Ordered GaN Nanowires on Nitrogen-Polar GaN

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In this work, the position-controlled growth of GaN nanowires on sapphire wafers and on N-polar GaN templates is presented using selective area vapor-liquid-solid growth in a metalorganic vapor phase reactor. Misoriented sapphire wafers and TMIn acting as surfactant are applied in order to achieve N-polar GaN buffer layers with high crystal and surface quality, suitable for a subsequent nano-patterning by electron-beam lithography.

1. Introduction

Gallium nitride (GaN) nanowires find strong interest in academic research due to their potential for future light emitting [1] and sensing [2] devices. While typically the ordered growth of nanowires can be well controlled with molecular beam epitaxy (MBE) [3], selective area epitaxy with metalorganic vapor phase epitaxy (MOPVE) on the nano-scale is still very challenging. Inhomogeneity from wire to wire and inhomogeneous growth of single wires is often observed [4]. Recently, a nanowire growth model based on a vapor-liquid-solid (VLS) process has been reported by Tessarek *et al.* using unpatterned sapphire substrates [5, 6]. Particularly, Ostwald ripening is discussed as one source for inhomogeneous growth of the nanowires in MOVPE [5, 6].

Depending on the growth conditions, GaN-based nanowires can be either grown with gallium- [1] or with nitrogen-polarity [7,8]. Growth in N-polar direction seems to be easier achievable than with Ga-polarity [1]. However, while high quality Ga-polar GaN templates are easily available, there exists a lack of MOVPE grown N-polar GaN buffer layers with high crystal and surface quality. Therefore, mainly structured sapphire substrates [4], polished freestanding GaN [8], or N-polar GaN templates realized in MBE [9] are applied for the nanowire growth. On sapphire, the N-polar GaN growth is achieved by *in-situ* nitridation of sapphire in ammonia (NH₃) ambient at high temperatures [10]. For selective growth of GaN nanowires in MOVPE, mainly two methods are reported in literature. Either a continuous growth [1], or a pulsed growth mode [11] with modulated metalorganic and hydride precusor flows is performed. Typically, small V/III-ratios and additional silane flows [12] are required in order to achieve a vertical growth. Recently, first studies on the diffusion processes occuring during the selective growth of GaN nanowires in MOVPE have been performed by Wang *et al.* [7].

Usually, the nanowire growth conditions are very different from growth conditions applied during nucleation of the wires. For nucleation, increased V/III-ratios, reduced temperatures, and reduced silane flows are applied. Small variations in the mask-patterning on the nano-scale typically have a strong influence on the latter nanowire growth. Additionally, due to charging effects, electron-beam lithography on sapphire is often more difficult



Fig. 1: Schematic illustration of the "selective area" vapor-liquid-solid nanowire growth in MOVPE based on [5] dominated by surface and gas phase diffusion (left). Scanning electron micrograph of GaN microrods on unpatterned sapphire. After cooldown without ammonia [6], Ga-droplets are visible at the tips (right).

than on slightly doped GaN templates. An improved homogeneity and better control during nanowire nucleation is excepted on structured N-polar GaN buffer layers. In recent years, the quality of N-polar MOVPE-GaN templates on sapphire could be significantly improved [13]. Particularly, the application of misoriented sapphire wafers [13] and TMIn acting as surfactant [14] enabled a reduced density of inversion domain boundaries (IDBs).

In this work, the growth of N-polar GaN nanowires on nano-structured N-polar GaN templates is demonstrated and compared to the direct growth on sapphire. In order to reduce Ostwald ripening effects [5,6] under Ga-rich growth conditions, the application of selective area VLS growth in MOVPE is investigated. A study on the gas phase and surface diffusion processes during nanowire growth with VLS is performed.

2. Experimental

N-polar GaN-nanowire and GaN-template growth is performed in an Aixtron AIX200 MOVPE reactor using ammonia (NH_3), silane (SiH_4), trimethylgallium (TMGa), trimethylindium (TMIn) precursors as well as hydrogen and nitrogen as carrier gases.

For growth of GaN nanowires on sapphire, conventional c-sapphire substrates are applied with a miscut of 0.3° towards the m-direction. The substrates are covered with a 20 nm thick SiO₂-layer deposited using plasma enhanced chemical vapor deposition (PECVD) and patterned with electron-beam (e-beam) lithography. For e-beam lithography, PMMA 950K is used as resist and a thin layer of germanium is evaporated onto the resist to avoid charging during exposure. After exposure, the germanium is wet chemically removed in diluted H₂O₂ and the resist pattern is tranferred into the SiO₂ using dry etching techniques. Resist residues are removed in oxygen plasma and wet chemically using potassium hydroxide and piranha etching. *In-situ* nitridation of the sapphire is performed in the MOVPE reactor, using nitrogen and ammonia ambient. The selective nanowire nucleation is realized with a V/III-ratio of ~ 200 at $T \sim 950$ °C using a hydrogen to nitrogen ratio of ~ 2 : 1. All temperatures are given as process temperatures measured inside the susceptor core. Subsequently, the GaN nanowire overgrowth is performed with a V/III-ratio of ~ 60 at $T \sim 1100$ °C in hydrogen ambient. Additionally, silane (~ 70 nmol/min) is applied to promote the vertical growth [1].

