The behaviour of optical and structural properties of GaInNAs/GaAs quantum wells upon annealing

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Abstract. Our experiments show that photoluminescence spectra from dilute nitride Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$/GaAs ($y < 2\%$) quantum wells (QW) are independent of growth temperature of the QWs in the range from 430 to 470 °C. Spectral blue shift upon annealing is large for the low-temperature QW (430 °C), and emission intensity is more enhanced than that of the high-temperature QW (470 °C). Raman scattering reveals that the 430 °C QW contains more In–N bonds than does the 470 °C QW. It seems, therefore, that the blue shift, which is proportional to a number of In–N bonds, originates from the presence of point-like defects of the alloy. Lower emission intensity from the annealed 470 °C sample may be attributed to more pronounced alloy fluctuations and interface roughening, seen in cross-sectional transmission electron micrographs.

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1. Introduction

Dilute nitride alloys, GaInNAs, based on the GaAs technology are promising semiconductors for optical fibre telecommunications applications [1]–[7]. Alloying nitrogen with GaInAs reduces compressive strain and decreases the band gap, pushing the emission wavelength up to 1.3 µm and beyond. However, in spite of the low nitrogen content in this alloy, the optical quality of as-grown materials is significantly worse than that of GaInAs, hindering extensive GaInNAs-based device application. The deterioration in luminescence is also due to the relatively low growth temperatures (usually in the 420–480 °C range), used in molecular beam epitaxy (MBE) growth to prevent phase segregation.

Post-growth annealing of GaInNAs/GaAs quantum well (QW) structures, by either rapid thermal annealing or in situ annealing improves photoluminescence (PL) intensity, but causes an undesired blue shift (BS) of emission. The annealing-induced enhancement of the PL intensity can be assigned to a partial removal of non-radiative centres. The BS has mainly been attributed to Ga/In/N atomic interdiffusion across the QW interfaces [5] and/or to an increase of In presence in the nearest-neighbourhood environment of nitrogen [8]. Another cause for BS could be homogenization of In-rich areas, promoted during epitaxial growth by MBE [9].

The annealing-induced enhancement in luminescence efficiency and the magnitude of BS have been often found to differ from one paper to another even if the alloy composition and layer structures were nearly the same [10]. These suggest that the annealing behaviour of the QW strongly depends on the structural quality of the alloy and its heterostructures, which in turn are controlled by the growth conditions. So far, growth temperature has proved to be the most important parameter controlling the quality of dilute-nitride semiconductors grown by MBE. In spite of numerous works on the post-growth annealing of GaInNAs QWs prepared by MBE, little is known about the influence of alloy temperature on the behaviour of its PL under thermal treatment. In this work, we investigate the effects of growth temperature and annealing on PL from MBE-grown GaInNAs/GaAs QWs subject to thermal annealing.

2. Experimental setup

Our samples consisting of 7 nm Ga0.63In0.37N0.01As0.99/GaAs QW structures were grown by solid-source MBE on a n-type GaAs (0 0 1) substrate under As-rich conditions and were nominally undoped. We prepared two samples, labelled S430 and S470, whose QW was grown at 430 and 470 °C, respectively. The top layer was about 20 nm and deposited at the temperature of 450 °C for 72 s. A relatively high growth rate of around 1.6 µm h⁻¹ was used for the QW growth. Growth took place in a layer-by-layer mode, as monitored by streaky reflection high-energy electron diffraction patterns and confirmed by post-growth transmission electron microscopy (TEM). This enabled investigation of the intrinsic effect of $T_{QW}$ on PL from QWs by avoiding the additional ‘extended’ defects promoted by a change in growth mode. The crystallographic structure was studied with a TEM by (0 0 2) dark field imaging. The TEM used was Jeol JEM 2010 and the cross-sectional specimens were prepared by mechanical polishing followed by Ar⁺-ion milling. PL for optical characterization was measured by a standard lock-in technique and a Cd-He laser for excitation and a close-cycle He cryostat for cooling. Thermal annealing was carried out with IR lamp in a separate chamber under N₂ environment. Temperature was measured with a pyrometer with an accuracy of ±10 °C and, during annealing, the samples
Figure 1. (a) 9-K PL spectra from the as-grown S430 and S470 samples. (b, c) (1 1 0) cross-sectional images under dark-field conditions with diffraction vector $g = 200$ for two as-grown samples, both containing one GaInNAs QW: (b) S430 grown at 430 °C and (c) S470 grown at 470 °C. Black arrows indicate the direction of $g$.

were capped with a GaAs wafer to prevent As evaporation. Raman spectra were recorded at 77 K in backscattering from the (1 0 0) growth surface, using the 568.2 nm line of a Kr+ laser. The incident and scattered light were both polarized parallel to the same (1 1 0) crystallographic direction, i.e. the $x (y', y')-x$ scattering configuration was employed.

