

CBE growth and characterization of InGaAsN / InP quantum well structures using NH₃

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Abstract: NH₃ is used successfully as nitrogen precursor for the growth of In_xGa_{1-x}As_{1-y}N_y / InP structures using Chemical Beam Epitaxy (CBE). In our system one high temperature injector is used for the introduction of NH₃ only. The maximum amount of N introduced in InGaAs is 1.4 %, estimated from X-ray and PL measurements. The N incorporation is strongly influenced by the temperature of the injector and by compressive strain. Additionally, the N incorporation is decreased when high strain values give rise to non-planar surfaces. Segregation, clustering and / or interface undulations are enhanced by a post-growth heat-treatment.

1. Introduction

Diluted alloys of N lattice matched to standard semiconductors such as GaAs received recently a considerable attention because of laser diode / VCSEL applications at 1.3 – 1.55 μm in the GaAs technology [1]. Due to the large difference in atomic size and electronegativity between N and In, Ga, As small amounts of N in the range of few percent cause a large reduction of the band gap, opening new possibilities for use of these materials for optoelectronic applications. The main problems for InGaAsN materials are related to the strong decrease of the radiative recombination efficiency associated with the increase of N content above 1-2 % [2,3] and with increasing difficulty of N incorporation in layers with high (≥ 33 %) In content [4,5]. This work concerns growth of InGaAsN alloys on InP substrates, thus in layers with In content ≥ 53 %. These layers have smaller bandgap / larger wavelength than the corresponding ternary alloy.

2. Experimental

Growth was performed in a Riber CBE reactor using triethylgallium (TEGa), trimethylindium (TMIn), arsine (AsH₃), phosphine (PH₃) and ammonia (NH₃). Arsine and phosphine were introduced through a high temperature cracker maintained at 900 °C. NH₃ was introduced through a separate high temperature injector. From growth chamber pressure measurements it was concluded that at a temperature of 1000 °C approximately 50 % of the NH₃ was cracked (to N₂ and H₂) while the remaining 50 % of the molecules is believed to be in a thermally excited state. The temperature of growth was 515 °C as measured with an optical pyrometer [6]. The (100) InP substrates were misoriented by 0.5 ° towards (111) B. All samples were investigated using high resolution X-ray diffraction and PL measurements.

The layer structure was chosen in order to have a high sensitivity in detecting small lattice constant differences between a reference InGaAs ternary QW and the next InGaAsN quaternary well which was grown under the same conditions as the first one, except that NH₃ was introduced in the reactor. The structure consists of 5 sequences of 4 nm In_xGa_{1-x}As QW / 60 nm InP barrier / 4 nm In_xGa_{1-x}As_{1-y}N_y QW / 60 nm barrier. Assuming that the In content is the same in both QW's of the same sequence the sensitivity of the X-ray diffraction measurement for N incorporation would be about 0.1 %. A heat treatment at 650 °C for 5 minutes was done on all samples after growth.

3. Results and discussion

3.1. Influence of the temperature of the NH₃ injector

In X-ray simulations we attribute the difference in the lattice constant only to N incorporation. There is a clear influence of the NH₃ injector temperature on the lattice constant of the second (quaternary) QW in the sequence. This is revealed by a series of samples with In content of 58 %, i.e. close to lattice match conditions. When the temperature of the NH₃ injector is 1100 °C the N content is equal to 0.35 %. At 1000 °C there is a maximum incorporation of 0.6 % while with the injector at 900 °C the N content is down to 0.35 % again. PL measurements did not reveal unambiguously two distinct peaks for this series of samples close to lattice matching. This is attributed to the small bandgap difference between the ternary and quaternary alloy with N content ≤ 0.6 %. This difference is expected to be about 20 meV [7].

3.2. Influence of lattice mismatch

It is known that an alloy in the region of solid immiscibility may be stabilized by the effect of the substrate [8]. Since the InGaAsN alloy has a large immiscibility gap, this so called 'lattice pulling' effect may be expected to play a role here. Indeed, when the In content is increased to 65 % (8 x 10⁻³ mismatch) the N incorporation estimated from X ray simulations is as high as 1.4 % using the same amount of NH₃ as during growth of the samples of In content equal to 58 %. When this sample was subjected to heat treatment at 650 °C for 5 minutes remarkable changes occurred both in X-ray and PL spectra. The PL spectrum of the as grown sample (Fig. 1a) and after heat treatment show that the FWHM and the peak position attributed to the ternary InGaAs QW do not change to a significant extent. However, after heat treatment there is a considerable increase of the emission intensity of the peak attributed to the quaternary InGaAsN QW. Furthermore, five regularly spaced distinct levels appear in a large (85 meV) localization potential. The spacing between these peaks is quite

