Luminescence Properties of Epitaxially Grown GaN and InGaN Layers Around ZnO Nanopillars

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GaN and InGaN layers grown around ZnO nanopillars by metalorganic vapor phase epitaxy (MOVPE) are investigated by means of photoluminescence (PL) and locally resolved cathodoluminescence (CL). A multi layer growth process involving deposition at different growth conditions in a step-wise manner has been employed for the coaxially grown GaN. Then InGaN/GaN quantum wells and barriers have been deposited as the final growth stage. A sharp peak at 3.46 eV in low temperature PL with FWHM of 23 meV confirmed the high quality of the deposited GaN layers. The existence of InGaN layers has been confirmed by another PL peak at 3.16 eV that has been shifted to 3.11 eV as the InGaN deposition temperature was reduced by 15°C and the trimethylindium (TMIn) flow was increased by 40 sccm. For more efficient investigations of single pillars, position control has been achieved through the growth of single ZnO nanopillars on top of GaN pyramids. Locally resolved CL mapping along single rods has revealed a relatively homogeneous indium distribution along the nonpolar side facets of the overgrown nano-pillars.

1. Introduction

The controlled synthesis of nano-structures based on GaN and related group III-N alloys has been receiving significant attention in recent years as possible candidates for the development of nanophotonic devices. Moreover, due to their high surface to volume ratio, tuneable direct band gap and high chemical stability, GaN based nanostructures promise a high potential as sensing elements for biomedical applications. As a first step towards the afore-mentioned goals, a process for producing high quality group III-N nanostructures with controlled positions is required. Well ordered and vertically aligned GaN nanorods have been recently achieved [1,2]. However, according to our experience, it is more difficult to obtain upright and well-ordered GaN nanorods directly by MOVPE in comparison to ZnO nanopillars grown by vapour-transport methods [3,4]. Moreover, the lattice constant of ZnO is close to that of GaN. Therefore, we have chosen such nanopillar structures as templates for the subsequent epitaxial sheathing by GaN-InGaN layers.

The ZnO nanopillars used as templates in these studies had typical diameters of 100-300 nm and heights of 1-2 μm. They have been grown by the vapour-transport method on a-plane sapphire substrates covered by a uniform ZnO nano-crystalline seed layer which was deposited in a preceding growth step via simple chemical vapour deposition [3]. The thin nano seed layer was formed rapidly on the substrate by sublimation and thermal decomposition of zinc acetate dihydrate at moderate temperatures and pressures. Subsequently, growth of ZnO nano-wires was performed by a carbo-thermal vapour-transport method yielding nano-wires with c-axis up-right orientation [3].

The ZnO pillars have then been transferred to our AIXTRON AIX 200 RF low pressure MOVPE system. Trimethylgallium (TMGa) and ammonia (NH_3) were used for the deposition of GaN layers whereas trimethylindium (TMIn) and triethylgallium (TEGa) have been used for the deposition of the quantum wells and the barriers.

2. GaN Layers Around ZnO Nanopillars

A major issue for the hetero-epitaxial growth of GaN on ZnO using MOVPE is the high sensitivity of ZnO in the GaN growth environment: At elevated temperatures, ZnO decomposes by reacting with hydrogen and ammonia. Therefore, we have established a multi-layer growth process based on our experience in the growth of GaN layers on ZnO templates by MOVPE [5]. In order to protect the ZnO from being etched at the onset of the growth process, the nanorods were first covered by GaN at 550 °C using N_2 as a carrier gas. Then, we raised the growth temperature in order to improve the GaN quality. As the temperature was increased to 1050 °C using H_2 as carrier gas, hollow GaN tubes were achieved. The corresponding SEM pictures are shown in our previous works [5] and [6]. Figure 1 shows a low temperature (25 K) photoluminescence spectrum of such a nanorod ensemble where the spot size of the exciting laser was around 100 µm. As the spectrum was taken from a large ensemble of nanorods, we believe that the sharp peak at 3.46 eV with a FWHM of 23 meV confirms relatively high material quality of the deposited GaN layers. However, a blue luminescence centered at around 2.9 eV is still observed which is either defect related or resulting from Zinc doping of GaN. Our assumption for defect related blue luminescence is based on the fact that the low temperature casting layers in our multi growth process are of very low material quality. Moreover, the other two peaks centered at 3.195 eV and 3.28 eV are believed to originate from stacking faults in GaN. TEM investigations are planned for confirmation.

