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Group III-Arsenide-Nitride Quantum Well Structures on GaAs for Laser Diodes Emitting at 1.3 µm

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ABSTRACT

We report the growth of GaNAsN heterostructures on GaAs substrates by conventional molecular beam epitaxy (MBE) using a radio frequency plasma source. Lattice-matched bulk samples and several strained single quantum well (SQW) and multiple quantum well (MQW) structures were grown. The QWs were sandwiched between two GaNAs strain-compensating layers (SCL) and AlGaNAs cladding layers. By the aid of SCL the photoluminescence (PL) wavelength red-shifted as much as 88 nm with the same strain. GaNAs strain-modulating layers (SML), having less strain than QW, were also used to obtain red shift and improved luminescence properties.

The structures were studied by room temperature (RT) PL, x-ray diffraction (XRD) measurements and atomic force microscopy (AFM). The indium and nitrogen compositions of the QWs varied from 34 to 38 % and 1.3 to 3.5 %, respectively. Most of the studied structures showed PL peak wavelength at over 1.3 µm. Depending on the structure and thermal annealing treatment conditions the wavelength blue shifted up to 55 nm and intensity increased ~4 times. Furthermore, as AFM image of a five QW sample showed very smooth surface indicating together with PL measurements that high quality MQWs can be realized. In addition, 1.32-µm continuous-wave GaNAsN edge-emitting lasers were demonstrated.

Keywords: Long-wavelength laser diode, GaNAsN, GaAs, quantum well, photoluminescence, rapid thermal annealing.

1. INTRODUCTION

Semiconductor lasers emitting at 1.3 µm are important for high-speed optical data links and optical networks. Traditionally, InP-based materials have been used for these applications but there is an increasing interest in expediting cheaper and more robust GaAs technology.

The GaAs system holds all the possibilities to reach light emission at 1.3 µm with only one decisive point missing – an easy way to do it, since the long-wavelength limit for GaAs QWs is at about 1.2 µm. Therefore several new routes are being investigated to reach this goal. One is the use of GaNAsN/GaAs quantum dot, which indeed allow emission at 1.3 µm. Secondly, despite uncertainties about the band lineups, Ga2O3/InAs/GaAs has been studied and this wavelength has also been reached. Both approaches, however, require layers that lie under a very high level of compressive strain.1,2

The third possibility, which is studied here, is the use of mixed group III-arsenide-nitride alloys first proposed by Kedrov et al.3 These alloys allow increasing amount of strain driven by both their long-range physical properties and their potential for applications by electronic and optoelectronic devices. In particular, in the last few years much work has been devoted to the epitaxial growth and characterization of GaNAsN layers and QWs.4,5 The huge band gap bowing of this ternary alloy together with the possibility to adjust its lattice parameter to GaAs enable their use in the next generation GaAs-based long-wavelength lasers. Furthermore, the large conduction band offset and improved

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electron confinement compared to conventional GaInAsP/InP QWs allow for a significant reduction of the temperature sensitivity of the lasing threshold and thus lasers with high characteristic temperature $T_c$ can be potentially achieved. $T_c$ is expected to be over 200K in GaInAsN/InP system due to an energy discontinuity of $\Delta E = 400$ meV in the conduction band$^7$.

High performance GaInAsN-based edge-emitting laser diodes operating around 1.3 $\mu m$ have been rapidly demonstrated$^{1,2}$ In addition, electrically pumped monolithic vertical-cavity surface-emitting lasers (VCSELs) operating at this wavelength can also be made of the GaInAsN/GaAs material system$^{3,4}$.

In this paper, we report the growth of GaInAsN material on GaAs substrates by conventional molecular beam epitaxy. The epitaxial crystal growth details are presented in section 2. The section 3 goes through the AFM and XRD measurements of a 2 $\mu m$-thick GaInAsN/InP/GaAs/InP/GaAs bulk sample. The PL measurements and RTA-related wavelength and intensity changes of SQW and MQW samples are shown in section 4 in addition to AFM and XRD studies. Also results on SCLs and SMLs are shown in this section. The characterization results of a 1.32-$\mu m$ edge-emitting ridge waveguide laser is presented in section 5. Finally, conclusions are drawn in section 6.

