Effects of the annealing temperature on the structural and electronic properties of MBE grown InGaN/GaN quantum wells

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Abstract. A sample consisting of a 2.5nm thick In\textsubscript{0.25}Ga\textsubscript{0.75}N quantum well grown by molecular beam epitaxy (MBE) was annealed for 2 hours in a hydride vapour phase epitaxy (HVPE) reactor under an NH\textsubscript{3} atmosphere at 880°C, 920°C and 975°C. High-resolution TEM and STEM combined with electron energy-loss spectroscopy (EELS) investigations on the local electronic properties have been carried out to correlate these with the structure evolution during annealing. Image processing techniques such as geometric phase analysis of HR-TEM images reveal significant fluctuations in the indium distribution inside the well on a nanometric scale. An increase of the emission characteristic has been observed for annealing at 920°C.

1. Introduction and experimental procedures

It is well known that the annealing process has great influence on a sample’s emission characteristics, so that the full understanding of the effects of such process reveals crucial to improve III-N heterostructures [1].

A sample consisting of a 2.5nm thick In\textsubscript{0.25}Ga\textsubscript{0.75}N quantum well grown by NH\textsubscript{3}-MBE on a sapphire/GaN template was annealed for two hours in an HVPE reactor under NH\textsubscript{3} atmosphere at various temperatures ranging from 800 to 975°C. The photoluminescence (PL) and micro-PL characteristics of these heterostructures show a more uniform and red-shifted emission from the sample annealed at 920°C. To understand this phenomenon we investigated the structural changes in the specimen during the annealing process and determined the influence of such changes on the electronic properties.

Investigations have been performed on a FEI TITAN Cubed 80-300kV microscope equipped with Cs-corrector, monochromator and a 966 quantum GIF detector (0.2eV resolution) for EELS analysis and a JEOL 2000EX microscope equipped with a LaB\textsubscript{6} electron gun operating at 200kV.

Observations have been performed in the [11-20] and [1-100] direction on cross-sectional samples prepared by two different methods: by focused ion beam (FIB) using a Helios Nanolab FIB-SEM integrated system and by mechanical polishing and dimpling followed by ion milling. Electron transparency was obtained by PIPS ion milling with 4kV accelerated argon ions and LN\textsubscript{2} cooled stage. The final acceleration voltage used for surface cleaning has been 200V.
Local strain distribution and compositional information has been collected by processing HR-TEM images by geometric phase analysis (GPA), analyzing the tetragonal distortion in the heterostructure using the method described in [2]. Thin foil relaxation has been taken into account with the help of finite element (FEM) calculations [3]. Two beam condition technique has been applied to obtain images of 0002 lattice fringes tilting the sample by 3-4 deg around [0001] direction away from the exact zone axis. The incident electron beam was inclined to the optical axis of the microscope midway between the [0002] and [0000] beams. The application of Vegard’s law allowed us to obtain detailed information on the indium distribution along the quantum wells.

2. Results and discussion

2.1. High resolution (S)TEM

Figure 1a shows a STEM low magnification cross-sectional image of the heterostructure prepared by FIB. It is evident that the presence of the mounds, formed due to kinetic roughening that takes place during NH$_3$-MBE growth [4], influences the morphology of the well, distorting its geometry evidently. From SEM images we could determine a periodicity of the mounds as ~500nm. These form plates in which the well runs parallel to the [0001] lattice planes and valleys in which the c-planes and the well are not parallel. In these regions a step growth of the quantum well can be observed. Atomic steps could be observed during STEM observations (fig.1b). V-pits or threading dislocations are preferentially to be found at the bottom of the valleys as figure 1a shows. Here the quantum well’s width decreases due to the distortion caused by the dislocation.

![Figure 1](image_url)

**Figure 1.** (a) V-pit dislocation at the bottom of an MBE mound; (b) STEM-HAADF image showing atomic steps at the InGaN/GaN interface at mound’s slope, (c) Indium content map obtained by GPA superimposed on a TEM image of the reference sample; (d) Laterally averaged profiles of REF, TA880 and TA920 samples. The blue curve is characterized by two peaks presumably due to defects at the upper InGaN/GaN interface.
Geometric phase analysis of the reference sample (fig. 1c) allowed us the determination of the exact strain distribution and indium content along and across the wells. Our results show a uniform distribution and a concentration of 25-28 at% of indium atoms in the wells. No phase separation or clustering has been observed. The average quantum well thickness could be determined to be 3nm. The originally 3nm thick quantum well reduces its width to 2.5nm after annealing at 880°C and to 2.2nm after annealing at 920°C. The indium concentration in the wells of these two samples has been determined to be respectively 23% and 22%. We observe a more homogeneous indium distribution in the well annealed at 880°C, which leads to a less broad PL spectrum. The indium concentration inside the well after the annealing process at 975°C could be determined to be 7-9%. We could observe an increase of the strain in the cap layer, which we suggest to attribute to vacancy activated indium diffusion towards the surface. Further investigations on the effects of the annealing on the vacancies in the cap layer will be carried out in future.

