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Controlling morphology and optical properties of self-catalyzed, mask-free GaN rods and nanorods by metal-organic vapor phase epitaxy

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A simple self-catalyzed and mask-free approach will be presented to grow GaN rods and nanorods based on the metal-organic vapor phase epitaxy technique. The growth parameter dependent adjustment of the morphology of the structures will be discussed. Rods and nanorods with diameters reaching from a few μm down to 100 nm, heights up to 48 μm, and densities up to 8.10^7 cm^-2 are all vertically aligned with respect to the sample surface and exhibiting a hexagonal shape with smooth sidewall facets. Optical properties of GaN nanorods were determined using cathodoluminescence. It will be shown that the optical properties can be improved just by reducing the Ga precursor flow. Furthermore, for regular hexagonal shaped rods and nanorods, whispering gallery modes with quality factors up to 500 were observed by cathodoluminescence pointing out high morphological quality of the structures. Structural investigations using transmission electron microscopy show that larger GaN nanorods (diameter > 500 nm) contain threading dislocations in the bottom part and vertical inversion domain boundaries, which separate a Ga-polar core from a N-polar shell. In contrast, small GaN nanorods (~200 nm) are largely free of such extended defects. Finally, evidence for a self-catalyzed, Ga-induced vapor-liquid-solid growth will be discussed. © 2013 AIP Publishing LLC.

I. INTRODUCTION

The group III nitride material system such as AlInGaN is a well established system for the application of optoelectronic devices.1 Although the defect density of nitride based light emitting structures is 6 orders of magnitude higher than in other material systems (e.g., GaAs), the structures are highly efficient.2 Nevertheless, it is desired to reduce the defect density in order to increase the device lifetime or to alleviate the efficiency droop.3 A possibility would be the use of low defect density GaN substrates, e.g., grown with the ammonothermal method.4 However, due to the high costs of these substrates, it is desired to grow on cheaper substrates such as, e.g., sapphire. Smooth GaN layers on sapphire can be grown via a two-step growth consisting of deposition of GaN islands followed by a coalescence process.5 However, different tilt and twist of the islands yield defect and strain generations during the coalescence of the islands into a layer.6 A possibility to achieve low defect GaN material on sapphire substrates is the growth of vertically aligned GaN rods and nanorods (NRs) because a coalescence process is not needed. Interface defects caused by different lattice constants such as threading dislocations are expected to eliminate at the basement of the rod due to bending towards the sidewall facets.7 Furthermore, in c-direction, grown GaN rods provide non-polar sidewall facets and quantum wells or quantum dots would not be affected by the quantum confined Stark effect.8 Another benefit is the high surface to volume ratio of dense rod structures. Compared to a two dimensional film, the optical activity per unit area is enhanced.

Many publications report about the bottom-up growth of GaN rods and NRs using different methods such as molecular beam epitaxy (MBE) or metal-organic vapor phase epitaxy (MOVPE). Due to higher growth rates and the expansion to large scale processes, MOVPE is the system of choice in view of industrial production. Concerning MOVPE, publications related to GaN rods are quite clear. There are publications about vapor-liquid-solid (VLS) grown GaN NRs using a metal catalyst,9 GaN NRs grown via a pulsed10 or a continuous-flux growth mode11 on prestructured substrates using a SiO2 mask and Si-induced GaN wires grown with12 or without13 an in-situ deposited SiNx mask. Our previous work concentrated on the growth of undoped, mask-free, and self-catalyzed GaN rods showing that vertical growth can be achieved just by setting the appropriate parameters and by using a simple two-step growth method consisting of nitridation and growth.14

This paper will start from the simple two-step growth method and will show the influence of Si doping on the growth of GaN rods. The temperature was varied in order to optimize the rod structures. The optical properties utilizing cathodoluminescence (CL) were determined and whispering gallery modes (WGMs) have been observed in regular hexagonal shaped GaN rods pointing out the high structural and

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morphological quality of these rods. The insertion of a GaN nucleation layer (NL) will be discussed leading to the formation of GaN NRs with diameters down to 100 nm and densities up to $8 \times 10^7$ cm$^{-2}$. Depending on the growth time, a height up to 48 $\mu$m can be achieved. The optical properties of the NRs are determined. Reduction of the yellow defect luminescence with respect to the GaN near band edge emission is possible by the reduction of Ga precursor flow. WGMs were also observed in NR structures. Structural investigations using transmission electron microscopy (TEM) were carried out showing a strong decrease of the defect density in vertical direction and the presence of both Ga and N polarity. Finally, evidence for a self-catalyzed, Ga-induced growth of NRs is presented.

