Chapter 7

One of the unique properties of NCs is their very high crystalline quality, even when grown on low quality substrates, due to an efficient strain relaxation caused by the NCs large surface-to-volume ratio following the principle of St. Venant [Love1944] and by the bending of threading dislocations that may be present at the bottom of the NC towards the NC sidewalls [Harui2008] [Li2010].

Figure 7.3.2.2: (a) Low temperature (12K) PL spectra of ordered GaN NCs and the UID GaN buffer; (b) bright-field TEM picture of ordered GaN NC, adapted from Nanotechnology 24, 175303 (2013).

This material improvement upon NC growth can be seen nicely in figure 7.3.2.2 a, where LT-PL spectra of the GaN buffer layer and SAG GaN NCs grown on top are shown. The dominant PL emission from the UID GaN buffer is a broad peak centered at 3.42 eV with a low energy shoulder, the former being attributed to Si-donor-bound excitons [Sanchez-Garcia1998b]. In contrast, SAG GaN NCs show a sharp and intense (2000 times higher than the buffer) D′X emission at 3.47 eV with a line width of 6.5 meV, representative of high quality, strain free material. However a line width value of 6.5 meV is higher than the one measured in SA GaN NCs presented in chapter 4.1 (2-3 meV) which may point towards the presence of extended defects in the selectively grown GaN NCs.

The bright field TEM image shown in figure 7.3.2.2b reveals the presence of two distinct NC types, namely defect free ones (type I), and defective ones (type II) showing the presence of threading dislocations and inversion domains. The origin of the formation of two distinct NC types is still under investigation. The presence of extended defects in some of the NCs most probably accounts for the observed broadening of the
D\textsuperscript{0}X emission due to an inhomogeneous strain distribution and disorder inside defective type II NCs (with zero average strain). When growing SA GaN NCs on bare Si(111) surfaces, the strong mismatch forces a Volmer-Weber nucleation mechanism, and the NCs grow defect free because they “disconnect” from the substrate lattice by generation of a dislocation network at the interface (discussed in more detail in chapter 4.1). However, in case of SAG NCs on buffered Si(111), the growth is a homoepitaxial process, in which dislocations already existing in the buffer are allowed to run through some of the NCs (type II). The lack of a strong radial strain field in the first stage of the growth may make the bending and annihilation of these running-through dislocations less efficient.
Chapter 7

7.3.3 Selective area growth of InGaN/GaN NCs on GaN-buffered Si(111) substrates

InGaN NCs were grown for 1h at different temperatures, III/V and In/Ga ratios on top of 550 nm high GaN NCs grown by SAG on GaN-buffered Si(111) for 3h at 810°C under the conditions described in section 7.2 (the growth conditions of the InGaN part are summarized in table 7.2.1). SEM images from samples of series G are shown in figure 7.3.3.1, from where the height of the InGaN portion can be estimated.

![Figure 7.3.3.1: Cross-sectional SEM pictures of InGaN/GaN samples: (a) G1, (b) G2, (c) G3, (d) G4, (e) G5, (f) G6, (g) G7 and (h) G8. The insets show top view SEM images of the respective samples, Nanotechnology 24, 175303 (2013).](image)

A growth rate increase from 5.7 nm/min for sample G1 to 8.2 nm/min for sample G3 is determined (temperature decrease from 700 to 600 °C). This can be explained by a decrease of In desorption, as well as by a lower InN decomposition rate [Gallinat2007] [Koblmüller2007]. This interpretation is confirmed by the PL measurements shown in figure 7.3.3.2, in particular figures 7.3.3.2a and c, that reveal an increase of In content as the growth temperature decreases.
Figure 7.3.3.2: PL spectra of samples (a) G1, (b) G2, (c) G3, (d) G4, (e) G5, (f) G6, (g) G7 and (h) G8. The insets show photographs of the respective samples taken during the PL experiments, Nanotechnology 24, 175303 (2013).
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The low temperature (T=12K) PL spectrum of sample G1 (figure 7.3.3.2a) reveals a peak at around 3.2 eV that could be related to InGaN, though with very low In content (~5%).

In agreement with an increased growth rate (7 nm/min) with respect to sample G1, a significantly higher In% can be found in sample G2, indicated by a broad low energy shoulder (figure 7.3.3.2b). The appearance of a broad PL emission points towards an inhomogeneous In content, most likely due to high InN decomposition at 650ºC. In addition to that it has to be noted that the low temperature PL spectra of samples G1 and G2 reveal a sharp emission at 3.47 eV, i.e. D⁰X excitonic emission of GaN.

Top-view SEM images from samples G1 and G2, shown as insets in figures 7.3.3.1a and b, clearly show strong morphological inhomogeneities of the topmost InGaN region of the NCs. For self-assembled InGaN NCs it has been shown in chapter 4 that structural inhomogeneities, such as those found here, induce a strong variation of In composition together with broad PL emission. Indeed, the absence of morphological inhomogeneities in sample G3 (figure 7.3.3.1c) grown at lower temperature (600ºC) also corresponds to a less broad PL spectrum with just two distinct peaks (figure 7.3.3.2c). The reduction of the line width is more evident in the samples G4-G6 grown at 550ºC, which is assumed to be related to a reduced InN decomposition, leading to a more homogenous indium distribution along the NCs.

When lowering the growth temperature from 600ºC to 550ºC (sample G4), the whole PL spectrum red-shifts by some 200 meV (figure 7.3.3.2d). On the other hand, while keeping the temperature at 550ºC, no significant PL shift is observed when changing either the In/Ga (figure 7.3.3.3e) ratio or the group III/N ratio (figure 7.3.3.2f) in samples G5 and G6. The effect of an increased In/Ga ratio is an improvement in the NC morphology, that is, a more homogenous NC diameter, as can be seen in figure 7.3.3.1e for sample G5. On the other hand, a reduction in group III/N ratio leads to a reduction in NC diameter along the growth direction (sample G6 in figure 7.3.3.1f) leading to a needle-like shape. Besides morphological changes, the reduction in group III/N ratio yields a strong increase of the internal quantum efficiency (IQE) estimated from PL data, from 2.6 % in sample G5 to around 22% in sample G6. The PL related IQE at RT is estimated from the ratio between the integrated PL intensities at RT and LT (T=12K), assuming an IQE of 1 at T=12K.

Lowering the temperature down to 500ºC a needle like morphology is observed for both sample G7 and G8 (figure 7.3.3.1 g and h). Remarkably no further red-shift of the PL
peak position is observed for both sample G7 and sample G8. However, an increase of PL-IQE to 10% is observed in sample G7 when compared to sample G5 (2.6%), i.e. a decrease of the growth temperature leading to an increase of PL-IQE. When comparing sample G7 with sample G8 (higher N-flux) a further increase of PL-IQE up to 30% is found. This issue will be discussed in more detail in the next chapter.

Finally the emission wavelength was pushed towards the infrared by increasing the In composition, up to 100% (samples of series H). Figure 7.3.3.3 shows SEM images of these samples. Starting from the same growth conditions as for sample G8, but using a lower growth temperature of 480ºC, sample H1 shows a broad PL emission at 2.1 eV (orange) as depicted in figure 7.3.3.3e. A further decrease of the growth temperature leads to a more pronounced red-shift of the PL emission down to 1.18 eV (sample H3 in figure 7.3.3.3e). Besides the growth temperature, the group III/N ratio can be used as well in order to change the In content. This is observed when comparing samples H2 and H3, grown at the same temperature. A lower group III/N ratio (higher N flux) used for sample H3 leads to an increase in the In incorporation. This behavior is in contrast to the behavior observed in samples G4-G6, where no dependence of In incorporation on the provided N-amount was found. It can be speculated that this difference relates to growth taking place under metal rich or nitrogen rich conditions, respectively. When growing under metal-rich conditions an increase of nitrogen favors In incorporation (discussed in chapter 4), but if the temperature is too high, and In desorption increases growth may take place under N-rich conditions and In-incorporation does not depend on the supplied N-amount (samples G4-G6).
In order to achieve the SAG of InN NCs (100% In) on top of GaN, sample H4 was grown at much lower temperature (300ºC) to drastically reduce the InN decomposition. As can be seen in figure 7.3.3.3d, the nanocolumnar shape, as well as the selectivity, is retained. The PL spectrum of sample H4 (figure 7.3.3.3e) shows a peak at 0.78 eV, which is higher than the energy corresponding to fully relaxed high quality InN layers, which is known to be at 0.63 eV [Gallinat2006]. Possible reasons for such a blue-shift in the PL emission from InN NCs are the presence of compressive stress (not commonly observed in NCs) or a high electron concentration. However, a high electron concentration can account for both the measured PL line width of around 70 meV, and the observed emission energy of 0.78 eV [Song 2008]. It has to be noted that the growth conditions for InN NCs are extrapolated from samples with lower In content, thus they are not the optimal ones. Low-loss EELS [Kong2012] has been used in order to study the axial indium distribution as a function of growth temperature in samples G5 (550ºC), G7 (500ºC) and H2 (450ºC). The axial line scans of low-loss EELS spectra performed along the GaN-InGaN section, are shown in figure 7.3.3.4. Depending on the growth temperature an increasing In content with decreasing temperature is found i.e. 25.5% in G5, 36% in G7 and 80.4% in H2.
Figure 7.3.3.4: Indium concentration profiles measured by line scans of low-loss EELS along axial direction of samples G5 (550ºC), G7 (500ºC) and H2 (450ºC), Phys. Status Solidi A, 1-4 (2015).

Regardless of the growth temperature all samples exhibit similar indium compositions profiles in spite of the different indium concentrations. In all samples a broad transition area with an increasing indium concentration above the InGaN/GaN interface is found (as before in case of SA InGaN/GaN NCs shown in chapter 4). The transition region is assumed to be caused by lattice pulling effects at the InGaN/GaN interface. Upon growth of the InGaN region, strain relaxation sets on and allows for a higher In incorporation. With increasing In-content the width of the lattice pulling region decreases from 50 nm for sample G5 to 20 nm for sample H2, which is assumed to be related to higher strain gradient for increasing In-content leading to an earlier onset of relaxation. At this point it has to be noted that these PL results (figure 7.3.3.2) do not agree with the low loss EELS measurements presented here, i.e. based on the PL no increasing In incorporation is found when decreasing the growth temperature (sample G5 vs G7) while low loss EELS measurements show a clear increase of In content when decreasing the sample temperature. The reason for this discrepancy is still under investigation.
7.4 Summary:

In summary, high quality, undoped and Si-doped GaN buffers were grown on Si(111). The buffers showed PL excitonic emission and no traces of the yellow band. The buffers were used as templates for SAG of In(Ga)N/GaN NCs. GaN NC arrays were grown on these templates with perfect selectivity and high quality, revealed by the PL emission of donor-bound excitons at 3.47 eV and a line width of 6.5 meV. The higher line width compared to self-assembled GaN NCs was attributed to the presence of threading dislocations in some of the NCs most likely propagating from the GaN buffer layer into the GaN NCs. InGaN and InN NC arrays were then grown with In content ranging from 5% to 100% covering the spectrum from ultraviolet (3.2 eV) to the infrared (0.78 eV). InGaN/GaN NCs grown on GaN/Si emitting in the green spectral range were found to have a double peak structure in PL. Low loss EELS-TEM measurements indicated the presence of a lattice pulled region at the InGaN/GaN interface. The size of the lattice pulled region was determined to decrease with increasing nominal In-content. For InGaN/GaN NCs emitting in the green spectral range, a decrease of growth temperature and/or group(III)/N ratio was found to have no impact on the PL peak position of the InGaN/GaN NCs but it was leading to an increase of the PL-IQE.
Chapter 8: Effects of growth conditions on morphology and optical properties of InGaN/GaN nanocolumnar heterostructures selectively grown by MBE
8.1 Introduction:

Selective area growth (SAG) of GaN nanocolumns (NCs), as well as InGaN/GaN NCs with thick InGaN segments (~500nm) on GaN/sapphire emitting in the whole visible spectrum, has been presented in chapters 5 and 6, as a way to overcome the limitations of self-assembled (SA) NCs, that undergo a strong dispersion in morphological, optical and electrical characteristics. Furthermore in chapter 7 SAG of InGaN/GaN NCs including long InGaN sections (530-830 nm) covering the whole alloy composition range was successfully demonstrated on cheap, easy to process Si(111). InGaN/GaN NCs with long InGaN segments, grown either on GaN/sapphire or GaN-buffered Si(111), may provide an effective and elegant way to reduce droop effects while ensuring high internal quantum efficiency (IQE), particularly for green emission where droop effects are stronger. First LEDs based on long ordered InGaN NCs (~500 nm) emitting in the blue, green and yellow spectral range have already been demonstrated in chapter 6. However, up to this point no analysis of the growth mechanism as well as optical properties of selectively grown InGaN segments has been performed, although this information is vital for future device optimization.

