Coaxial InGaN Epitaxy Around GaN Nano-tubes: Tracing the Signs

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This work focuses on investigations of the luminescence properties of coaxial InGaN layers around single GaN nano-tubes on top of GaN micro-pyramids. The nano-tube structure was formed after the controlled desorption of ZnO nano-pillar templates during the coaxial GaN epitaxy. An intense and broad photoluminescence (PL) peak centered around 2.85 eV is attributed to transitions from a shallow donor or from the conduction band to a Zn_{Ga} acceptor level above the valence band edge. A thin layer near the area around the inner diameter of the nano-tube is believed to be heavily doped with Zn impurities. These are believed to hinder the luminescence from coaxial InGaN quantum wells (QWs) around the GaN nanotube. Comparing samples with and without QWs, where the thickness of the GaN tube wall before the QW growth was doubled, a clear indication of In incorporation in low temperature PL was observed via an intense peak around 3.1 eV. Moreover, as the temperature of the QW growth was changed from 830°C to 780°C, a shift of the peak corresponding to an increase in In incorporation from 3.5 % to 7.5 % was noticed.

1. Introduction

Nano-structures based on GaN and related group III-N alloys have been receiving significant attention in recent years as possible candidates for the development of nano-photonic devices. Moreover, due to their high surface to volume ratio, tuneable direct band gap and high chemical stability, GaN based nano-structures promise a high potential as sensing elements for biomedical applications. Developing a scalable process for the realization of these novel structures with high crystal quality is necessary as a first step towards their realization. We have reported in [1] our approach using coaxial casting of ZnO nano-pillars for the generation of high crystal quality GaN nano-tube structures after the controlled desorption of the ZnO nano-pillars (Fig. 1). Such a nano-tube structure has a larger surface to volume ratio than a GaN nano-pillar in addition to possible different optical wave-guiding properties. We have also reported in [2] about our approach for the position control of the ZnO nano-pillars on top of GaN micro-pyramids, where a high degree of scalability is achieved, thus enabling a consistent investigation of epitaxial parameters. As a further challenge, the epitaxial optimization of coaxial InGaN hetero-structures around our GaN nano-tubes was set. In addition to their non-polar characteristics with reduced Quantum Confined Stark Effect (QCSE), the afore-mentioned coaxial InGaN nano-hetero-structures could be optically interfaced to measure their luminescence response to surface conditions. An SEM picture of the afore-mentioned structure with coaxial InGaN layers is shown in Fig. 2. Due to the reduction of growth temperature to realize epitaxial InGaN

layers, the top part of the tubes was sealed by a pyramid-shape cap. In this study, we report on the challenges for generating highly luminescent coaxial InGaN layers with the help of photoluminescence and locally resolved cathodoluminescence characterization for a series of samples with and without coaxial InGaN layers of varying In content.

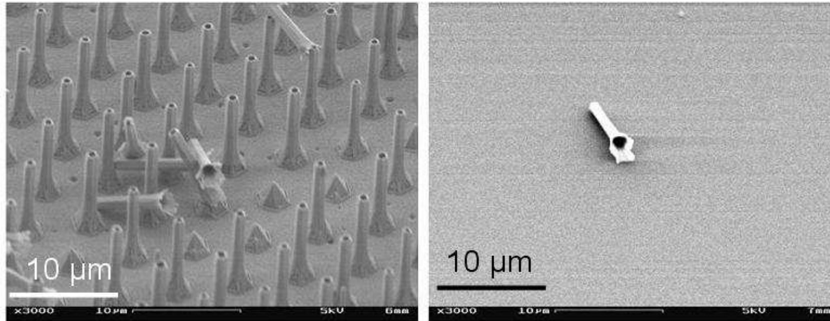

Fig. 1: SEM picture of single hollow GaN nano-tubes on top of GaN pyramids (left). Hollow GaN nano-tube separated on a sapphire substrate confirming the complete desorption of ZnO (right).

