboring gallium atoms and after annealing nitrogen atoms have one or more bonds with indium atoms [9,16]. Laser treatment enhances only the luminescence efficiency of the QW peak, especially in the case of a GaAsN QW. Thus, the defect affected by the laser treatment is related to the layer containing nitrogen. When annealing GaInNAs the local configuration around a nitrogen atom changes and the defect in question disappears.

The laser treatment procedure affects the defects in the lattice likely due to recombination enhanced defect reaction [8,17]. When pairs of electrons and holes are recombined within a short period of time through a non-radiative defect, the band gap energy E_g is transformed into lattice vibration energy by a series of coherent carrier captures. To be effective this reaction needs a high concentration of electrons and holes. Laser light is used to generate carries, but the effect should also be seen under strong forward bias in diode structures. When reaching a long-wavelength (1.55 µm) laser-operation on GaAs with GaInNAs structures the recombination enhanced defect annealing might be a better solution than the thermal annealing. However, the recombination enhanced defect reaction affects only one specific defect associated with a high non-radiative recombination rate. Thermal annealing also reduces the FWHM of the GaInNAs PL peak, which is found to be an important parameter in reducing the laser threshold current density [18].

Figure 5 shows the integrated PL intensity of a $GaAs_{0.98}N_{0.02}$ and a $Ga_{0.68}In_{0.32}N_{0.015}As_{0.985}$ QW as a function of reciprocal temperature. Laser treatment was performed on these samples before every measurement, because the laser spot is focused to a different location on the sample surface at different temperatures due to thermal expansion of the sample holder. An activation energy of 50 meV is obtained by fitting the data to a theoretical model equation. The temperature dependence of the PL intensity of the annealed and of the laser treated GaAsN is very similar to that of GaInNAs.

4 Conclusion

The effect of laser treatment on Ga(In)NAs QWs has been studied. Laser treatment and thermal annealing were found to have similar effects on optical properties of GaAsN and the largest luminescence intensity was obtained by utilizing both of them. For GaInNAs, the effects of the post-growth treatments were found to differ from each other. Thermal annealing resulted in a large blue shift and a 10-fold increase in the luminescence intensity. The laser treatment did not shift the energy of the PL peak and the luminescence intensity was not increased as much as after the thermal annealing. Laser irradiation could offer advantages in the cases like long-wavelength structures, where the blue shift of the PL peak should be avoided. The laser treatment effects should also be known when measuring optical properties of arsenide-nitrides.

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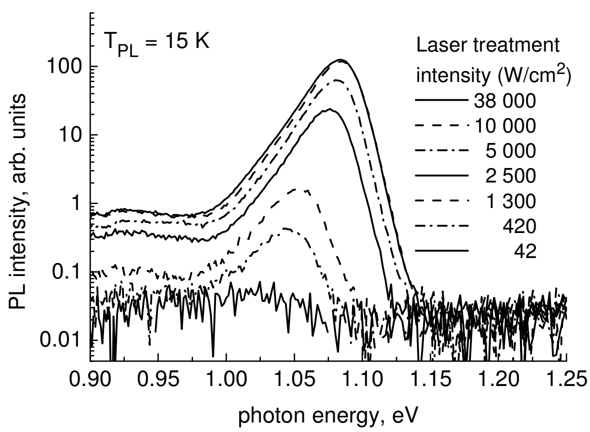

FIG. 1. Photoluminescence spectra measured at 15 K before and after laser treatments of a $GaAs_{0.955}N_{0.045}$ quantum well structure. The PL excitation intensity was 42 W/cm^2 for all spectra.

