Realization of Nitrogen-Polar GaN Micro- and Nanostructures

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We report on the selective area growth of N-polar GaN micrometer and sub-micrometer sized structures on structured sapphire wafers for applications in optical gas sensing. Optical lithography has been applied for patterning a SiO_2-mask on the micrometer scale, whereas electron-beam lithography has been used on the nanometer scale. Subsequently, prismatically shaped GaN rods have been fabricated by selective area metal organic vapor phase epitaxy (MOVPE) and first experiments for the realization of GaInN quantum wells on the facets of such structures have been made.

1. Introduction

Today, nanowires find strong interest in research due to their potential applications as light emitting diodes [1], nanolasers [2], as well as single photon emitters and detectors [3, 4]. Morerover, interdisciplinary applications beyond classical optoelectronics are increasingly investigated in particular sensor systems for biomolecules [5], DNA [6], liquids or gases [7, 8]. Due to their large surface to volume ratio, nanowires are in general predestinated as sensing devices [9]. Due to their large bandgap in particular GaN nanostructures are promising candidates for optical gas sensing [10], and furthermore provide a good thermal, chemical, and mechanical stability.

Such a sensing mechanism may be based on the adsorption of oxidative or reductive atoms on the surface which introduces a band bending in the semiconductor which is well understood for ZnO nanowires [11]. This effect corresponds with a change in the photoluminescence emission which in particular can be visible for nanoresonator structures with quantum wells located close to the surface. Uniformly arranged GaN nanowires have been achieved previously within our group by overgrowing ZnO nanowires grown on micrometer-scale GaN pyramids [12]. During this overgrowth the ZnO template desorbs and allows the realization of GaN nanotubes with an even higher surface to volume ratio. However, the inavoidable Zn-doping of GaN in this approach is disadvantageous for potential optical devices with integrated GaInN quantum wells [12].

In this work, we investigate a new approach by growing GaN nanopyramids and nanorods directly on structured sapphire substrates without using a ZnO template. GaN nanorods grow preferably with nitrogen-polarity, while Ga-polar GaN in general results in pyramidal structures [9]. Here, the N-polarity of GaN is achieved by an in-situ nitridation of the sapphire substrate in a hot ammonia atmosphere before growth [13]. During this nitridation step a thin AlN nucleation layer is formed from the Al_2O_3 substrate [14] which

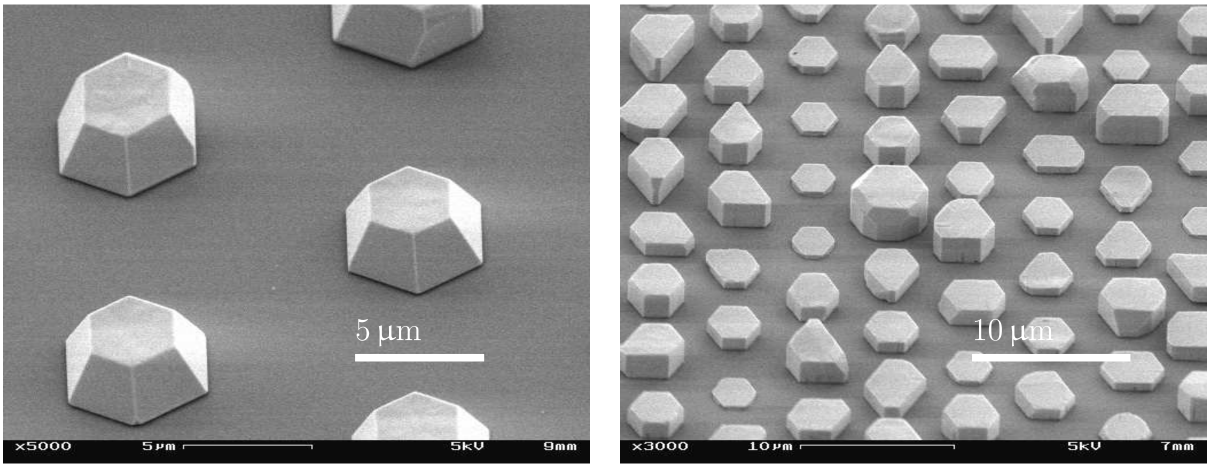

Fig. 1: SEM micrographs of GaN micrometer structures grown on structured sapphire substrates, with a V/III ratio of ≈ 230 (left) and a V/III ratio of ≈ 160 (right).