3. InGaN Layer Overgrowth

After the deposition of GaN as the final layer of the multi-layer growth process at 1050 °C, the temperature was reduced for the deposition of three coaxial thin InGaN/GaN layers and barriers, respectively. We have demonstrated in our previous work [6] the successful growth of a single coaxial quantum well with about 4 nm thickness as confirmed by transmission electron microscopy (TEM). For these layers, we used growth conditions optimized for c-plane GaN resulting in well/barrier thicknesses of 3 - 4 nm and 7 - 8 nm, respectively. We would then expect an In incorporation of about 9 % in the QWs. In low temperature PL, the expected InGaN peak was found at 3.16 eV with a FWHM of 190 meV (solid line in Fig. 2). Now considering that the 4 nm quantum well is formed only along the non-polar side facets of the rods, this corresponds to an In content of 9.7 %. Moreover, in comparison to the result in Fig. 1, another higher intensity peak at 3.35 eV was observed indicating the possible existence of ZnO remains. As a further check for the

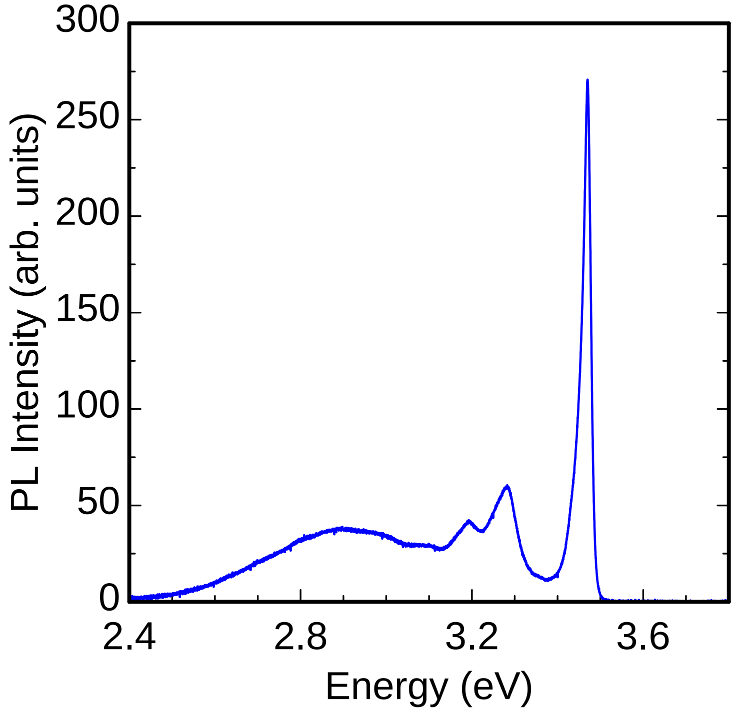

Fig. 1: Low temperature (25 K) PL spectrum for an ensemble of ZnO nanopillars overgrown with GaN layers.

In incorporation into the InGaN layers, the InGaN deposition temperature was reduced by 15 °C and the TMIn flow was raised by 40 sccm. In low temperature PL, a shift in the InGaN peak from 3.16 eV to 3.11 eV was observed, whereas no shift was observed for the assumed ZnO peak at 3.35 eV (dashed line in Fig. 2). This confirmed the expected increase of In incorporation into the quantum wells and it was calculated to be 1.5 %.

4. Position Control of ZnO Nanopillars

As mentioned in the introductory section, the ZnO nanopillar templates were prepared using the seed layer (SL) approach. This process is quite random and did not involve position control measures. However, for the purpose of simple addressing and efficient characterization of single rods, an effective position control approach needed to be implemented. An efficient approach that avoids the expense of e-beam lithography has been investigated. Growth of single ZnO nanorods on top of GaN micro-pyramids has been achieved (Fig. 3 (a)) where we made use of growth selectivity on the different surface planes of GaN pyramids [7]. The GaN micro-pyramids were prepared using the epitaxial lateral overgrowth (ELOG) technique employing a SiO_2 mask and photolithography. The degree of control of the subsequently grown ZnO rod diameters is relatively low since they range between 200 nm to 700 nm. However, this process is still investigated to reveal a narrower deviation window. Figure 4 shows the result of overgrowing such pillar-pyramid complex with GaN where the degree of ZnO desorption proved to be higher compared to the more densely packed nano-pillars prepared by the seed layer approach due to the