2. EPITAXIAL CRYSTAL GROWTH

All samples were grown by conventional molecular beam epitaxy on 'as-received' (001) Si-doped substrates in a VG Semicon V600 system equipped with a solid-source valved As cracker and radio-frequency (rf) plasma source for incorporating nitrogen radicals. Ga, In and Al were supplied from Knudsen effusion cells. For each sample the substrate was desorbed at 600°C for 10 minutes and then a GaAs buffer layer was grown at 580°C. In the case of the GaInAsN bulk layer the growth temperature was lowered to 460°C and the growth rate was 1.6 $\mu m/h$. The background pressure was around 3 $\times$ 10$^{-6}$ mbar during the growth of the nitrogen containing layer. No GaAs cap layer was added.

The basic QW sample (Fig. 1) consisted of a SQW which was sandwiched between two tensile-strained GaInAsN SCLs or compressively-strained GaInAs SMLs. The bottom Al$_{0.8}$Ga$_{0.2}$As cladding layer was 300 nm thick and it was grown at 680°C at the growth rate of 1.1 $\mu m/h$. The 100 nm-thick top Al$_{0.8}$Ga$_{0.6}$As cladding layer was grown at 600°C to minimize growth related annealing effects. A GaAs cap layer (10 nm) was grown at the same temperature as the buffer layer. In more complicated structures, the number of QWs was increased to 2 and 5. No growth interruptions were used during any growth. In addition, the growth was monitored in-situ by using reflection high energy electron diffraction (RHEED).

![Figure 1. The structure of basic GaInAsN SQW sample with GaInN SCLs.](image-url)
3. BULK SAMPLE

For a lattice-matched GaInAsN bulk sample an undoped 2-μm-thick GaInAsN_{2.0}As_{0.6}N_{0.4} bulk layer was grown on a GaAs substrate. A Nicolet 3600 atomic force microscopy (AFM) was used to determine the surface roughness. In Fig. 2a and 2b a surface profile and AFM image (area 5 × 5 μm) are shown. The scanning distance along the surface was 1.5 μm. By scanning different parts of the sample the maximum vertical distance difference was found to be approximately 1.0 nm. The root mean square (RMS) value for the sample was 0.4 nm. AFM measurements show that the surface is very smooth.

![AFM image](image)

Figure 2. Atomic force microscopy a) surface profile graph and b) surface image of the 2-μm-thick GaInAsN_{2.0}As_{0.6}N_{0.4} bulk layer.

A reflection (004) double-crystal x-ray diffraction (XRD) measurement was used to determine the nitrogen content in the GaInAsN_{2.0}As_{0.6}N_{0.4} bulk layer. A separate GaInAs sample was grown to determine the In content. Two well defined rocking curve peaks were observed in the XRD plot. The peak splitting between the substrate and spilayer indicates the GaInAsN layer was not perfectly lattice-matched to GaAs. Nevertheless, the crystal quality of GaInAsN layer was high because the peak intensity of the layer is high and peak width is narrow.

The nitrogen composition, \( x \), was calculated to be 2.15% by using formula (1)

\[
x = 0.35y + (2.0 \times 10^3)\Delta \theta,
\]

where \( x \) is the nitrogen and y indium composition and \( \Delta \theta \) is the peak splitting. Indium composition of 0.6585 and peak splitting of 49 arcsec was used in the formula. The lattice-matched condition would have been obtained if the nitrogen content had been 2.05% \((y = 2.85x)\).

4. QUANTUM WELL STUDIES

Several GaInAsN_{2.0}As_{0.6}N_{0.4} quantum well samples were grown with different indium and nitrogen compositions, 34 to 35% and 1.3 to 3.5%, respectively. Samples with one, two and five QWs were grown. The N content was determined using XRD on separate GaInAsN epitaxial calibration layers grown under the same growth conditions (e.g., plasma cell operation, substrate temperature, arsenic pressure) and assuming nitrogen content to be the same in GaInAsN QW.

The TPL measurements were mostly carried out by using the 488 nm line of an Ar+ laser as an excitation source. A 532 nm Nd:YAG solid state laser was used to measure samples with five QWs.
Generally, it was observed that the more nitrogen was incorporated into the structure the longer the wavelength was. In addition, PL intensity decreased rapidly with increasing nitrogen content indicating dramatic degradation in the crystal quality. These are well-known effects of nitrogen when incorporating it into GaInAs QWs.

The crystal quality deterioration is due to a large miscibility gap and phase separation, even though the amount of average strain in the layer decreases. GaAsN alloy tends to phase separate when N composition increases, resulting in the formation of highly inhomogeneous material with inclusions of GaN, GaAsN, and GaAs phases.

