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On the Origin of the Unexpected Annealing Behavior of GaInNAs Quantum Wells

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Studies of the annealing of GaInNAs quantum wells under argon or hydrogen atmosphere revealed a significant dependency of the annealing behavior on the growth temperature. Structural investigation by means of transmission electron microscopy reveals the formation of vacancy type dislocation loops after argon annealing only for quantum wells grown at low temperature. This was not observed for hydrogen annealing. The formation of these loops leads to enhanced nonradiative recombination reducing the luminescence efficiency. In contrast, samples grown at high temperatures show improved luminescence efficiency upon both annealing atmospheres. This is attributed to the growth-induced formation of different kinds of defects. [DOI: 10.1143/JJAP.46.L614]

KEYWORDS: dillute nitrides, quantum wells, annealing, luminescence efficiency, transmission electron microscopy, time-resolved spectroscopy

The quaternary GaInNAs alloy acts as active region in quantum well (QW) lasers for the infrared spectral range.[1)] A well known phenomenon of this alloy system is a strong decreases of the luminescence efficiency upon N incorporation.[2)] Annealing improves the optical properties significantly. The cause for this improvement has been the subject of controversial debate. Compositional homogenisation, local ordering of the alloy and annealing of atomic defects has been put forward. In the last years several groups performed detailed studies on the optimal combination of growth temperature, annealing temperature, and annealing time.[3,4)] Although the increase of the light output is often accompanied by an improvement of the QW homogeneity, previous work demonstrated that the reduction of nonradiative recombination centers through annealing is the key to GaInNAs laser structures with better light output, while the improvement of structural properties (QW roughness, compositional homogeneity) is of minor importance.[4)] Based on this work we study the nature of these defects and their annealing behavior under different annealing atmospheres. Structural investigations in combination with time-resolved optical data show completely different effects for low and high temperature grown structures, respectively, and their influence on nonradiative recombination mechanisms.

The investigated single GaInNAs QWs are part of an extensive study on the optimal combination of the growth and the annealing process.[4)] They were grown by molecular beam epitaxy at different temperatures between 360 and 480 °C. The indium content is 37%, the nitrogen content is 1.7%. The growth procedure and structural investigations using transmission electron microscopy (TEM) are described elsewhere.[4)] These studies show a transition from pure two-dimensional (2D) growth to island-like structures with increasing growth temperature. The two presented samples, grown at 402 and 453 °C, respectively, strongly differ concerning their growth mode. While the 402 °C QW has smooth interfaces, the 453 °C QW shows a strongly undulated upper interface and compositional fluctuations.[4)] After growth the samples were cut into three parts. Two parts were annealed for 109 min at 680 °C under argon and under hydrogen atmosphere, respectively. As already mentioned, the aim of this work is not to find the optimal annealing conditions. Therefore, in contrast to previous work,[4)] all samples were annealed under the same conditions apart from the atmosphere. In order to investigate the annealing behavior and its influence on the carrier relaxation and recombination processes, time-integrated and time-resolved photoluminescence (TIPL and TRPL) experiments were performed at low temperature and at elevated temperatures up to room temperature (RT). TIPL was excited by a tungsten lamp and was detected by an InGaAs photodetector. TRPL investigations were performed using a Nd:YAG pumped dye laser with a cavity damper. The temporal width of the laser pulses was 4 ps at a repetition rate of 3.78 MHz. The detection system consisted of two 0.35 m McPherson monochromators in subtractive mode and an ultra-fast photodetector (multi-channel plate) providing a spectral resolution of about 1 meV and a time resolution better than 30 ps. From selected as-grown and annealed samples, cross-sectional and plan-view samples were prepared for TEM by subsequent mechanical grinding, polishing and ion milling with 4 keV Ar+ ions to achieve electron transparency. High resolution as well as conventional bright field images were obtained in a Philips CM300 operated at 300 keV.

Figure 1 shows the low temperature TIPL spectra of the GaInNAs QWs grown at 402 and 453 °C, respectively. The as-grown samples emit at 1.00 eV (402 °C) and 0.93 eV (453 °C). The lower emission energy of the 453 °C grown QW and the larger full width at half maximum (FWHM) of its emission band can be explained by the strong compositional/strain fluctuations in this structure. For both QWs the annealing leads to a significant blue-shift of the PL and a decrease of the FWHM. This effect was studied by several groups and can be attributed to the interdiffusion of nitrogen atoms[5)] and a change of their nearest-neighbor configuration.[6–8)] In the case of the hydrogen annealing also the formation of N–H complexes and the resulting reduction of the effective N content could be responsible for the blue shift.[9)] The decreasing FWHM leads to the assumption that the interdiffusion during the annealing procedure leads to