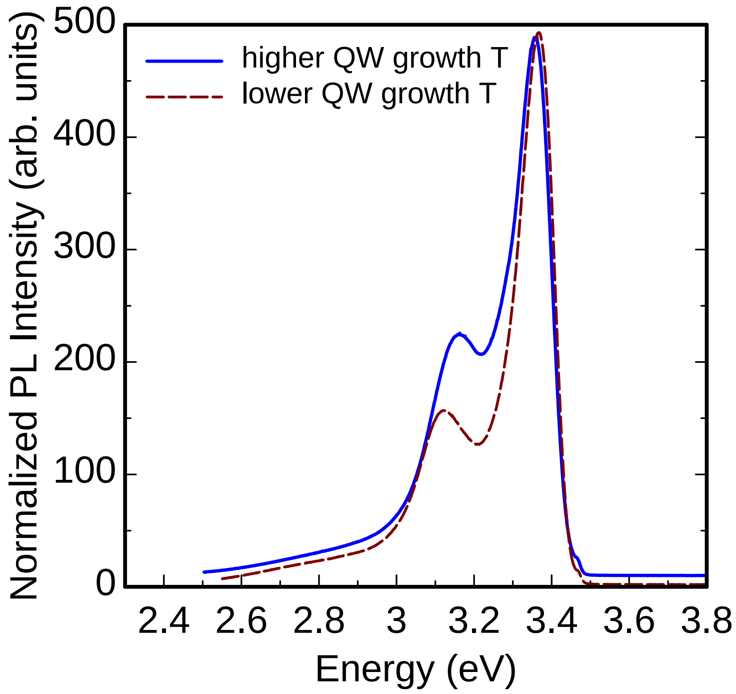

Fig. 2: Low temperature PL spectrum of coaxially overgrown ZnO nanopillars with GaN and 3 InGaN quantum wells. Solid line: quantum well grown at 855 °C. Dashed line: quantum well grown at 840 °C and TMIN flow increased by 40 sccm.

higher local V/III ratio.

5. Spatially Resolved Cathodoluminescence Mapping Along Single Pillars

The In distribution and defect distribution profile along these novel structures were still open questions. Overgrown single ZnO rods grown on top of GaN pyramids have been chosen as the best candidate structure for efficient cathodoluminescence studies. The rod-pyramid complexes were overgrown using the afore-mentioned step-wise multi growth procedure for GaN described in section 2, in addition to three InGaN/GaN wells and barriers (Fig. 3 (b)). Due to the much lower density for these samples, the increase of pillar diameter is relatively larger than for our other templates prepared without position control measures. An average diameter increase of around 500 nm was observed in comparison to around 200 nm for our previous templates. Moreover, the top of the rods was covered by a pyramid-like cap with semi-polar facets closing the top part of the hollow tubes, and we could clearly see the hexagonal symmetry formed by the non-polar side facets. Figure 5 shows a low temperature CL line scan from top to bottom of a single overgrown rod, where an electron acceleration voltage of 5 kV and a spectral resolution of 3.2 nm have been used. Each spectral scan in Fig. 5 is shifted in intensity for comparison of each position along the rod. Line-scans 1 and 2 were measured at the pyramid-like cap structure on top of the pillar, while line-scan 10 was measured at the interface between the