This chapter reports on a detailed study providing insight into the growth mechanism as well as optical properties of ordered InGaN/GaN NCs with thick InGaN sections emitting in the green range grown on GaN/sapphire as well as GaN-buffered Si(111).
8.2 Experimental details:

In order to compare the optical properties of SAG InGaN/GaN NCs emitting in the green spectral range, two series of samples, I and G (series of chapter 7), were grown/analyzed.

Table 8.2.1: Growth conditions of the InGaN segments. Series G was grown on GaN buffered Si(111) while series I was grown on GaN/sapphire.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Impinging fluxes in nm/min (x10^{14} atoms/(s cm^2))</th>
<th>III/V ratio</th>
<th>In/Ga ratio</th>
<th>T_{sample} in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga</td>
<td>In</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>I1</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>14 (10.3)</td>
<td>0.49</td>
</tr>
<tr>
<td>I2</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>17 (12.5)</td>
<td>0.40</td>
</tr>
<tr>
<td>I3</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>20 (14.7)</td>
<td>0.34</td>
</tr>
<tr>
<td>G5</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>10 (7.37)</td>
<td>0.68</td>
</tr>
<tr>
<td>G6</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>14 (10.3)</td>
<td>0.49</td>
</tr>
<tr>
<td>G7</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>10 (7.37)</td>
<td>0.68</td>
</tr>
<tr>
<td>G8</td>
<td>2.3 (1.7)</td>
<td>6.3 (3.33)</td>
<td>14 (10.3)</td>
<td>0.49</td>
</tr>
</tbody>
</table>

In series I nanoholes were arranged in a compact hexagonal lattice, with a pitch of around 270 nm and an average diameter of 170 nm. The initial GaN NC sections were grown on GaN/sapphire templates with a Ga-flux (Φ_{Ga}) of 18 nm/min and N-flux (Φ_{N}) of 5 nm/min at 880°C (thermocouple) during 3h (GaN sections around 450 nm long). The InGaN sections were subsequently grown during 1h on top of the GaN NCs under the conditions described in table 8.2.1 (series I).

Details about the growth procedure of samples of series G can be found in the experimental section of chapter 7 and table 8.2.1. It has to be noted, that the growth temperatures given in table 8.2.1 correspond to thermocouple readings taken at the backside of the sample (without physical contact to the sample), hence the higher temperature values measured when growing on GaN/sapphire do not necessarily relate to a higher sample temperature at the sample top surface (lower thermal conductivity of
sapphire compared to silicon). All samples were characterized by means of scanning electron microscopy (SEM), photoluminescence (PL) and cathodoluminescence (CL).
8.3 Results and discussion:

Figure 8.3.1a shows cross-section and top-view SEM pictures of samples (I1-I3), as well as pictures of the corresponding PL emission color.

Figure 8.3.1: a) SEM images and PL emission pictures of InGaN/GaN NCs of series I grown on GaN/sapphire and magnified cross-section SEM pictures of single NCs with similar GaN section diameter (~170 nm) of b) sample I1, c) sample I2, and d) sample I3, showing different diameter changes. The dotted lines are guides for the eye indicating the position of the nominal InGaN/GaN interface.
In the three cases, ordered InGaN/GaN NCs with flat top facet, emitting in the green spectral range were obtained. The growth rates for the InGaN sections, as determined from SEM pictures in figure 8.3.1b-d, are 5.5 nm/min, 6.0 nm/min, and 6.8 nm/min for samples I1, I2 and I3 respectively, indicating a trend of increasing growth rate with increasing nitrogen. Cross-section SEM pictures in figure 8.3.1b and 1.c show an increasing diameter towards the NC top starting at (or slightly below) the InGaN/GaN interface, i.e. 40% increase for sample I1 and 20% for sample I2. This diameter increase is rather abrupt for sample I1 at the InGaN/GaN interface (figure 8.3.1.b) and then gradual up to the top, whereas sample I2 shows a gradual diameter increase starting below the nominal the InGaN/GaN interface (figure 8.3.1.c).

Figure 8.3.2: a) Cross-section SEM pictures from InGaN/GaN NCs of sample I3 having different GaN diameters (sample I3), the GaN diameter as well as the relative diameter change upon InGaN growth are shown in the figure. In all three cases similar top diameters between 130 and 140 nm are observed; b) sketch showing the different contributions to the InGaN section growth in sample I3.

However, for sample I3 (figure 8.3.1.d) the diameter beyond the GaN/InGaN interface is almost constant but for the topmost NC region where a sudden and asymmetric
diameter reduction (20%) is observed. Notice that the diameter comparison in figures 8.3.1.b, 8.3.1.c and 8.3.1.d is done selecting on purpose individual NCs with the same starting GaN diameter of ~170 nm.

Taking advantage of the colloidal lithography process, where a certain nanohole diameter variation is present, figure 8.3.2 shows individual NCs from sample I3 with different starting GaN diameters. The final shape and diameter of these NCs are strongly dependent on the starting diameter, and, in fact, for initial diameters of 130 nm, no changes are observed.

The different diameter changes observed in samples I1, I2 and I3 (or the absence of changes in sample I3 for a 130 nm starting diameter) seem closely related to the nominal III/V ratio and the initial NC diameter. Both factors affect the “local” III/V ratio on the NC top, which depends on the directly impinging metal flux and the diffusion flux along the NC sidewalls to its top.

It has been shown for SA GaN NCs that the NC diameter is directly related to the local Ga/N ratio at the growth front (NC top) where the system always moves towards stoichiometry during the growth [Fernández-Garrido2013]. A similar mechanism is found to be present in the SAG InGaN/GaN NCs presented here.
While no significant active nitrogen diffusion along the NC sidewalls occurs [Lymperakis2009], nitrogen plays a crucial role to determine stoichiometry at the NC top, since the total amount of metal atoms reaching the upper growth front can be larger than the nominal impinging flux. The overall metal flux reaching the NC top is given by:

\[
\Phi_{\text{total,metal}} = \Phi_{\text{imp,top}(\text{In/Ga})} + \Phi_{\text{diff}(\text{In/Ga})} + \Phi_{\text{dec}(\text{In/Ga})} - \Phi_{\text{des}(\text{In/Ga})}
\]  

(1)

All relevant contributions are shown in figure 8.3.3. The decomposition fluxes (\(\Phi_{\text{dec, Ga}}, \Phi_{\text{dec, In}}\)) as well as desorption fluxes (\(\Phi_{\text{des, Ga}}, \Phi_{\text{des, In}}\)) play a crucial role for the temperature used as can be seen by the rather small growth rates compared to the
impinging fluxes. While the direct impinging metal fluxes \( \Phi_{\text{imp.pop}}^{\text{Ga In}} \) are independent of the NC diameter, the metal diffusion flux \( \Phi_{\text{diff}}^{\text{Ga In}} \) arriving to the NC top depends on the diameter of the NC as follows (from simple geometrical argumentation):

\[
\Phi_{\text{diff}}^{\text{Ga In}} \propto \frac{\Phi_{\text{imp.pop}}^{\text{Ga In}} \cdot 2 \pi r L_{\text{diff}}^{\text{Ga In}}}{\frac{2 L_{\text{diff}}^{\text{Ga In}}}{r}} = \Phi_{\text{imp.pop}}^{\text{Ga In}} \cdot \frac{2 L_{\text{diff}}^{\text{Ga In}}}{r}
\]

(2)

with \( r \) being the NC radius and \( L_{\text{diff}}^{\text{Ga In}} \) the diffusion lengths of Ga and In atoms along the c-direction at the NC sidewall. Then, an increase (decrease) of the NC diameter leads to a net decrease (increase) of the diffusion flux towards the top. At this point it has to be noted that the diffusion length of Ga-atoms \( L_{\text{diff}}^{\text{Ga}} \) was found to be significantly higher than that of In-atoms \( L_{\text{diff}}^{\text{In}} \) at the given growth temperature of 650ºC, meaning that the diffusion flux contribution to the overall metal amount at the NCs top is higher for Ga [Sekiguchi2010]. This will be a relevant point for the interpretation of the spatial indium distribution within the NC later on.

The diameter increase observed in the InGaN section of samples I1 and I2 can be interpreted as originating from the local III/V ratio at the NC top being too high to reach stoichiometry for the given diameter defined by the underneath GaN section (although ratios of nominal impinging fluxes are below 1), that is:

\[
\frac{\Phi_{\text{metal}}^{\text{total}}}{\Phi_{\text{N}}^{\text{imp.pop}}} > 1.
\]

(3)

In order to compensate for this metal excess at the NC top, its diameter increases in order to decrease the metal atoms diffusion contribution to the top, i.e. a lower metal density at the top to accommodate with the impinging \( \Phi_{\text{N}} \). The higher the metal excess, the higher the diameter increase needed, as shown in figure 8.3.1b and 8.3.1c for InGaN/GaN NCs with the same starting GaN diameter of 170 nm but different nominal III/V ratios (40% in sample I1 grown with nominal III/V of 0.49 versus 20% in sample I2 grown with nominal III/V of 0.4). On the other hand, a net nitrogen excess at the growth front would lead to a diameter decrease, following the same mechanism to reach stoichiometry. In that case, the condition would be:

\[
\frac{\Phi_{\text{metal}}^{\text{total}}}{\Phi_{\text{N}}^{\text{imp.pop}}} < 1
\]

(4)

then causing a diameter decrease to increase the diffusion contribution of metal atoms.
In the light of this model the evolution of the InGaN section diameter should then depend on the fulfilled condition, either by eq. (3) or eq. (4). Figure 8.3.4 shows this dependence on NCs from samples I1 and I2 that start from different initial GaN diameters (due to diameter variations inherent to the colloidal lithography process).

![Figure 8.3.4: Diameter variation of InGaN sections in NCs from samples I1 (left) and I2 (right) starting from different initial GaN diameters (indicated). The diameter variations are indicated in percent.](image)

It is clear from data in figure 8.3.4 that the diameter increase of the InGaN section is determined by the condition imposed by eq.(3), that is, local metal-excess. In addition it is clearly seen that a higher metal-excess condition (smaller GaN diameter) leads to a higher relative diameter change. The main behavior difference between samples I1 and I2 is just the onset value of the initial diameter for the regime established by eq.(3), but not the trend which is quite similar. In sample I2, an initial diameter of around 210 nm is nearly sufficient for reaching stoichiometry at the NC top (only rather small diameter change of around 8% of the InGaN section), whereas a similar diameter still leads to a significant diameter change in sample I1 upon InGaN growth (diameter change of 25%). This difference is attributed as mentioned before to the different nominal impinging III/V ratios used (table 8.2.1).

Considering the NCs from sample I3 shown in figure 8.3.1d, with an initial GaN diameter of 170 nm (same as for samples I1 and I2 in figure 8.3.1b and 8.3.1c), the observed decrease of InGaN top diameter (20% smaller than the initial GaN one) suggests that the growth regime is determined by eq. (4), that is, local nitrogen excess. As can be seen in figure 8.3.2, an increase of the initial GaN diameter does not affect
the InGaN top diameter, i.e. in both cases the InGaN top diameter is around 140 nm. On the other hand no change in NC diameter upon InGaN growth with respect to the GaN diameter is observed at all for a GaN starting diameter of around 130 nm. A possible explanation is illustrated in the sketch shown in figure 8.3.2b. The InGaN section grows under the regime given by eq.(4) forcing a diameter reduction to a value determined by the NCs top stoichiometry condition directly at the InGaN/GaN interface. This will expose a portion of the initial GaN NC top surface where growth can proceed as well but with a different growth rate. The combination of the two processes would give rise to a complex structure where two different diameters are observed, inner and outer. This model would also predict that, for a small enough initial GaN diameter the growth front at the NC top would be at stoichiometry, so that, no diameter changes would be expected. This is shown in figure 8.3.2a for an initial diameter of 130 nm.