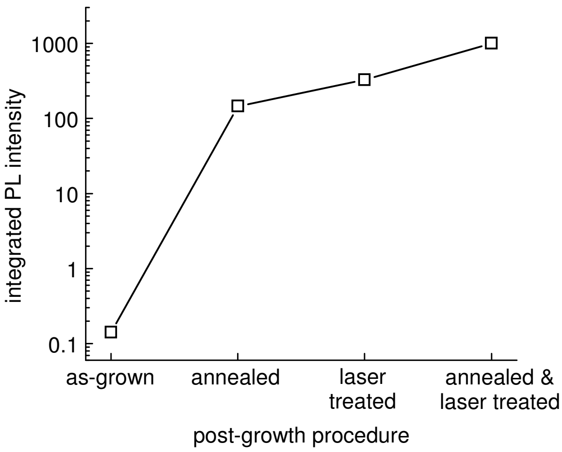

FIG. 2. Integrated photoluminescence intensity of a $GaAs_{0.968}N_{0.032}$ quantum well structure before and after post-growth treatments. The line is guide to the eye.

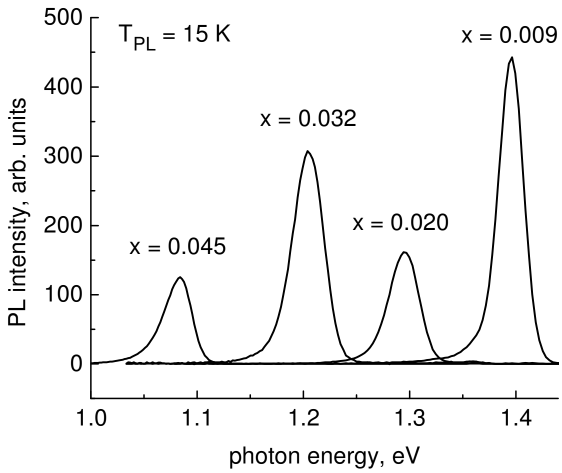

FIG. 3. Photoluminescence spectra of $GaAs_{1-x}N_x$ (annealed & laser treated) quantum well (QW) structures. The optical quality of the QWs is similar through the N content x from 0 to 0.045.

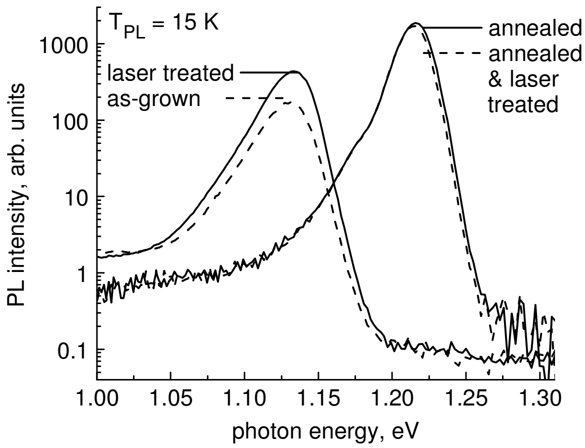

FIG. 4. Photoluminescence (PL) spectra measured at 15 K before and after thermal annealing and laser treatment of a $Ga_{0.80}In_{0.20}N_{0.02}As_{0.98}$ quantum well structure. The PL excitation and the laser treatment intensities were 42 W/cm^2 and 10 000 W/cm^2, respectively.

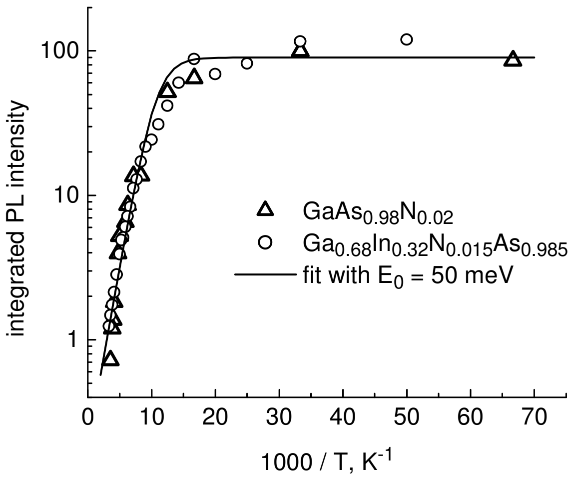

FIG. 5. Measured and calculated photoluminescence intensity (I) as a function of reciprocal temperature of GaInNAs (annealed) and GaAsN (annealed & laser treated) quantum well structures. The intensities are normalized.