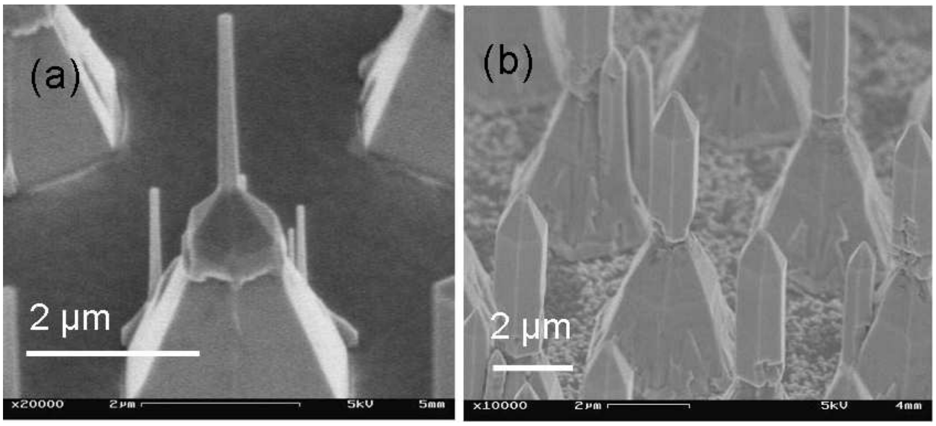

Fig. 3: SEM pictures of (a) a single ZnO nanorod grown on top of GaN pyramids and (b) these ZnO nanorods overgrown with GaN and InGaN quantum wells.

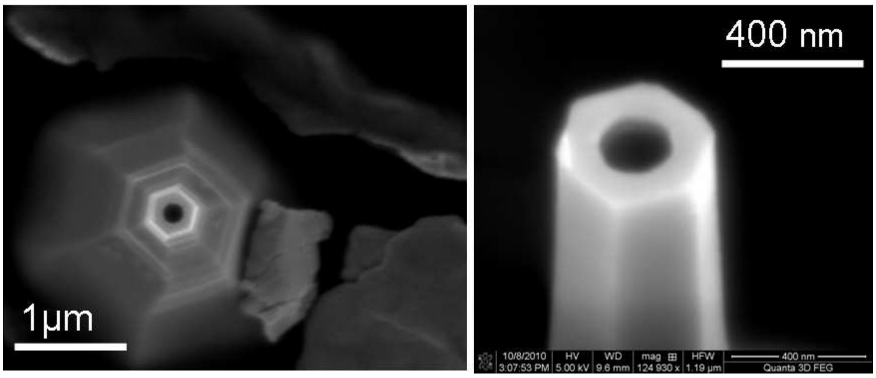

Fig. 4: SEM pictures of hollow GaN nanotubes grown on top of GaN micro-pyramids after desorption of ZnO. Left: top view and right: angular view.

GaN micro-pyramid's top and the pillar's bottom. The high luminescence contribution at 388 nm emerges mainly from the middle part of the rod with the non-polar side facets (line-scans 3 to 8), whereas it dies out at the afore-mentioned top and bottom areas of the pillar. The emission's full width at half maximum for line scans taken from the middle of the rod were measured to have an average of 170 meV, which is slightly narrower than those measured by photoluminescence from an ensemble of nanorods in section 2. For the interface between the pillar and the pyramid, this is assumed to be related to unintentional impurity incorporation during the nucleation of the ZnO nano-pillar. This could be excessive zinc or oxygen doping into GaN or excessive gallium doping into ZnO. For the pyramid-like cap structure on top of the pillar, the nature of defects is still not clear but further TEM investigations are planned for clarification.

The luminescence distribution of the peak at 388 nm along the middle part of the rod with the non-polar side facets (Fig. 6 (b)) shows a relatively homogeneous profile without signs of localized luminescent centers. Tracing the luminescence along the lateral direction perpendicular to the rod's axis, we do not expect to see perfect homogeneity since there exist the edges between the different m-plane side facets that could cause disturbances in