Figure 8.3.5: Top view SEM, cross-sectional SEM, and PL emission pictures from InGaN/GaN NCs of series G.

Figure 8.3.5 shows cross-section and top-view SEM pictures of InGaN/GaN NCs of series G (NCs grown on GaN buffered Si(111)). From the GaN section height (450 nm) the growth rates for InGaN sections can be estimated from cross-sectional SEM data (figure 8.3.6). For both temperatures (550°C and 500°C) the growth rate increases with
increasing nitrogen from 9 and 13.8 nm/min for samples G5 and G6 grown at 550ºC, and 10 and 10.8 nm/min for samples G7 and G8 grown at 500ºC.

Figure 8.3.6: Higher magnification cross-sectional SEM pictures of a) sample G5, b) G6, c) G7 and d) G8. The dotted lines are guides for the eye, indicating the position of the nominal InGaN/GaN interface.

In contrast to samples of series I, dramatic changes of the overall NC morphology are found in samples of series G, namely NC flat top for sample G5 and needle-like for samples G6, G7 and G8 (figure 8.3.6). In principle the same mechanisms as discussed for samples of series I should be present here as well. However at this point it has to be noted that GaN growth on Si(111) by PAMBE is known to lead to the growth of N-polar GaN layers [Gangopadhyay2006] and due to that the formation of N-polar InGaN/GaN NCs is assumed to be present in samples of series G (opposite as for samples of series I grown on GaN/sapphire). Based on that, the different morphology
compared to samples of series I could be related to different polarities in the two sets of samples, i.e. metal-polar in series I and N-polar in series G. This is backed up by findings for SA N-polar InN NCs grown on Si(111) which were shown to develop a needle like shape (similar to the ones observed here), when growth was performed under nitrogen rich conditions [Stoica2006]. At this point it is unclear how exactly the polarity of the SAG GaN NCs influences the InGaN growth and in particular the NC morphology and further studies are needed in order to gain more insight into this issue.

Figure 8.3.7: Low-temperature (T=7K) PL spectra of samples of (a) series I and (b) series G. Temperature dependence of integrated PL intensity and corresponding PL-IQE values of samples of (c) series I and (d) series G (all plots are normalized to a laser power of 0.2 mW).

Low temperature PL spectra of samples of series I and G are shown in figures 8.3.7a and b. PL spectra in figure 8.3.7a show a clear red-shift with increasing nitrogen in samples I1 to I3, pointing towards an increasing In incorporation with increasing
nitrogen. However, this red shift, significantly pronounced between samples I1 to I2 (27% to 31% In content) is much smaller between samples I2 and I3 (32% In content in I3). This behavior is expected, when moving from the metal rich to the nitrogen rich growth regime [Averbeck1999], i.e. samples I1 and I2 were grown under (local) metal rich growth conditions at the growth front (NC top), while in sample I3 (local) stoichiometric or N-rich conditions were present. This finding backs up the suggested model for the morphology evolution for sample of series I.

On the other hand a different behavior is found for samples of series G (figure 8.3.7b). Here no red-shift of the PL peak position with increasing nitrogen or decreasing temperature is present. In fact the lowest PL peak position is found for sample G5 (2.22 eV), which when taking into account the growth conditions, is expected to have the lowest In-content (high temperature, low nitrogen), i.e. highest PL peak energy, of all samples of series G.

In figures 8.3.7c and d the integrated PL intensities versus temperature of samples of series I (figure 8.3.7c) and G (figure 8.3.7d) are shown. For all three samples of series I similar integrated low temperature PL intensities are found. On the other hand clear differences in integrated low temperature PL intensities are observed for the samples of series G, i.e. a decrease of temperature and/or increase of nitrogen leads to a lower integrated PL intensity at low temperature. This behavior can, a prior, be ascribed to a variety of effects, namely (i) different defect densities, (ii) different NC densities due to the use of colloidal lithography or (iii) different light extraction efficiencies due to the morphology changes. Considering the stable integrated intensity in the low temperature range, different defect levels can be excluded since their thermal activation would reflect in an immediate drop of the emission intensity with increasing temperature. On the other hand differences in NC density may play a role due to the use of colloidal lithography. However, the systematic change of the low temperature intensity with temperature and nitrogen, makes the (random) variation of the NC density as the main source seem unlikely. Due to that the observed changes in low temperature intensity may be related to changes in the light extraction from the individual columns due to the strong morphology changes among samples of series G (figure 8.3.6).
In addition to its impact on the NC morphology as well as the average In-content, changes in the local III/V and In/Ga ratio at the NC top are expected to affect as well the In-distribution inside the NCs. In order to gather information about the In distribution inside the individual NCs along the growth direction, as well as among different InGaN/GaN NCs, RT-CL measurements were performed on samples I1 to I3 (figure 8.3.8). Results show that spectra are identical for single NCs and ensembles, which points to a good homogeneity and an identical average In incorporation from NC to NC, as expected from SAG. As a consequence, the line width of around 200 meV in all three cases can be attributed solely to the specific In distribution within individual NCs.

Figure 8.3.8: RT-CL spectra of a single NC and an ensemble of ~400 NCs of samples I1-I3 measured in top-view. In addition spatially resolved CL data from single NCs from samples I1 to I3 are shown.

Spatially resolved CL measurements of samples I1 and I2 (figure 8.3.8) show a red shift of the emission towards the NC top, pointing towards an increase of the In composition along the NC. This change of In composition was reported before in chapter 6 for red emitting SAG InGaN/GaN NCs grown on GaN/sapphire (sample D6) and attributed to partial InGaN decomposition and In segregation during the growth. A similar mechanism may be present here as well. However, sample I3 shows a different
behavior, i.e. no red shift but a blue shift towards the NC top. At this point it has to be noted that all samples were grown at the same temperature (650ºC), hence InGaN decomposition an In segregation can be assumed to be similar in all cases. Due to that, an additional mechanism that gives rise to the observed changes of In-content must be present.

It is reasonable to assume that this mechanism relates to the morphology evolution observed in samples I1-I3. Upon NC diameter increase (sample I1 and I2) the amount (density) of metal atoms at the growth front (NC top) is reduced following eq. (2), that determines the metal flux reaching the NC top by diffusion along the sidewalls. This reduction is the same for In and Ga fluxes along the sidewall, but given the differences between the directly impinging fluxes (Φ_{In}=6.3 nm/min for In and Φ_{Ga}=2.3 nm/min for Ga), the overall effect is a net increase of the In/Ga ratio at the growth front as the NC diameter increases (higher diffusion flux contribution for Ga than for In to total flux). In addition the increasing diameter would lead to an reduction of the local III/V ratio at the NC top which leads to an increased In-incorporation as well, given the local metal rich conditions at the NC top [Averbeck1999]. This mechanism should not be present in an InGaN section with constant or reduced diameter towards the NC top (sample I3).

At this point it can only be speculated about the origin of the observed blue shift. In principle a diameter decrease should lead to an increase of the local Ga/In ratio, which in turn would lead to a decreasing In-content towards the top (blue shift) under local N-rich conditions. However given the more complex morphology of InGaN segments of sample I3 no conclusive explanation for the observed blue shift can be provided at this point and further studies will be needed in order to clarify this issue.

As in case of series I, the comparison of the RT-CL spectra of a single NC with an ensemble of NCs of the samples of series G shown in figure 8.3.9, reveal almost identical peak positions and shapes indicating an excellent homogeneity of the In incorporation in these samples as well. However, whereas the spatial emission properties in samples of series I do show a rather straightforward dependence from the growth conditions, a more complex behavior is observed in samples of series G (insets in figure 8.3.9). Samples G5, G6 and G7 show a double peak structure (figure 8.3.9a, b, c), while sample G8 shows only single peak emission (figure 8.3.9d).
Figure 8.3.9. RT-CL spectra of single NC versus ensemble and spatially resolved CL measurements (insets) of a single InGaN/GaN NC from a) sample G5, b) sample G6, c) sample G7 and c) sample G8.

The optical performance of the samples was further evaluated using the PL related internal quantum efficiency (PL-IQE) at room temperature. The samples of series I do not show any clear tendency of the PL-IQE as a function of the nitrogen used, i.e. I1: 3.7%; I2: 1.4%; I3: 2.6% (figure 8.3.7c). On the other hand a reduction of the growth temperature and/or increase in nitrogen leads to a strong increase in the PL-IQE in samples of series G, i.e. G5: 2.6%; G6: 22%; G7: 10%; G8: 30% (figure 8.3.7d).
Figure 8.3.10: PL peak position and line width versus temperature of a) sample I1, b) sample I2 and c) sample I3. An s-shape of the PL peak positions is observed for all samples. The dotted lines are guides for the eye.
A reasonable explanation for this finding may be a change of carrier localization in the InGaN/GaN NCs of series G by changing the growth conditions. A lower growth temperature and group(III)/N ratio apparently prevents the photo-excited carrier more effectively from recombining via non-radiative recombination channels (point defects, NC surface) thus increasing the PL-IQE. It was shown that localization of carriers in InGaN QWs leads to high IQEs despite a high defect density commonly observed in planar InGaN QWs [Kaneta2008].

In order to gain insight into the carrier localization, temperature dependent PL experiments were performed on samples of series I (figure 8.3.10) and compared to the samples of series G (figure 8.3.11). A clear s-shape behavior of the PL peak position as well as a weak w-shape behavior of the line width is found for samples of series I, which indicates the presence of carrier localization-delocalization mechanisms [Kazlauskas2003]. In InGaN this behavior is generally attributed to alloy potential fluctuations (APFs). Several mechanisms such as In-rich clusters [Bartel2007], the random formation of In-N-In chains [Bellaiche1999], quantum dot like formations [Jia2007] and areas of increased In-content at extended defects [Chiu2009] have been identified as potential sources for the APF.

At low temperatures around 7K, all photo-excited carriers are randomly distributed among the potential minima. As the temperature increases up to a certain characteristic freeze-out temperature weakly localized carriers are thermally activated and relax down into other strongly localized states via hopping and reach eventually a saturated distribution [Monroe1985] [Baranovskii1998] [Grünewald1985]. This process reflects in a red-shift of the peak energy. At temperatures above the freeze-out temperatures, the carriers are enabled to occupy higher energy levels of the localized states resulting in a blue-shift until the free-exciton ground state is reached at a second characteristic temperature allowing finally for the Varshni like behavior to dominate. At RT a clear Varshni like behavior is observed for samples I1 and I2.

Taking into account the efficient carrier de-localization (blue-shift of peak position with increasing temperature) at RT in samples of series I (figure 8.3.10), the low PL-IQE in these samples can be understood as a consequence of a strong nonradiative surface recombination at the InGaN sidewalls [Nguyen2013] as discussed previously in chapter 6.
Figure 8.3.11: PL peak position versus temperature of samples G5, G6, G7 and G8. A complete s-shape when going up to RT is only observed for sample G5 which has the lowest IQE. The dotted lines are guides for the eye.

The temperature dependent PL of samples of series G shows a different behavior than samples of series I. Only sample G5 (lowest PL-IQE) shows clear de-localization behavior as indicated by the pronounced blue-shift of the PL peak position at higher temperatures (figure 8.3.11a) as well as the pronounced w-shape of the line width, which would account for the observed PL-IQE of only 2.6%.

In samples G6, G7 and G8, no significant blue-shifts of the PL peak positions at higher temperatures are found. The PL peak position becomes virtually temperature independent, i.e. localization prevails up to room temperature in these samples. This finding would explain the improvement of the PL-IQEs observed in these samples and indicates the presence of deeper localized states. The formation mechanism of these states, which is apparently related to the growth temperature and group(III)/N ratio and which is specific to the growth on GaN/Si templates, is unclear at the moment. Commonly it is assumed that carrier localization increases with In-content, i.e. a higher In-content leads to a higher disorder which causes a higher localization. However this
explanation does not apply here, since carrier recombination takes place in regions of similar In-content in all samples of series I and G as indicated by the optical emission in the same spectral range (green). As a reasonable assumption the dependence of carrier localization may be related in some way to differences in crystal polarity, i.e. metal-polar on GaN/sapphire (series I) and N-polar on GaN/Si (series G). Further studies will be needed in order to resolve this issue.
8.4 Summary:

In summary InGaN/GaN NCs with thick InGaN segments (330 nm-830 nm) emitting in the green spectral range, were grown selectively on GaN/sapphire and GaN/Si templates.

