PUBLICATION IV

ELSEVIER

Journal of Crystal Growth 234 (2002) 631–636

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

GaInNAs quantum well structures for 1.55 μm emission on GaAs by atmospheric pressure metalorganic vapor phase epitaxy

T. Hakkarainen*, J. Toivonen, M. Sopanen, H. Lipsanen

Optoelectronics Laboratory, Helsinki University of Technology, P.O. Box 3000, FIN-02015 Hut, Finland

Received 15 June 2001; accepted 26 September 2001
Communicated by K. Nakajima

Abstract

GaInNAs/GaAs multiple quantum well (MQW) structures for long wavelength emission were grown by atmospheric pressure metalorganic vapor phase epitaxy using trimethylgallium, trimethylindium, tertiarybutylarsine and dimethylhydrazine precursors. The dependence of the N concentration and the emission wavelength on the In concentration was investigated. The longest wavelengths were obtained with In concentrations of around 23%. Post-growth rapid thermal annealing was performed to enhance the optical quality of the material. Low-temperature photoluminescence (PL) down to 0.77 eV (1.61 μm) was obtained from a $Ga_{0.74}In_{0.26}N_{0.03}As_{0.97}$ MQW structure. After annealing the PL wavelength of 1.51 μm was obtained at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 81.15.Gh; 78.55.−m

Keywords: A1. Photoluminescence; A1. Rapid thermal annealing; A3. Metalorganic vapor phase epitaxy; B2. Semiconducting materials

1. Introduction

GaInNAs grown on a GaAs substrate has been under great research interest in recent years due to its potential applications in optoelectronic devices for fiber-optic communications. The large band gap bowing of GaInNAs makes it suitable to be used as an active material in long wavelength (1.3 or 1.55 μm) laser diodes on GaAs [1]. The addition of nitrogen into GaInAs also increases the conduction band offset [2], which results in improved high-temperature performance of lasers. Moreover, it can be used to improve the conversion efficiency of multi-junction solar cells [3], and as an active material in vertical-cavity surface-emitting lasers (VCSELs) with GaAs/AlAs distributed Bragg reflectors (DBRs) [4].

GaInNAs/GaAs structures for long wavelength emission have recently been fabricated by different techniques. Low-temperature (LT) emission at 1.68 μm has been achieved very recently from GaInNAs quantum wells (QWs) grown by solid-

*Corresponding author. Tel.: +358-9-451-2325; fax: +358-9-451-3128.

E-mail address: thakkara@cc.hut.fi (T. Hakkarainen).

PII: S0022-0248(01)01750-X

source molecular beam epitaxy (SS-MBE) [5]. GaInNAs/GaAs laser diodes operating at 1.52 μm have also been grown by SS-MBE [6]. Room-temperature (RT) emission at 1.52 μm has been demonstrated from self-assembled GaInNAs quantum dots grown by gas-source MBE [7]. One previous report shows 1.5 μm emission from GaInNAs QWs on GaAs fabricated by metalorganic vapor phase epitaxy (MOVPE) [8]. However, these structures were grown at low pressure, and in the present study GaInNAs/GaAs multiple quantum wells (MQWs) for 1.55 μm emission were fabricated by atmospheric pressure MOVPE.

2. Experimental procedure

The samples were grown on semi-insulating GaAs (1 0 0) substrates in a horizontal MOVPE reactor at atmospheric pressure. Palladium-purified hydrogen was used as a carrier gas. Trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as sources for gallium, indium, arsenic and nitrogen, respectively. The sample structure consists of a 100-nm-thick GaAs buffer layer, a 10-period $Ga_{1-x}In_xN_yAs_{1-y}$/GaAs MQW and a 20-nm-thick GaAs cap layer. In concentrations between 10% and 30% in gas phase were used. All the layers excluding the buffer layer were grown at the same temperature, varied in the range of 500°C–580°C. All the temperatures mentioned here are thermocouple readings. The growth rate of the GaInNAs layers was 1.4 μm/h and the TBAs/III ratio and the DMHy/V ratio were varied from 2 to 3.5 and from 0.936 to 0.97, respectively.