is then overgrown with nitrogen-polar GaN rods. Moreover, investigations on nitrogen-polar GaN layers have been performed (see the article by M. Fikry in this Annual Report). These buffer layers shall be applied as templates for growth of homogeneously arranged, high quality nanowires. Here, an improved crystal quality and a high fraction in nitrogen-polarity is expected compared to structures directly grown on sapphire.

2. Fabrication

All structures are realized on *c*-oriented sapphire wafers using an horizontal flow Aixtron MOVPE reactor.

For the realization of micrometer sized structures, a thin SiO_2 layer has been deposited onto the sapphire by plasma enhanced chemical vapor deposition. Subsequently, a photoresist layer has been patterned by optical lithography on the SiO_2. Then, reactive ion etching (RIE) with a CF_4 plasma has been applied to etch a hole mask with an opening diameter of $3\,\mu m$ and a period of $3\,\mu m$ and $10\,\mu m$ into the SiO_2, corresponding to a filling factor of approximately 21% and 93% respectively. Finally, in-situ nitridation in hot ammonia and selective area MOVPE at 1100°C has been applied to grow GaN rods. A mixture H_2:N_2 of 2 : 1 has been used as carrier gas during growth.

In case of nanometer sized structures, a spin-coated PMMA layer and subsequent electron-beam lithography has been applied for the etching-mask pattering. Then, holes with a diameter of approximately 100 nm and periods in the µm-range have been etched into the SiO_2 by RIE.

3. Micrometer Rods

For realization of GaN rods a low V/III ratio [1] of approximately 160 and high temperatures of approximately 1110°C were necessary in order to suppress the stable $(10\bar{1}1)$ side facet (compare Fig. 1). This is different than growth conditions for three-dimensional