The use of SAG allowed for a detailed and systematic study of the optical properties and growth mechanism of InGaN alloys, not possible before with self-assembled InGaN/GaN NCs due to their strong dispersion in NC dimension and optical properties. The evolution of NC morphology as well as the distribution of In inside the InGaN/GaN NCs grown on GaN/sapphire as a function of III/V ratio and NC diameter was explained by changes of the local III/V and In/Ga ratio at the NC top.

On the other hand a more complex evolution of the NC morphology and with that of the In distribution as a function of III/V ratio as well as growth temperature was found for samples grown on GaN/Si(111). This different behavior was related to different polarities of the NCs in the two case i.e. metal polar when growing on GaN/sapphire and nitrogen polar when growing on GaN-buffered Si(111). Furthermore a decrease of growth temperature and/or an increase of active nitrogen amount was found to lead to an increase of the PL-IQE in samples grown on GaN buffered Si(111). With temperature-dependent PL, this increase of the IQE value was explained by the formation of highly localized states, leading to PL-IQEs of up to 30%. On the other hand no dependence of carrier localization on the growth conditions was found for InGaN/GaN NCs grown on GaN/sapphire where PL-IQEs no higher than 3.7% were achieved.
Chapter 9:
Growth and characterization of ordered InGaN/GaN core-shell structures
Chapter 9

9.1 Introduction:

Axial InGaN/GaN nanostructures have been studied thoroughly in the last chapters. Drawbacks of this axial approach are certain practical limitations due to the polar character and rather small emission area (top part of the structure).

In order to exploit an enhanced emission/absorption and a reduced (or zero) internal electric field in NC-based LEDs, the growth of high aspect ratio InGaN/GaN core-shell structures was addressed and successfully achieved by metal organic vapor phase epitaxy (MOVPE) [Qian 2004] [Qian2005] [Dong2009] [Bavencove2011] [Koester2011] [Jacopin2012] [Wierer2012]. For maximizing the ratio between active areas of core-shell structures with respect to planar structures, large aspect ratios and filling factors are necessary. In addition, if phosphor materials, whose grain size is in the micron range, are to be embedded between the columns for light conversion in order to achieve white light emission, the diameter and pitch of the core-shell structures must be in the micron range, so that from now on these heterostructures are referred to as micropillars (MPs). This approach was followed by a number of authors using MOVPE that provides a high enough growth rate [Li2012], but no successful attempts were made by PAMBE until now due to difficulties with the promotion of lateral InGaN growth at the pillar sidewalls while keeping selectivity and avoiding merging.

![Figure 9.1.1: SEM (a) top view and (b) bird view of SAG GaN MPs 300 nm high.](image)
The growth of InGaN/GaN core-shell structures by PAMBE would be quite relevant for high In content shell layers that are not straightforwardly obtained by MOVPE due to the much higher growth temperatures involved.

First attempts to selectively grow micron size GaN MPs by PAMBE were successful, as it can be seen in figure 9.1.1. However, the growth rate was too small (300 nm in 6 hours) in order to achieve micropillars several microns high in reasonable time. Thus, a different approach based on the conformal overgrowth of GaN micropillars etched from a GaN template (4 microns thick) or MOVPE grown GaN pillars with GaN and InGaN shells was followed.
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9.2 Experimental details:

For the InGaN overgrowth of etched GaN MPs all samples were grown on GaN/sapphire templates patterned by etching down a geometrically aligned array of GaN MPs, as follows: (i) definition of an hexagonally ordered hole pattern with photolithography using AZ 5214 positive photo-resist, (ii) deposition of Ni and removal of the resist with isopropyl alcohol and acetone resulting in an array of ordered Ni micro-discs which were used as mask, (iii) inductively coupled plasma (ICP) etching of the GaN template using Cl:Ar (10 sccm:25 sccm), a pressure of 5 mTorr, an RF power of 150 W and an ICP power of 300W, resulting in an etch rate of around 400 nm/min, and (iv) removal of the Ni disks with HCl and HNO$_3$. As a result, templates of well ordered GaN pillars were obtained. The pillar diameter and length were 1.6 µm and 2.1 µm, respectively. After a standard degreasing in pyrrolidone, the samples were loaded into the PAMBE system.

Since the original GaN templates have a significant defect density ($10^9$-$10^{11}$ cm$^{-2}$), the etched MPs are expected to have defects as well. Relaxation of residual strain is expected upon etching down the MPs. Moreover, the etching process may produce crystal damage that could have an influence on the epitaxial growth of conformal GaN layers on the MPs.

The InGaN shell overgrowth on SAG MOVPE GaN MPs was performed on arrays grown on n-type GaN/sapphire masked with patterned SiO$_x$ (OSRAM Opto Semiconductors) [Mandl2013] having a diameter of 550 nm, a length of 7.3 µm, and 2.4 µm pitch with an aspect ratio of 13.

Before growth the MOVPE pillars were cleaned ex-situ with pyrrolidone and in-situ by a two-step thermal cleaning in the PA-MBE system for 30 min at both 350ºC and 550ºC.

In a first series of growths (series J), the conditions for conformal growth of GaN and InGaN over the etched GaN pillars were studied. GaN was grown under conditions described in table 9.2.1 (sample J1) for 2h to determine morphology changes (from MPs initial shape) and optical properties. Once characterized, the sample was re-loaded into
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the PAMBE system and growth of GaN was continued for 1h under the same conditions as in sample J1, in order to assure the presence of a clean GaN surface, before growing InGaN for 2h under the conditions described in table 9.2.1. The sample is now referred to as sample J2.

Table 9.2.1: Growth conditions of the samples grown in this chapter.

<table>
<thead>
<tr>
<th>sample number</th>
<th>impinging fluxes in nm/min (x10^15 atoms/(s cm²))</th>
<th>III/V ratio</th>
<th>In/Ga ratio</th>
<th>T&lt;sub&gt;sample&lt;/sub&gt; in ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga</td>
<td>In</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>J1</td>
<td>18 (13.2)</td>
<td>-</td>
<td>5 (3.7)</td>
<td>3.57</td>
</tr>
<tr>
<td>J2</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
<tr>
<td>O1</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
<tr>
<td>O2</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
<tr>
<td>O3</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
<tr>
<td>O4</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
<tr>
<td>P1</td>
<td>3 (2.2)</td>
<td>9.6 (5.1)</td>
<td>12 (8.8)</td>
<td>0.83</td>
</tr>
</tbody>
</table>

As will be seen later on, the InGaN core-shell growth over etched down pillars suffers from rather strong limitation in terms of aspect ratio (length of pillar limited by template thickness of around 4µm) as well as a low GaN quality (determined by the template). Due to that, the growth on high aspect ratio (>10) MOVPE grown GaN pillars is very appealing for more detailed studies as well as the actual device fabrication (LEDs).

Two series O and P of InGaN/GaN core-shell structures were grown in a similar fashion as in series J and K on MOVPE grown GaN pillars. The purpose of series O was to demonstrate InGaN core-shell growth as well as to study the In incorporation mechanism in the InGaN shell. For that sample O1 was grown in a similar way like sample J2 i.e. 1h growth of GaN under the condition used for sample J1 (table 9.2.1) followed by a two hour growth of InGaN under the conditions given in table 9.2.1 (sample O1). The sample was reloaded into the MBE system and growth was continued for 2h (sample O2), once characterized. After characterization this procedure was
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repeated two more times (samples O3 and O4) under the conditions described in table 9.2.1 where InGaN was grown for 2h and 1h 30 min, respectively. After characterization, the sample was cleaned each time ex-situ using pyrrolidone at 75ºC and in-situ by a two step thermal cleaning in the PA-MBE system for 30 min at 350ºC and 400ºC. During the thermal cleaning at 400ºC a nitrogen flux of 5 nm/min was provided.

In series P one sample P1 with stacked GaN:Mg/InGaN/GaN:Si sections (p-i-n structures) was grown. The GaN and InGaN section was grown in the same way as in sample O1 except of the use of Si-doping during the GaN growth (Si-cell temperature of 950ºC). In addition the structure was capped/surrounded with GaN:Mg grown for 1h at 625ºC ($\Phi_{Ga} = 8$ nm/min and $\Phi_{N} = 12$ nm/min) with a Mg-cell temperature of 365ºC. At this point it has to be noted that the GaN:Mg was grown at a much lower sample temperature than the GaN:Si to avoid/reduce InN decomposition.

The morphology of the samples was investigated by using SEM and STEM. The optical properties of the MP ensemble were characterized by LT-PL. In order to obtain the local luminescence properties spatially and spectrally resolved CL was performed using the SEM as well as the STEM at RT and LT, respectively. Electroluminescence (EL) of the MP-LEDs, performed at the Technical University of Braunschweig, was measured using a piezo-driven tungsten probe tip mounted inside a CL-SEM. The contact position of the tungsten probe tip was depicted by means of secondary electrons (SE) while the e-beam was blocked during the EL measurements. With this technique spatially resolved excitation can be performed, hence local properties with respect to the contact position can be extracted. No additional processing steps were needed for these measurements.

The results regarding InGaN/GaN overgrowth of etched MPs presented in this chapter were published in ref [Albert2014].
9.3 Results and discussion:

Figure 9.3.1: Top view and cross-sectional SEM pictures of etched GaN pillars (a-c) as well as of samples J1 (d-f) and J2 (g-i), J. Cryst. Growth 392, 5 (2014).

Images in figure 9.3.1 show the sequence from the bare etched GaN MPs to samples J1 and J2. The etched GaN MPs have cylindrical symmetry and rough sidewalls (figures 9.3.1b and 9.3.1c) as a consequence of etching. Sample J1 starts to develop facets upon the GaN growth (figures 9.3.1e and 9.3.1f), while sample J2 has a perfectly defined hexagonal geometry (figures 9.3.1h and 9.3.1i). In both samples J1 and J2, the growth is conformal with a significant radial growth rate. The top of sample J1 resembles a truncated pyramid with a hexagonal c-plane top facet of around 540 nm in diameter.

LT-PL spectra taken from the initial GaN template, the GaN etched MPs and samples J1 and J2 are shown figure 9.3.2a. Figure 9.3.2a reveals the GaN near band-edge (NBE)
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emission in all cases, and two InGaN-related emissions in sample J2. The yellow band emission (2.3 eV), typical signature of defects, is present in the GaN template and consequently in the etched GaN micropillars as well as on samples J1 and J2, in the latter merging with the low energy InGaN related peak.

Figure 9.3.2: Low temperature (7K) PL spectra of: (a) GaN template, GaN MPs and samples J1 and J2, (b) high resolution PL spectra of the GaN template, GaN MPs and sample J1, J. Cryst. Growth 392, 5 (2014).

Figure 9.3.2b shows in more detail the red-shift of the GaN NBE emission peak (from 3.485 eV to 3.472 eV) as a consequence of the relaxation of compressive strain upon etching down the GaN MPs. It has been found that a significant reduction of PL intensity quenching is present in sample J1 compared to the GaN MPs. The PL-IQEs estimated from the PL intensity of the near band edge emission of GaN at 12K and RT were found to be 0.89% for the GaN micropillars and 4.72% for sample J1, indicating the presence of etching induced crystal damage in the GaN pillars which was removed/reduced during the GaN overgrowth.

The LT-PL spectrum of sample J2 (figure 9.3.2a) reveals a main emission peak at around 3 eV, corresponding to InGaN with an In content of about 10%. In addition, a broad emission centered at around 2.4 eV can be observed.

RT-CL measurements of a single core-shell microstructure from sample J2 shown in figure 9.3.3 reveal two InGaN related emissions localized at different regions, a high energy one at 3.03 eV (already observed by PL in figure 9.3.2a) originating from the micropillar sidewalls (m-planes), and a lower energy one at 2.4 eV that stems from the
micropillars top region. This result points to a different In incorporation depending on the crystal plane, as already reported [De Mierry2009] [Wernicke2012].

