Improvement in the optical quality of GalnNAs/GalnAs quantum well structures by interfacial strain reduction

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Abstract: The authors report on the use of thin (2 nm) layers with intermediate strain placed between the barriers and the quantum wells of GaInNAs/GaInNAs structures in order to reduce the effect of strain on the quantum wells. A comparison between samples with and without these strainmediating layers has been performed using various optical and structural techniques, such as photoluminescence, high-resolution X-ray diffractometry and transmission electron microscopy. The results show that the introduction of strain-mediating layers brings beneficial effects to the structural quality of the active region which, in turn, is reflected by a two orders of magnitude improvement in the photoluminescence intensity. It is thought that this structural design approach can be successfully used to obtain high performance 1.3 and 1.55 μ m lasers based on dilute nitride materials grown on GaAs.

1 Introduction

Recently GaInNAs dilute nitride alloys have received much attention owing to their novel characteristics, in particular the large bandgap bowing [1] and the reduction of the lattice parameter of the alloy with respect to GaInAs. Both effects allow for an extension of the wavelength range achievable using GaAs substrates. Since the earliest reports made by Kondow *et al.* [2], dilute nitrides and particularly GaInNAs have been investigated as a potential material for telecommunication wavelength sources and detectors.

Unfortunately, however, the incorporation of increasing quantities of nitrogen in the alloy rapidly degrades the optical quality of the material and, therefore, the amount of nitrogen that can be used to process efficient sources is limited to a few percent (<5%). As a result, substantial progress has been made towards efficient emission at 1.3 µm [3–6] using typically 1–2% nitrogen, while extension into the 1.55-µm waveband (3–5% nitrogen) at present still looks difficult.

In this paper, we report on the use of thin (2 nm) layers inserted between the quantum well (QW) and the barriers in order to grade the strain on the QW. This approach has been proposed by Pavelescu *et al.* [7], who suggested the insertion of such layers, named strain mediating layers (SMLs), between tensile-strained barriers and highly compressive-strained QWs. In their study they concentrated on optimising the thickness of these layers. In our study we investigated the effectiveness of this approach in a structure

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with barriers lattice-matched to the GaAs substrate and we have optimised their composition for samples emitting at $1.3 \,\mu$ m. We also investigated the effect of the surface nitridation on the optical quality.

2 Growth

All the samples in our study were grown by MBE using a VG80H system equipped with all solid sources except for the atomic nitrogen source which is an Oxford Applied Research HD25 radiofrequency plasma source. The growth was monitored *in situ* by reflection high-energy electron diffraction (RHEED) and the substrate temperature was measured using a pyrometer. The substrates used were (001) GaAsn⁺-doped.

During the growth of the active region we lowered the temperature down to $375 \,^{\circ}$ C, since our previous studies showed that this temperature provides us with the best results in terms of optical and structural quality [8, 9]. To reduce the effects of nonradiative defects we annealed all the samples *in situ* at 660 $^{\circ}$ C for one hour immediately after the end of the growth under an arsenic overpressure. For all the samples, if not otherwise stated, the nitrogen plasma was ignited immediately before the growth of the first quaternary barrier, keeping the main shutter in front of the sample, to try to reduce the amount of unintentional nitrogen incorporation during this stage.

For this study we grew two sets of single quantum well (SQW) samples. The first set of samples was used to investigate the effectiveness of the SML approach and to optimise the composition of the SML layers and the second set was used to investigate the role of the surface nitridation on the optical quality of the material. To complete our study two other samples were grown: a reference sample with no strain-mediating layers and without any technique to reduce the effect of the surface nitridation and a three-quantum-well sample containing the SMLs with the best composition.

All the quantum wells in the samples for this study consist of 8-nm $Ga_{0.62}In_{0.38}N_{0.02}As_{0.98}$ and the barriers are 52 nm of $Ga_{0.97}In_{0.03}N_{0.01}As_{0.99}$. The active region is surrounded by 50 nm of GaAs and all this is placed between $Al_{0.4}Ga_{0.6}As$

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cladding layers. All the epitaxial layers are nominally undoped.

