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Nitrogen-dependent effects on GaInNAs photoluminescence upon annealing

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Abstract

In order to assess the effects of nitrogen on GaInNAs during the annealing process, we analyzed several quantum wells (QWs) with different nitrogen contents after annealing at different rapid thermal annealing (RTA) conditions. When only the RTA temperature was varied, we found two blueshift regimes. Up to 700 °C (strong blueshift regime), the blueshift experiences a rapid increase with increasing RTA temperature, while above this temperature (weak blueshift regime) it saturates. The activation energies of the blueshift mechanism in the strong blueshift regime decrease with increasing nitrogen content. In the weak blueshift regime, the blueshift saturates more slowly with respect to RTA temperature and to higher values the higher the nitrogen content. When only the RTA time was changed, the blueshift again saturated to higher values the more the nitrogen content. The photoluminescence (PL) efficiency improvement is, on the other hand, unaffected by the nitrogen concentration and depends only on the RTA conditions used. Moreover, short-time annealing at high temperatures results in a smaller PL broadening and is therefore preferable for the growth of active GaInNAs. In outdiffusion from the QW is evident only for long-time annealing. Therefore, the blueshift effects seen for the short-time annealing are related to a different mechanism.

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1. Introduction

The quaternary dilute nitride GaInNAs has recently gathered much interest in the scientific community. Kondow et al. [1] were the first to propose it as a substitute for InGaAs because the addition of N to InGaAs decreases the bandgap energy allowing for emission wavelengths interesting for telecommunication applications (1.3 and 1.5 μm). Optimized growth conditions for GaInNAs require the use of relatively low growth temperature and high growth rates which, combined with the introduction of N generated by a plasma source, contribute to the low as-grown photoluminescence (PL) efficiencies of this material. Post-growth thermal annealing is essential to heal the defects generated during growth and fabricate active materials with PL efficiencies adequate for lasers [2,3]. However, annealing also causes a drastic blueshift of the emission wavelength, which has not yet found a clear explanation [4,5].

We present here, a detailed study of GaInNAs single-quantum wells (SQWs) blueshift and PL efficiency improvement depending on the N concentration and on the annealing parameters of temperature and time.

2. Experimental procedure

For our studies, we grew a total of five samples: one N-free 10 nm-InGaAs-SQW with 35% In content (reference sample) and four 10 nm GaInNAs SQWs with In content of 35% and N content varying from 1.3% to 2.5%. The concentrations of N were chosen to cover the range of PL emission wavelengths from 1350 to 1513 nm. The growth conditions for the quantum wells (QWs) are outlined in

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Ref. [6]. These conditions were used for the growth of the absorber layers of semiconductor saturable absorber mirrors used to successfully passively modelock solid-state lasers [7–10]. All SQWs were capped by a 60 nm-GaAs-layer also grown at the same growth temperature as the QWs to avoid *in-situ* thermal annealing. The N was provided by an RF plasma source at a constant plasma power of 200 W and the N flow was instead varied from 0.03 to 0.08 sccm to obtain the N contents mentioned above. The SQWs thicknesses and materials concentrations were measured by high-resolution Xray diffraction (HRXRD) and the N concentration was found to increase with increasing N flow. All the PL measurements were carried out at room temperature at an excitation wavelength of 785 nm and a power of 40 mW. The emission wavelength of the SQWs increases almost linearly with N concentration from 1350 to 1513 nm, while the PL efficiency (integrated intensity) decreases almost linearly with N concentration.

For all these samples, we wanted to compare two different rapid thermal annealing (RTA) conditions: short-time annealing at various temperatures and long-time annealing at a fixed temperature. For the first annealing condition, we cleaved six pieces from each GaInNAs SQW sample and from the InGaAs SQW sample to perform RTA for 1 min at temperatures ranging from 550 to 800 °C in intervals of 50°. For the second RTA conditions, we took one more piece from each sample and annealed it at 600 °C up to 140 min in several time steps. Moreover, we annealed the GaInNAs sample with the lowest N content and the InGaAs reference sample at 700 °C for 1 h.

The post-growth RTA was performed by placing a GaAs wafer in contact with each sample to provide As over-pressure in order to prevent surface damage due to As evaporation from the GaAs cap layer. Two pieces of the GaInNAs sample with lowest N content, the one annealed at 750 °C for 1 min and the one annealed at 600 °C for 140 min, were also measured in a low-temperature (LT) PL setup at liquid He temperature (4 K) and with an excitation of 1 mW at 483 nm. Finally, for some samples HRXRD rocking curves of the (0 0 4) reflex were measured before- and after-annealing to attest whether the blueshift was due to In outdiffusing from the QW.