Figure 9.3.3: Spatially resolved CL measurements of sample J2 showing the overlaid monochromatic CL intensity images with the secondary electron contrast of individual MPs.

An InGaN/GaN single MP (sample J2) was further characterized by LT-STEM-CL. Cross-sectional annular dark-field (ADF) STEM images confirm the presence of threading dislocations from the GaN template, that remain within the MPs after etching (figure 9.3.4a). A darker ADF density observed at the MP apex relates to the upper InGaN region (750 nm thick) having a defective morphology. The thickness of the InGaN shell can be estimated to be around 100 nm and is found to slightly increase towards the MP topside. Figure 9.3.4c shows the CL integral intensity distribution, which is maximum in the InGaN shell (side facets) and in the top region (yellow color coded). Figure 9.3.4d represents the peak wavelength distribution, with a distinct emission at 407 nm (3.05 eV) originating from the side facets and a broad luminescence band (510-640 nm, or 2.43-1.94 eV) coming from the InGaN cap region. The CL red-shift along the InGaN cap layer is assumed to result from an increasing In composition towards the tip due to InN thermal decomposition and segregation as well as strain relaxation, as discussed before in chapter 6. The observed difference in In incorporation between the InGaN cap and shell regions is due to a lower (2-3x) In incorporation at m-planes as compared to c-plane [Yamada 2008].
Figure 9.3.4: Highly spatially resolved STEM-CL analysis at 16K of sample J2: (a) annular dark-field (STEM-)image of an individual single MP, (b) magnified view of (a) depicted top part of MP including an InGaN cap layer in the apex, (c) integral CL intensity image in semi-logarithmic scale of the single MP, and (d) CL wavelength image showing the distribution of the peak wavelength; dashed lines in wavelength scale indicate the emission wavelength of GaN near band edge emission (359 nm) as well as yellow band (560 nm) and the InGaN emission at 407 nm and at 520 nm, respectively, J. Cryst. Growth 392, 5 (2014).
Figure 9.3.5 shows top and cross-section SEM pictures of the SAG MOVPE MPs and sample O1. Figure 9.3.5b shows a hexagonal shape with smooth sidewalls of the MOVPE GaN MPs. The subsequent growth of InGaN/GaN leads to a clear increase in diameter from the initial MOVPE GaN MPs (550 nm) to 640 nm at the MPs bottom and 770 nm at the MPs top in sample O1.

A clear increase in pillar diameter is observed upon InGaN/GaN overgrowth.

The LT-PL spectrum of sample O1 (figure 9.3.6a) reveals a main emission peak at around 3.1 eV, corresponding to an In content of about 10%. In addition, a second InGaN-related broader emission centered at 2.3 eV can be observed. The internal quantum efficiency (IQE) estimated from the low to room temperature PL-intensity ratio is ~4%, which is about the same as the PL-IQE for axial SAG InGaN/GaN NCs grown on GaN/sapphire templates under similar conditions (chapters 6, 8). Weak localization is expected in an (bulk) InGaN layer of 10% In, so that recombination via non-radiative channels (e.g. strong nonradiative surface recombination at the InGaN sidewalls) is pronounced, adding to a low IQE value.
Figure 9.3.6: a) RT- and 8K PL spectra of sample O1, b) RT-CL spectra of a single MP and an ensemble of ~300 MPs of sample O1 measured in top-view, and c) spatially resolved CL measurements of sample O1 showing the overlaid monochromatic CL intensity images (color) with the secondary electron image (grayscale) of an individual MP.

Figure 9.3.6b shows RT-CL spectra of a single MP and an ensemble of ~300 MPs from sample O1. The first apparent fact is that both spectra are quite similar, pointing to a high MPs uniformity. In addition, two emission peaks contribute to the spectra at 2.3 and 3.0 eV, in agreement with those observed by PL. Spatially resolved SEM-CL measurements (figure 9.3.6c) reveal that the emission at 3.0 eV originates at the MP side facets (m-plane), whereas the emission at 2.3 eV comes from the MPs topmost region. These two InGaN emission peaks are attributed as before to a different In-
incorporation depending on the crystal plane, i.e. m-plane for the lateral shell and \{10-11\} planes for the top region. This agrees with findings of Wernicke et al. [Wernicke2012] which reported the In incorporation on the \{10-11\} planes to be significantly higher than on the m-plane in case of MOVPE growth. Furthermore it has to be noted that similar results were found for InGaN/GaN core-shell structures grown on etched GaN MPs shown before.

In addition, a red-shift of the InGaN shell-related emission towards the MP top can be observed (figure 9.3.6c upper side) indicating the presence of an In-gradient in the InGaN shell towards the pillar top. In composition gradients are generally attributed to thermal InN decomposition and In segregation towards the NC top side as reported for axial SAG InGaN/GaN NCs. However, the composition gradient observed in figure 9.3.6c could also be due to lattice pulling effects (increase of In incorporation upon strain relaxation) or changes of the local III/V ratio at the side facet along the MP (shadowing effects). The presence of lattice pulling effects is suggested by the shell thickness increase towards the MP top (bottom diameter of 640 nm to top one of 770 nm) as observed in figure 9.3.5f. RT-CL point spectra along a single MP sidewall (figure 9.3.7) clearly show the increase of In composition towards the top side. At the MP bottom (point P1) the CL spectrum is dominated by the GaN emission while emission from the InGaN shell is barely seen, meaning that this shell, if present, must be very thin.
In order to further check for the presence of lattice pulling effects, sample O2, with double InGaN growth time (2 more hours) compared to sample O1, was grown. SEM pictures in figure 9.3.8 show the diameter evolution of individual MPs, where the top diameter changes from 770 nm (sample O1 grown for 2h) to 970 nm (sample O2 grown for 4h) as a consequence of the increased growth time.

Figure 9.3.8: Top- and cross sectional SEM pictures of samples O1-O4.
If pulling effects were present, a thicker InGaN-shell should lead to an increasing average In-content, as well as to a reduction of the emission energy red-shift towards the MP top (P1 to P7). RT-CL point measurements along single MPs of samples O1 and O2 shown in figure 9.3.9a reveal that, upon thickness increase, the same In-gradient and average In-content is present in sample O2, as indicated by the negligible change of peak positions. Based on this result, lattice pulling effects can be ruled out as the origin of the increasing In-content towards the MP top in the InGaN shell.

Figure 9.3.9: a) RT-CL point measurements of samples O1, O2, O3 and O4; b) RT-CL measurements of samples O2, O3 and O4, c) spatially resolved CL measurements of samples O2, O3, O4 showing the overlaid monochromatic CL intensity images with the secondary electron contrast of an individual micro-pillar. Inset in a) shows cross-sectional SEM pictures of measured pillars with indication of positions at which CL measurements were performed.
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To study the potential effects of InN thermal decomposition and In desorption on the shell In-graded composition and average In-content, samples O3 and O4 were grown at temperatures of 600°C and 525°C (remember samples O1 and O2 were grown at 625°C). It can be seen in figure 9.3.8, that while a reduction of growth temperature down to 600°C (sample O3) does not lead to any morphological degradation, a reduction of the growth temperature down to 525°C leads to a highly inhomogenous top morphology. On the other hand well defined hexagonally shaped side facets are present in both; sample O3 and O4 (figures 9.3.8 g, h). Given the nominally nitrogen rich conditions during the InGaN growth, a decrease of the growth temperature should in principle lead to an increasing average In-content (due to reduced InN decomposition and In desorption) and a concomitant reduction of the In-gradient in the shell towards the MP top.

RT-CL spectra taken of sample O3 and O4 (figure 9.3.9b) show a main emission peak at around 3.0 eV, identical to that of sample O2, indicating that a reduction of growth temperature does not have any impact on the average In content of the InGaN shell. Only the CL emission from the MP top, at around 2.2 eV, reveals an increase of the In content for sample O3 and O4. The reason for this most likely relates to In accumulation close to and at the MP top, which has already been implied by the CL emission peak deviation observed in figure 9.3.9a (points P7 and P8).

Spatially resolved CL measurements (figure 9.3.9c) confirm that the emission at 3.0 eV originates from the MP sidewalls while the low energy emission at ~2.2 eV comes from the MP top. Furthermore, RT-CL point measurements in samples O3 and O4 (figure 9.3.9a) indicate again the presence of an In gradient towards the MP top, which is quite similar to that found in samples O1 and O2. Based on these findings, it can be concluded that neither lattice pulling effects, nor decomposition, nor In desorption are responsible for the In-gradient observed in the shell.

The last possibility envisaged that may account for this In-graded shell relates to different local III/V ratios at the MP sidewalls along the axial direction caused by changes of the impinging fluxes (particularly the N-flux) due to geometrical effects such as shadowing of impinging metal fluxes as well as active nitrogen by surrounding MPs.
Figure 9.3.10: a) Top-view and b) cross-section SEM images of a single core-shell microLED (sample P1); c to f) SEM images at 30° tilt showing the probe tip contact at four different positions on the top and sidewall of a single microLED to obtain EL; g) normalized EL spectra taken at the respective positions P1-P4 with an injection current of 50 µA.
Shadowing would also account for the observed tapering of the MPs, which can be understood as a result of different lateral growth rates of the (In, Ga)N shell along the pillar. At this point it is worth noting that shadowing effects were already found to play a crucial role in the growth of SAG InGaN quantum disc structures [Sekiguchi2010].

The potential of PAMBE grown core-shell MPs for LED applications was checked by growing a p-i-n microLED (sample P1), as shown by the SEM top and side view in figures 9.3.10a and b. Starting from the same structure as that in sample O1, the microLEDs include a Mg-doped top GaN shell layer. The microLEDs morphology shows a flat top with an outer and inner hexagonal structure, in contrast to the pyramidal top in sample O1, which is assumed to relate to the growth of the Mg-doped shell.

EL measurements were performed by current injection via micro probe tip placed at the sidewall and top facet of the MP-LED, as shown in figures 9.3.10c-f. Due to the absence of a current spreading layer, the current injection takes place at localized areas around the contact point which results in a localized injection of carriers into the active region.

EL spectra obtained with a driving current of 50 µA measured at different contact points on the microLED are shown in figure 9.3.10g. It can be seen that while the spectrum taken at P1 (pillar top) shows a main emission peak at about 2.3 eV together with a second emission peak at about 3.0 eV, spectra taken at points P2-P4 show emission at about 3.0 eV with decreasing emission energy towards the pillar top (from 3.27 eV at pillar bottom to 3.13 eV at pillar top). Based on the results for samples of series O, the higher energy peak observed at P1 is believed to originate at the lateral shell (m-plane) close to the MP top, which is weakly excited by injected electrons from the top contact, while the emission at 2.3 eV relates to an axial diode grown on the pillar top. The observed red-shift of the EL emission energy (from P4 to P1) coming from the InGaN shell (lateral diode) is in agreement with the findings presented for samples of series O, where an In-gradient towards the MP top was found to be present in the InGaN shell (figure 9.3.9a).
In addition it has to be noted that the EL emission peak of the lateral diode shows a pronounced low energy tail, which is absent in the EL emission peak of the axially grown diode. Based on the discussion presented in chapter 6 (axial pin junctions), this difference in peak shape can be attributed to the presence of different distribution, densities and depths of localized states in both regions depending on the In-content.
9.4 Summary:

In the first section growth of InGaN/GaN core-shell microstructures was achieved by PAMBE using a combination of top-down and bottom up steps. Growth was performed on GaN MPs that were produced using ICP etching. When growing InGaN layers on a patterned array of GaN MPs, a significant radial growth took place that led to the formation of a shell layer, as it was confirmed by spatially resolved CL and STEM measurements.