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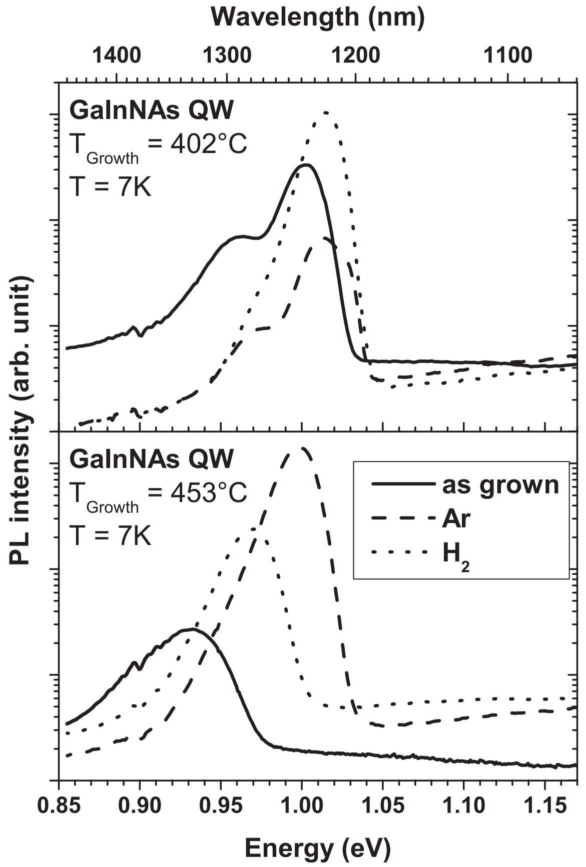

Fig. 1. Low temperature PL of GaInNAs QWs grown at 402 and 453 °C, as grown, annealed under argon and hydrogen atmosphere, respectively.

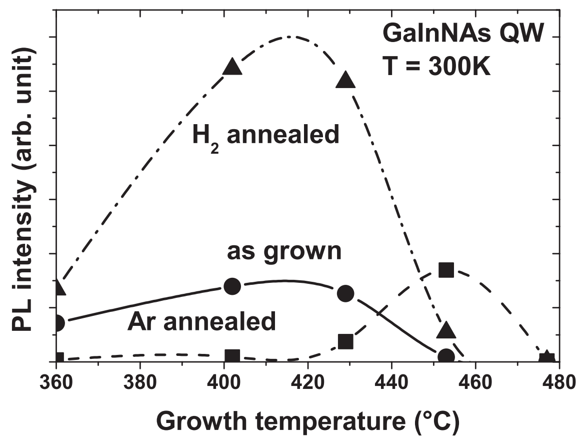

Fig. 2. PL intensity vs growth temperature, as grown (solid line), annealed under argon (dashed line), and annealed under hydrogen (dashed-dotted line).

a higher homogeneity of the QWs.

From Fig. 2 it can be seen that the PL intensity of the QWs grown at low temperatures is increased after annealing under hydrogen atmosphere, while it is decreased after annealing under argon atmosphere. Only for the QW grown at high temperatures the luminescence intensity increases more upon argon annealing than after hydrogen annealing. This supports previous results.[4] The luminescence efficiency is not correlated with the homogeneity of the QW. Although the argon annealing improves the compositional homogeneity of the 402 °C QW, its luminescence decreases.

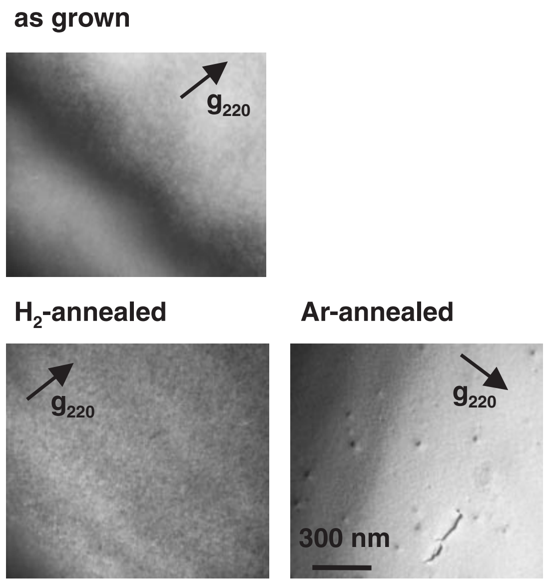

Fig. 3. Plan-view TEM images of the GaInNAs QW grown at 402 °C, as grown, annealed under argon and hydrogen atmosphere, respectively.