A high-resolution X-ray diffractometer (HR-XRD) with a four-crystal Ge (2 2 0) monochromator was used to determine the layer thickness and the indium and nitrogen concentration of the samples by comparing measured and simulated rocking curves. The optical properties of the samples were investigated by LT, i.e., 10 K, and RT photoluminescence (PL) measurements. The 488 nm line of an argon ion laser was used for excitation. The luminescence was dispersed with a 0.5 m monochromator and detected by a liquid-nitrogen-cooled germanium detector. To enhance the optical quality of the samples, post-growth rapid thermal annealing was performed under excess As ambient in the MOVPE reactor.

3. Results and discussion

It is generally known that the band gap energy of $Ga_{1-x}In_xN_yAs_{1-y}$ decreases with increasing N and In concentration. If the electron effective mass in GaInNAs is assumed to be two to three times heavier than that in GaAs [9], the effect of quantization on the PL peak energies of the MQWs with the QW thickness of 10 nm is less than 50 meV. Fig. 1 shows the PL peak energies of the $Ga_{1-x}In_xN_yAs_{1-y}$(10 nm)/GaAs(30 nm) MQW samples fabricated with different In concentrations. The PL peak energy decreases strongly with increasing N concentration, but with a slightly reduced curvature at high In concentrations compared to GaAsN for the N concentrations of less than 1%. This may indicate a reduction in the bowing parameter of GaInNAs/GaAs material system with increasing In concentration, as previously suggested by Koch [8]. It should be noticed, though, that there is some uncertainty in the evaluation of the N concentration, which is discussed later in this paper. It has been reported

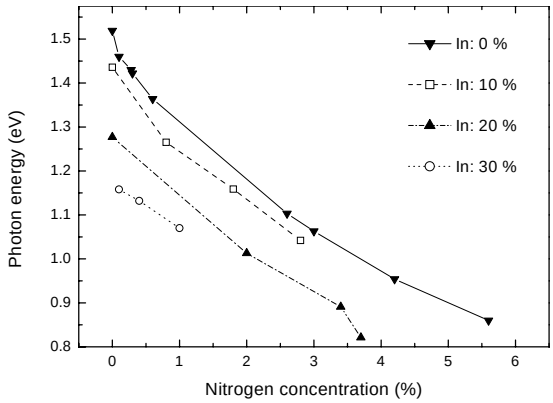

Fig. 1. LTPL peak energies of the $Ga_{1-x}In_xN_yAs_{1-y}$(10 nm)/GaAs(30 nm) MQW samples fabricated with different In concentrations. A slight reduction in the band gap bowing is observed for N concentrations of less than 1% when the In concentration is increased.

that the N incorporation is seriously hindered by the presence of In during MOVPE growth of $Ga_{1-x}In_xN_yAs_{1-y}$ [10,11]. In contrast, the In content does not significantly affect the N incorporation during SS-MBE growth [5]. We investigated the effect of In on N incorporation and optimized the growth conditions in order to achieve long wavelength emission from $Ga_{1-x}In_xN_yAs_{1-y}$/GaAs MQW structures.

First, the growth temperature was varied from 500°C to 580°C using relatively low DMHy/V ratio of 0.936 and TBAs/III ratio of 3.1. The effect of the growth temperature on the N concentration with In concentrations of $x = 0.1$ and 0.3 is shown in Fig. 2. The N concentration increases when the growth temperature is decreased, and the maximum N concentration is achieved at 520°C. Decreasing the growth temperature further results in poor crystal quality. Therefore, all the subsequent samples were grown at 520°C. It can also be seen from Fig. 2 that increase in the In concentration results in decrease of the N concentration. Friedman et al. [11] suggested that this behavior could be due to surface segregation of In, which creates a surface layer with a much enhanced In content relative to the bulk. They also speculated that the presence of In adatoms at the growth surface changes the surface reconstruction and thereby decreases the surface N solubility. We have also observed that negligible amount of nitrogen is incorporated in MOVPE-grown GaInNAs quantum dots (QDs) with the In concentration of 60%.