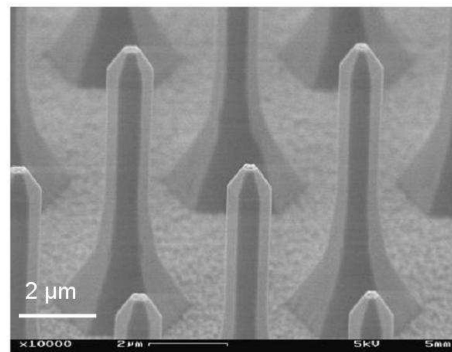

Fig. 2: SEM picture of single hollow GaN nano-tubes on top of GaN pyramids with epitaxial InGaN layers.

2. Experimental

Single ZnO nano-pillars used as templates in these studies with diameters of 150–300 nm and heights of 4–6 µm were grown using the vapor-transport on top of GaN pyramids. ZnO/carbon powder mixture and oxygen were used as precursors in a three heating zones furnace [3]. The GaN pyramids were patterned and subsequently grown using optical lithography and selective area epitaxy, respectively, in our AIXTRON AIX 200 RF low pressure MOVPE system with a SiO_2 mask of 5 µm openings [2]. Trimethylgallium (TMGa) and ammonia (NH_3) were used for the deposition of GaN layers around the well positioned ZnO pillars, whereas trimethylindium (TMIn) and triethylgallium (TEGa) have been used for the deposition of the quantum wells and the barriers. Low temperature photoluminescence measurements (around 18 K) were performed using a He-Cd laser with

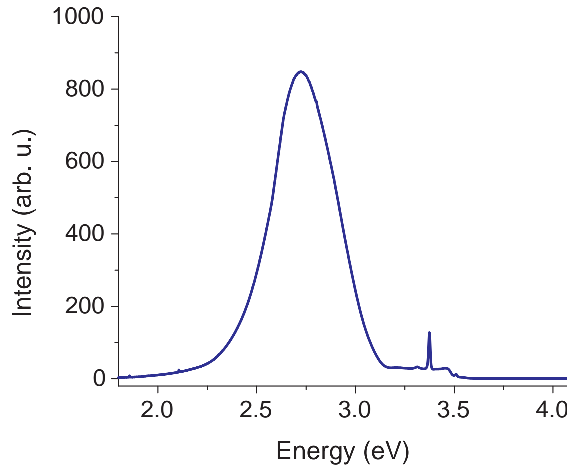

Fig. 3: Low temperature photoluminescence spectrum of a single coaxial InGaN layer around GaN nanotubes grown at 835 °C.

a wavelength of 325 nm and a spot size of around 150 µm. Locally resolved cathodoluminescence was performed at a temperature of 9 K employing excitation voltages between 2 and 5 keV and a detector window of 5 nm. The deposition of a single coaxial GaInN quantum well which was finally coated by a GaN layer was done at reduced growth temperatures ranging between 760 °C and 850 °C [2]. In order to examine the presence of InGaN layers, a series of samples epitaxially designed to have different In incorporations were developed. By mechanical contact, we were able to separate single rods on different substrates, where measuring the thickness of the tube was possible and consequently the growth rate of our GaN and InGaN layers was estimated to be 2.5 nm/min.

3. Photoluminescence and Cathodoluminescence Investigations

As reported in [4], due to the desorption of TMIn during growth, an Arrhenius plot of the indium incorporation coefficient k_{In} defined as

$$K_{\mathrm{In}} = \frac{x}{1-x} \cdot \frac{f_{\mathrm{TEGa}}}{f_{\mathrm{TMIn}}}. \tag{1}$$

is expected, where x is the In mole fraction in the InGaN layer[1], f_{TEGa} and f_{TMIn} are the molar flow rates of triethylgallium and trimethylindium, respectively. The coefficient is expected to increase with decreasing substrate temperature with an activation energy of 1.6 eV for c-plane growth [4] (Fig. 4 (left)). Although we are expecting InGaN growth on non-polar planes, we still expect a similar Arrhenius plot behavior but possibly with a different activation energy.

[1]We have evaluated the In mole fraction x by measuring the center peak position in low temperature photoluminescence where a thickness of 10 nm of InGaN layers was assumed, neglecting the piezoelectric field (since they are grown coaxially on non-polar planes) and assuming a conduction band offset of 40 %.