In a second step InGaN overgrowth was performed using MOVPE grown pillars, leading to ordered InGaN core-shell structures with aspect ratios of around 13. The InGaN/GaN core-shell microstructures were found to have an optical uniformity similar to InGaN/GaN structures that were grown using bottom-up selective area growth presented in chapter 8. In spatially resolved CL, a red-shift of the CL emission of the InGaN shell towards the top was observed, indicating an increasing In content in the shell towards the top, which has been explained by different local group(III)/N ratios at the pillars sidewall due to shadowing effects. It was demonstrated as well, that a reduction of growth temperature down to 525ºC (starting from 625ºC) has no impact on the In content of the InGaN shell. Finally the successful fabrication of a core-shell pin structures was demonstrated. Spatially resolved EL measurements, performed at a single pillar, confirmed emission from the InGaN shell at around 3.0 eV, with a red-shift towards the top. In addition a second pin junction was formed at the pillar top emitting at around 2.3eV.
Chapter 10: Growth and characterization of ordered (In)GaN nanostructures on non-polar and semi-polar GaN/sapphire templates
10.1 Introduction:

Most of the work presented up to this point focused on group(III)-nitrides grown along the polar [0001] direction, with emphasis on developing InGaN-based nanocolumnar active structures for LEDs. However, the internal polarization fields are very strong in InGaN/GaN heterostructures grown along the polar direction. The associated quantum confined Stark effect affects detrimentally the IQE, and causes a blue shift of the EL peak with increasing current, due to screening of the internal electric field. In order to reduce or even avoid this internal polarization field, growth on semi-polar and non-polar crystal orientations has been suggested and demonstrated [Waltereit2000] [Farrel2012]. Up to now, the best results have been obtained when growing on nonpolar or semipolar bulk substrates [Yoshizumi2009] but due to limitations of bulk GaN substrates (in terms of size and price), heteroepitaxy on r-plane and m-plane sapphire has been the most common approach. This heteroepitaxial growth results typically in GaN templates with large density of stacking faults (>10^5 cm⁻¹) and of their associated partial dislocations [Vennéguès2012]. Different strategies are used in order to increase the material quality [Scholz2012]. As in case of polar GaN, the epitaxial lateral overgrowth (ELO) technique has been implemented in metal organic chemical vapor deposition (MOCVD) to grow semi-polar (11-22) GaN layers with reduced defects density [Kriouche2010] [Lacroix2011].

An alternative approach is the use of selective area growth (SAG), which already demonstrated in chapters 5-8 the growth of high quality GaN and InGaN NCs on c-plane GaN/sapphire and GaN/Si templates. As discussed in chapter 5, the most frequent upper shape (corresponding to the initial growth front) of SAG GaN NCs grown on c-plane GaN templates is pencil-like formed by semi-polar planes, where a subsequently grown InGaN region keeps the same geometry. Though in these NCs with semi-polar top planes the effects of internal fields in the active region of the device are reduced compared to polar planes, the most effective solution remains the growth along non-polar directions, either by growing core-shell heterostructures on the lateral non-polar facets (presented in chapter 9), or by growing axial heterostructures on semi-polar or non-polar substrates, where internal electric fields are reduced or nominally zero.

The first part of this chapter presents results on the SAG of GaN nanostructures, with and without an insertion of InGaN, on semi-polar (11-22) GaN templates. In the second
part SAG of GaN NCs on non-polar a-plane (11-20) GaN templates are presented, studying the vertical and lateral growth rates (anisotropy) in comparison to SAG on c-plane substrates. In addition the pseudo-substrates are produced by coalescing individual non-polar SAG GaN NCs.
10.2 Experimental details:

For the SAG on semi-polar substrates, GaN templates grown by MOCVD on m-plane sapphire were used. Prior to the growth, Ti nanohole masks were fabricated on (11-22) GaN templates by colloidal lithography. Nanoholes were arranged in a compact hexagonal lattice with an average pitch of 270 nm and diameters of 200 nm. The resulting nanohole density was around $1.6 \times 10^9 \text{ cm}^{-2}$. The growth of the GaN NCs was performed with $\Phi_{\text{Ga}}=18.5 \text{ nm/min}$ and $\Phi_{\text{N}}=5 \text{ nm/min}$ at 880ºC for 3h. Following that two more samples were grown, i.e. i) one sample with an InGaN insertion grown at 625ºC, with $\Phi_{\text{Ga}}=4.3 \text{ nm/min}$, $\Phi_{\text{In}}=4.3 \text{ nm/min}$, and $\Phi_{\text{N}}=14 \text{ nm/min}$ during 160s which was capped with a GaN layer grown for 5 min, at the same temperature (625ºC) and with $\Phi_{\text{Ga}}=4.3 \text{ nm/min}$ and $\Phi_{\text{N}}=14 \text{ nm/min}$ (just closing the In shutter) (sample N1) and ii) one sample with long InGaN section grown at 650ºC, with $\Phi_{\text{Ga}}=2.3 \text{ nm/min}$, $\Phi_{\text{In}}=6.3 \text{ nm/min}$, and $\Phi_{\text{N}}=14 \text{ nm/min}$ during 1h (sample N2). Results of this section were published in ref [Bengoechea-Encabo2013].

For the second section, i.e. SAG on (11-20) a-plane substrates in comparison to c-plane substrates (series L) as well as the production of non-polar pseudo-templates (series M), nanohole masks were fabricated by colloidal lithography on the respective templates with an average pitch of 260 nm and a diameter of 150-200 nm. The growth of GaN NCs was performed under the conditions shown in table 10.2.1. In series L different growth conditions and templates were used in order to study vertical and lateral growth rates while in series M the development of optical properties as a function of the coalescence degree was tracked using the same sample, i.e. the sample numbers in series M correspond to different stages of growth in the same sample. GaN was grown under the conditions described in table 10.2.1 (sample M1) for 3h. Once characterized, the sample was re-loaded into the PAMBE system and growth was continued for 2h (sample M2). After characterization this procedure was repeated two more times (samples M3 and M4) under the conditions described in table 10.2.1. After SEM and PL characterization, the sample was cleaned ex-situ using pyrrolidone at 75ºC and in-situ by a two-step thermal cleaning in the PA-MBE system for 30 min at 550ºC and 6 min at 880ºC.

The results of this section were published in ref [Bengoechea-Encabo2012] and ref [Albert2014b].
Table 10.2.1: Growth conditions of the SAG GaN samples grown in this chapter.

<table>
<thead>
<tr>
<th>sample number</th>
<th>growth time</th>
<th>impinging fluxes in \text{nm/min (x10^{14} \text{ atoms/(s cm}^2\text{)}}</th>
<th>III/V ratio</th>
<th>substrate</th>
<th>T_{\text{sample in °C}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>1h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>L2</td>
<td>1h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>c-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>L3</td>
<td>3h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>L4</td>
<td>1h</td>
<td>16 (11.7) 10 (7.4)</td>
<td>1.58</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>M1</td>
<td>3h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>M2</td>
<td>M1+2h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>M3</td>
<td>M2+3h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>880</td>
</tr>
<tr>
<td>M4</td>
<td>M3+2h</td>
<td>16 (11.7) 5 (3.7)</td>
<td>3.16</td>
<td>a-plane GaN/sapphire</td>
<td>820</td>
</tr>
</tbody>
</table>
10.3 Results and discussion:

10.3.1 Growth of InGaN/GaN nanostructures on semi-polar GaN/sapphire templates

SEM images shown in figures 10.3.1.1a and 10.3.1.1b show nanostructures tilted around 32° relative to the substrate.

Figure 10.3.1.1: SEM images of the ordered GaN NCs on a semi-polar (11-22) GaN template: top- a) and bird’s-eye b) views. In c), TEM image showing the tilted NCs with the long axis being parallel to the Ga-polar [0001] and the filtering effect for the stacking faults originating from the template. The three facets exposed to the molecular beam are indicated in the figure, Appl. Phys. Lett. 103, 241905 (2013).
TEM measurements (figure 10.3.1.1c) give more details on the dominant facets of these nanostructures i.e. polar, semi-polar, and non-polar, with a preferential growth along the [0001] Ga-polar direction which leads to the inclined growth. In addition, most of the GaN nanostructure volume is free of defects because the basal plane stacking faults coming from the substrate at a given angle (very high density) are effectively "filtered" leaving the upper part of the nanostructures free of them (see inset in figure 10.3.1.1c).

Figure 10.3.1.2: Low temperature (T=8K) PL spectra of the bare (11-22) GaN template and the SAG GaN NCs, Appl. Phys. Lett. 103, 241905 (2013).

The improvement in structural quality is accompanied by a strong improvement of the PL emission, as shown by the LT-PL spectra in figure 10.3.1.2. A rather broad featureless spectrum peaking at 3.43 eV is measured in the (11-22) GaN template, which is commonly assigned to basal plane stacking faults (BSFs) [Liu2005]. After GaN NCs SAG, a strong and narrow (FWHM of only 2.7 meV) near band edge emission at 3.473 eV, identified as strain-free $D^{0}$X, is observed. In addition, a weak emission at 3.42 eV, originating from BSFs, is still detected, most likely originating from the template or the nanostructures bottom part (figure 10.3.1.1c).

In a second step, an InGaN insertion was embedded into the GaN nanostructures and capped by GaN, as explained in the experimental section 10.2. Figures 10.3.1.3a and b show SEM images of GaN/InGaN/GaN SAG nanostructures grown on semi-polar GaN templates, having a similar morphology like the bare GaN nanostructures previously described, also aligned along a preferential growth (0001) polar direction (c-axis).
Figure 10.3.1.3: SEM pictures of sample N1 in top view a), and bird view b). Spatially resolved InGaN-related emissions are shown in the SEM-CL measurements in c) and d).

In e), a comparison of RT-CL spectra of a single InGaN/GaN nanostructure and an ensemble of around 2000 InGaN/GaN nanostructures is shown, Appl. Phys. Lett. 103, 241905 (2013).
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The comparison of RT-CL spectra of a single nanostructure with an ensemble of more than 2000 nanostructures (figure 10.3.1.3e) reveals an almost identical shape and peak position, indicating an excellent reproducibility of the In incorporation into the nanostructures. Up to three emission peaks are observed, being the two ones at lower energies related to InGaN (2.43 eV and 3 eV) and the third one to the near band edge emission of GaN. Spatially resolved CL results, shown in figures 10.3.1.3c and d reveal that the lowest energy InGaN related peak at 2.43 eV originates from the NC apex (along c-direction), while the peak at 3 eV comes mostly from a larger area below the apex. Assuming strain-free material, those emissions would correspond to $\text{In}_x\text{Ga}_{1-x}\text{N}$ with $x$ equal to 26% and 10%, respectively.

According to the morphology of the GaN and InGaN/GaN nanostructures determined by TEM (figure 10.3.1.1c) and SEM (figures 10.3.1.3a and b) it can be assumed that the InGaN region with lower In content (3 eV emission) is grown on non-polar planes, while the higher In content InGaN (2.43 eV) is grown either on polar or semi-polar planes. Regarding the In incorporation on semi-polar or polar planes, no definite statement can be made. It has been shown for PAMBE, that In incorporates easier on (0001) polar planes than on (11-22) semi-polar planes [Das2010] [Das2011]. In addition it has been shown for InGaN/GaN core-shell structures in chapter 9 that In incorporates easier on semi-polar (10-11) planes than on m-planes.

To finish up this section one more sample with thick InGaN segment (growth time 1h) on top of SAG GaN NCs on semi-polar GaN templates was grown (sample N2). The top-view and cross-sectional SEM pictures shown in figure 10.3.1.4a and b reveal the formation of InGaN/GaN nanostructures which are tilted with respect to the template. The nanostructures have a hexagonal top which presumably corresponds to a c-plane facet.
Figure 10.3.1.4: SEM pictures of InGaN/GaN nanostructures with thick InGaN (sample N2) in top view a), and cross-section b). Low temperature (8K) PL measurement revealing the presence of two distinct emission bands is shown in c).