The samples from the first set have the QW enclosed between two 2-nm-thick layers of $Ga_{1-x}In_xN_{0.02}As_{0.98}$, which we term strain-mediating layers (SMLs) after Pavelescu *et al.* [7]. These layers are grown as short-period superlattices, with a thickness chosen as 2 nm also following [7]. We grew three samples in this set which differ from each other only in the In content in the SMLs (x = 0.12, 0.18 and 0.24 labelled A1, A2 and A3, respectively) in order to understand which composition gives the optimum results for this particular QW and barrier composition.

The second set is again composed of three samples; for the first one (B1) we tried to minimise the effects of unintentional surface nitridation during the plasma start-up phase by reducing the substrate temperature to 200°C and keeping an arsenic overpressure on the sample before igniting the plasma and then raising the temperature to 610°C in order to try to desorb the nitrogen species that could have been adsorbed on the surface. The second sample in this set (B2) has the same structure as the reference sample (single quantum well and no SMLs), but in this case the RF plasma was started before starting the growth run and then kept to a stable plasma power minimum with the k-cell shutter closed until nitrogen incorporation was required. Under these conditions we would expect minimal nitrogen incorporation. The last sample in this set (B3) was grown similarly to sample B2, but with 18% indium composition SMLs between the quantum well and the barriers. The technique used for these last two samples had the objective of keeping the nitrided surface as far as possible from the active region.

Finally we grew a sample using the same recipe as sample B3 but containing three quantum wells instead of a single well. This sample was used mainly to investigate the structural properties of the samples containing the SMLs in a multi-quantum well (MQW) environment by transmission electron microscopy (TEM).

3 Results

The photoluminescence (PL) measurements were performed using a 532 nm solid-state green laser as excitation source and a 0.55 m monochromator was used to disperse the PL spectra that was detected by a liquid-nitrogen-cooled Ge detector. Low-temperature and temperature-dependent measurements were performed using a closed-cycle helium cryostat.

High-resolution X-ray diffractometry measurements were performed using a Bede D1 system and an estimation of the material composition was obtained by the simulation of the (004) and (115) glancing incidence rocking curves, using the Bede RADS software and keeping the In and N compositions as free parameters in the layer fitting procedure.

Figure 1 shows a comparison of the PL intensities and the full width at half maximum (FWHM) of the samples measured at 10 K for the first set and the reference sample. As can be clearly seen, the optical quality improves dramatically with the introduction of the SMLs. The best sample was A2, which is the one with 18% indium in the SML. From our data, increasing the indium content (to 24%) further decreases the optical quality. This latter result could be due to the fact that a higher indium composition can reduce the valence band offset between the strain-mediating layers and the quantum well below an acceptable minimum value, so that the holes are effectively not confined [10]. If this is the case, the overlap between the



Fig. 1 Comparison between the photoluminescence intensities and full width at half maximum values measured at 10 K of samples in set A and the reference sample

electron (the confinement of which should be strong and not significantly affected by the introduction of the SMLs) and the hole wavefunctions could be strongly reduced.

The results show that the reduction in strain obtained using the SMLs, in combination with the low growth temperature, creates conditions to grow much higher quality material.

Room-temperature PL measurements show similar results to those obtained at 10 K, although at room temperature it was impossible to take the spectrum of sample A3 due to its poor optical quality. The degradation of the room-temperature PL supports the hypothesis that the valence band offset is not enough to confine the holes as previously mentioned.

Figure 2 shows the HRXRD (004) rocking curves for the reference sample and sample A2. From these we can see that the introduction of the SMLs does not degrade the quality of the QW and, in fact, the QW diffraction peak appears better defined and narrower compared to the reference sample.

Nitridation of the exposed surface [11] is the unintentional incorporation of nitrogen species (atoms, molecules and ions), when the growth is interrupted during the ignition of the plasma, which requires significantly higher RF power than is used during the growth.

By analysing the PL results from the second set of samples and comparing them to the reference sample, we



Fig. 2 *High-resolution X-ray diffractometry (HRXRD) (004)* rocking curves of the reference sample and sample A2

Graphs show that the peak on the left-hand side, due to the QW, in sample A2 is narrower than in the reference sample, which is a sign of better structural quality and uniformity



Fig. 3 *Photoluminescence spectra at 10 K of the samples in set B and the reference sample*

Table 1: Summary of the photoluminescence intensity and FWHM values of all the samples used in this study, taken at $10 \, \text{K}$

Name	Description	(meV)	Intensity
Ref	Reference sample	21.9	1
A1	SML 12% In	14.14	17.3
A2	SML 18% In	10.8	193.6
A3	SML 24% In	24.7	0.3
B1	plasma-effect minimisation	19.5	1.5
B2	early plasma ignition	15.9	7
B3	SML 18% In $+$ early plasma	10.8	357
С	as B3, but 3QWs	12.4	2234.7

can see that nitridation is indeed a degrading factor on the optical quality of the material.