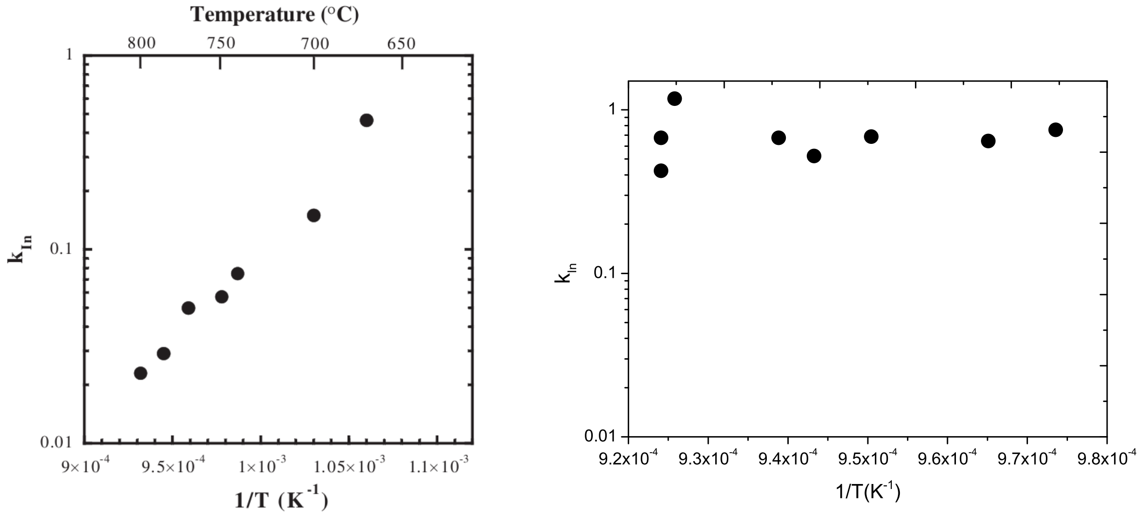

Fig. 4: Arrhenius plot of a series of InGaN layers grown at different temperatures on c-plane bulk GaN [4] (left) and a similar series of single coaxial InGaN layer around GaN nano-tubes related to a peak around 2.85 eV (right).

Figure 3 shows a PL spectrum for a coaxial InGaN layer grown at 835 °C. In order to check if the main peak at 2.85 eV is related to the InGaN layer luminescence, a series of growth temperatures and indium flows was examined. The corresponding data revealed a negligible shift with temperature (Fig. 4 (right)). This result indicated that another source of luminescence is dominant. As reported in [5] and [6], a similar peak has been always observed for Zn impurities in GaN and is attributed to transitions from a shallow donor or from the conduction band to a Zn_{Ga} acceptor level above the valence band edge. So our next approach was to examine the local luminescence distribution from single rods with and without InGaN layers by means of cathodoluminescence. We have separated single rods on TEM grids to exclude any parasitic luminescence from the substrate. The spectrum of a nano-pillar without a QW gave a similar peak at 2.85 eV with homogeneous distribution of luminescence (Fig. 5). This has confirmed that this peak is attributed to transitions to a Zn_{Ga} acceptor level of 0.4 eV above the valence band edge [6]. The luminescence at 2.85 eV for the rods with a single QW was less homogeneous and a new peak around 3.3 eV gave more localized luminescence near the top and bottom of the rod (Fig. 6). This indicated that the epitaxial structure is clearly different. We do believe that this peak at 3.3 eV originates from the InGaN layer (also supported by experiments described in the next section), however, the question remains why does it give higher luminescence from the top or bottom of the rod. Further investigations using CL are planned using different excitation voltages for clarification.

