

Growth of InGaAsN / InP structures by Chemical Beam Epitaxy

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Abstract: In III-V semiconductors incorporation of small amounts of nitrogen cause a relatively large bandgap reduction. The problem of InGaAsN is the decrease in luminescence with nitrogen content above 1 - 2%. We have grown a.o. $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}_{0.985}\text{N}_{0.015}$ quantum wells. The as-grown samples show poor photoluminescence at 4K but after a high temperature anneal clear peaks are observed. In comparison to ternary layers of $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$, the bandgap has decreased by approximately 70 meV due to 1.4 % of nitrogen. A further increase in the nitrogen content could result in layers with a bandgap of 800 meV at room temperature ($\lambda = 1.55 \mu\text{m}$).

1. Introduction

Diluted alloys of N lattice matched to standard semiconductors such as GaAs are currently under investigation for possible laser diode / VCSEL applications at 1.3 – 1.55 μm in the GaAs technology [1]. The main problems in the InGaAsN materials are related to the strong decrease of the radiative recombination efficiency associated with an N content above 1-2 % [2] and with increasing difficulty of N incorporation in layers with high (≥ 33 %) In content [3]. This work concerns growth of InGaAsN alloys on InP substrates, thus layers with In content ≥ 53 %. These alloys have smaller bandgap / larger wavelength than the corresponding ternary alloy. It is required to introduce at least 0.2% of nitrogen in the layer before a bandgap reduction will take place. With lower nitrogen content one cannot speak of a true alloy, the nitrogen is then present as an isoelectronic impurity, comparable in properties to a donor or acceptor level [4].

2. Experimental

Growth was performed in a Riber 32 P CBE system using as starting compounds triethylgallium (TEGa), trimethylindium (TMIn), arsine (AsH_3), phosphine (PH_3) and ammonia (NH_3). The pressure during growth is on the order of 10^{-5} torr. As substrates, semi-insulating (Fe doped) (100) InP was used misorientated by 0.5° towards (111)B. The temperature of the substrate during growth was 515°C as measured with an optical pyrometer. All samples were investigated using PL measurements and high resolution x-ray diffraction.

The layer structure consists of 5 sequences of 4 nm $\text{In}_x\text{Ga}_{1-x}\text{As}$ QW / 60 nm InP barrier / 4 nm $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ QW / 60 nm InP barrier. The reference InGaAs ternary QW and the InGaAsN layer were grown under the same settings of all components, except that NH_3 was introduced for the quaternary. A heat treatment at 650°C for 5 minutes was done in N_2 on all samples after growth with an InP substrate covering the samples.

3. Results and discussion

In CBE it is required to decompose the thermally stable components such as the hydrides (AsH_3 , PH_3 and NH_3) in a high temperature “cracker cell”. Thus, one of the growth parameters is the temperature of the injector used for the introduction of the hydrides into the growth chamber. Arsine and phosphine were introduced through a cell maintained at 900°C . At this temperature decomposition of AsH_3 and PH_3 to give As_2 and P_2 as well as molecular hydrogen (H_2) is 100% complete [5]. However a nitrogen molecule (N_2) is not a suitable molecule for the growth of nitrogen containing layers so the injector through which the NH_3 is introduced should not be set to 100% conversion. In order to produce an unstable, reactive nitrogen containing species the injector temperature was varied from 100°C to 1100°C . By varying the NH_3 injection temperature one does indeed influence the nitrogen content of the InGaAsN layers, as can be seen in Table I, samples 1, 3, 5 and 6. Maximum N incorporation of 0.6 % is achieved at 1000°C , whilst higher (1100°C) and lower (900°C) injector temperatures give rise to only 0.35 % N in InGaAsN. With the injector at 100°C (sample 3) virtually no nitrogen is incorporated. However, when the NH_3 flow is increased (samples 2 and 7) the N content of the layer does not increase further. Figure 1 shows a measured X-ray diffraction curve as well as the simulated spectrum of sample 11 using the layer thicknesses and compositions as given in table I.

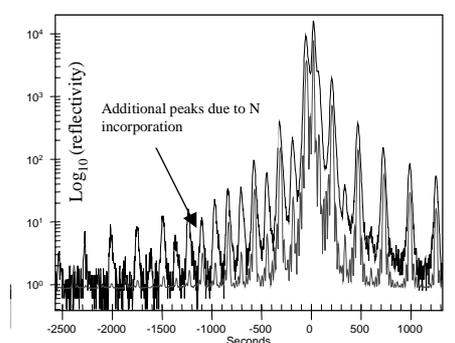


Fig. 1 High resolution 002 diffraction curve for the sample C709

It is known that an alloy in the region of solid immiscibility may be stabilized by the effect of the substrate [6]. Since the InGaAsN alloy has a large immiscibility gap, this so called ‘lattice pulling’ effect may be expected to play a role here. In our case, when the In content is increased to 65 % (8×10^{-3} mismatch) the N incorporation estimated from X ray simulations is as high as 1.4 % using the same amount of NH_3 as during growth of the samples with In content of about 58 %, which contain only 0.6 % N. The excellent quality of the “high” nitrogen content sample is evident from the narrow peaks of the superlattice satellites in the x-ray diffraction curve shown in figure 1.

Figure 2 shows the PL spectra of sample C709, after annealing for 5 minutes at 650°C . We attribute the higher energy PL peak to emission from the ternary $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ layers. Peaks from the quaternary layer are present at lower energy and are present at comparable intensity to the InGaAs related luminescence. Note that at the intermediate excitation level, five peaks can be observed. The separation between the peaks is about 25 meV. Such an equidistant level spacing points to a parabolic, not rectangular potential distribution.