From Fig. 3 and Table 1 it is evident that trying to minimise the nitridation of the surface by keeping an arsenic overpressure in the growth chamber and a low substrate temperature (sample B1) is not very effective, as the improvement in optical quality relative to the reference sample is within the experimental uncertainty. Better results have been obtained by keeping the nitrided surface as far as possible from the active region (sample B2). Comparing sample B3 (grown with 18% indium SMLs) and sample A2, the optical quality improves by having the nitrided surface away from the active region, in this case in the GaAs buffer. The PL intensity is almost doubled using this technique, whilst the linewidth is the same in both samples. From these results we can suppose that the nitridation introduces mainly nonradiative recombination centres affecting the PL intensity, but that the linewidth broadening is not affected.

In a previous study of MQW samples without the SMLs, the first well at the bottom of the structure was identified as having a much lower optical quality than the subsequent ones. In structural observations by cross-sectional TEM, a thickness modulation of the first well was observed in some of these samples. Comparisons between PL measurements of SQW and MQW samples showed that the former had intensities orders of magnitude weaker than the latter, again demonstrating the poor quality of the first well. We have demonstrated that the growth temperature plays an important role, especially on this undulation, since the samples grown at higher temperatures show a higher level of undulation in the first well and a tendency to propagate this modulation to the other wells [8].



Fig. 4 TEM image of sample C

It can be seen that the QW quality is very high, no visible defects or dislocations are present, the QWs look flat within the resolution and their interfaces are abrupt

For this reason we include in our study the results of sample C, which is an MQW containing three wells, grown in an identical manner to sample B3 and characterised by TEM and PL.

Figure 4 shows the compositionally sensitive (002) darkfield image of the MQW sample. In this sample all the quantum wells appear flat, with no thickness modulation, no composition modulation and with abrupt interfaces. The structural quality of this sample is very high, amongst the highest we have seen, and no defects are evident from the picture.

From these results and from the analysis of the PL FWHM we can see that this growth recipe, consisting of the SMLs along with a low-growth temperature and the removal of the nitrided surface from the active region, gives improved reproducibility through the MQW in terms of composition and of thickness of the QW.

If we compare the PL results from this sample with those from sample B3 we can see that the optical quality of the first quantum well, or the SQW in sample B3, is comparable to that of the other wells. However, there still exists a discrepancy between the PL intensity of sample B3 and the one of sample C. We would expect the latter to be approximately three times brighter than the former, but instead the difference is approximately six times. This factor of two could suggest that the quality of the first QW, although dramatically improved, could be enhanced more.

The broadening of the linewidth due to the presence of three quantum wells instead of a single one is rather low, indicating that the three quantum wells are very similar to each other in terms of composition and thickness and that a good growth uniformity was achieved.

4 Conclusions

We have demonstrated the value of inserting strainmediating layers between the barriers and the QW and the minimisation of the effect of the surface nitridation on the QW by placing the plasma ignition before the beginning of the growth for high structural and optical quality dilute nitride material for 1.3 µm applications.

The narrowing of the quantum well peak in X-ray rocking curves and the improved photoluminescence data indicate better structural quality. However, the precise mechanism for this is as yet unclear. The structural benefits of the SMLs could be an improvement in interfacial morphology or a reduction in relaxation, such as that from dislocation loops [8]. However, we have no direct evidence for these effects. Such improvements are on a microscopic scale and beyond the limits of our analysis techniques at present. Another effect could be the compensation of inhomogeneities in the distribution of In and N along the growth direction, such as segregation of nitrogen to the interfaces [12]. Further work is needed to investigate this possibility.