**In-situ** postgrowth annealing and rapid thermal annealing (RTA) are found to be powerful and, thus, important methods in improving the crystal quality and PL properties. This has been attributed to a significant reduction in the concentration of competing nonradiative defects but it also results in a blue shift of the emission. The blue shift has been attributed to nitrogen codiffusion and group III interdiffusion. Annealing at a temperature of around 650°C was reported to improve the luminescence significantly with a small blue shift of the PL peak wavelength. RTA at high temperatures (around 950°C) was also reported to improve the PL properties but caused a large wavelength shift. RTA has also been made successfully at 750°C.

We performed RTA treatments for our QW samples at medium temperatures (700°C and 750°C) in a flowing N2 ambient. It was found that by using annealing procedures (several minutes) were needed to greatly enhance the crystal quality and luminescence properties. Actually, these long treatment periods were made in 5 min steps. Furthermore, all samples were covered with a GaAs cap.

### 4.1 Strain-compensating GaAsN and strain-mediating GaInAsN layers

It is well known that nitrogen concentration in GaInAsN should be as low as possible. Therefore, in order to achieve the desired wavelength (0.2–1.3 μm) large In content is used. A very high In content can introduce too much strain in GaInAsN / GaAs interfacial regions and the structure may relax. The strain reduces the critical thickness of GaInAsN well and, hence, imposes an upper limit to its width. In an attempt to relax strain and critical thickness limitations in the QW researchers have placed a thin GaAsN layer strain-matched to GaAs between the QW and the GaNAs barrier. The inserted layer decreases the effective width of the QW, shifting the PL spectrum towards longer wavelengths as desired. Because it leaves high strain at the walls of the QW misfit dislocations are readily formed at high temperatures during device fabrication or laser operation.

Another attempt includes the growth of a strain-compensating GaNAs barrier layer (SCL) adjacent to the QW. This layer causes a red-shift of emission due to the formation of a reduced barrier potential. Because strain is compensated in part by the barrier, the QW can be made wider and any strain can be bandgap compatible with strain relaxation. Recently, we proposed a novel structure in which a strain-compensating layer (SCL) is grown in between the GaNAsN QW and the GaNAs SCL. Having less indium, i.e. compressive strain, than that of the well the GaNAsSCL reduces the high effective strain in the compressive / tensile interfaces, leading to improved luminescence properties. At the same time, the SCL shifts emission towards longer wavelengths as shown later in this paper.

We made 6-μm-thick GaInAsN/GaAsN/GaAsN/GaAsN/GaAsN/GaAsN/GaAsN/GaAsN/GaAsN/Si QW samples (structure presented in Fig. 1.) for PL measurements. The thickness of the GaNAs SCL was varied from 0 to 30 nm. The in-situ annealing (RTA) treatment at 700°C was performed for 30 s. The effect of the SCL is presented in Fig. 3a. It can be seen that only by changing the thickness of the GaNAs layer a strong red shift as high as 85 nm was obtained. The intensity was the highest when using 5 nm SCLs. Moreover, the intensity was basically equal to a sample without the SCLs and to a sample with 30 nm SCLs.

In Fig. 3b the PL spectra of two 6-μm-thick double quantum well (DQW) samples (In and N contents were 56% and 1.6%, respectively) are shown. One was grown without SCLs (0 nm) and the other had a 5-μm-thick SCL. In-situ annealing for 60 min at 700°C was performed in the growth chamber immediately after the growth was finished. The sample without GaNAs layers showed shorter wavelength than the sample with 5 nm SCL. The observed wavelength difference was 18 nm and the full width at half maximum (FWHM) values were 32 nm and 37 nm. This result confirms our observation that the GaNAs layer on both sides of the QW introduces a red-shift and helps to maintain or even improve the PL intensity.
GaNAsN SMLs were studied by growing six SQW samples under similar conditions. The samples were identical in all parts except the SML width was changed (0.1, 2, 3, 5 and 7 nm). The samples were In-diffused in-situ in the growth chamber at 700°C for 10 minutes prior to PL measurements. The PL spectra are shown in Fig. 4. As seen from the figure the optimum SML width was found to be 2 nm from the intensity point of view. When wider layers were used the intensity decreased. Furthermore, the obtained red shift was 33 nm when comparing to the sample without SML and the sample with 7 nm SML. Both samples are almost equal in intensity.