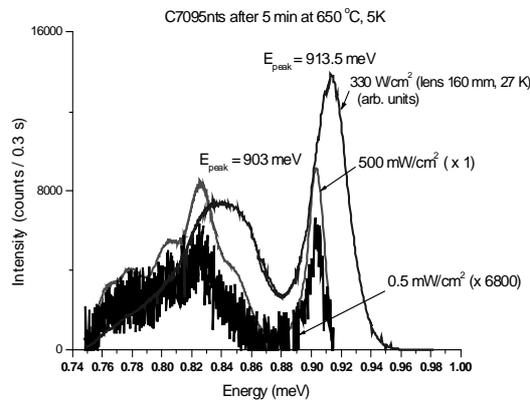


Fig. 2: PL spectra of C709

During the high temperature post growth heat treatment atomic rearrangements can lead to segregation and alloy fluctuations within the layer. Triple axis measurements on sample C709 reveal more crystallographic details. Figure 3a and 3b show these plots, taken perpendicular and parallel to the misorientation, after the high temperature annealing step. Parallel to the steps (Fig 3a) one can observe a symmetric broadening of the substrate peak. We attribute this to symmetric undulations of the quaternary layer surface. The triple axis plot taken perpendicular to the steps (Fig. 3b) reveals clearly asymmetric broadening. It is known that the combination of steps and coherent strained layers gives rise to lattice tilting. In the region of the steps the strain field is different than in planar regions. The compressive strain field there can be reduced when the larger atoms (In and As) are replaced by the smaller atoms, Ga and N. Hereby a lateral periodicity is introduced in the quaternary quantum wells giving an additional confinement.

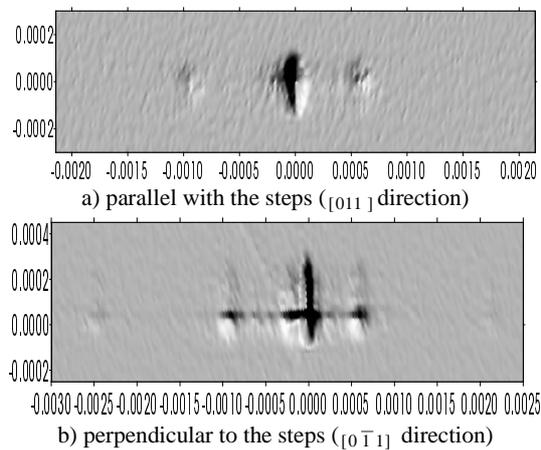


Fig. 3 Triple axis plot near 004 reflection for C709 after heat treatment

4. Conclusions

- InGaAsN / InP structures were successfully grown by CBE using ‘thermally activated’ NH_x molecules
- The maximum N content in layers close to lattice matching was 0.6 % and in compressively strained layers the N incorporation is enhanced. This is a clear indication of the lattice pulling effect which should occur in the growth of alloys having a miscibility gap. Up till now, the maximum amount of nitrogen which could be incorporated was 1.4%. A higher concentration is required for emission at $\lambda = 1.55 \mu\text{m}$ at room temperature.
- Post growth heat treatment is required in order to “activate” the InGaAsN luminescence. It also results in atomic rearrangements within notably the InGaAsN layer. We propose that regions have been formed in the InGaAsN with both lateral and vertical confinement. They have a parabolic localization potential of about 85 meV.

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table I: Growth parameters for InGaAsN / InP superlattice samples

No	Sample	NH_3 injector Temp.	Ga/III _{tot}	AsH_3 (torr)	NH_3 (torr)	In in the solid (x)	N content in the solid (y)	PL peak (meV) (ternary QW)	FWHM (meV)	Peak splitting (arcsec)	PL peak (meV) After heat treatment	FWHM (meV) After heat treatment
1	C6975nts	1000 °C	0.556	1.55	1.55	0.57	0.6%	932.4	9	-42	935.3	8.1
2	C6985nts	1000 °C	0.556	1.2	3.60	0.57	$a_q > a_i$ poor fringes	930	6	-40	908	13
3	C6995nts	100 °C	0.556	1.55	1.55	0.57	0.18 %	937.4	7.0	-52	941	8.7
4	C7005nts	1000 °C	0.556	1.2	1.55	0.57	$a_q > a_i$ poor fringes	934.4 (two peaks)		-50	929.7	10
5	C7015nts	1100 °C	0.556	1.55	1.55	0.57	0.35 %	930.7	7	-41	936.3	7.74
6	C7025nts	900 °C	0.556	1.55	1.55	0.57	0.35 %	930.2	7	-40	923.4	two peaks
7	C7035nts	1000 °C	0.556	1.55	3.60	0.57	0.30 %	933.4	7	-41	935	7.5
8	C7045tsl	1000 °C	0.556	1.2	-	0.57	$a_q > a_i$ poor fringes	932	9	-44	918.8	two peaks
9	C7055nts	1000 °C	0.556	1.55	1.55	0.58	0.50 %	931.5	8.6	-67	928	12
10	C7085nts	1000 °C	0.525	1.55	1.55	0.72	0.50 %	-		-250	835	
11	C7095nts	1000 °C	0.541	1.55	1.55	0.65	1.40 %	901	14.2	-181	903	7.54