The low temperature (8K) PL spectrum of sample N2 (figure 10.3.1.4c) shows the existence of two emission peaks at around 2.2 eV and 2.8 eV, leading to white light emission. Based on the finding for InGaN Qdisc structures (figure 10.3.1.3) the distinct emission peaks could a priori be related to emission from non-polar and polar facets, respectively. In order to gain information about the origin of the two emission peaks spatially resolved CL measurements were performed (figure 10.3.1.5). Figure 10.3.1.5a reveals that the two peaks originate from distinct areas of the same sample and not from each single NC as reported before for InGaN Qdisc structures (figure 10.3.1.3). The two regions are referred to as region I emitting at 2.7 eV and region II emitting at 2.1 eV. RT-CL spectra and spatially resolved CL measurements taken of the respective regions (figures 10.3.1.5 a and b) reveal that the emission at 2.7 eV originates from partially coalesced regions.
Figure 10.3.1.5: a) RT-CL spectra of sample N2 taken of different samples regions, i.e. in low magnification (ensemble), partially coalesced areas (region I) and well separated areas (region II); b) shows spatially resolved CL measurements of distinct regions of samples N2.
At the moment no clear statement can be made about the driving mechanisms of the coalescence in these areas. On the other hand the emission at 2.1 eV is dominant in areas where well separated NCs can be found. In principle these results agree with the findings of sample N1 (InGaN Qdisc) i.e. a low energy emission (high In-content) coming from the top of the NCs which is most likely related to growth along the c-direction and a high energy emission (low In-content) from the side-facet of the NCs which has been identified to be the m-plane facet (figure 10.3.1.1).
10.3.2 Growth and characterization of selectively grown GaN nanostructures and pseudo-substrates on non-polar GaN/sapphire templates

Figure 10.3.2.1 shows the SEM images of sample L2 (figure 10.3.2.1a and b) and sample L1 (figure 10.3.2.1c and d), grown under the same conditions.

![SEM images of sample L2 and L1](image)

In both cases, selective area growth of GaN nanostructures with different morphologies was achieved. The c-plane GaN NCs have a typical hexagonal structure with pyramidal top surfaces (pencil-like), as expected from the results presented in chapter 5. On the other hand, nanostructures grown on a-plane templates show elongated geometries with distinct lateral facets, observed by SEM and AFM (figure 10.3.2.1c). The vertical growth rates (estimated from SEM) measured for c- and a-plane SAG were 3.5 nm/min and 1.3 nm/min, respectively. The measured ratio between both growth rates (2.7) is in the range of the factor derived from the kinetic Wulff’s plots calculated for GaN in reference (factor 4) [Jindal2009].
In order to check the morphology evolution of the a-plane nanostructures with time and nitrogen, two more samples L3 (same conditions as L1 but grown for 3h) and L4 (same conditions as L1 except double active nitrogen) were grown. A similar arrow-headed morphology was observed for both samples, similar to those reported by MOVPE [Jindal2009].

Figure 10.3.2.2: SEM pictures of a-plane SAG GaN NCs grown under the same conditions as sample L1 but: a) twice as much active nitrogen (sample L4) and b) same growth conditions but grown for 3h (sample L3). Magnified images of the typical morphologies are shown in: c) for sample L1, d) for sample L4 and e) for sample L3, J. Cryst. Growth 353, 1-4 (2012).

The main difference is an onset of nanostructure coalescence in case sample L4 (higher nitrogen). This feature is going to be discussed in more detail later on. At this point it has to be noted that a strong lateral growth rate is present in the a-plane nanostructures. For TEM measurements shown in figure 10.3.2.3 a thin foil lamella was prepared using focused ion beam (FIB). The cross-section was obtained along the direction perpendicular to the elongation of the nanostructures i.e. orthogonal to the arrow in
Figure 10.3.2.2e. Figure 10.3.2.3a shows a general view of the whole lamella where Pt and Au layers, previously deposited to protect the sample surface from the ion beam during the thinning process, are clearly observed.

Figure 10.3.2.3: a) General view of the lamella prepared using focused ion beam in cross-section perpendicular to the arrow in figure 10.3.2.2e, b) view of the nanocolumn marked in (a) exhibiting faceting along planes perpendicular to corresponding g vectors for most of the spots in 0001 axis diffraction pattern (inset), J. Cryst. Growth 353, 1-4 (2012).

In figure 10.3.2.3b, an isolated NC is presented at higher magnification. The top most facet is confirmed to be (11-20). The NC exhibits lateral faceting perpendicular to [1-100] and top facets perpendicular to [10-10] and [01-10], i.e. m-planes. The corresponding selected area diffraction pattern along the [0001] axis is shown in the inset, confirming the elongation of the NCs in that direction.

Figure 10.3.2.4 shows the measured vertical and lateral growth rates for c-plane GaN and a-plane GaN nanostructures (in the last case, lateral growth was measured along the arrow direction in figure 10.3.2.2e, [0001], the corresponds to the largest value) under the two different active nitrogen conditions.
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While the lateral growth for c-plane NCs was almost negligible, for a-plane nanostructures the lateral growth rate was almost half of the vertical one (lateral to vertical ratio, approximately 0.4). A similar ratio was observed in a-plane nanostructures when the active nitrogen is doubled.

Based on these findings it can be concluded that one of the main differences observed between SAG on c-plane GaN/sapphire and a-plane GaN/sapphire templates is the dominant growth direction, which is perpendicular to the template in the first case, and parallel to the template surface in the second. However, it is worth to notice that in terms of crystal plane, in both cases the dominant growth direction is along the Ga-polar c-direction. Due to the enhanced lateral growth rate in case of SAG on a-plane GaN/sapphire templates, compared to the vertical one, one might expect lateral coalescence of the GaN nanostructures when grown on a-plane GaN/sapphire templates, which may allow for the fabrication of non-polar pseudo-substrates. This has been explored in samples of series M. The top view SEM pictures shown in figure 10.3.2.5 show the nanostructures of series M at the respective growth stages. For sample M1, well separated nanostructures can be observed (figure 10.3.2.5a). Upon continuation of the growth and due to the significant lateral growth, an increasing degree of coalescence
is found, leading finally to a continuous film of around 700 nm thickness (figure 10.3.2.5e).

Figure 10.3.2.5: Top view SEM pictures of SAG GaN nanostructures (series M) grown on a-plane GaN templates showing different degrees of coalescence: (a) separated (M1), (b) partially coalesced (sample M2), (c) and d) fully coalesced (samples M3 and M4). Arrow in (b) indicates the c-direction based on results shown in figure 10.3.2.2. (e) The cross-sectional SEM of sample M4. (f) AFM measurement (5x5 µm$^2$) of sample M4 revealing a RMS roughness of 20 nm, Appl. Phys. Lett. 105, 091902 (2014).

The AFM measurement (figure 10.3.2.5f) of a 5x5 µm$^2$ area of sample M4 reveals a RMS roughness of 20 nm. The high RMS roughness is expected due to: (i) the use of colloidal lithography which leads to different coalescence degrees and (ii) the top morphology of the isolated nanostructures itself, which is faceted with a-planes and m-planes (figure 10.3.2.3b). At this point, it has to be noted that the high roughness may even facilitate the fabrication of high quality templates by further overgrowth (with techniques such as MOVPE) since the irregular and rough surface can effectively bend threading dislocations and prevent their propagation [Son2014]. In order to evaluate the quality improvement of the non-polar SAG GaN nanostructures upon SAG before coalescence, LT-PL spectra shown in figure 10.3.2.6 were taken of sample M1 and the a-plane GaN template (prior to growth).
Figure 10.3.2.6: LT-PL (7K) spectra of: (a) a-plane GaN template and SAG GaN nanostructures grown on it (sample M1), and (b) higher resolution PL spectra of the near band edge emission of sample M1 and the a-plane GaN template, Appl. Phys. Lett. 105, 091902 (2014).

The PL spectrum from the a-plane GaN template shown in figure 10.3.2.6a reveals a strong yellow band peaking at 2.28 eV, known to be related to V$_{Ga}$-related defects [Neugebauer1996] and/or C impurities [Lyons2010]. In addition, a strong and broad luminescence is observed at 3.43 eV (figure 10.3.2.6b), most likely related to Basal Stacking Faults (BSFs), being slightly blue shifted by residual compressive strain (template is grown on sapphire) compared to the accepted value of 3.42 eV for I1-type BSFs [Lähnemann2012].

On the other hand, sample M1 with ordered GaN nanostructures grown on the a-plane GaN template show no traces of yellow band and six distinct emission peaks (figure 10.3.2.6b), i.e. free exciton emission at 3.478 eV, donor bound exciton D$^0$X emission at 3.472, an emission at around 3.45 eV labeled as UX, Y2 (3.42 eV) [Liu2005] [Lähnemann2012], Y4 (3.36 eV) [Lähnemann2012] and Y6 (3.32 eV) [Tischer2011a] [Tischer2011b] defect related lines, which point towards the presence of I1 and I2 BSFs (respective peak positions are marked in figure 10.3.2.6b). It should be noted that the origin of the 3.45 eV line is still under debate: initially, it was tentatively ascribed to the two-electron satellite (TES) of the D$^0$X transition [Lefebvre2011] [Corfdir2009] more recent experiments point rather towards a surface-related transition [Pfüller2010] [Sam-Giao2013]. In addition, GaN nanostructures are strain free, so that the PL spectrum is not blue shifted.
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The presence of strong and dominant BSF-related emission in the PL spectrum is in contrast to what is observed in SAG GaN nanostructures grown on semi-polar (11-22) and polar (0001) templates. Indeed, in the semi-polar case an efficient filtering of BSFs from the underlying GaN template was observed, which was explained by the growth direction being inclined with respect to the BSFs plane and a small footprint on the initial template. In a-plane GaN templates there is not such an effect because BSFs propagate along [11-20], which is now the growth front, i.e. perpendicular to the c-plane direction [0001] (no filtering effect).

A sharp ($D^0_X$) emission with a line width of only around 5 meV is observed in sample M1 (figure 10.3.2.7b) that, in combination with the presence of the free exciton emission at 3.478 eV, indicates a much higher quality material than the template (aside from BSFs).

![Image](image.png)

Figure 10.3.2.7: LT-PL (7K) spectra of: (a) samples of series M and (b) corresponding line width values of ($D^0_X$) emission of these samples, Appl. Phys. Lett. 105, 091902 (2014).

Similar PL spectral features are observed for all stages of coalescence (figure 10.3.2.7a). Upon coalescence, a strong reduction of the relative intensities of peaks associated with BSFs in combination with a steady decrease of the ($D^0_X$) line width down to 2 meV (sample M4 in figure 10.3.2.7b) is observed. This behavior is typical of improved material quality and the absence of extended defects, opposite to what should be expected upon coalescence of GaN “islands”. Furthermore, note that the overall intensity does not show a continuous trend as a function of layer thickness, probably due to the interplay between improved optical quality and extraction efficiency. In
addition, a decrease of the (UX) intensity relative to the D\(^{0}\)X intensity with increasing degree of coalescence is observed (figure 10.3.2.7a), i.e. the ratio $\frac{I_{D^{0}X}}{I_{UX}}$ is 0.6, 8, 11 and 11 for samples M1, M2, M3 and M4, respectively. This finding can be explained as follows. It has been shown that the relatively high intensity of the (UX) peak in GaN NCs is related to the proximity of the donor to the NCs lateral surface [Lefebvre2011]. With increasing degree of coalescence, the surface area of the structures is reduced and, thus, the relative (UX) intensity decreases.

A similar mechanism is assumed responsible for the observed narrowing of the D\(^{0}\)X line, with increasing coalescence degree. Whereas “bulk” donors have symmetric electrostatic potentials, electrostatic potentials of donors close to the surface are highly asymmetric, leading to a substantial broadening of the (D\(^{0}\)X)-line [Levine1965] [Satpathy1983]. In the case of individual GaN nanostructures grown on a-plane templates, the lateral surface is rather high in comparison with their volume, and the surface to volume ratio strongly decreases upon coalescence until a continuous film is achieved. This means that, in the absence of other mechanisms (dislocations), a reduction of line width should be expected upon coalescence. With respect to defect generation upon coalescence, it is worth to distinguish the case of vertical (polar) SA GaN NCs, where the natural surface is large and tilt/twist may play a substantial role in dislocation generation, and the present case, where all nanostructures have a rather small lateral surface area and are well aligned along the c-direction as imposed by the orientation of the template (figure 10.3.2.5b). In this context, the most important feature is the fact that voids exist among neighboring NCs, as seen in figure 10.3.2.5e, and that these voids might block both threading dislocations and BSFs. In other words, the coalescence of non-polar (a-plane) GaN nanostructures may be understood as Epitaxial Lateral Overgrowth (ELOG) enabled by nanomasking. Transmission Electron Microscopy studies will certainly clarify this point, which is quite important since the aim of this approach is to provide the basis for a further overgrowth of a thicker layer by other epitaxial techniques (MOCVD, HVPE).
10.4 Summary:

In summary, ordered GaN/InGaN/GaN nanostructures were grown by SAG MBE on semi-polar (11-22) GaN templates. PL and TEM analysis showed a strong improvement in crystal quality after SAG due to an efficient filtering of most BSFs coming from the template. After SAG, PL emission is dominated by a strong donor-bound exciton line at 3.473 eV with a full width half-maximum of 2.7 meV. Due to the SAG growth mode, embedding an InGaN insertion into the GaN NCs yielded a homogenous array of nanostructures that have the same optical signature for both a single nanostructure and an ensemble. CL spectra showed two InGaN-related emission peaks at 2.43 eV and 3 eV that relate to regions with different In content within each single NC: Higher In-contents are related to In incorporation at polar or semi-polar planes (at the NCs apex) while lower In contents are achieved at non-polar facets.