Plan-view TEM images of the low-temperature QW (Fig. 3) show the appearance of dislocation loops after argon annealing, while the samples grown at high temperatures are completely free of such loops. For the hydrogen annealing this effect could not be observed. A detailed contrast analysis using inside outside contrast proves these defects to be vacancy loops. From these observations we conclude that the different annealing behavior of samples grown at low and high temperature is due to the existence of two competing defects. The defect in the low temperature samples is vacancy related, the defect in the samples grown at high temperatures is still unknown. Thinh *et al.* report the growth induced formation of two nonradiative defects (AsGa-antisite complex and unknown deep-level defect) in GaAsN, the formation of which strongly depends on the growth temperature.[10] We assume a similar situation in GaInNAs QW structures. The formation of the first defect is favored by the low temperature growth far away from the thermal equilibrium. During the annealing under argon it reasons the appearance of dislocation loops. Under hydrogen this defect is passivated, comparable to the observed hydrogen induced passivation of nitrogen.[9] The second defect dominates the recombination mechanisms of the GaInNAs QW grown at high temperature. Its density can be efficiently reduced by argon annealing. No dislocation loops were observed. The growth induced incorporation of defects is always accompanied by an increase of nonradiative processes.[4,10]

TRPL at low temperature and at elevated temperatures up to RT is a powerful tool to investigate nonradiative recombination. Figure 4 shows the PL intensity after a pulsed laser excitation as a function of time at liquid helium temperature and RT, respectively. The PL transients at low temperature show the typical nonexponential decay of a strongly disordered system due to the QW roughness and the compositional inhomogeneity. At RT the PL decays are exponential and much shorter compared to low temperature. A decrease of the time constants with increasing tempera-

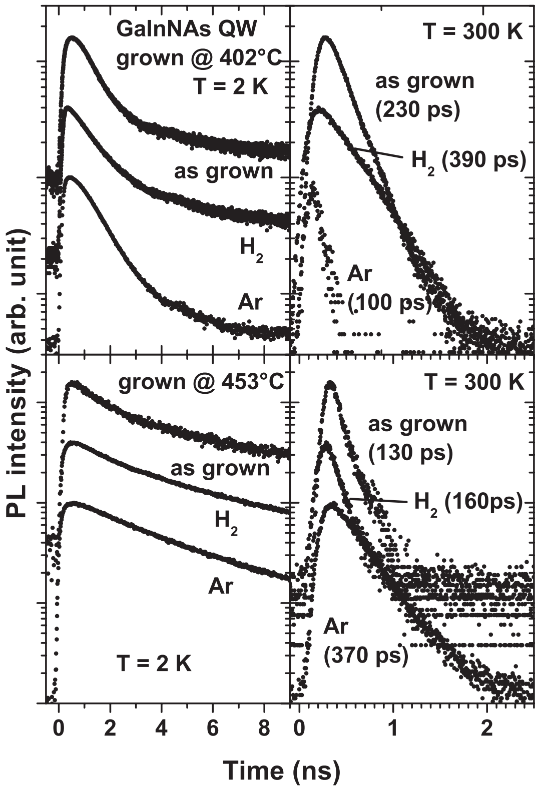

Fig. 4. 2 K and room temperature TRPL of GaInNAs QWs grown at low and high temperature, respectively.

ture is evident. While at low temperature the carriers are localized and recombine radiatively, at higher temperature the carriers are thermally activated and reach the defects where they recombine nonradiatively. Thus, nonradiative processes govern the recombination dynamics at RT leading to the shorter PL decay. With the argon-annealed 402 °C QW the structure with the lowest RT PL intensity has the shortest PL decay (100 ps). The bright hydrogen-annealed 402 °C QW has the largest decay time at RT (390 ps). The clear correlation of the RT time constant with the integral PL intensity (Fig. 2) leads to the conclusion that nonradiative processes are responsible for the decrease or the increase of the luminescence efficiency after annealing.

In conclusion the influence of annealing under two different atmospheres on the luminescence properties of GaInNAs QWs grown at low and high temperatures, was studied. Additional dislocation loops emerged during the argon annealing of the low temperature grown structure. The different annealing behavior of the low and high temperature structures could be attributed to the growth-induced formation of two competing defects. Both defects act as nonradiative recombination centers. Thus, the reduction of these defects is the main key to improve the quantum efficiency. Introducing the atmosphere as annealing parameter in addition to growth temperature, annealing temperature, and annealing time an optimized annealing procedure could be developed to achieve GaInNAs laser structures with better light output.

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