

Investigation of optical and concentration profile changes of InGaNAs/GaAs heterostructures induced by thermal annealing

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Abstract. In this contribution we compare optical and structural properties of $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}_{0.024}\text{As}_{0.976}$ quantum wells before and after annealing at 550 °C and 600 °C in an N_2 atmosphere. We measure strain and chemically sensitive contrast to determine local indium and nitrogen concentrations using a TEM 3-beam image formed by the 000, 220 and 200 beams. For quantification of the concentrations Bloch wave simulations are used, which include bonding and static atomic displacements. The samples were grown by metal-organic vapour phase epitaxy, prepared with focused ion beams (FIB), thinned with low energy ion milling and investigated in a Cs-corrected Titan 80/300 microscope using an L-shaped objective aperture. Imaging conditions with the Laue circle centre at (0 4.2 0) are used as they show a weak dependence on the lamella thickness.

Absorption measurements show a blueshift of the band gap of 19 ± 7 meV (550 °C) and 36 ± 7 meV (600 °C) after annealing. The average nitrogen concentration was found to be $2 \pm 1\%$ and is unaffected by the annealing temperature. In contrast, the mean indium concentration appears to decrease from $18.5 \pm 2\%$ before to $15 \pm 1\%$ after annealing. Together with the blueshift, this observation is discussed in terms of a modification of electron structure factors, caused by preferred coordination of N to In atoms.

1. Introduction

Introducing even small amounts of nitrogen into an InGaAs crystal reduces band gap and lattice parameter, allowing to tune both of them [1, 2]. Hence, $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ is an interesting material for optoelectronic devices emitting at the telecommunication wavelengths of 1.3 μm and 1.55 μm [3, 4]. Post-growth annealing leads to an increase of the originally low luminescence intensity of these devices but also to a band gap blueshift [5, 6]. The blueshift can reach up to 100 meV depending on indium content, growth mode and the annealing conditions temperature, time and atmosphere. To explain the blueshift of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ during annealing, structural properties were investigated. Some authors found evidence for an increase of preferred indium-nitrogen bonding [5, 7, 8], while others found evidence for long-range redistribution of nitrogen or indium [6, 9]. So there might be different mechanisms contributing to the band gap increase.

To investigate these structural changes, atomic-scale nitrogen and indium content has to be detected with highest possible accuracy. To this end, two sources of information are needed.

Grillo et al. developed a TEM-method based on measuring strain and the amplitude of the chemically sensitive (200) reflection of a single well, using a zone axis high-resolution and an off-zone dark field micrograph [10] under kinematic approximation, whereby imaging of exactly the same specimen area is difficult.

Another method was presented by Müller et al. [9] recently, using the 200, 220 and 000 beams to determine strain and 200 reflection amplitude simultaneously from a single TEM image. Strain and 200 amplitude provide the two pieces of information needed to determine the concentration of indium and nitrogen. This method is used here to investigate the reason for the blueshift observed after annealing a metal-organic vapour phase epitaxy (MOVPE) grown $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}_{0.024}\text{As}_{0.976}$ quantum well.

2. Experimental Setup

A 15 nm thick quantum well with nominal composition $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}_{0.024}\text{As}_{0.976}$ was grown with MOVPE at 520 °C. The sample was annealed under N_2 atmosphere at 550 °C for 10 minutes and afterwards for another 10 minutes at 600 °C. For each annealing step, optical experiments were performed using a JASCO V-670 spectrophotometer. The cross-sectional TEM specimens have been prepared in zone axis [001] using an FEI focused ion-beam machine Nova Nanolab 200. The specimens were thinned by argon ion milling at 400 eV using a Technoorg Linda gentle mill in order to remove the amorphous layer and to reduce the thickness. Before thinning the specimen thickness was measured with an accuracy of ± 15 nm using STEM as described in [11]. The thinning time was chosen in order to reach the same thickness for each lamella of about 20 nm. All (S)TEM measurements were performed with an FEI Titan 80/300 equipped with a corrector for the spherical aberration of the objective lens, operated at 300 kV. The TEM images were recorded on a 2048×2048 pixel CCD camera.

3. Optical properties before and after annealing

In order to determine the band gap of the quantum well, absorption spectra are evaluated in the range of 0.75 eV to 1.5 eV photon energy. The absorption $A(E)$ is calculated from the measured transmission $T(E)$ and the determined reflectance $R(E)$, via $A(E) = 1 - T(E) - R(E)$. In the investigated range, the reflectance depends almost linearly on the photon energies [12], giving $R(E) = m \cdot E + b$. Below the band gap of the investigated wells, no absorption occurs and only transmission and reflection take place. Here, the assumed linear reflectance is determined.

Figure 1 shows the obtained absorption spectra for each annealing step. Energies below 0.85 eV do not show absorption. Towards higher energies the absorption increases exponentially, caused by the impurity band. For higher energies the absorption shows a square-root-like behavior caused by the combined density of states of the valence and conduction bands. The square root functions fitted to these energies give the band gaps. The band gap is 944 ± 5 meV before annealing. After annealing at 550 °C and 600 °C blueshifts of 19 ± 7 meV and 36 ± 7 meV occur.