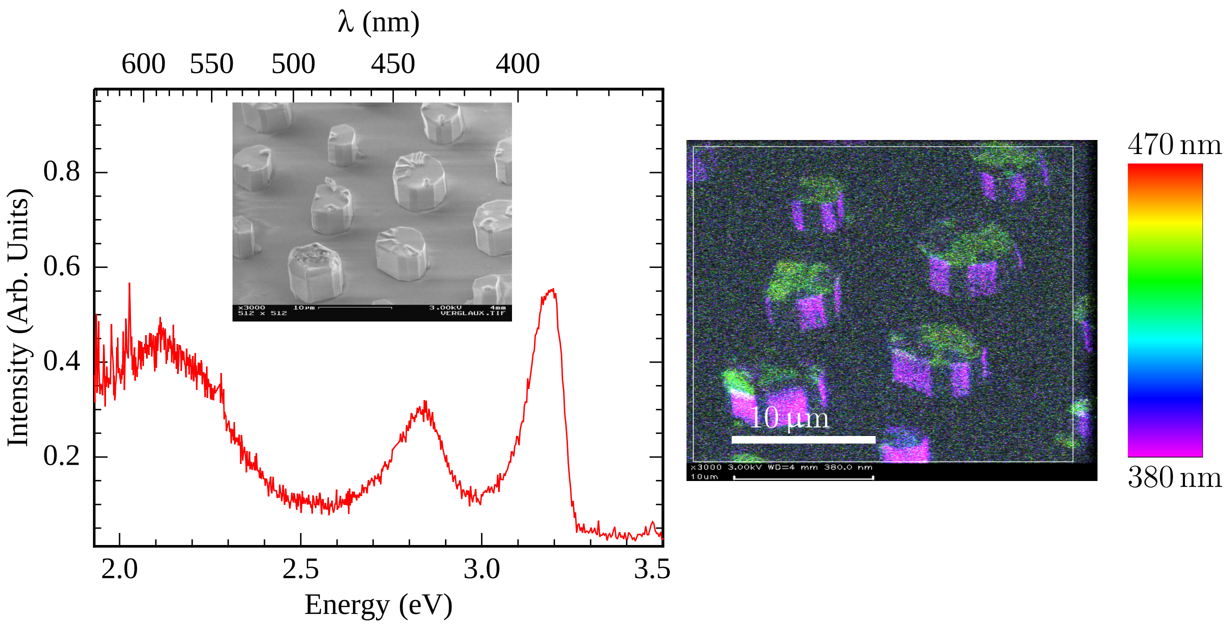

Fig. 2: Low temperature cathodoluminescence measurements of GaN microrods with integrated GaInN quantum well have been performed by I. Tischer at Ulm University. Integrated sprectrum (left) and spatially resolved map (right) demonstrating two contributing kinds of quantum wells located at the top and at the side facets of the structures.

Ga-polar structures where a lower temperature of $\approx 950°C$ and a higher V/III ratio of ≈ 250 is required [15]. The introduction of an in-situ nitridation is crucial for achieving prismatically shaped N-polar structures. In case of pure hydrogen as carrier gas a reduced selectivity, but an improved vertical growth was observed. This can be contributed to the more efficient cracking of NH_3 in pure hydrogen which results in a higher V/III ratio in contrast to the diluted carrier gas. Especially for very high V/III ratios of approximately 1000 no selective growth was observed, which is different to the expected behaviour of Ga-polar GaN structures.

However, while good hexagonal homogeneity in shape was observed for structures with inclined side facets (Fig. 1, left), prismatic structures show a reduced accuracy to the hexagonal shape and stronger height differences (Fig. 1, right). This reduced accuracy can be attributed to the circular mask openings, which in contrast to pyramidal structures apparently show a stronger influence for prismatically shaped structures. However, photoluminescence shows relatively good crystal quality with a FWHM of 42 meV for the near bandedge luminescence located at 3.465 eV.

Subsequently, structures with an additional GaInN quantum well have been realized. Low temperature cathodoluminescence measurements have been performed on both kinds of structures (Fig. 2). In contrast to structures without quantum wells, two additional spectral contributions could be observed at approximately 2.8 and 3.2 eV, which can be attributed to quantum wells located at the c-plane like top of the rods and in addition quantum wells located at the m-plane side facets.