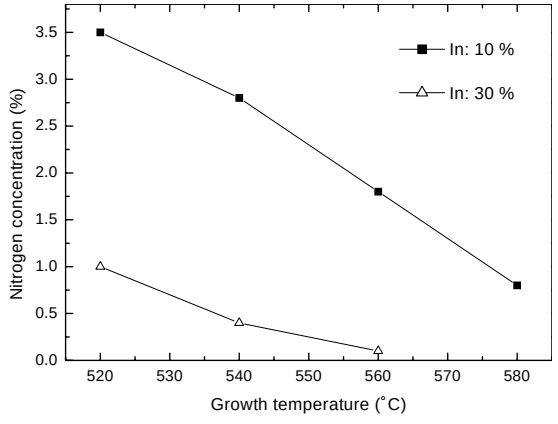

Fig. 2. Effect of growth temperature on the N concentration for two In concentrations of 10% and 30%. The N concentration increases when the growth temperature is decreased and the maximum is achieved at 520°C. Increase in the In concentration results in decrease of the N concentration.

The thickness of GaAsN samples grown at low temperatures was reduced due to decrease in growth rate as a result of incomplete decomposition of TMGa. Based on the growth rates of the GaAsN samples, it was observed that the decomposition of TMGa decreases by 10% at 540°C and by 15% at 520°C. At higher growth temperatures the decomposition was observed to be complete. Consequently, the In concentration of GaInNAs in solid is a few percent larger than in gas phase at low temperature. This was used as a guideline when the concentration was determined by comparing simulated and measured X-ray diffraction curves. Fig. 3 shows an X-ray rocking curve of a GaInNAs/GaAs MQW structure. The lower curve is the simulated X-ray rocking curve, which agrees well with the measured curve. The N and In concentrations of the 9 nm thick QWs are 3.0% and 26%, respectively, and the thickness of the GaAs barrier layer is 24.5 nm.

Fig. 4 shows the 10 K PL peak energies of the samples fabricated with two different DMHy/V ratios (0.936 and 0.96) and TBAs/III ratios (3.1 and 2) as a function of the In concentration. The QW thickness is 10 nm in all these samples. It can be seen that there exists an optimum growth window at In concentration of around 23% for both DMHy/V ratios, where the smallest PL peak

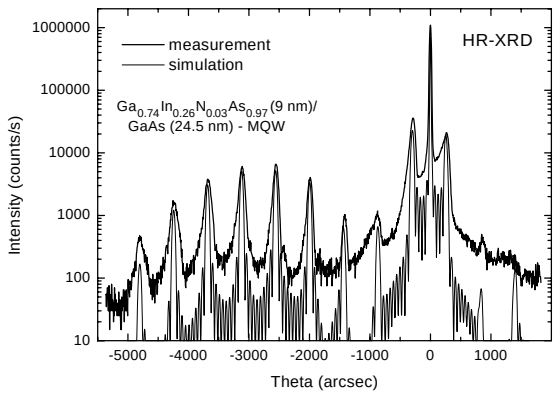

Fig. 3. Measured and simulated X-ray rocking curves of a $Ga_{0.74}In_{0.26}N_{0.03}As_{0.97}$(9 nm)/GaAs(24.5 nm) MQW structure.

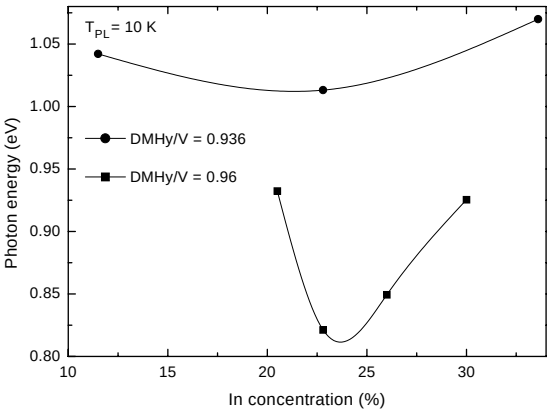

Fig. 4. Dependence of the PL peak energy on the In concentration with two different DMHy/V ratios. There exists an optimum window at the In concentration of around 23% for the smallest PL peak energies.