3. Results and discussion

In figure 1(a), 9-K PL spectra for the as-grown S430 and S470 samples are presented. The spectral line has the same energy for both samples, indicating a similar composition and width of the QWs, as expected on the basis of growth conditions [11]. The PL intensity for S470 was higher (25%) than that of S430, most likely due to the decrease in growth temperature. The broad luminescence band observed in figure 1(a) at $\sim 1100$ nm is substrate-related. We used TEM to study the structural properties of the samples under investigation. In figures 1(b) and (c), TEM dark field images of the as-grown S430 and S470 samples are presented. The diffraction vector was $g = (0 0 2)$ [12]. This orientation is sensitive to the chemical composition of the alloy. The two thin dark lines, approximately 1 nm thick, in the images correspond to the interfaces of GaInNAs QW. The dark line closer to the free surface seems to be somewhat thicker than the line defining the lower interface. The origin of these parallel dark lines is the minimum of the intensity due to the actions of both the In and N composition at the interfaces [9]. Both sample show a clear QW structure with a similar QW thickness. This is consistent with the PL results, which showed the same emission wavelength for the as-grown S430 and S470 samples. Both interfaces seem to be abrupt with no increase in interface roughness with increase in $T_{QW}$ and no island-like structures are seen in the image. This is in contrast to what have been reported for (0 0 2) dark-field analysis [14, 15], where an increase in $T_{QW}$ from 420 to 475 °C was found to
Figure 2. (a) 9-K PL spectra from the 6 min at 580 °C annealed S430 and S470 samples. (b, c) cross-sectional images under dark-field conditions with diffraction vector \( \mathbf{g} = 200 \) for two annealed samples, both containing one GaInNAs QW: (b) S430 grown at 430 °C and (c) S470 grown at 470 °C. Black arrows indicate the direction of \( \mathbf{g} \) and white arrows show the interface roughness.

induce contrast modulations at the GaInNAs/GaAs interfaces and it was attributed to a growth-mode change from two-dimensional to three-dimensional Stranski–Krastanow with increase in \( T_{QW} \).

When the samples were annealed for 6 min at \( T_{ann} = 580 °C (\gg T_{QW}) \) in a way which mimics the substrate temperature variation when 100 nm GaAs cap would be grown on top of the QW at a similar growth rate as that used in the QW, a remarkable BS and enhancement in PL intensity is seen for both samples (figure 2(a)). A striking point is that both the BS and enhancement in PL showed a strong dependence on the \( T_{QW} \): their magnitudes increase with decrease in \( T_{QW} \). Thus, upon annealing, there is an apparent red shift of PL emission as well as a deterioration of PL intensity with increase in \( T_{QW} \). A similar behaviour of BS in GaInNAs/GaAs QWs has been reported previously but no explanation was given. As long as a similar annealing could occur when the layers capping the QW are grown by MBE at a temperature much higher than that of the QW, we suggest that self-annealing is the main cause of the previously observed dependence of QW emission on \( T_{QW} \) [13]–[15]. For the sake of clarity, in our previous study [16], we grew two samples at 430 and 470 °C where the top GaAs layers were grown at the temperature of 580 °C for 6 min, a temperature usually used for GaAs growth by MBE. The PL spectra of these as-grown samples reminded those of the annealed S430 and S470 samples, confirming our afore-mentioned suggestion.

Figures 2(b) and (c) show the TEM dark field images of the annealed S430 and S470 samples. The (0 0 2) dark field images show increased variations in the contrast inside the QW for the S470 sample. These contrast variations may be caused by fluctuations of the In or N mole fractions. An absolute variation of \( \sim \pm 1\% \) in the [In] is reported to be sufficient to induce variations in the contrast when the GaInNAs QWs In mole fraction is in the range 25–35\%, while a variation of \( \sim \pm 2\% \) in the nitrogen mole fraction would be needed to observe changes in the contrast when [N] = 2.5\% [14, 15]. This is due to the lower sensitivity of the (0 0 2) dark-field intensities to N variations [14, 15]. In our case, [N] = 1\%, therefore the contrast fluctuations are easier to
relate to fluctuations of the In mole fraction than to the N mole fraction. However, N fluctuations cannot be excluded with this technique alone. Recently, In-concentration homogenization and N out-diffusion from the well after annealing has been reported [9]. For the S430 sample, the interface is quite smooth, whereas for S470 some roughening of the interface near the free surface is observed. The deterioration of the upper interface for the annealed S470 sample did not necessarily cause the observed decreased PL intensity. It should be mentioned that the decrease of PL intensity with increase in surface roughness is usually connected to the formation of non-radiative recombination centres, e.g. point defects [17]. Despite the observed interface roughening, the PL peak (figure 1(b)) is not split, which rules out a dot-like behaviour of the GaInNAs alloy as reported by Chauveau et al [14, 15]. One could expect that, due to the improved crystal quality after RTA, the PL peak widths will be narrower for the S430 sample than for the as-grown sample. This is not true in our case. Also, the annealed S470 sample having the rough interface shows decreased peak width compared with the as-grown S470 sample. These results are contradictory to the commonly assumed PL line narrowing with improved QW interface quality. Evidence of an opposite phenomena, where the narrow exciton lines do not necessarily imply that the interfaces are of very good quality, has been recently reported [18].