When growing thick InGaN segments on top of SAG GaN NCs on semi-polar templates, LT-PL showed two emission peaks at 2.2 eV and 2.8 eV. Spatially resolved CL revealed that the peaks are related again to emission originating from distinct areas of the sample, i.e. the low energy emission coming from the apex of non-coalesced NCs (most likely growth along c-direction) and the high energy emission (low In%) from coalesced NCs side-facets (growth along m-plane).

In the second section of this chapter, the SAG on (11-20) a-plane templates was performed, and compared to conventional c-plane SAG. In agreement with results obtained by other epitaxial techniques, the vertical growth rate is lower when growing on a-plane as compared to c-plane, under the same growth conditions. While the lateral growth rate is negligible for SAG growth on c-plane, it is significant in the case of SAG on a-plane. The high lateral growth rate was used for fabricating non-polar pseudo-templates by merging individual nanostructures. By PL a clear improvement of optical quality compared to the template is observed upon SAG, although the presence of stacking faults which propagate from the template into the nanostructures has been detected. Upon coalescence a decrease of line width down to 2.0 meV is found, indicating the formation of high quality, non-polar GaN pseudo-substrates.
Chapter 11:  
Conclusions and future work
11.1 Conclusions:

The following results were achieved in the framework of this thesis:

1. Fabrication and characterization of self-assembled GaN and InGaN/GaN nanocolumns (NCs) on Si(111).

2. Fabrication and characterization of ordered GaN NCs with and without InGaN insertion on GaN/sapphire templates.

3. Study of the impact of growth temperature, In/Ga ratio and III/V ratio on the selective area growth of (bulk-like InGaN) InGaN/GaN NCs grown on GaN/sapphire.

4. Achievement of white-light emission from single ordered NCs using i) a composition graded InGaN active region and ii) a RGB stacked InGaN structure.

5. Fabrication and characterization of blue (441 nm), green (502 nm) and yellow (568 nm) light emitting diodes (LEDs), using ordered InGaN/GaN NCs with long InGaN active regions (250 nm to 500 nm).

6. SAG and characterization of GaN NCs and InGaN/GaN NCs on Si(111).

7. Development of growth model for selectively grown InGaN/GaN NCs on GaN/sapphire.

8. Growth and characterization of InGaN/GaN core-shell microstructures using a combination of top-down (etching) and bottom up (epitaxy) steps.

9. InGaN overgrowth was performed using MOVPE pillars, leading to ordered InGaN core-shell structures with aspect ratios of around 13.
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10. Fabrication of core-shell pin structures.

11. Ordered (GaN/InGaN/GaN) nanostructures were grown by SAG MBE on semi-polar (11-22) GaN templates.

12. The SAG of GaN was performed on (11-20) a-plane templates and compared to conventional c-plane SAG.

11.2 Future work:

As a direct consequence of the work presented in this thesis the following topics are already scheduled as future work.

1. Further studies on the SAG of axial pin structures will be performed. In particular the role of InGaN segment thickness for the presence/absence of droop will be studied further. Furthermore surface passivation of the pin structures will be performed in order to improve current injection as well as decrease surface recombination at the NC sidewalls.

2. Growth and characterization of InGaN/GaN core-shell structures with In-contents higher than 20% will be performed in order to allow for the fabrication core-shell pin structures emitting in the green spectral range.

3. Development of InGaN/GaN high In-content core-shell solar cell structures, which are expected to be superior over axial structures (layer and NC), since absorption and current extraction are perpendicular with respect to each other.

4. Fabrication of non-polar (11-20) and semi-polar (11-22) InGaN pseudo-templates using SAG of InGaN/GaN nanostructures.

Besides their applications for light generation (LEDs) as well as power generation by light absorption (solar cells) at which most research effort in this thesis was focused, selectively grown (In)GaN based nanocolumnar structures are anticipated to have a major impact on sensor applications and in the field of water splitting. Water splitting is addressing one have mankind’s major concerns i.e. the efficient storage of energy. Both applications will be addressed in the near future.

Since these applications make use of different material aspects (compared to LEDs or solar cells) a short overview which may serve as a brief introduction to the respective fields is given in the following.
Chapter 11

11.2.1. Selectively grown GaN and InGaN nanostructures for photo-electrochemical sensors.

The excellent electrical and optical properties of group(III)-nitrides, in combination with their high thermal, chemical and radiation stability [Ambacher1998] [Pearton2004] as well as their biocompatibility [Young2006] [Jewett2012], make them very appealing for sensing applications, in particular under harsh environments, which can be found in industry and space. Since the first demonstration of pH sensing using GaN surfaces [Kocha1995], much effort was made for the development of III-nitrides for (bio)chemical sensors. Most of the work up to now, was focused on planar 2D devices leading to a large variety of applications, like pH sensors [Steinhoff2003], cell activity recording [Steinhoff2005], DNA hybridization monitoring [Shih2008] and gas sensing [Schalwig2002]. In the last years, following the demonstration of Si nanowire based sensing [Cui2001], attention moved to nanocolumn (NC) and nanowire (NWs)-based sensors. As for lighting applications, limitations planar devices suffer from, can be overcome by the use of NCs. Due to their large surface-to-volume ratio, NC-based sensing allows for a better performance and sensitivity compared to planar devices. The adsorption or binding of molecules on the NCs surface can modify the surface sites (surface states) and/or the depletion region inside the NCs, affecting the electrical conductance and/or radiative recombination efficiency of the NCs. Based on the type of monitorization, NC-based sensors can be classified as electrical or optical sensors. In electrical sensing, changes of the electrical properties of the NCs (current or voltage) are monitored, while in optical sensing changes of the optical properties of the NCs are monitored. Another classification is based on the differentiation between sensors consisting of an ensemble of NCs, or single NCs.

Among all the applications of III-nitrides NCs as sensors, detection of H$_2$ is particularly relevant, due to its potential application in industrial processes. H$_2$ is a promising candidate for large scale energy storage as will be discussed later, but at the same time, its hazardous and flammable nature demands for thorough leak monitoring. A high H$_2$ sensitivity of reliable sensors able to operate in harsh environments is needed in e.g. aircrafts, spacecrafts and automobiles.

Recently, Pt- or Pd-coated (In)GaN NCs have been demonstrated to be efficient transductors for changes in H$_2$ concentration. Using electrical detection, the group of
Prof. Pearton in Florida (USA) demonstrated room temperature detection of H$_2$ concentrations down to 200 ppm (monitored as a change in electrical resistance of 7.4%) with a power consumption <0.6 mW [Lim2008]. Using optical detection (changes in PL intensity of (In)GaN NCs), Prof. Eickhoff’s group in Giessen (Germany) reported detection limits of 10 ppm at room temperature [Paul2012]. In these structures H$_2$ dissociates upon absorption at Pt or Pd. Following that it diffuses to the metal/semiconductor interface and alters the surface recombination sites (hence the radiative recombination efficiency affecting the PL intensity) and/or the depletion region of the NCs (changing the electrical conduction).

In ISOM first experiments using self-assembled InGaN/GaN NCs have already been conducted, and it was found that these structures are sensitive to gases such as oxygen [Lefebvre2012]. Due to the exposure to oxygen a quenching of the PL intensity of the uncoated nitride NCs was observed, which was reported as well in ref [Teubert2011].

Up to now, all studies published on nitride NCs for sensors were based on self-assembled NCs, mostly grown by MBE and CVD. However while enabling the fabrication of proof-of-concept devices, the growth of self-assembled NCs leads to a strong dispersion of the dimensions and properties among NCs, which is highly undesirable for processing and in terms of reliability. Moreover, for a better performance of the sensors, factors like diameter and carrier concentration need to be optimized which cannot be done properly with the self-assembled process. In the particular case of electrical sensors, where the modulation of the depletion region is essential for the sensor operation, NCs with too large diameter can loose sensitivity, while NCs with to small diameter would not contribute at all since they are completely depleted, leading to situations where only some small percentage of the NCs would contribute to the sensor operation (similar as in case of self-assembled InGaN/GaN pin structures for LEDs). In ref [Dobrokhotov2006] it was shown, that in case of NCs with carrier concentrations of around 2.2x10$^{17}$ cm$^{-3}$, only NCs with radii between 90 to 100 nm are sensitive to the gas changes. A solution of all these problems would be the use of selectively grown NCs.
The specific aim of this upcoming work will be the application of high quality ordered (In)GaN NCs for sensors, aiming for hydrogen detection, exploiting their superior homogeneity and the controllability of properties and dimensions.
11.2.2. Selectively grown GaN and InGaN nanostructures for water splitting systems.

The dependence on fossil fuels as well as the alarming increase of greenhouse gas emissions demands for the development of clean renewable energy sources. Of all candidates, solar energy is seen as the most promising due to the magnitude of solar power striking earth (around 120000 TW). With current state of the art technology this solar energy received on earth’s surface can be converted into electricity with an efficiency of up to around 40%. However with current technology the electricity is difficult to store and distribute over long distances. This issue can be solved by converting photochemical energy directly into fuel, i.e. the storage of solar energy in the chemical bonds of fuel like hydrogen which can be achieved by solar water splitting for production of hydrogen in a carbon free process. At this point it has to be noted that current hydrogen fuel cells can generate electricity with comparable or higher efficiencies than a combustion engine making hydrogen an overall appealing alternative to gasoline. In addition hydrogen could be used as an energy-rich reagent for the exothermic formation of methane, methanol, or even hydrocarbons using atmospheric CO$_2$ as a carbon feedstock. With that it may be used to generate conventional fuels for transportation, which currently account for around 30% of all human energy consumption.

A particularly important feature of photoactive materials is a large surface area to promote efficient surface reactions with water, thus requiring special attention to semiconductors with nanoscale morphology. During water splitting, a semiconductor undergoes or assists photon absorption, charge separation and diffusion/migration as well as H$^+/\text{H}_2$ reduction and H$_2$/O$_2$ oxidation at the surface. One-dimensional structures such as nanocolumns (NCs) can potentially provide benefits for each of these processes: i) since NCs can effectively trap light through scattering [Garnett2010] [Zhu2009] their use can reduce material cost by decreasing the amount of material required to absorb the same fraction of light and ii) by decoupling directions of photon absorption and charge separation, NCs can allow for a geometric optimization of the active region [Hochbaum2010]. An improved photocatalytic activity has already been demonstrated for self assembled GaN NCs structures [Wang2011] [Jung2008], due to a large surface-to-volume ratio, a rapid charge carrier separation and an enhanced optical absorption.
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All work related to NC based InGaN photo-electrochemical cells presented up to now was based on the use of self-assembled nanocolumnar structures which are known to suffer from a strong dispersion in morphological, optical and electrical characteristics. The use of selectively grown GaN and InGaN NCs as anode material in PECs would be appealing for the following reasons: i) the surface band bending and electrochemical properties of GaN NCs as well as InGaN NCs are influenced strongly by the NC diameter, ii) an enhanced $H_2$ production and incident-photon-to-current-conversion efficiency (IPCE) can be achieved by optimizing the NCs length and density, and iii) a further improvement in the IPCE can be achieved by increasing the thickness of the InGaN segments and band gap engineering both of them requiring a higher level of control than self assembled growth allows for. With that the incorporation of different In levels in each InGaN segment which allows for the fabrication of triple or even quadrupole-band NC photo-electrodes with further enhanced efficiency could be performed.
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