II. EXPERIMENTS

The samples were grown utilizing an Aixtron 200RF horizontal flow MOVPE reactor. The temperature was measured with a thermocouple inside the susceptor. As there is no set up to measure the surface temperature, the thermocouple temperature will be given as a measure for the used growth conditions. It is estimated that the real surface temperature is roughly 50–100 °C lower.

In our previous publication, the growth of undoped GaN rods is presented and discussed. Structures were achieved not exceeding an aspect ratio of 1. $^{14}$ Basically, the structures have a non-regular hexagonal shape and the edges are not sharp. In Subsection III A 1, the massive influence of Si doping conditions on the GaN rod growth on these aspects is shown. There is a variation of the size of the structures and aspect ratios below and above 1 can be found on a single sample. In order not to confuse the reader, the description “rod” will be used for all discussed structures although there might be different definitions for different aspect ratios such as disk, rod, and wire.

1. Influence of Si doping on the shape of GaN rods

GaN was deposited at 1200 °C for 5 min using different TMG/silane (Ga/Si) ratios in the gas phase. The V/III ratio was set to 6. The SEM images of the samples are shown in Fig. 1. The samples (a), (b), and (c) are grown without Si supply, with a Ga/Si ratio of 12 050 and 1339, respectively. In Fig. 1(a), non-regular hexagonal rod structures with a diameter ranging from 0.6–1.5 $\mu$m have formed not exceeding an aspect ratio of 1. The density is $5 \times 10^7$ cm$^{-2}$. The top facets exhibit rounded edges. GaN growth with a Ga/Si ratio of 12 050 significantly changes the morphology as it is shown in Fig. 1(b). Rods and disks have formed on the surface. Compared to sample (a), the maximum height and average diameter of the rods is increased whereas the density is decreased. The top edges are more pronounced. A further increase of the silane flux to a Ga/Si ratio of 1339 again drastically influences the morphology. Diameter and height have increased at the expense of the rod density. Some rods have exceeded their height above 10 $\mu$m comparable to a growth
rate of 120 \mu m/h. The sidewalls of the rods are not flat; many steps and tilted facets are visible.

A Ga/Si ratio of 12 050 should correspond to a doping concentration in the range of $10^{18} - 10^{19}$ cm$^{-3}$, i.e., these are ordinary doping conditions.\textsuperscript{21} For the growth of two dimensional layers usually carried out at V/III ratios above $10^3$, no morphology effect for Si doping is reported.\textsuperscript{21} The role of Si during the growth of rods and NRs will be in detail discussed elsewhere.

### 2. Influence of growth temperature

In Figs. 2(a) and 2(b), SEM images are shown of two samples, which have been grown at a temperature of 1150°C and 1100°C, i.e., they are comparable to the sample shown in Fig. 1(b). The GaN rods grown at 1100°C have a rough top facet and an increased diameter compared to the sample grown at 1200°C. At 1150°C, almost perfect regular hexagonal shaped GaN rods with sharp edges, smooth top, and sidewall facets have formed, i.e., an optimized structure in terms of morphology was achieved.

Generally, no additional GaN deposition is found on the surface in between the rods, i.e., all material is either incorporated into the rods or re-evaporated into the gas phase. The results are showing that an additional masking procedure acting as an antisurfactant for GaN, e.g., an \textit{in-situ} deposited SiN/SiO$_2$ mask, is not necessary resulting in a simplified total process. It is expected that the surface mobility of the atomic species is enhanced due to high temperature and low V/III ratio. Therefore, nucleation of GaN on the sapphire surface is suppressed promoting vertical growth of GaN rods.