4. Investigations of InGaN Layers Around Thicker GaN Nano-tubes

We believe that a thin layer near the inner surface of the nano-tube is heavily doped with Zn_{Ga} acceptors as compared to deeper layers along the coaxial growth direction. This

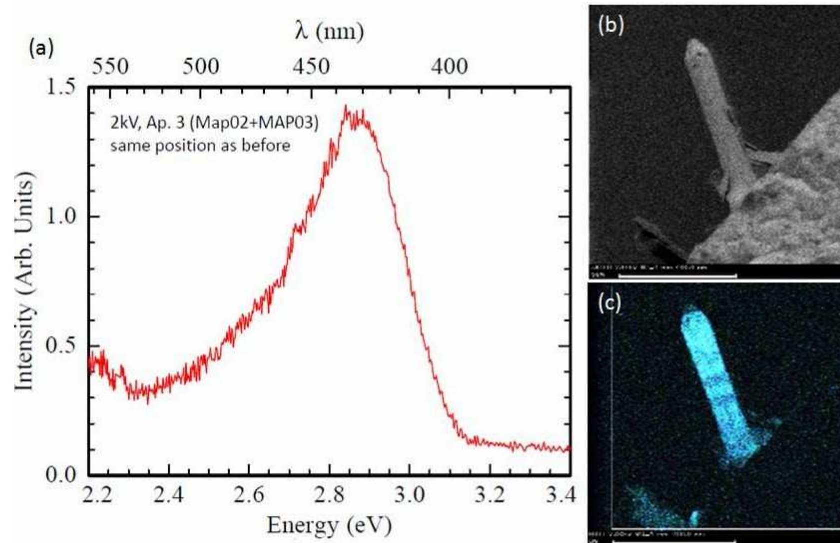

Fig. 5: Locally resolved cathodoluminescence distribution and spectrum from a single GaN nanotube without InGaN QW separated on TEM grid.

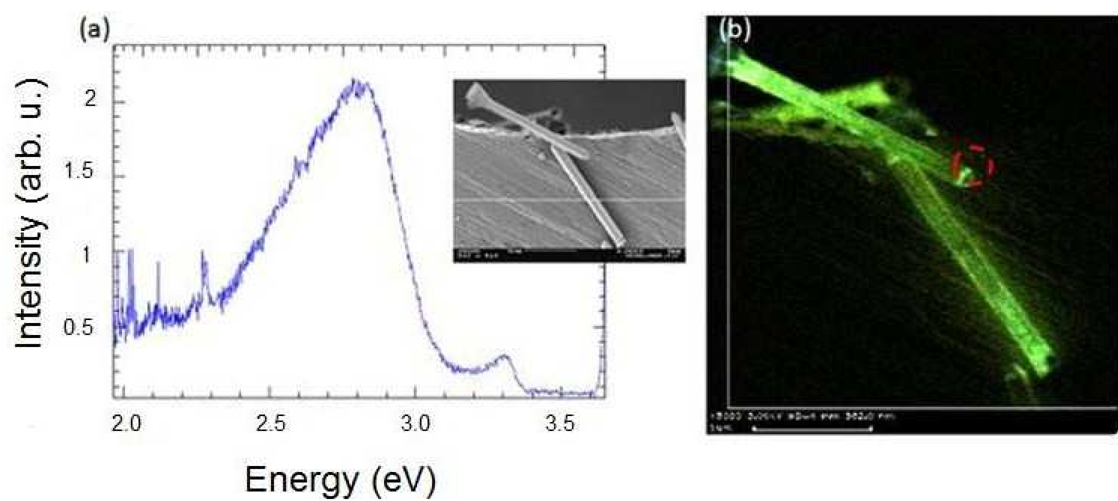

Fig. 6: Locally resolved cathodoluminescence distribution and spectrum from single GaN nanotubes with InGaN QW separated on TEM grid.

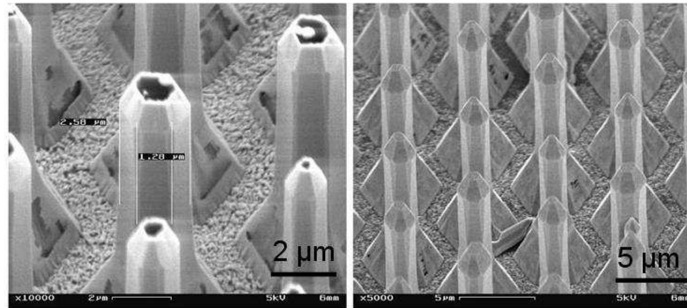

Fig. 7: SEM picture of thick hollow GaN nano-tubes on top of GaN pyramids (left). Thick GaN nano-tubes with a single QW of 10 nm (right).