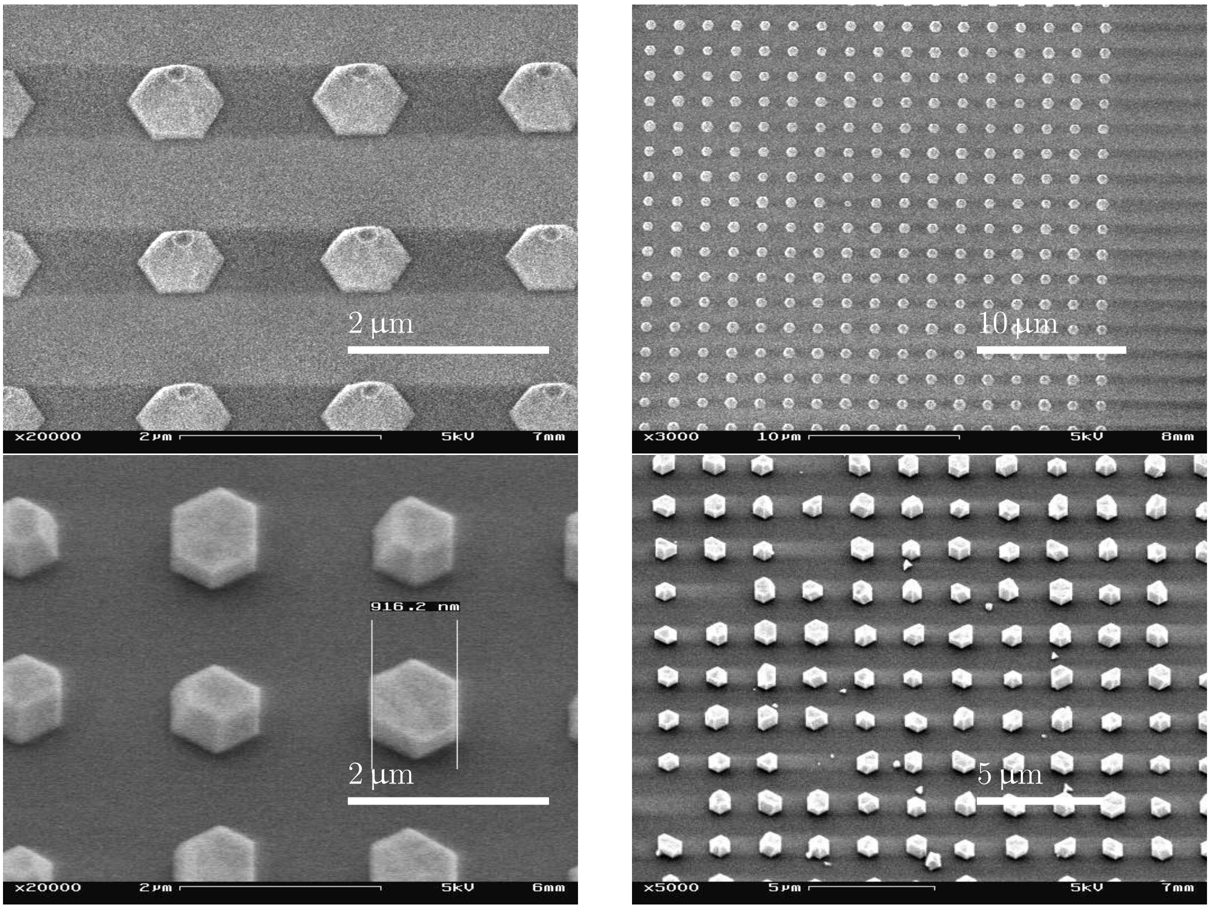

Fig. 3: SEM micrographs of GaN pyramids (top) and rods (bottom) grown on structured sapphire substrates.

4. Sub-Micrometer Rods

The realization of GaN nanowires requires a significant reduction in the diameter of the realized rods and additionally an improved vertical growth rate. In particular, applications as nanoresonators require small dimensions in the range of the investigated wave length. Therefore, the epitaxial process has been transferred from the micro to the nanometer scale by using electron beam lithography. Realized GaN sub-micrometer pyramids and rods are given in Fig. 3.

Good selectivity as well as a homogeneous developement of semipolar $(10\bar{1}1)$ side facets was achieved for pyramidal structures. In constrast, GaN rods show good selectivity in their arrangement. However, inhomogeneities are observed in their hexagonal shape similar to the micrometer structures. As for the micrometer structures, a very low V/III ratio of approximately 100 has been adjusted for growth, not including the additional reduction in the V/III ratio by the high filling factor of the mask with approximately 99.9%. In order to enable an optical read-out of individiual rods in µ-PL with different gas atmospheres a large period of 2 µm was chosen. The observed diameter of the structures lies in the range of 900 nm and therefore requires further reduction.

5. Summary

In this work the realization of GaN rods on the micrometer as well as sub-micrometer scale has been investigated. Instead of using foreign templates like ZnO nanowires, vertical growth was directly achieved on sapphire substrates. Here, selectivity and homogeneity could be significantly improved by adjusting growth parameters while N-polarity was achieved by introduction of an in-situ nitridation step. GaInN quantum wells could be successfully deposited on the side facets of micrometer structures and spatially identified by low temperature cathodoluminescence. In future, in particular the vertical growth rate will be further enhanced to promote the growth of wires with high aspect ratios.

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