These type of optimized GaN rods were used to extract plasticity parameters of GaN with high-temperature \textit{in-situ} micro-compression.\textsuperscript{22}

### 3. Optical properties of GaN rods

The optical properties of a single GaN rod were investigated using CL. The spectrum of a rod with a regular hexagonal shape (cf. Fig. 2(a)) having an inner diameter and height of 1.7 \mu m and 1.3 \mu m, respectively, is depicted in graph A of Fig. 3. The electron beam was fixed at a central position of the sidewall. GaN near band edge emission in the UV spectral part as well as the broad yellow defect band in the lower energetic range is visible. The yellow defect band is modulated by optical modes. Comparing the height of the single rod and the spectral distance between each dominant mode, it can be excluded that top-bottom Fabry-Perot modes are responsible for the modulation. A very good agreement is achieved if hexagonal WGMs are assumed.\textsuperscript{23,24} A detailed CL analysis and classification of the WGMs is discussed in Refs. 25 and 26.

The CL spectrum B shown in Fig. 3 of another GaN rod with a larger diameter of 3.8 \mu m (height 1.7 \mu m) exhibits many sharp WGMs with single modes having a quality factor $Q (Q = \lambda_0/\Delta \lambda)$ above 500. The spectral distance between the WGMs is reduced due to the larger diameter. $Q$-factors of the same magnitude have also been observed in GaN microrods of similar diameters in \textit{\mu}-photoluminescence (PL) investigations.\textsuperscript{27} Even higher $Q$-factor WGMs ($Q \sim 1000 - 4000$) were observed in \textit{\mu}-PL measurements on the GaN rods discussed here.\textsuperscript{25} The appearance of high $Q$-factor WGMs in these GaN rods is unique and pointing out the high morphological quality of the GaN rods.

### B. Growth of GaN NRs

#### 1. Deposition of a GaN nucleation layer

\textit{a.} Adjusting diameter and density of GaN NRs. In order to achieve GaN NRs, the previous discussed two-step method for GaN rods is extended. A GaN NL step is introduced during nitridation. The main growth steps to achieve GaN NRs are as follows:

- Nitridation
- Deposition of GaN NL + 2 min nitridation
- Growth of GaN NRs

![FIG. 2. SEM images of two samples with lower GaN growth temperatures (compared to sample (b) shown in Fig. 1): (a) 1150°C and (b) 1100°C. The Ga/Si ratio was set to 12 050.](image)

![FIG. 3. CL spectra of a single GaN rod similar to the structures presented in Fig. 2(a) is shown in graph A. The yellow defect band is modulated due to hexagonal WGMs. In graph B, a CL spectra of another rod with a larger diameter are shown. Many sharp WGMs are visible. The single WGM at 587 nm has a $Q$-factor of 562.](image)
The NL is grown under H₂ atmosphere at a V/III ratio, NH₃ flow and susceptor temperature of 373, 1500 sccm and 1200 °C, respectively. Note that these parameters are quite different to a similar NR approach discussed in Ref. 12.

Two samples without GaN NRs were grown to check the morphology of the GaN NL. The NL was deposited for 1 s and 4 s, respectively, and nitridated for further 2 min. Flat flake-like structures have formed on the surface of both samples as shown in Figs. 4(a) and 4(b). The density and diameter of the flakes increases with increasing the NL deposition time from 3 · 10⁶ cm⁻² to 1 · 10⁷ cm⁻² and 50–100 nm to 100–150 nm for 1 s and 4 s, respectively.

Two further samples have been grown in order to investigate the influence of the NL deposition time on the NR growth. After NL deposition for 1 s and 4 s, respectively, and nitridation, the system was switched in 3 min to NR growth condition, i.e., reducing the temperature to 1150 °C and the NH₃ flow to 25 sccm. Si-doped GaN was grown for 5 min. The SEM images of these samples are shown in Figs. 4(c) and 4(d).

After 1 s, NRs and rods have formed with a density of 8 · 10⁴ cm⁻². The diameter varies from 400 nm to a few µm. A further increase of the NL deposition time to 4 s yields smaller NRs with a higher density up to 8 · 10⁷ cm⁻². The diameter varies from 200 nm to a few µm.