For growth of GaN nanowires on N-polar GaN, buffer layers are realized on c-plane sapphire wafers with a miscut of 0.3° towards the m-direction and compared to layers grown on c-plane with 3.5° miscut towards the a-direction [13] and a-plane sapphire wafers. The sapphire wafers are nitridized and subsequently a N-polar GaN nucleation layer and buffer layer are grown using TMIn as surfactant [14]. For the nucleation layer growth, a high V/III-ratio of ~ 8200 at $T \sim 1020 \,^{\circ}$ C and nitrogen as carrier gas are applied. Buffer layers are realized with a reduced V/III-ratio of ~ 500 at $T \sim 1170 \,^{\circ}$ C. Finally, the templates are patterned ex-situ using SiO₂ as mask material and electron-beam lithography in accordance with the previously mentioned procedure. A second MOVPE step is carried out and GaN nanowires are selectively grown out of the mask openings without nucleation step.

3. Ordered Growth of N-Polar GaN Nanowires on Sapphire

In order to allow investigations on diffusion processes and local V/III-ratios, the masked substrates are patterned with a hole mask with fields of varying period (1 μ m, 2 μ m, 5 μ m, and 10 μ m), but same opening diameter. Scanning electron micrographs of the selectively grown GaN nanowires on sapphire are given in Fig. 2. Unintentional parasitic growth on masked areas can be observed which can be attributed to the Ga-rich growth conditions. The density of the clusters appears to be highest in the areas with smallest period and corresponding smallest mask filling factor. Partly, the clusters can be related to coalescence of neighboring nanowires which mainly appears for small periods. The corresponding larger local V/III-ratio for smaller periods might promote lateral growth of the wires in these regions.

Surprisingly, the height and diameter of the nanowires appears to be to a large extend independent of the filling factor of the mask and the local V/III-ratio. This could be related to the VLS growth mode reported by Tessarek *et al.* [5] which is different than the typically observed selective area growth in MOVPE. During VLS growth, the formation of gallium droplets at the tip of the nanowires is assumed while the side facets of the wires are passivated by Si-compounds [5]. The droplet-formation requires Ga-rich growth conditions, where Ga-atoms from surface and gas-phase diffusion are adsorbed in the droplet. In areas with large filling factor, only Ga-atoms within the surface diffusion length are able to reach the droplet. Adsorbed Ga-atoms at larger distances either desorb back to gas-phase or promote the formation of parasitic growth.

The total amount of deposited GaN per unit area is significantly reduced in areas with large periods. The estimated surface diffusion length is in the range of $1-2 \mu m$ [15] which is in good agreement with results obtained by others [7]. Interestingly, most wires have a uniform length of about 1.3 µm which is in good agreement with the estimated diffusion length. Increasing the growth time (not shown) does not increase the length of the wires but promotes cluster formation. As the Ga-droplet at the wire-tip is mainly fed by surface diffusion, droplets can completely desorb if the wires reach a length larger than the surface



Fig. 2: Scanning electron micrographs of ordered N-polar GaN nanowires on sapphire at the border between the 1 µm and 5 µm period region (left). Density of parasitic GaN clusters with varying mask filling factor (right).

diffusion length. Without Ga-droplet the wires can easily be completely passivated due to the high silane flows and a stop of growth occures. Additionally, due to the VLS growth, Ostwald ripening has to be taken into account [5]. For small periods, accidentally smaller droplets at the tips of the wires can easily desorb and promote the formation of larger neighboring droplets and thereby cluster formation. This phenomenon was also observed for nanowires grown on unpatterned substrates without size-control due to the unavoidable size fluctuations of the droplets [5].

4. Realization of N-Polar GaN Templates

A comparison is made for N-polar GaN grown on different sapphire orientations with varying thickness, carrier gas, and TMIn surfactant flows. While Ga-polar GaN is typically grown on c-sapphire wafers, c-oriented GaN with good crystal quality can also be realized on a-sapphire wafers [16]. According to our knowledge, the growth of N-polar GaN on a-plane sapphire and the influence of TMIn acting as surfactant has not been reported in literature. Additionally, the influence of the carrier gas is investigated, e.g., hydrogen is known to result in a strongly reduced lateral growth compared to nitrogen [12]. Particularly, a strong influence on the nucleation and coalescence of the buffer layers is expected.