regular and amounts to 17-20 meV. This regularity suggests a parabolic potential distribution with an extension of about 25 nm. The same value of the localization potential (energy) could be extracted from temperature dependent PL measurements. High resolution X ray triple axis measurements show a good crystal quality of the as grown sample and a coherent tilting in the direction of the misorientation after heat treatment associated with a slight degradation of the crystal quality. The tilt ζ is related to the mismatch according to the formula:
$$Z = \frac{\alpha \Delta a_0}{c} \times a$$
 where α is the misorientation angle. Fig.

2a, b show the triple axis plot after heat treatment at 650 °C. From these findings we conclude that the heat treatment has resulted in atomic rearrangements in the InGaAsN layer. Whether this gives rise only to segregation or whether this also gives rise to nonplanar surfaces is not clear at this point.

When the In solid composition in the QW layers is increased further to 72 % (1.3 % mismatch), both PL spectra and triple axis X ray diffraction reveal that segregation and / or interface undulations are present already in the sample as grown, probably due to alloy clustering and faceting [6]. Most likely, the ternary InGaAs layer is already non-planar / inhomogeneous. Remarkably, this negatively affects the N incorporation which decreases to about 0.5 % in this sample containing 72 % In.

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 % while lattice pulling is the most probable cause of the higher N content (1.4 %) in layers grown at 8×10^{-3} compressive mismatch. Such a value of mismatch is on the limit of surface stability and layers grown with 1.3 % compression contain inhomogeneous / non planar ternary and quaternary QW layers, due to alloy clustering and faceting.
- Post growth heat treatment results in atomic rearrangements within notably the InGaAsN layer. Very clear features appear in the PL spectra while the triple axis X-ray diffraction plots show formation of elongated regions aligned parallel to the steps of the InP substrate in the [011] direction. The localization potential in these regions give rise to evenly spaced optical transitions.

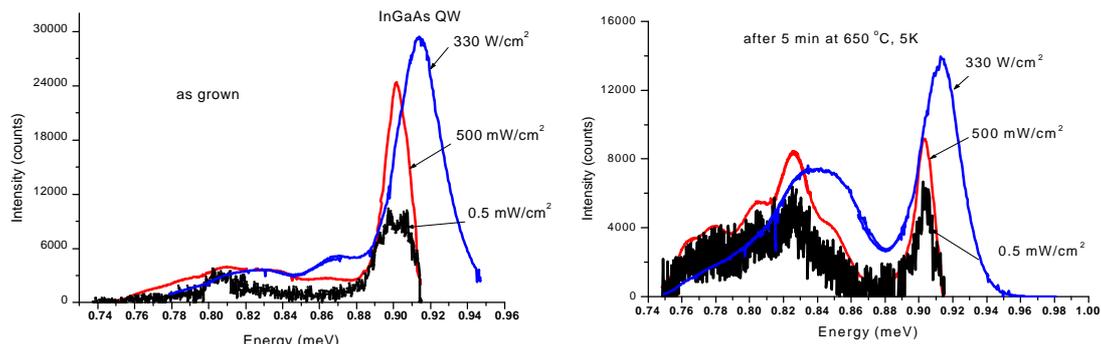


Fig. 1: PL spectra of QW sample with In content of 65 %

a) as grown

b) after heat treatment

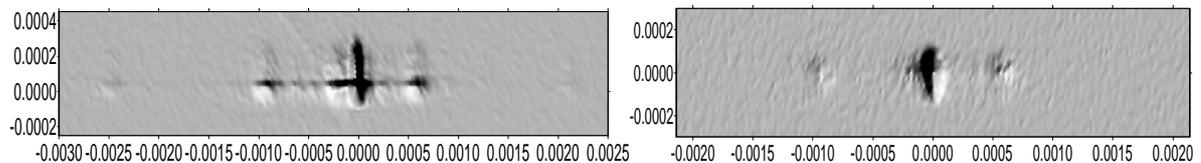


Fig. 2 Triple axis plot near 004 reflection for the QW sample with In content of 65 % after heat treatment

a) perpendicular to the steps ($[0 \bar{1} 1]$ direction)

b) parallel with the steps ($[0 1 1]$ direction)

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