The density of NRs correlates with the density of the NL flakes. It is expected that the flakes act as nucleation sites for the subsequent NR growth. However, not every flake is the origin of a NR. The density of NRs is at least one order of magnitude lower than the density of flakes. We note that our trend, higher NL deposition time leads to higher NR density, is in opposite behavior to similar reports in Refs. 12 and 28.

There is an anti-correlation between the size of the flake and the NR: increasing the NL deposition time yields flakes with a larger diameter but NRs with a smaller average diameter. It is expected that not the flake size is determining the rod diameter rather than the density. It is observed that the average height of the NRs of samples grown with different NL deposition time is constant. Therefore, if the supplied material is spread over a larger number of flakes, consequently, the diameter of the NRs should be reduced.

### b. Increasing the height of NRs

A detailed GaN NR growth time study is presented in Ref. 26. Increasing the growth time leads to an increased height and after 1 h slight tapered wires were obtained having a height of up to 48 µm (cf. Fig. 5). Even higher structures can be obtained with this approach as shown in Ref. 33.

![SEM images showing the influence of GaN NL](image)

**FIG. 4.** SEM images are showing the influence of a GaN NL. (a) and (b): GaN NL deposited on sapphire for 1 s and 4 s, respectively. (c) and (d): GaN NRs grown after deposition of a GaN NL for 1 s and 4 s, respectively. Please note the different scale bars of (a), (b) and (c), (d).

**c. Homogeneity.** As visible, e.g., in Fig. 4(c), there is a large inhomogeneity in the morphology of the NRs. Especially, the diameter varies from a few hundred nm to a few µm. In order to improve the homogeneity, three samples were grown with different total reactor fluxes of 2000 sccm, 4000 sccm, and 8000 sccm, respectively. For that purpose, only the amount of carrier gas supply (H₂) was changed. The corresponding SEM images are shown in Fig. 6. A large inhomogeneity of the height and diameter is visible in Fig. 6(b) for a sample with a standard reactor flow of 4000 sccm, which was also applied for all previous discussed samples. The height and diameter is varying from 1–10 µm and 100 nm to a few µm, respectively. Increasing the total reactor flow to 8000 sccm (Fig. 6(c)) leads to an increase of the overall size of the rod. However, the sidewalls are multi-faceted and NRs are not present anymore.

The influence of the total reactor flow on the rod/NR morphology is quite different to the report of Koester et al. 12 They refer to an increase of the growth rate by a factor of 5 if the total flow is increased from 2000 sccm to 8000 sccm. A morphological change as shown in Fig. 6 is not reported. We expect that the different behavior is related to the reactor architecture. The vertical flow close-coupled showerhead reactor, used in Ref. 12, allows the gas inlet ~1 cm above the sample; whereas in the horizontal flow reactor used in this work, the gas species passes ~10 cm of the hot susceptor until they reach the sample. A change in the residence time of the gas species in the reactor might have different growth effects in the two different reactor architectures. A gradient of the growth rate in a horizontal flow reactor with respect to the susceptor position was reported in Ref. 34. Another reason might be the supposed higher temperature used in this study, which would shift the growth into a stronger etching regime and would increase the mobility of atomic species on the surface. However, the surface temperature is not exactly known in our case as already mentioned and only speculative statements are possible.

### 2. Structural characterization of NRs

TEM measurements have been performed on GaN NRs with a diameter >500 nm in order to reveal their defect structure and crystal polarity. Figs. 7(a) and 7(b) show TEM bright-field images of typical GaN NRs on sapphire. A high density of dislocations and related strain are located at the GaN/sapphire interface. Further away from the interface, the dislocations are quickly eliminated by bending towards the
sidewall facet. After approximately 500 nm, the rods are nearly free of dislocations and strain. This is one of the advantages expected from freestanding GaN NRs compared to two-dimensional films.\textsuperscript{5} Approximately in the center of the NRs, a pair of vertical planar defects occur which, in contrast to the dislocations, extend over the full rod height. The subsequent analysis proves that these defects are inversion domain boundaries (IDB) separating an inner cylinder ("core") with Ga polarity from an outer "shell" with N polarity (see below). In fact, the SEM image of two GaN NRs in Fig. 7(c) shows small hillocks, which terminate the core cylinders. The inclined facets already indicate Ga polarity of the core, which is confirmed by CBED (see below).\textsuperscript{16,26} In order to prove that the core really forms a cylinder inside the GaN NRs Fig. 7(d) depicts a TEM bright-field image of a sample cut perpendicular to the rod axis. The image has been taken with the sample tilted $\sim30^\circ$ from the (0001) zone axis in order to get pronounced contrast from the inclined IDB. The image clearly shows that the IDB surrounds an inner cylinder, which has the same faceting as the outer rod surface.