3. Results and discussion

3.1. Blueshift after short-time and long-time RTA

In the experiments aimed at observing the effects of RTA temperature on blueshift, we annealed all the samples for 1 min at various temperatures. Fig. 1(a) shows the blueshift, ΔE, vs. RTA temperature. The difference between the InGaAs reference (open markers) and all the GaInNAs samples is evident. The blueshift of InGaAs is comparable with that of GaInNAs only upto 600 °C (about 10 meV for all samples). This is a bit surprising for InGaAs, the blueshift being too large to be attributed to In outdiffusion

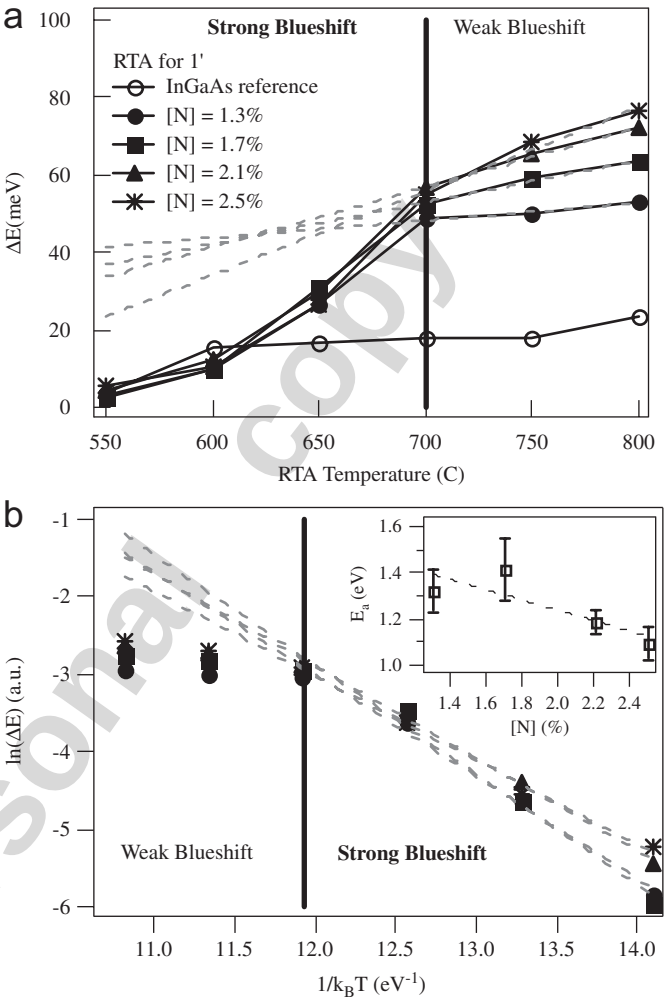

Fig. 1. Energy blueshift, ΔE, vs. RTA temperature of the GaInNAs SQWs and a reference InGaAs SQW with the same In content and growth conditions. The gray dashed lines are the linear fits of the GaInNAs samples in the weak blueshift regime. (b) Arrhenius plots of the data in (a) (the InGaAs sample is excluded from this graph). The gray dashed lines are the linear fits in the strong blueshift regime. Inset in (b): activation energies of the blueshift mechanism in the strong blueshift regime (obtained from the Arrhenius plot in (b)) vs. N content.

after only 1 min annealing. Probably the very low growth temperature (~60° below the ideal one for InGaAs) results in an effective bandgap reduction of the as-grown material due to clustering of the In atoms. However, it is evident that after this small blueshift the InGaAs sample reaches a stable situation. On the other hand, the GaInNAs samples experience a much more dramatic blueshift. As shown in the figure, we can categorize the blueshift in two regimes, a "strong" blueshift regime (below 700 °C), where the blueshift increases rapidly with RTA temperature, and a "weak" blueshift regime (above 700 °C), where the blueshift tends to saturate.

We can trace linear fits (gray dashed lines in Fig. 1(a)) in the weak blueshift regime region for all the GaInNAs samples data and then it is clear that the slopes of these fits increase with increasing N content of the QW. This

indicates that the samples with higher N content have a higher saturation blueshift than those with less N, a result which is in agreement with Klar et al. [4].