![Graph showing intensity versus wavelength for different SML widths.](image)

Figure 4. The effect of GaNAsN SMLs on the photoluminescence wavelength and intensity.

As shown in Fig. 5a and d the both the SCL- and SML-technique can be very useful in increasing the PL wavelength while improving or maintaining PL intensity. It will be shown later in this paper that the generally observed blue shift related to the annealing of GaNAsN material can be reduced by using SMLs.

4.2 Growth temperature and annealing of single quantum wells

6.8 nm-thick Ga0.62In0.38As0.62N0.38 SQWs were grown at different temperatures under similar conditions as described in the section 2. The purpose of these samples was to find the best growth temperature conditions GaNAs SQWs with thickness of 5 nm were used in all samples. The PL measurements were performed for as-grown samples and the intensity and full width half maximum (FWHM) results are shown in Fig 5a. The highest intensity was obtained from the sample grown at 460°C. This sample was then annealed as-sit and these results are presented in Fig. 5b.
From Fig. 5a it can be seen that by increasing growth temperature the PL peak wavelength red shifts 75 nm in this case. The lowest FWHM which was 27 meV at the peak wavelength of 1375 nm is also seen. It was obtained from the sample grown at 440°C. Recently, we reported even lower FWHM value of 24.4 meV at 1314 nm\(^2\). These are among the lowest reported values around 1900 nm\(^3\).

The best annealing time at 700°C for the sample grown at 460°C was found to be ~10 minutes (Fig. 5b). The increase of the peak intensity was roughly 8 times. The peak wavelength red shifted as much as 51 nm.

In addition to these SQW samples, more GaInAsN SQW samples were grown with higher indium (~38%) and nitrogen composition (estimated to be >3.5%). The longest achieved wavelength was 1480 nm for an as-grown sample. The PL intensity was, however, weak but still clearly noticeable in the room temperature PL measurements using 532 nm Nd:YAG laser (excitation power was 46.2 mW). Recently, pitted R1 operating GaInAsN-based edge-emitting laser emitting at over 1.5 um has been achieved\(^4\) indicating the GaInAsN/GaAs material system to be potentially suitable also for 1.55 um fiber-optic telecommunication applications.

4.3 Multiple quantum wells

Three samples (called S1, S2 and S3) with five GaInAsN quantum wells (5QW) were grown in a similar way as described in section 2. 2-nm-thin GaInAsN QW were used adjacent to every QW. The width of the GaAs barrier was 10 nm. The growth of the Si was stopped immediately after the last QW. AFM images were taken on the as-grown surface. The samples S2 and S3 were grown with 5-nm GaAs cladding layer (simplified structure shown in Fig. 1) for PL measurements. The S2 (N content of ~2.5%) was treated at 700°C and the S3 (N content of ~1.83%) at 750°C to find the best RTA conditions.

2 and 3-dimensional images of the sample S1 are shown in Fig. 6. The images indicate the surface to be high quality and smooth. The RMS was 0.922 nm. The RMS is about double comparing to the bulk sample but nevertheless it is still a small value. The Ra value was 0.767 nm.
Figure 6. a) 2-dimensional and b) 3-dimensional image of as-grown Ga$_{0.5}$In$_{0.5}$As$_{0.95}$N$_{0.05}$ sample with five quantum wells. The topmost layer is a QW layer.

The samples S2 and S3 were cut into eight pieces for the RTA treatment. All the pieces were measured before annealing and the value for the as-grown wavelength peak was taken from the average of all the pieces of one sample. Then each piece of S2 was treated at 700°C for different RTA time period (3, 5, 10, 15, 20 and 25 min) and correspondingly each piece of S3 was annealed at 750°C for the times (1, 2, 3, 4, 5, 6 and 7 min). The annealing influence on the PL intensity and wavelength of the S2 is shown in Fig. 7a. The annealing results for S3 are presented in Fig. 7b. The intensity of the S2 as-grown piece was set to 1 and all the other intensities are comparable to this value (also in Fig. 7b).

Figure 7. Rapid thermal annealing effect on the PL peak wavelength and intensity in two samples with nitrogen composition of a) S2: 2.3 % (annealed at 700°C) and b) S3: 1.85 % (annealed at 750°C).