In order to determine the signs of crystal polarity in the core and shell of GaN rods, CBED has been applied to complete rods extending from a cross-section sample (Fig. 8). Thin areas appropriate for polarity analysis of the shell and core regions are available at the sidewall and the hillock protruding from the top surface of the rod, respectively (Fig. 8, bottom). The two experimental CBED patterns have been taken in $\langle10\bar{1}0\rangle$ zone axis at identical sample thickness of 135 nm and clearly show the inverted crystal polarity. Comparison with the simulated CBED pattern reveals that the core has Ga polarity whereas the shell has N polarity. The size of the core visible in Fig. 7(d) is in agreement with the size of the flakes shown in Fig. 4(b). It is expected that a Ga-polar core forms above such a GaN flake and it is furthermore assumed that the GaN flakes itself exhibit Ga-polarity. However, due to the small size of the GaN flakes as well as the presence of defects at the nearby interface, it was not possible to perform CBED measurements. In order to achieve NRs with uniform polarity, the GaN nucleation layer has to be optimized in terms of obtaining N-polar GaN flakes.

A TEM image of a GaN NR with a diameter of $\sim200$ nm is depicted in Fig. 9. In contrast to the NRs with a larger diameter (>500 nm) shown in Fig. 7, the NR is completely free of extended defects. (The dark lines in the NR correspond to bend contours, which result from pronounced bending of smaller rods in the TEM samples.) This observation clearly shows that GaN NRs are more suitable for growing defect-free GaN on a substrate with different lattice constant such as sapphire. Furthermore, Fig. 9 shows that

![FIG. 6. SEM images of samples grown with different total reactor flux: (a) 2000 sccm, (b) 4000 sccm, and (c) 8000 sccm.](image)

![FIG. 7. (a) and (b) Cross-section TEM bright-field images of GaN rods showing the presence of dislocations in the bottom part and vertical IDB extending across the whole rod height. (c) SEM image of two rods with typical hillocks terminating an inner GaN cylinder with inverted crystal polarity (cf. Fig. 8). (d) TEM bright-field image of an IDB in a plan-view section showing that the core with inverted polarity has the same side facets as the outer rod surface.](image)

![FIG. 8. Crystal polarity analysis of a GaN rod by CBED showing that the inner core with faceted tip and the outer shell possess Ga and N polarity, respectively. Both experimental CBED patterns as well as the simulated pattern were taken along $\langle10\bar{1}0\rangle$ zone axis at a sample thickness of 135 nm.](image)
vertical nanorod growth is possible without inversion domain formation. Additionally, it is expected that the microrods, which are not grown on the flakes arising from the nucleation layer, also exhibit single N-polarity. In general, hillocks as in Fig. 7 are not observed in microrods (cf. Sec. III A and Ref. 25). In Sec. III C, it will be shown that the vapor-liquid-solid growth mode is responsible for the vertical growth of rods.

3. Optical properties of GaN NRs

a. Improving optical properties. A further parameter which is strongly influencing morphology and optical properties of GaN NRs is the amount of TMG supplied during growth. A series of four samples were grown with different TMG fluxes and different deposition times of 40 sccm, 20 sccm, 10 sccm, and 5 sccm for 5 min, 10 min, 20 min, and 40 min, respectively, i.e., the total amount of TMG supplied into the reactor was constant for each sample. The NH$_3$ flow was not changed, i.e., the V/III ratio for each sample was 6, 12, 24, and 48, respectively.

The SEM images of the samples are shown in Figs. 10(a)–10(d). Decreasing the TMG flux/increasing the deposition time shows a trend towards lower density, increased height, and increased diameter of GaN NRs. The density is reduced from $5 \times 10^7$ cm$^{-2}$ for sample (a) to a very low density less than $1 \times 10^5$ cm$^{-2}$ for the sample shown in (d). The reduced density is attributed to the high growth temperature.