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References 6

- 1 Shan, W., Walukiewicz, W., Yu, K.M., Ager, J.W., Haller, E.E.,
- Shan, W., Walukiewicz, W., Yu, K.M., Ager, J.W., Haller, E.E., Geisz, J.F., Friedman, D.J., Olson, J.M., Kurtz, S.R., and Nauka, C.: 'Effect of nitrogen on the electronic band structure of group III–N–V alloys', *Phys. Rev. B, Condens. Matter*, 2000, 62, (7), pp. 4211–4214
 Kondow, M., Kitatani, T., Nakatsuka, S., Larson, M.C., Nakahara, K., Yazawa, Y., Okai, M., and Uomi, K.: 'GaInNAs: a novel material for long-wavelength semiconductor lasers', *IEEE J. Quantum Electron.*, 1997, 3, (3), pp. 719–730

- 3 Tansu, N., Yeh, J.Y., and Mawst, L.J.: 'Low-threshold 1317-nm InGaAsN quantum-well lasers with GaAsN barriers', *Appl. Phys. Lett.*, 2003, **83**, (13), pp. 2512–2514
- Gupta, J.A., Barrios, P.J., Aers, G.C., Williams, R.L., Ramsey, J., and Wasilewski, Z.R.: 'Properties of 1.3 µm InGaNAs laser material grown by MBE using a N₂/Ar RF plasma', *Solid-State Electron.*, 2003, **47**, pp. 399-405
- 5 Coldren, C.W., Spruytte, S.G., Harris, J.S., and Larson, M.C.: 'Group III nitride-arsenide long wavelength lasers grown by elemental source
- III nitride-arsenide long wavelength lasers grown by elemental source molecular beam epitaxy', J. Vac. Sci. Technol. B, Microelectron. Nanometer Struct., 2000, 18, pp. 1480-1483
 6 Li, W., Jouhti, T., Peng, C.S., Konttinen, J., Laukkanen, P., Pavelescu, E.M., Dumitrescu, M., and Pessa, M.: 'Low-threshold-current 1.32-µm GaInNAs/GaAs single-quantum-well lasers grown by molecular-beam epitaxy', Appl. Phys. Lett., 2001, 79, (21), pp. 3386-3388
 7 Pavelescu, E.M., Peng, C.S., Jouhti, T., Konttinen, J., Li, W., Pessa, M., Dumitrescu, M., and Spânulescu, S.: 'Effects of insertion of strain-mediating layers on luminescence properties of 1.3-µm
- Buintrescu, M., and Spannescu, S.: Effects of insertion of strain-mediating layers on luminescence properties of 1.3-µm GaInNAs/GaAs quantum-well structures', *Appl. Phys. Lett.*, 2002, 80, (17), pp. 3054–3056
 Herrera, M., González, D., Hopkinson, M., Navaretti, P., Gutíerrez, M., Verrez, M., Verrez
- 8 Herrera, M., González, D., Hopkinson, M., Navaretti, P., Gutíerrez, M., Liu, H.Y., and García, R.: 'Influence of growth temperature on the structural and optical quality of GaInNAs/GaAs multi-quantum wells', *Semicond. Sci. Technol.*, 2004, 19, pp. 813–818
 9 Liu, H.Y., Hopkinson, M., Navaretti, P., Gutíerrez, M., Ng, J.S., and David, J.P.R.: 'Improving optical properties of 1.55 μm GaInNAs/GaAs multiple quantum wells with Ga(In)NAs barrier and space layer', *Appl. Phys. Lett.*, 2003, 83, (24), pp. 4951–4953
 10 Dumitras, G., and Riechert, H.: 'Determination of band offsets in semiconductor quantum well structures using surface photovoltage', *J. Appl. Phys.*, 2003, 94, (6), pp. 3955–3959
 11 Wang, S.Z., Yoon, S.F., and Loke, W.K.: 'Effects of surface nitridation during nitrogen plasma ignition on optical quality of GaInAsN grown

- during nitrogen plasma ignition on optical quality of GaInAsN grown by solid source molecular beam epitaxy', Appl. Phys. Lett., 2003, 94, (4), pp. 2662–2666 12 Grillo, V., Albrecht, M., Remmele, T., Strunk, H.P., Egorov, A.Y., and
- Riechert, H.: 'Simultaneous experimental evaluation of In and N concentrations in InGaAsN quantum wells', *J. Appl. Phys.*, 2001, **90**, (8), pp. 3792-3798