4. Structural properties before and after annealing

Before discussing the structural properties, we outline the used method shortly. See [9] for more details. An L-shaped objective aperture is used to select only the 200, 220 and 000 beams. Fourier filtering the 3-beam image gives the 220 fringe and the 200 amplitude image as depicted in figure 2, which are used to measure the strain and the 200 amplitude locally. To determine the indium and nitrogen concentration maps from the locally measured strain and the 200 fringe amplitude, reference tables were used as depicted in figure 3. To calculate these, elasticity theory was applied and Bloch wave simulations were performed [13]. The structure factors used account for static atomic displacements (SADs) via empirical potentials [14]. Furthermore, bonding is included in form of modified atomic scattering amplitudes (MASAs) [15]. In order to achieve a

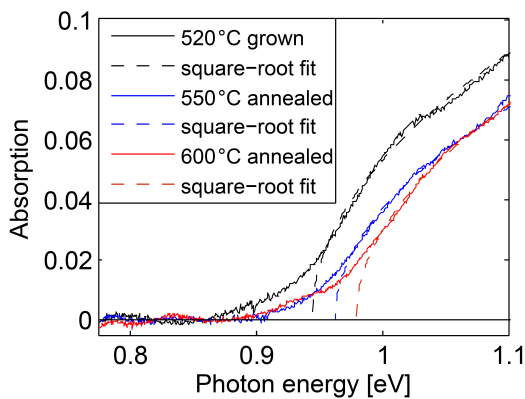


Figure 1. Absorption spectra before and after thermal annealing at 550 °C and 600 °C.

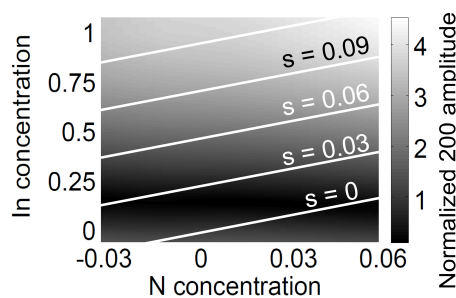


Figure 3. Reference data for the normalized 200 fringe amplitude and the normalized [220] fringe distance in [100] direction (white lines) as a function of indium and nitrogen concentration for a Laue circle centre of (0 4.2 0) and a thickness of 20 nm [13].

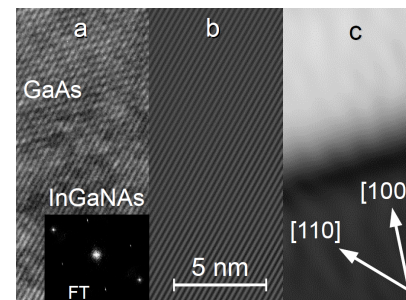


Figure 2. (a) Experimental 3-beam image of the $\text{In}_{0.2}\text{GaN}_{0.024}\text{As}/\text{GaAs}$ well before annealing acquired near zone axis [001] with a Laue circle center at (0 4.2 0). Filtering the diffractogram shown in (a) as insert gives (b) 220 fringe image and (c) the chemically sensitive amplitude of the 200 beam.

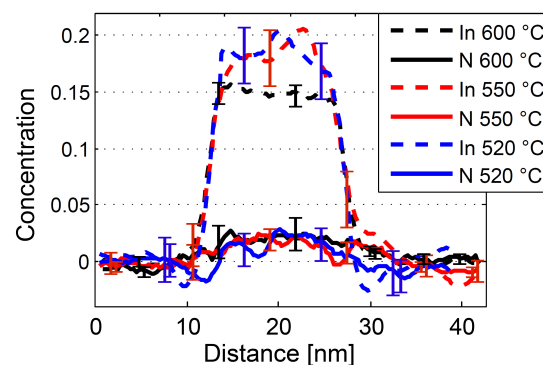


Figure 4. Indium and nitrogen concentration profiles before (520 °C) and after annealing at 550 °C and 600 °C.

weak dependency on the lamella thickness, imaging conditions were optimized [13]. By the use of a Laue circle center of (0 4.2 0) this dependency is minimized.

Figure 4 shows indium and nitrogen concentration profiles before and after annealing. Each profile is obtained by averaging the concentration maps parallelly to the well over a distance of 10 nm. With increasing annealing temperature, the average indium content decreases from $18.5 \pm 2\%$ to $15 \pm 1\%$ in the well, while the nitrogen content of $2 \pm 1\%$ is not measurably affected by the thermal annealing. The given precision accounts for inaccurately known specimen thickness, unknown relaxation in electron-beam direction and concentration fluctuations.

5. Discussion

Upon annealing a band gap blueshift of 36 ± 7 meV is observed, whereas the indium concentration seems to decrease by $3.5 \pm 2.5\%$. The blueshift could be explained by the diffusion of indium out of the InGaNAAs quantum well. In case of a diffusion into the GaAs layers one would expect a broadening of the indium concentration which was not observed (see fig. 4). As there are no indications of indium diffusion after annealing, this does not seem to occur. The

indium concentration decrease can be explained by an increasing number of In-N bonds, leading to a change of the 200 structure factors [8], and hence to a misassignment of the concentrations. A growing number of In-N bonds is also plausible because it minimizes the strain energy of the crystal [7] and it is discussed as a reason for the blueshift after thermal annealing [5].

To investigate the dependence of the 200 structure factor F on the number of In-N bonds, calculations were performed accounting for SADs as well as bonding via MASA. To account for SADs, super-cells with a size of $30 \times 30 \times 30$ unit cells have been relaxed [14], where every nitrogen atom is surrounded only by gallium atoms (N-4 Ga), indium atoms (N-4 In), or by a random distribution according to the gallium/indium ratio. For the observed concentrations before annealing, we find a decrease of the 200 structure factor with increasing frequency of N-In bonds. Compared to F_{random} , F_{N-4Ga} and F_{N-4In} show an increase of 5% and a decrease of 18%, respectively. A redistribution towards preferred N-In coordination leads to an underestimation of the indium content, which was observed after annealing. Hence, the observed band gap blueshift is attributed to an increase of the N-In bonds.

6. Conclusion

The seeming decrease of indium concentration and the observed blueshift after thermal annealing are explained by preferred coordination of nitrogen and indium. If long range redistributions of indium or nitrogen had been present here, they would have been observed with the used 3-beam method [9].

7. Acknowledgements

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