FIG. 10. (a)–(d) SEM images of four samples with different TMG flux rates and deposition times. (a) 40 sccm for 5 min, (b) 20 sccm for 10 min, (c) 10 sccm for 20 min, and (d) 5 sccm for 40 min. (e) CL spectra of the samples. The scale bar corresponds to 1 $\mu$m for samples (a)–(c) and 2 $\mu$m for sample (d). The spectra of the four samples shown in (e) were recorded collecting light from an ensemble of NRs (field of view $\sim 20 \times 20 \mu$m$^2$). (f)–(h) are the SEM image, panchromatic CL map, and monochromatic CL map recorded at 367 nm, respectively, for a NR fabricated with a variation of the TMG flux during growth. (i) is showing the CL spectra of the NR from (f) recorded with a fixed electron beam at the positions 1–4. (j) is showing another SEM view of sample (c). (k) is the corresponding panchromatic CL map. (l) and (m) are the monochromatic CL maps recorded at 367 nm and 560 nm, respectively.
and low NH₃ flux, i.e., growth takes place in a strong etching regime. If the TMG flux is further reduced (below 5 sccm), no growth takes place at all.

CL measurements were performed exposing an ensemble of GaN NRs. The spectra of each sample are shown in Fig. 10(e) and are normalized with respect to the GaN near band edge emission. For the sample with 40 sccm TMG for 5 min, the yellow defect luminescence is dominating the spectrum. Furthermore, an additional peak appears around 450 nm. The origin remains to be unclear but might be attributed to surface related emission. Reducing the TMG flux/increasing the growth time decreases the yellow defect luminescence compared to the GaN near band edge emission by two orders of magnitude, and the GaN near band edge emission is dominating the spectra. In order to exclude that the size is responsible for the improvement of the optical properties, a further sample was grown with a variation of the TMG flux during growth. The sample was grown with the following sequence for the TMG flux: 40 sccm for 20 s, 10 sccm for 400 s, 40 sccm for 20 s, and finally 10 sccm for 400 s. The flux was changed applying a linear ramp with a duration of 32 s. The SEM image, the panchromatic CL map, and the monochromatic CL map recorded at 367 nm are shown in Figs. 10(f)–10(h). An expressive monochromatic CL map at 560 nm could not be recorded due to the weak intensity of the yellow luminescence. Bright and dark regions are visible which are related to the change in the TMG flux. In Fig. 10(f), four positions of the fixed electron beam are marked; and the corresponding CL spectra are shown in Fig. 10(i). At position 1 and 3, the spectra show strong GaN near band edge emission, and only weak yellow defect luminescence is visible. These regions are related to the growth sequence with 10 sccm TMG. At position 2 and 4, the intensity of the GaN near band edge emission and the yellow defect luminescence is decreased and increased, respectively, compared to positions 1 and 3. These regions are related to the growth sequence with 40 sccm TMG. The peaks in the spectra are related to whispering gallery modes. The results are pointing out that the improvement of the optical properties shown in Fig. 10(e) is not related to the change in size. The optical properties of GaN NRs can be improved just by reducing the amount of TMG supplied during growth.