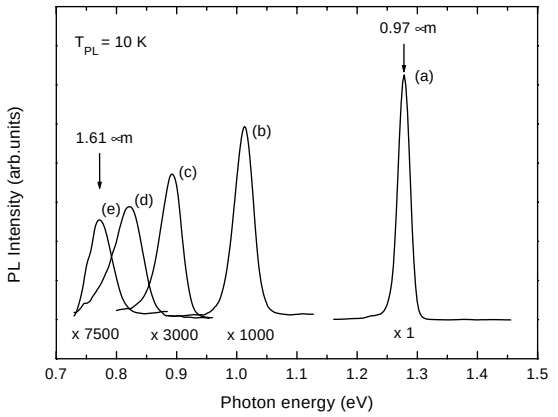

Fig. 5. LTPL spectra of $Ga_{1-x}In_xN_yAs_{1-y}$(9 nm)/GaAs(24.5 nm) MQW samples fabricated with different DMHy/V ratios. The In and N concentrations of the samples are: (a) $x = 0.228$ and $y = 0$, (b) $x = 0.228$ and $y = 0.02$, (c) $x = 0.228$ and $y = 0.034$, (d) $x = 0.228$ and $y = 0.037$ and (e) $x = 0.26$ and $y = 0.03$. The PL spectrum of the sample (e) peaks at 0.77 eV (1.61 μm).

energies are achieved. The well-known effect of the DMHy/V ratio on the N concentration can also be seen from Fig 4. The N concentration increases with increasing DMHy/V ratio, which explains the energy difference between the two curves. The change in the PL peak energy as a function of the In concentration is more drastic with larger DMHy/V ratio. Unfortunately, the reason for this effect is yet not known.

Also the V/III ratio was varied by changing the TBAs/III ratio while the DMHy/V ratio was kept constant (DMHy/V = 0.936). The N concentration and thus the PL peak energy were found to be fairly insensitive to the V/III ratio. However, we have previously reported for MOVPE growth of GaAsN that when the DMHy/V ratio increases, the N concentration becomes more sensitive to the V/III ratio [12]. Also no high-quality crystal growth of GaAsN was obtained with TBAs/III ratios below 2. Therefore, a TBAs/III ratio of 2 was chosen for all the subsequent samples.

The LTPL spectra of the $Ga_{1-x}In_xN_yAs_{1-y}$ (9 nm)/GaAs(24.5 nm) MQW samples fabricated with different DMHy/V ratios are shown in Fig 5. Samples (a)–(d) are grown with the In concentration of 22.8% while the In concentration of the sample (e) is 26%. Sample (a) is a $Ga_{0.772}In_{0.228}As$ reference sample with the maximum of the PL peak at 1.28 eV (0.97 μm) and the full-width at half-maximum (FWHM) of 23 meV. The growth conditions for the reference sample are similar to the other samples, but no DMHy flow was used. Samples (b), (c), (d) and (e) are grown with DMHy/V ratios of 0.936, 0.95, 0.96 and 0.97, respectively. While the PL peak energy decreases with increasing N concentration, the PL intensity decreases rapidly and the FWHM increases. The PL intensity of the sample (a) is three orders of magnitude larger than that of the as-grown sample (b) containing about 2% nitrogen. The FWHM of the PL peak of the sample (b) is 37 meV. However, further increase in the N concentration does not result in such a drastic decrease of the PL intensity. The PL intensity of the sample (e) is less than one order of magnitude smaller than that of the sample (b). The PL spectrum of the sample (e) peaks at 0.77 eV (1.61 μm) and the FWHM of the peak is 50 meV.