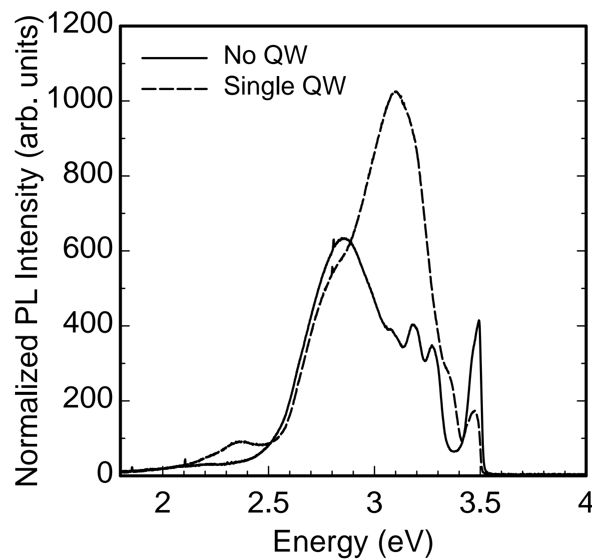

Fig. 8: Low temperature photoluminescence spectrum of thick GaN nanotubes with and without a single coaxial InGaN layer.

might be due to the fact that the growth rate of our layers is assumed to be much faster than the diffusion of Zn atoms through the material. This fact has been also reported in [7] using EDX investigation of the Zn concentration across the nano-tube structure.

As a counteract to this presumed effect, we tried to investigate thicker GaN nano-tubes where the QW is positioned further away from the inner tube surface. GaN nano-tubes with doubled wall thickness with and without a single QW were realized and compared (Fig. 7), where the same original ZnO template was used and the QW was grown at 800 °C. As shown in Fig. 8, the peak around 2.85 eV was observed in both samples whereas a highly luminescent new peak around 3.1 eV emerged for the sample with a single QW, corresponding to In incorporation of 10 %. Furthermore, another ZnO template was split into two halves and the InGaN layers were grown at 780 °C and 830 °C, respectively. The resulting PL spectrum at low temperature indicated a clear shift in the main peak with peak positions of 3.21 eV and 3.345 eV respectively (Fig. 9). This indicated an In incorporation of 7.5 % and 3.4 %, respectively. Comparing this result to the PL spectrum

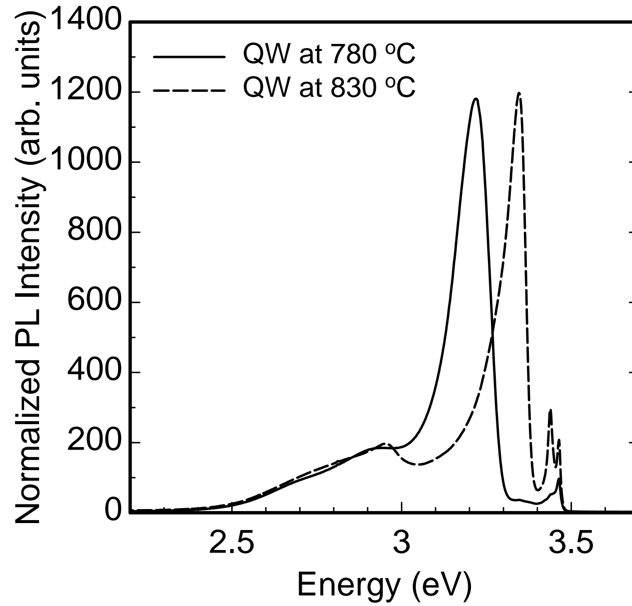

Fig. 9: Low temperature photoluminescence spectrum of thick GaN nanotubes with single coaxial InGaN layers grown at 830 °C and 780 °C.

in Fig. 7, we expected an In incorporation higher than 10 % for the sample grown at 780 °C. However, since the original ZnO template was different, we assume that the InGaN layer luminescence energy depends on the original ZnO template. These last results are to be confirmed by locally resolved cathodoluminescence measurements for single nano-pillars separated on TEM grids.