In the case of S2 (Fig. 7a) the best annealing time at 700°C was found to be 10 min. The luminescence intensity started to degrade when longer treatments were used. The reason for this is not yet fully understood. The intensity was increased ~45 times compared to the as-grown piece. Moreover, the peak wavelength decreased until it saturated in pieces which were annealed over 10 min. A 31-mm blue shift was observed.

The as-grown S3 piece had about 70 % higher peak intensity than the peak intensity of S2 as-grown piece indicating better crystal quality in S3. Indeed, there is less N in S3 so its crystal quality should be better. The best annealing time for the S3 pieces (annealed at 750°C) was 3-5 minutes. During this period no change in the PL intensity was observed. Similarly to the results of S2 the intensity dropped quickly if annealing was continued. Here, the intensity increased max. ~30 times (and 53 times comparing to the as-grown S2 piece) and the blue shift was 26 nm.

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By comparing the blue shift of the SQW samples with GaInN SQCLAs (described in subsection 4.2) with the SQW samples (this subsection) we can see that the blue shift is much lower (about a half) when using GaInAsN SMLAs. Of course, because the samples were not exactly similar (anyway, they were grown under similar conditions) we cannot fully verify this. However, the preliminary results obtained here indicate a remarkable reduction of blue shift in GaInAsN QWs grown with GaInAsN SMLA.

5. EDGE-EMITTING LASER

We succeeded in making GaInAsN/GaAs SQW edge waveguide Fabry-Perot lasers operating at 1.32 μm. Under pulsed (pulse length 50 ns, repetition rate 5 kHz) conditions the threshold current density \( J_T \) was 175 mA/cm², corresponding to the threshold current density \( J_T \) of 560 A/cm², for a laser with a 19.4-μm-wide and 1600-μm-long cavity. The maximum output power was over 150 mW and the slope-efficiencies ranged from 0.2 to 0.28 W/A per facet. The spectrum at \( I = 1.011 I_T \) showed multi-mode emission centered at 1319 nm. At \( I = 2.5 I_T \), the main peak of multi-mode emission shifted to 1321.6 nm. The mode-width (Δλ) was 0.11 nm and the mode separation (Δλ) 0.15 nm. Therefore, we obtained from the formula (2)

\[
\lambda_0 = \frac{h}{e} \frac{J_T}{\Delta \lambda}
\]

that the average refractive index \( n \) was 3.64 for the active region (L is the cavity length). This is a bit smaller than the theoretical prediction of Saitoh et al. (n = 3.7) assuming that the band gap of GaInAsP with 904 eV (L = 1.32 μm²)[16]. The internal quantum efficiency (\( \eta_i \)) was 80% and the material loss \( \eta_m \) was 7.6 cm⁻¹. By plotting the threshold current densities versus the inverse of cavity length, a transparency current density of 227 A/cm² was determined.

The lasers worked also under continuous-wave (cw) operation. The threshold current density was \( I_T = 780 \) A/cm² for lasers with the cavity length of 1000 μm. The maximum output power of 40 mW at room temperature was thermally limited, due to the p-side-up mounting for which heat transfer from the active region was inefficient. The temperature behaviour indicates that the laser has low- and high-temperature regimes of \( n_c \), which is 133 K in the range from 10 to 40°C and 97 K in the range from 50 to 80°C. More details of the lasers can be found in the reference 13.

6. SUMMARY

In this paper, we report the growth of GaInN heterostructures on GaAs substrates by conventional molecular beam epitaxy (MBE) using a radio frequency plasma source. Lattice-matched bulk samples and several strained single and multiple quantum well structures were grown. The structures were studied by room temperature photoluminescence, x-ray diffraction measurements and atomic force microscopy.

The indium and nitrogen compositions of the QW varied from 34 to 38 % and 1.3 to 3.5 %, respectively. The longest achieved wavelength from RT PL measurements was 1480 nm. Depending on the structure and thermal annealing treatment conditions the wavelength blue shifted up to 55 nm and intensity increased 45 times. Furthermore, the AFM image of the sample with five QWs showed very smooth surface indicating together with FL measurements that high quality MQW can be realized.

GaInN strain-compensating layers were used to reduce the strain at the GaInAsN/GaAs interface and to increase PL wavelength up to 88 nm. No photoluminescence degradation was observed compared to the samples without GaAsN layers. GaInAsN strain-mediating layers were also used to obtain red shift and improved luminescence properties. In addition, 1.3-μm continuous-wave GaInAsN edge-emitting lasers with very low threshold current density (563 A/cm²) were demonstrated.

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