To enhance the PL intensity, the structures were annealed post-growth in the MOVPE reactor under excess As ambient. Fig. 6 shows the PL peak energy and intensity of a $Ga_{0.772}In_{0.228}N_{0.037}As_{0.963}$(9.4 nm)/GaAs(24 nm) MQW structure after post-growth annealing at different temperatures for 10 min. The PL peaks blueshift for all annealing temperatures. Annealing at 700°C increases the PL intensity by a factor of 300 and

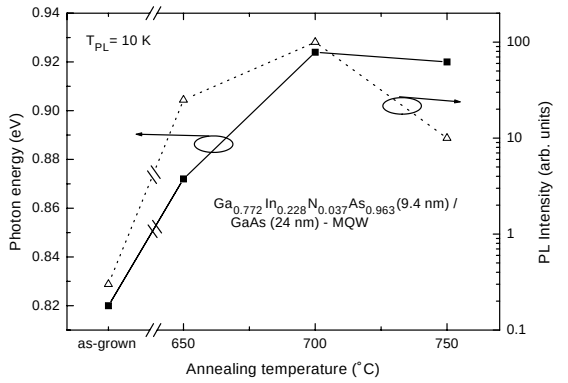

Fig. 6. PL peak energies and intensities of a MQW structure after post-growth annealing at different temperatures for 10 min.The PL peaks blueshift for all annealing temperatures. Annealing at 700°C increases the PL intensity over two orders of magnitude.

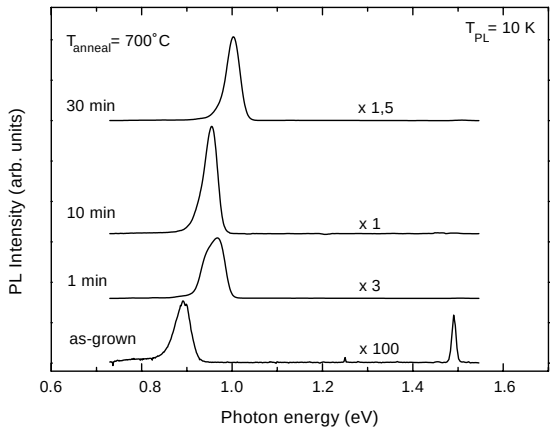

Fig. 7. PL spectra of a $Ga_{0.772}In_{0.228}N_{0.034}As_{0.966}$(10 nm)/GaAs(24.3 nm) MQW structure annealed at 700°C for different times. Annealing for longer times than 10 min does not enhance the PL intensity further, but results in larger blue shift of the PL peak.

shifts the PL peak by 104 meV to blue. The increase in the PL intensity is due to the reduction of nonradiative centers [13]. Since the blueshift for the ternary $GaAs_{1-y}N_y$/GaAs with y up to 4.2% is much smaller after identical annealing [12], the blueshift for $Ga_{1-x}In_xN_yAs_{1-y}$ could be caused by Ga and In interdiffusion [14]. When the annealing temperature is increased from 700°C to 750°C, the PL intensity decreases by one order of magnitude due to thermal generation of new nonradiative defects, but no further blueshift occurs. Since the Ga–In interdiffusion is more likely at higher temperature, the blueshift could be caused by some other mechanism like nitrogen out-diffusion. However, we have not observed any annealing induced reduction of the N concentration by X-ray diffraction measurements, so the reason for the lack of further blueshift is not known yet. Annealing also reduces the PL linewidth which could be due to improved composition uniformity in the GaInNAs QWs. The PL spectra of a $Ga_{0.772}In_{0.228}N_{0.034}As_{0.966}$(10 nm)/GaAs(24.3 nm) MQW structure after a post-growth annealing at 700°C for different durations is shown in Fig. 7. The spectrally integrated PL of the sample annealed for 10 min is about 100 times more intense than that of the as-grown sample. Annealing for longer times does not introduce further enhancement of the PL intensity, but the blueshift of the PL peak is increased. Therefore, the optimum relation between the annealing time and the annealing temperature is found to be 10 min at 700°C.