5. Conclusion

We reported about an investigation of epitaxial InGaN layers grown epitaxially around GaN nano-tubes on top of GaN micro-pyramids involving low temperature photoluminescence and locally resolved cathodoluminescence. An intense and broad peak centered around 2.85 eV is attributed to transitions from a shallow donor or from the conduction band to a Zn_{Ga} acceptor level above the valence band edge. This peak did not shift with varying InGaN layer growth temperature and TMIn flows and it had homogeneous luminescence distribution in locally resolved cathodoluminescence mapping for samples without InGaN layers. A thin layer near the inner surface of the nano-tube is believed to be heavily doped with Zn_{Ga} acceptors as compared to deeper layers along the coaxial growth direction. This layer is also assumed to prevent efficient carrier recombinations in the QW. A clear indication of In incorporation in low temperature PL was observed via an intense peak around 3.1 eV by growing double GaN layer thicknesses before the QW growth. Furthermore, a shift of a similar peak by growing at different InGaN layer growth temperatures from 3.34 eV to 3.21 eV supported the argument of In incorporation into the coaxial layers.

Acknowledgment

We like to thank Zhe Ren for his scientific contributions and investigations of the samples in this work throughout his master thesis, Manfred Madel for growing the ZnO nanopillars used in these studies, Ingo Tischer for undertaking the cathodoluminescence measurements, S.B. Thapa for his previous work on the epitaxial growth of GaN on ZnO as well as I. Argut for her assisstance with sample processing. This work has been partly financially supported by the Helmholtz Association within the project "PINCH Photonics".

References

[1] S.B. Thapa, J. Hertkorn, T. Wunderer, F. Lipski, F. Scholz, A. Reiser, Y. Xie, M. Feneberg, K. Thonke, R. Sauer, M. Dürrschnabel, L.D. Yao, D. Gerthsen, H. Hochmuth, M. Lorenz, and M. Grundmann, "MOVPE growth of GaN around ZnO nanopillars", *J. Cryst. Growth*, vol. 310, pp. 5139–5142, 2008.

[2] M. Fikry, M. Madel, I. Tischer, K. Thonke, and F. Scholz, "Luminescence properties of epitaxially grown GaN and InGaN layers around ZnO nanopillars", *Phys. Status Solidi A*, vol. 208, pp. 1582–1585, 2011.

[3] A. Reiser, V. Raeesi, G.M. Prinz, M. Schirra, M. Feneberg, U. Röder, R. Sauer, and K. Thonke, "Growth of high-quality, uniform c-axis-oriented zinc oxide nano-wires on a-plane sapphire substrate with zinc oxide templates", *Microelectron. J.*, vol. 40, pp. 306–308, 2009.

[4] Y. Kobayashi, V. Perez-Solorzano, J. Off, B. Kuhn, H. Gräbeldinger, H. Schweizer, and F. Scholz, "Investigations of growth of self-assembled GaInN islands on SiC substrate by metalorganic vapor phase epitaxy", *J. Cryst. Growth*, vol. 243, pp. 103–107, 2002.

[5] M.A. Reshchikov, and H. Morkoc, "Luminescence properties of defects in GaN", *J. Appl. Phys.*, vol. 97, pp. 061301-1–95, 2005.

[6] M.A. Reshchikov, A.A. Kvasov, M.F. Bishop, T. McMullen, A. Usikov, V. Soukhoveev, and V.A. Dmitriev, "Tunable and abrupt thermal quenching of photoluminescence in high-resistivity Zn-doped GaN", *Phys. Rev. B*, vol. 84, pp. 075212-1–14, 2011.

[7] J. Goldberger, R.R. He, Y. Zhang, S. Lee, H. Yan, H.J. Choi, and P. Yang."Single-crystal gallium nitride nanotubes", *Nature*, vol. 422, pp. 599–602, 2003.