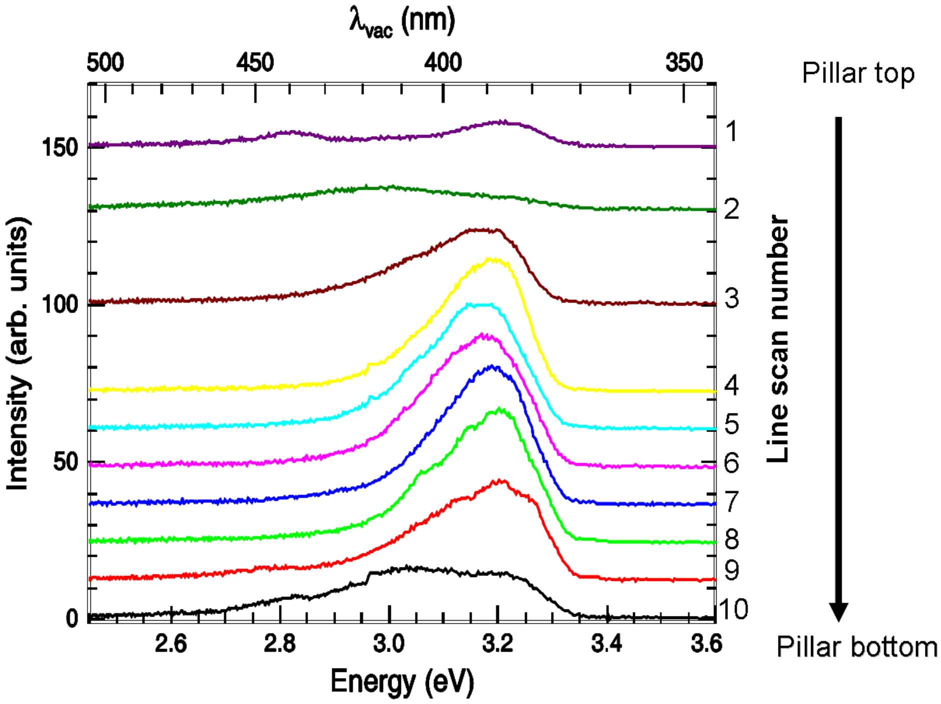

Fig. 5: Low temperature CL linescan from top to bottom along a ZnO nanopillar overgrown with GaN and InGaN layers.

strain and In incorporation. For the same growth experiments on the more densely packed seed layer samples, cathodoluminescence studies revealed randomly distributed localized luminescent centers along single m-planes (not shown here). Moreover, blue shifting of the center peak positions are observed near the pillar's top and bottom (comparing line-scans 3 to 9 in Fig. 5). These small shifts in peak position are assumed to be predominantly caused by different degree of strain at the top and the bottom parts of the pillar compared to the middle part. However, slightly different In incorporation can not be excluded.

The luminescence contribution from the pyramid was weaker than from the rod and was observed at a wavelength of 420 nm (not shown here). Such luminescence peak shift between the nonpolar and semipolar facets of the rod and the pyramid, respectively, is believed to result from possible different In incorporation, different quantum well thicknesses as well as the effect of presence and absence of the piezoelectric field.

6. Conclusion

We have studied the luminescence properties of coaxially deposited GaN and InGaN layers around ZnO nanopillars by MOVPE and we were able to conclude their fairly high material quality. Moreover, successful position control of these novel structures was achieved by growth of single rods on top of GaN pyramids. This has facilitated efficient locally resolved cathodoluminescence mapping along single rods. A high contribution with

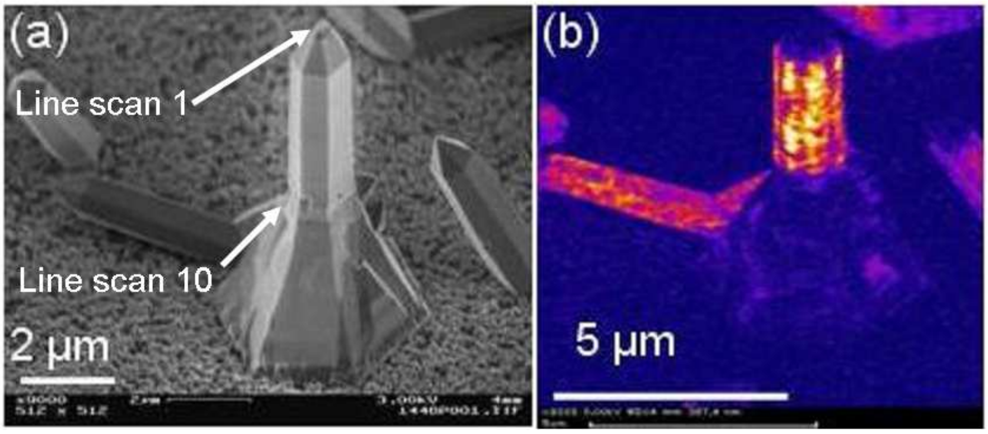

Fig. 6: (a) SEM picture of a single ZnO rod overgrown with GaN and InGaN on top of a GaN pyramid. (b) Spatial distribution of the CL emission at 3.195 eV for the rod-pyramid complex shown in (a).

a relatively uniform luminescence distribution at 388 nm emerges from single non-polar side facets of the rod indicating the existence of InGaN quantum wells.

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