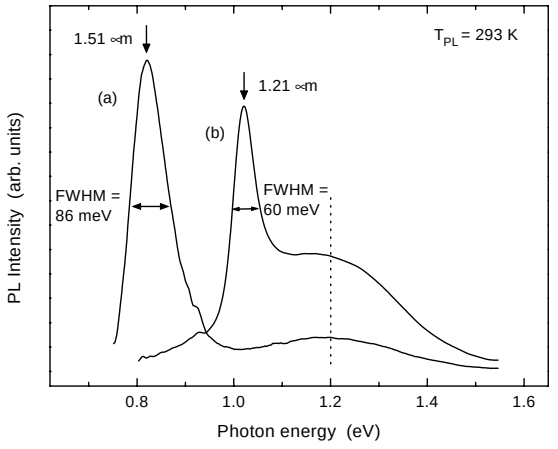

Fig. 8. RTPL spectra of two annealed MQW structures. (a) $Ga_{0.74}In_{0.26}N_{0.03}As_{0.97}$(9 nm)/GaAs(24.5 nm) and (b) $Ga_{0.772}In_{0.228}N_{0.02}As_{0.98}$(9.5 nm)/GaAs(26.5 nm). The PL spectrum of the sample (a) peaks at 0.82 eV (1.51 μm).

Fig. 8 shows the RTPL spectra of $Ga_{0.74}In_{0.26}N_{0.03}As_{0.97}$(9 nm)/GaAs(24.5 nm) and $Ga_{0.772}In_{0.228}N_{0.02}As_{0.98}$(9.5 nm)/GaAs(26.5 nm) MQW structures. The sample (a) was annealed at 650°C for 10 min while the sample (b) was annealed at 700°C for 10 min. The maximum of the PL peak of

the sample (a) is at 0.82 eV (1.51 μm) and the FWHM of the peak is 86 meV. It should be noticed that there exists a broad peak around 1.2 eV in these spectra. This peak is related to diffusion of nitrogen into the GaAs barriers and we have observed it in all the annealed samples measured at RT.

4. Conclusions

$Ga_{1-x}In_xN_yAs_{1-y}$/GaAs MQW structures for 1.55 μm emission on GaAs were successfully fabricated by atmospheric pressure MOVPE using TMGa, TMIn, TBAs and DMHy precursors. The dependence of the PL peak energy on the In concentration was investigated. The longest PL wavelengths were obtained with the In concentrations of around 23%. Post-growth annealing was found to enhance the PL intensity. The LTPL peak wavelength of 1.61 μm was observed from an as-grown $Ga_{0.74}In_{0.26}N_{0.03}As_{0.97}$/GaAs MQW structure. After post-growth annealing the PL peak wavelength of 1.51 μm was obtained at room temperature.

References

[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, Y. Yazawa, Jpn. J. Appl. Phys. 35 (1996) 1273.
[2] W. Shan, W. Walukiewicz, J.W. Ager III, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, Phys. Rev. Lett. 82 (1999) 1221.
[3] S.R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J. Banas, B.E. Hammons, Appl. Phys. Lett. 74 (1999) 729.
[4] C. Ellmers, F. Höhnsdorf, J. Koch, C. Agert, S. Leu, D. Karaiskaj, M. Hoffmann, W. Stolz, W.W. Rühle, Appl. Phys. Lett. 74 (1999) 2271.
[5] E. Tournié, M.-A. Pinault, S. Vézian, J. Massies, O. Tottereau, Appl. Phys. Lett. 77 (2000) 2189.
[6] M. Fischer, M. Reinhardt, A. Forchel, Electron. Lett. 36 (2000) 1208.
[7] M. Sopanen, H.P. Xin, C.W. Tu, Appl. Phys. Lett. 76 (2000) 994.
[8] J. Koch, F. Höhnsdorf, W. Stolz, J. Electron. Mater. 29 (2000) 165.
[9] E.D. Jones, A.A. Allerman, S.R. Kurtz, N.A. Modine, K.K. Bajaj, S.W. Tozer, X. Wei, Phys. Rev. B 62 (2000) 7144.
[10] R. Bhat, C. Caneau, L. Salamanca-Riba, W. Bi, C. Tu, J. Crystal Growth 195 (1998) 427.
[11] D.J. Friedman, J.F. Geisz, S.R. Kurtz, J.M. Olson, R. Reedy, J. Crystal Growth 195 (1998) 438.
[12] J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Crystal Growth 221 (2000) 456.
[13] S.G. Spruytte, C.W. Coldren, J.S. Harris, W. Wampler, P. Krispin, K. Ploog, M.C. Larson, J. Appl. Phys. 89 (2001) 4401.
[14] H.P. Xin, K.L. Kavanagh, C.W. Tu, J. Crystal Growth 208 (2000) 145.