To further investigate the annealing effect, we annealed the S430 and S470 samples over the temperature range of 460–600 °C for 6 min (figure 3). As seen from the figure, the $T_{QW}$-dependent BS is remarkable even at annealing temperatures below the typical temperature range used for GaAs cap layer growth (570–600 °C). Also, the BS increases as the $T_{QW}$ of the QW decreases to 430 °C, especially when the annealing temperature $T_{ann} > 540$ °C. Furthermore, as our studies show, over the whole range of $T_{ann}$ investigated, the PL from S430 was significantly higher than that of S470 (about 2–4 times). This suggests that the observed increase in luminescence efficiency with decrease in $T_{QW}$ is mainly due to the annealing effect mimicking the GaAs top-layer growth.

**Figure 3.** Dependence of BS on the annealing temperature $T_{ann}$ for S430 and S470. Inset: the difference ($BS_{S430}−BS_{S470}$) between annealing-induced BS for S430 ($BS_{S430}$) and S470 ($BS_{S470}$) versus annealing temperature $T_{ann}$. The broken lines connecting the symbols are drawn to guide the eye.
To study the possible cause of the $T_{QW}$-dependent BS, the formation of In–N bonds during annealing was investigated. In the Raman spectra, the formation of such bonds (In–N) is seen as a formation of In–N-like LO2 modes, which are centred at the wavenumbers around 460 and 485 cm$^{-1}$ [19]. Raman spectra recorded from the as-grown and annealed S430 and S470 samples are presented in figure 4. All spectra were normalized to the intensity of the GaAs LO2 modes. The formation of In–N bonds during annealing can be seen only for the S430 sample as a featureless broad band partially overlapping the GaAs-like 2TO phonon spectrum. This indicates the formation of In–N bonds during annealing [19, 20]. For the as-grown S430, S470 and annealed S470, no peaks at wavenumbers around 460 and 485 cm$^{-1}$ have been resolved. This result suggests that the amount of possible In–N bonds in S470 formed during annealing was smaller than that in S430, impeding a well-resolved signal. Since the growth temperature is lower for the S430 sample than for the S470 sample, the number of point defects is higher in the S430 sample [21]. This hints that the annealing-induced In–N bond formation is a point-defect-assisted phenomenon. Thus, the lower the $T_{QW}$, the higher the defects, the easier is the formation of In–N bonds. As a consequence, as more In–N bonds are created, a larger band gap is obtained, giving rise to a larger BS upon annealing. It is also possible that the same mechanism that blueshifts the PL upon annealing also contributes to an increase in the PL efficiency by creating additional N–In ‘active sites’ [22].

4. Conclusions

In summary, we have investigated the effect of QW growth temperature on PL properties of GaInNAs/GaAs QWs with respect to the QW growth temperature. When the top GaAs layer is deposited at the same temperature as the QW, no noticeable differences in PL properties and QW microstructure could be seen. When the samples were annealed to simulate the top GaAs deposition at temperatures normally used for GaAs growth, significant BS and intensity decrease of the spectra with respect to the as-grown samples were observed. The magnitudes of
the BS and intensity deterioration are growth temperature-dependent. QW interface roughening is observed with increasing growth temperature, explaining lower PL intensity for the sample grown at higher temperature. This roughening is most likely caused by variations in the In mole fraction with increase in growth temperature. One possible explanation for our results is that the annealing or growth of the top GaAs layer at a typical substrate temperature anneals the QW and induces a BS on PL emission whose magnitude increases as growth temperature decreases. On the basis of Raman data, the main cause for the increase in BS with decrease in growth temperature seems to be an enhancement in the amount of In–N bonds formed by annealing, likely through a defect-assisted mechanism. Our results suggest that the observed increase in luminescence efficiency with decrease in growth temperature can be caused by the annealing effect during upper layer growth. According to the results presented, the top-layer annealing effect must be taken into consideration when making conclusions about the effect of growth temperature on the luminescence properties of the as-grown GaInNAs QWs grown by MBE. This is the case, especially when the capping layers are grown at a temperature above what is used for the GaInNAs QW, e.g. AlGaAs layers.

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