In the strong blueshift regime, the trend of the blueshift with N concentration in the sample is not as clear. Since we could not assume that group III materials outdiffusion is the only process governing the blueshift, it was impossible to derive diffusion lengths based on the blueshift itself (as commonly done with InGaAs [11]). Therefore we used a different analysis mechanism. We plotted the same data as that of Fig. 1(a) in an Arrhenius plot in Fig. 1(b). Then we fitted the data in the strong blueshift regime linearly. The slopes of these lines represent the activation energy, E_a, of the blueshift process. This analysis is justified by the fact that the blueshift rate calculated from the RTA time-dependent studies also provided the same results. In the inset in Fig. 1(b) the activation energies found for each sample are plotted vs. N concentration with error bars calculated from the standard deviation of the linear fits coefficients. We notice that the average is about 1.25 eV and that they decrease with increasing N. This implies that it is easier for the blueshift process to occur for samples with more N content. In the experiments aimed at studying the effects of RTA time on the blueshift, the samples were annealed always at 600 °C up to 140 min. Also here we noticed that the GaInNAs SQWs continue to blueshift drastically compared to the InGaAs reference. The blueshift of the GaInNAs samples starts to saturate only after 2 h and GaInNAs samples with more N content have a higher saturation blueshift.

3.2. Stoichiometric analysis with HRXRD

We used HRXRD to find out if there was a difference in composition or shape of the annealed SQWs compared to the as-grown ones. One of the possible causes of blueshift is in fact In outdiffusion from the QW. In Fig. 2 we see the XRD scans of two samples before (thick black line) and after (thick gray line) annealing at 700 °C for 1 h. The lower set of data belongs to the InGaAs reference sample and the top one to the GaInNAs SQW with the lowest N content (1.3%). The QW peak is the low-intensity peak to the left of the GaAs substrate peak. Its distance from the substrate peak represents the perpendicular mismatch of the QW material with respect to GaAs. A decrease in this distance after annealing would indicate a loss of In in the QW. This is usually accompanied by a decrease in the half-width of the QW peak, which indicates a broadening of the QW due to the In outdiffusion from the QW. The shift of the QW peak towards the GaAs substrate peak is evident when we compare the as-grown InGaAs SQW XRD scan (thick black line) with the annealed one (thick gray line) in Fig. 2. The annealed InGaAs SQW could be fitted (thin gray line) with a square well profile with a thickness about 3 Å larger than the as-grown QW (fit, thin black line) and an In concentration about 0.7% smaller. The GaInNAs SQW could also be fitted by a square well with a similar loss in In

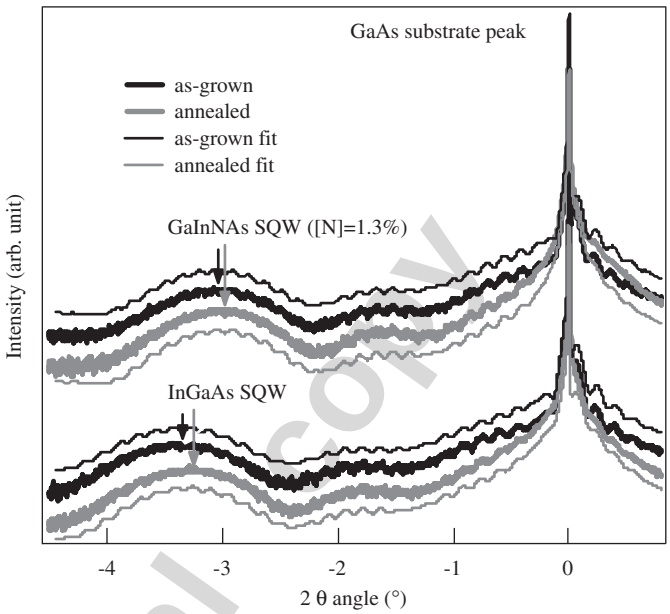

Fig. 2. HRXRD of the GaInNAs SQW with 1.3% [N] and reference InGaAs SQW before (black lines) and after (gray lines) annealing at 700 °C for 1 h. Fits of annealed SQWs before (thin black lines) and after (thin gray lines) annealing.

content and no other changes in the QW stoichiometry were required. Therefore, the larger PL blueshift observed in GaInNAs cannot be explained just by In outdiffusion. For annealing conditions at lower temperature or for shorter times, In outdiffusion is hardly noticeable from HRXRD. From Fig. 2 it is also evident that the pendellösung fringes present in the as-grown material are less visible after annealing (feature that the fit does not display). The lower visibility is attributed to surface roughness generated during the annealing process, which is clearly visible on the annealed samples by phase-contrast microscopy. We found out that it is preferable to use *in-situ* instead of *ex-situ* annealing in order to avoid this problem.