The spatial distribution of electron beam induced CL of the sample shown in the SEM image in Fig. 10(c) is depicted in Figs. 10(k)–10(m). The panchromatic CL map in (k) and the monochromatic CL map recorded at 367 nm in (l) show a homogeneous distribution of CL intensity all over the NRs. Only the bottom part with the high defect density and the vertical IDB is visible as non-radiative recombination centers. Moreover, yellow defect luminescence visible in the monochromatic CL map (m) recorded at 560 nm is more located at the bottom part of the NRs, illustrating the correlation between yellow luminescence and the high defect density at the interface (cf. Figs. 7(a) and 7(b)). The CL maps are showing that the NR concept is reasonable. The upper part is not anymore influenced by the substrate and by the high defect density interface, which leads to high quality optically active NRs. As an exception, there is also yellow defect luminescence visible at the top of the largest rod. Here, the rod has not a flat top surface. Instead, a pyramid has formed which is the origin of the yellow defect luminescence. As shown in Fig. 8, a pyramid is related to a Ga-polar core. The optical properties of pyramids are worse compared to GaN rods/wires as reported in Ref. 16. It is expected that the material incorporation in Ga-polar and N-polar GaN is different. Ga-polar GaN might suffer from Ga-vacancies and higher C incorporation, which increases yellow defect luminescence. It is concluded that the yellow luminescence is further suppressed if single N-polarity can be achieved. b. Whispering gallery modes in GaN NRs. WGMs are also present in GaN NRs. The SEM image of a single GaN NR is shown in Fig. 11(b). The CL spectrum recorded with a fixed electron beam at a central position of the NR is shown in Fig. 11(a). Spectrally, well separated WGMs are visible. Due to the small radius of the rod, the spectral distance between the WGMs is large (72 nm for the first two modes). However, the modes are not as sharp as the modes shown in Fig. 3. The highest Q-factor is 125. A reason is the diameter dependence of the Q-factor (Q ∝ D, D: diameter), i.e., a smaller diameter of the rod leads to smaller Q-factors. Another reason reducing strongly the Q-factor is the non-regular hexagonal shape of the NR, which is clearly visible in Fig. 11(b). Generally, it was found that the deposition of a GaN NL yields to mostly non-regular hexagonal shaped GaN NRs as it is shown in the top view SEM image in Fig. 11(c). However, WGMs are also possible in deformed hexagonal resonators but are more probably not stable. It is expected that stimulated emission of a single WGM can be achieved if the NRs are covered with an efficient optically active region as, e.g., InGaN quantum wells or quantum
dots. In combination with a tapered NR, this could lead to a tunable monomode laser.26

4. Overview of the growth parameters controlling the rod properties

In all previous sections, it was shown that basically each important GaN rod property such as morphology and optical properties can be controlled by a growth parameter. The rod properties and the corresponding parameters are summarized in Table I.

C. Evidence for a self-catalyzed, Ga-induced growth

The catalyst-induced VLS growth is an established method to form NRs/nanowires from different kind of materials.37 Generally, a metal-catalyst such as, e.g., Ni or Au is necessary to achieve VLS grown nanowires. A self-catalytic Ga-induced (without any additional Ni or Au catalyst) VLS growth was only reported for GaAs nanowires synthesized by MBE but, to the best of our knowledge, not for GaN up to now.38 The following experiments point out that a self-catalyzed, Ga-induced VLS mode drives the formation of GaN rod/NRs by MOVPE.

For all previous samples, an NH3 flow of 25 sccm was supplied during the cooling down process/after growth in order to stabilize the structures, i.e., to prevent desorption of GaN at high temperature. To test the influence of the NH3 flow during cooling, another standard sample (comparable to the sample shown in Fig. 6(b)) was grown without NH3 supply during cooling down. The corresponding SEM images are shown in Fig. 12. Droplets are found at the top and sidewall facets of the GaN rods and NRs. Etching experiments and x-ray photon spectroscopy (XPS) measurements were performed on this sample. After HCl etching, all droplets are removed (not shown here). Compared to the non-etched sample, a reduction of the Ga peak in the XPS spectra was recorded (not shown here). Therefore, it is clear that Ga-droplets are present on the GaN rods/NRs.

In order to clarify that the droplets do not form after growth due to annealing, a sample with NH3 supply during cooling down after the GaN NR growth was fabricated, i.e., no droplets are present. The sample was cleaved into three pieces. The first piece is the reference sample shown in Fig. 13(a). In a further process, the second and the third pieces were annealed for 30 s at 1150 °C in a H2 and N2 atmosphere, respectively, without NH3 supply during the total process. Strong etching of the NR structures occurred for the H2 annealed sample (c.f. Fig. 13(b)). No etching is visible for the sample annealed in an inert N2 atmosphere. However, no Ga-droplets have formed at the rods/NRs for both the annealed samples. Therefore, Ga-droplets are already present during the growth giving rise to a self-catalyzed VLS growth mode.