Optical micrographs of buffer layers grown on c-sapphire with 0.3° miscut, c-sapphire with 3.5° miscut and a-sapphire using nitrogen as carrier gas and $20 \,\mu$ mol/min TMIn are given in Fig. 3. High densities of inversion domain boundaries (IDBs) can be observed for N-polar GaN buffers grown on conventional c-plane and a-plane sapphire wafers. IDBs are known to result in hexagonal hillock formation during growth which are also clearly visible in the optical micrographs [13]. In contrast, much smaller and fewer hillocks can be observed on the strongly misoriented c-sapphire wafers in accordance to findings reported by Keller et al. [13]. Pronounced cracks are visible in the N-polar GaN layers on c-sapphires with 3.5° miscut caused by tensile strain. All layers are almost completely etched after 10 min in 5M potassium hydroxide solution (KOH) at 80 °C confirming the predominant



Fig. 3: Optical micrographs of N-polar GaN templates on conventional c-sapphire with 0.3° miscut towards m (left), c-sapphire with 3.5° miscut towards a (middle) and a-sapphire (right) using nitrogen as carrier gas and 20 µmol/min TMIn surfactant flow.

N-polarity [17] (not shown). For increased TMIn flows (40 µmol/min), smoother layers can be found on conventional c- and a-plane while a reduced quality is observed on the misoriented c-sapphire wafers. In contrast, a lower TMIn flow of 10 µmol/min results in a reduced surface quality on all sapphire wafers (not shown). Using hydrogen instead of nitrogen as carrier gas results in crack-free and almost hillock-free N-polar GaN layers on 2"-substrates. Hall-measurements show an increased unintentional n-type carrier concentration of $n \sim 3 \cdot 10^{19}$ cm⁻³ for layers grown with nitrogen compared to $n \sim 7 \cdot 10^{18}$ cm⁻³ for layers grown with hydrogen as carrier gas. High resolution X-ray diffraction analysis furthermore confirms an improved crystal quality of the N-polar GaN layers grown with hydrogen (see Table 1).

Table 1: Full widths at half maximum of the high resolution (0002) X-ray diffraction rocking curves of N-polar GaN layers grown with nitrogen and hydrogen as carrier gas.

| thickness | $0.8\mu\mathrm{m}$ | $1.6\mu{ m m}$ |
|-----------|--------------------|----------------|
| hydrogen | 509'' | 381'' |
| nitrogen | 800" | 621'' |

5. Ordered Growth of N-Polar GaN Nanowires on GaN

An homogeneous resist patterning is achieved on N-polar GaN templates with circular openings and diameters of approximately 150 nm (Fig. 4 top, left). Scanning electron micrographs of the selectively grown GaN nanowires are given in Fig. 4. Compared to the mask openings, an increased diameter of about 300 nm can be observed for the hexagonally-shaped wires caused by lateral growth over masked regions. Surprisingly, despite of their N-polarity, the nanowires form semipolar side-facets and a flat *c*-plane like plateau at the tips. In fact, the plateau turns out to be rather circularly-shaped and slightly raised with respect to the semipolar facets. The diameter of the plateau is corresonding to the diameter of the circular mask openings. It is expected that the initial size of the Ga-droplet is mainly determined by the size of the mask openings.



Fig. 4: (top) Scanning electron micrograph of a structured resist on N-polar GaN created by electron beam lithography (left) and corresponding micropraphs of N-polar GaN nanowires with 1 µm periodicity after overgrowth in MOVPE (right); (bottom) indicated positions of the former Ga-droplet (left); height fluctuations and observable hillocks (see white arrow in magnified region) at the nanowire tips (right).

We conclude, that under Ga-rich growth conditions the plateau formation of the nanowires is closely related to the VLS growth mode. Due to the VLS growth, layer-by-layer growth occurs on the *c*-plane like plateau at the tips which are covered by the droplet (compare Fig. 1, left). Occasionally, smaller circular hillocks are visible at the nanowire tip (Fig. 4 bottom, right). These features presumably develop during the final stage of the nanowire growth or even during cooldown due to the nitridation of the deposited Ga-droplet after stopping the Ga-supply. Additionally, height fluctuations can be observed for GaN nanowires grown on the N-polar templates similar to wires grown on sapphire. These fluctuations are likely not resulting from an inhomogeneous mask patterning but might be related to fluctuations in the size of the Ga-droplets. Particularly, Ostwald ripening is known to result in competition between individual droplets for the Ga-supply. Smaller droplets desorb more easily and result in a passivation of the GaN-nanowire at an early stage. Increasing height fluctuations appear more pronounced on the nano-scale and for closely-packet nanowires compared to micrometer-sized rods. This can be explained by the increasing challenge to prevent Ostwald ripening on the nanometer-sized structures.

6. Summary

The ordered realization of N-polar GaN nanowires by a selective area VLS growth in MOVPE was demonstrated. The influence of surface and gas phase diffusion on the nanowire growth was investigated with respect to the mask filling factor. High quality N-polar GaN buffer layers were realized suitable for nano-lithographic processing. Furthermore, a comparison between nanowires grown on structured sapphire substrates and on patterned N-polar GaN templates was performed.

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