3.3. Effects of RTA on PL efficiency improvement and linewidth

To obtain adequate PL efficiencies for laser materials from GaInNAs, it is necessary to anneal it post-growth in order to reduce the non-radiative defects incorporated during the low-temperature epitaxy. For all our samples we analyzed the integrated intensity of the PL spectrum over energy before and after annealing. In general, samples with more N, which had a lower as-grown PL efficiency, consistently have a lower PL efficiency after annealing compared to samples with less N. In Fig. 3 we show the improvement of the PL integrated intensity, η, defined as the ratio of the PL integrated intensity of the annealed sample normalized to the as-grown PL integrated intensity, vs. RTA temperature. As expected, for the InGaAs reference no significant improvement can be seen. In contrast, for all the GaInNAs samples there is a large

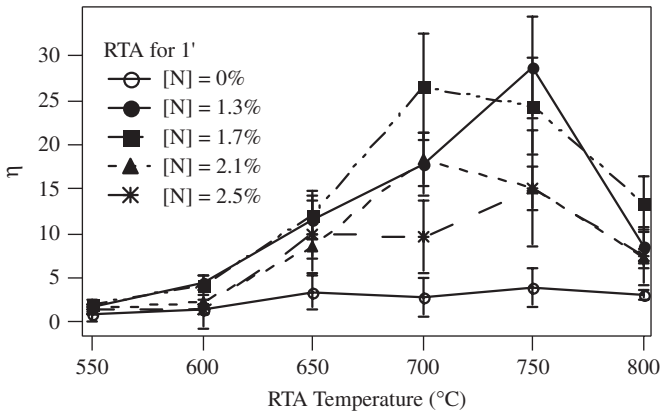

Fig. 3. PL integrated intensity improvement of GaInNAs SQWs and InGaAs SQW reference vs. RTA temperature for 1 min annealing time.

improvement, which increases up to an RTA temperature of about 750 °C (the decrease experienced at higher temperatures is due to surface damage). However, the improvement is similar for all the samples regardless of N content. This is in clear contrast with the blueshift, which shows an unambiguous dependence on the N content.

For all our samples, we obtained similar blueshifts and PL integrated intensity improvements for samples annealed for 1 min at 750 °C and samples annealed for 140 min at 600 °C, indicating that both methods can be used to improve the PL efficiency of GaInNAs. The difference in the material quality can, however, be seen in another important parameter, the linewidth of the PL spectrum. For this analysis we used LT PL with low-intensity pumping. Similar to the InGaAs material system [12], we notice a slightly larger half-width (18 meV compared with 16.4 meV) for the long-time annealed sample. Therefore, shorter annealing times at higher temperatures are preferable to obtain the best material quality.

4. Summary

The main conclusion of our systematic studies of RTA on GaInNAs SQWs with different N content is that the blueshift of the energy bandgap upon annealing is dependent on the N content of the QW while the PL integrated intensity improvement is not. In our short-time RTA studies, in which we analyzed the blueshift vs. RTA temperature, we found out two blueshift regimes, a strong one (below 700 °C) and a weak one (above 700 °C). In the strong blueshift regime we extrapolated activation energies for the blueshift mechanism from an Arrhenius-type model. These energies varied from 1.09 to 1.32 eV and decreased with increasing N content, implying that a higher N concentration facilitates the blueshift mechanism. In the weak blueshift regime, we noticed that the blueshift saturates to higher values the higher the N content of the QW. The same conclusion as in the weak blueshift regime could be reached after the long-time RTA experiments, where the RTA temperature was kept constant and the time duration of the RTA was varied. A clear In outdiffusion from the QW was observed by HRXRD analysis only for samples annealed at 700 °C for 1 h. Therefore it cannot be responsible for the drastic blueshift of GaInNAs at lower RTA temperatures and times. Even though similar PL integrated intensity improvement and blueshift can be obtained by both long-time annealing at relatively low temperatures and short-time annealing at high temperatures, better PL linewidths are obtained in the latter case. Hence this method is better for the growth of active materials based on GaInNAs.

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