Surface diffusion effects have been observed. For increasing annealing temperatures the valleys and mounds observed in the as grown sample level and create a smoother surface. The thickness of the cap layer along the samples is then inhomogeneous.

From the lateral averaged profile of the strain maps calculated by geometric phase analysis shown in figure 1d, we see a clear increase of the strain inside the quantum well as well as a reduction of the full width at half maximum (FWHM). For the sample annealed at 975°C a reduction of the strain and a leveling of the averaged profile confirm the out-of-plane diffusion and desorption of indium atoms. Integration along the calculated profiles allowed us to confirm the decrease in the total indium content in the samples for increasing annealing temperatures.

2.2. Electronic properties

EELS investigations of the annealed samples have been performed on cross-sectional samples and correlated to theoretical calculations made using the Wien2k program. This simulation software is based on full augmented plane wave (FLAPW) methods for the calculations of the energy loss spectra of the chosen compounds [5]. Our calculations have been performed for $q$ perpendicular to $c$. We used for GaN lattice parameters of $a_{\text{GaN}} = 0.3189 \text{nm}$ and $c_{\text{GaN}} = 0.5185 \text{nm}$. For the simulation of different indium contents we used lattice parameters derived by Vegard’s law with $a_{\text{InN}} = 0.3548 \text{nm}$ and $c_{\text{InN}} = 0.5760 \text{nm}$.

Through the simulation of various low loss spectra for different indium contents we calculated the dependence of the plasmon position on the atomic indium content. We notice a slight shift of the peak position for the annealed samples in comparison to the as-grown one. This is consistent with the difference in indium content revealed by GPA analysis. For 880°C and 920°C the differences in the plasmon peak position are minimal.

The measured bandgap for the sample annealed at 880°C has been determined through the acquisition and averaging of several spectra. Deconvolution of the zero loss peak from the acquired low loss spectrum and Kramers-Kronig analysis (KKA) have been applied to remove the contribution of surface losses to the acquired spectra [6]. Cerenkov effects could be neglected since the thickness of the investigated specimen fulfilled the requirements described in [7]. We measured in this way a bandgap of ~2.5eV. A narrower bandgap could be measured for the reference sample and the one annealed at 920°C (~2.3eV).

PL measurements showing a 55meV shift of the emission for the sample annealed at 880°C and an opposite shift for the one annealed at 920°C can be explained by the narrowing as well as by the different indium concentrations in the quantum wells and by the formation of clusters for higher temperatures.

In contrast to other groups that observed a relation between measured spectra and core-hole calculations, we find our measurements well correlated to ground state calculations of the low loss region of the investigated material [8].
3. Conclusions
We investigated the influence of different annealing temperatures on the structural properties of InGaN/GaN quantum wells with nominal 25% of indium content. We observed diffusion of In atoms to the sample surface and consequent desorption. A decrease of the total indium content in the samples for increasing annealing temperatures could be determined from laterally averaged profiles of strain maps. A more homogeneous indium distribution along the wells annealed at lower temperatures (<900°C) has been observed.

Electronic properties and the structure have been correlated through EELS measurements. A shift towards longer wavelength has been observed by measurement of the band-gap in the quantum well region for annealed samples at 920°C even though a slight decrease of the total indium content was observed in comparison to the as-grown sample. Indium diffusion and desorption is compensated by the narrowing of the well thickness, leading to a stronger QCSE and by indium clustering introducing size effects.

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References
[1] Tournie E et al. 2002 Appl. Phys. Lett. 80, 4148
[2] Kret S et al. 2001 Phys. Stat. Sol. (b) 227, 247
[3] Kret S et al. 2007 Nanotech. 19, 465707
[4] Vezian S et al. 2004 Physical Review B 69, 125329
[5] Blaha P et al. 1990 Comput. Phys. Commun. 59, 399
[6] Stoeger-Pollach M. 2008 Micron 39, 1092
[7] Gu L et al. 2007 Phys. Rev. B 75, 195214
[8] Keast VJ et al. 2002 Phys. Rev. B 66, 125319