Due to the high temperature and the low V/III ratio, the formation of a liquid phase at the GaN NL or at defects is more probable. The Ga-droplet supports the NR growth. After growth, the droplet is still present and can be transformed into GaN during the cooling down procedure if NH3 is supplied. If NH3 is not supplied, the droplet remains liquid (down to ~30 °C) on the top facet or is spread at the sidewall facets. The VLS growth mode also explains the decrease in NR density with increasing the growth time as observed in Ref. 26. Due to Ostwald ripening, larger droplets shrink at the expense of smaller droplets.39 Once the droplet vanishes the NR stops to grow and starts to desorb. We think that Ostwald ripening is also responsible for the inhomogeneity regarding diameter and height present in our structures (cf., e.g., Figs. 4(c) and 4(d)).

As discussed in Ref. 37, Ostwald ripening can be suppressed by increasing the pressure, which reduces the

![FIG. 12. SEM images of a sample without NH3 supply during cooling down process showing (a) NRs and (b) rods covered with Ga-droplets.](image1)

![FIG. 13. SEM images of annealed samples: (a) reference sample without annealing which was cooled with NH3 supply after growth of GaN NRs; (b) GaN NR sample annealed under H2 atmosphere; (c) sample annealed under N2 atmosphere. No NH3 was supplied during the complete annealing process.](image2)
mobility of atomic species on the surface. Two samples have been fabricated to demonstrate that suppression of Ostwald ripening during growth is possible according to the VLS model. The reference sample was grown at a pressure at 100 mbar for 1 h. The corresponding SEM image in Fig. 14(a) is showing large structures with diameters of 10 μm in between the GaN rods. The second sample was grown with a higher pressure of 200 mbar. In the SEM image in Fig. 14(b), only rods with an extended height are visible. The disappearance of the large structures with diameters of 10 μm is attributed to the suppression of Ostwald ripening caused by the higher pressure. The appearance of Ostwald ripening is a further proof that the rods are grown via a VLS growth mode.

A further effect typically for a VLS growth mode is a variation of the diameter in vertical direction depending on the droplet size.\(^{37}\) During the growth of self-catalyzed GaN rods, the droplet size can be adjusted by the amount of Ga supplied via the precursor TMG. A sample was grown with a variation of the TMG flux: 40 sccm for 20 s, 10 sccm for 400 s, 40 sccm for 20 s, and finally 10 sccm for 400 s. The flux was changed applying a linear ramp with a duration of 32 s. The SEM image in Fig. 14(c) is showing rods and nanorods, which are affected by the flux change. There is a step visible at the sidewall facet for some rods (indicated with a black arrow). The diameter of the rods is slightly increased due to the high TMG flux of 40 sccm. The second reducing ramp from 40-10 sccm is also visible for some structures (indicated with a white arrow). The results show that a change of the TMG flux which is expected to change the Ga droplet size on top of the NR is affecting the rod diameter as it is expected from the VLS growth mode.

Not all the rods exhibit a step as visible for the NR shown in Fig. 14(c), which was grown in the same growth run as the sample in Fig. 14(c). Basically, rods with steps are found closer to the edge, rods without steps can be found closer to the center of the sample. Due to the architecture of the horizontal flow reactor, there is a slight total growth rate gradient present from the edge to the center of the rotated sample. Slightly more TMG material is reaching the outer regions of the sample leading to an increase of the Ga-droplet. Slightly less TMG material is reaching the center, which is not sufficient to increase the droplet size to induce steps. Rods with and without steps are coexisting on this sample.

IV. CONCLUSIONS

GaN rods and NRs can be grown on sapphire by MOVPE, applying a simple two-three step approach. Rod and NR structures were achieved with heights up to 48 μm, diameters from 100 nm to a few μm, and densities up to \(8 \times 10^7 \text{ cm}^{-2}\) depending on the growth parameters. WGMs in rods and NRs were observed showing the high quality of the morphology. The optical properties can be improved in terms of reducing the yellow defect luminescence with respect to the GaN near band edge emission. TEM investigations show that both polarities are present in the NRs. Furthermore, the bottom part of the NRs suffers from a high defect density while the upper part is nearly defect-free. This is also confirmed by spatially resolved CL maps. Finally, it was shown that the rods and NRs grow via a self-catalyzed VLS mode.

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