TEM characterization of catalyst- and mask-free grown GaN nanorods

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Abstract. Catalyst- and mask-free grown GaN nanorods have been investigated using transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and energy filtered transmission electron microscopy (EFTEM). The nanorods were grown on nitridated r-plane sapphire substrates in a molecular beam epitaxy reactor. We investigated samples directly after the nitridation and after the overgrowth of the structure with GaN. High resolution transmission electron microscopy (HRTEM) and EFTEM revealed that AlN islands have formed due to nitridation. After overgrowth, the AlN islands could not be observed any more, neither by EFTEM nor by Z-contrast imaging. Instead, a smooth layer consisting of AlGaN was found. The investigation of the overgrown sample revealed that an a-plane GaN layer and GaN nanorods on top of the a-plane GaN have formed. The nanorods reduced from top of the a-plane GaN towards the a-plane GaN/sapphire interface suggesting that the nanorods originate at the AlN islands found after nitridation. However, this could not be shown unambiguously. The number of threading dislocations in the nanorods was very low. The analysis of the epitaxial relationship to the a-plane GaN showed that the nanorods grew along the [000-1] direction, and the [1-100] direction of the rods was parallel to the [0001] direction of the a-plane GaN.

1. Introduction

Despite intensive research in the last decade, heteroepitaxy of GaN-based light emitting diodes still suffers from the high density of defects such as threading dislocations and stacking faults that form due to the large lattice mismatch to the used substrate, as e.g. sapphire or SiC. On the other hand, GaN homoepitaxy is avoided due to the high costs of GaN substrates. Growing single crystalline and defect-free GaN nanorods could overcome such problems [1,2], since they could be grown almost strain-free. Usually, nanorods are grown on patterned or masked substrates, or growth may be initiated by a seed of metal droplets [3,4,5]. However, the seed metals often result in an incorporation of impurities and extended defects into the nanorods [6]. Catalyst- and mask-free grown nanorods exhibit the possibility to circumvent that, enabling fabrication of more effective optical devices. Catalyst-free growth of nanorods was reported for GaN on Si(111) and c-plane sapphire using AlN buffer layers [7,8]. However, the nanorods were only moderately ordered. In contrast, Aschenbrenner et al. [9] recently showed that highly ordered nanorods can be achieved by growth on nitridated r-plane sapphire substrates. In this paper, we report on the structural characterization of the catalyst-free grown GaN nanorods of Aschenbrenner et al. [9,10] using transmission electron microscopy (TEM) and related techniques. We determine the epitaxial relationship between the GaN nanorods with the
substrate and investigate the stage of growth directly after the nitridation of the sapphire substrate and after the growth of the GaN nanorods.

2. Growth of the structures and experimental setup
The samples were grown using the following approach. The r-plane sapphire substrates were nitridated in a Thomas Swan vertical shower head reactor using a mixed NH$_3$/H$_2$ ambient with a ratio of 1:1 at 1050 °C [10] and overgrown with a thin GaN layer. In a second step the nitridated substrates were transferred to a molecular beam epitaxy (MBE) reactor and the nanorods were grown at a temperature of 830 °C with a background pressure of 1.3·10$^{-4}$ Pa and 6·10$^{-7}$ Pa of the N and Ga flux, respectively.

TEM specimens were prepared with the lift-out technique in a FEI focused ion beam (FIB) facility or by conventional thinning with a tripod holder to a thickness of about 15 µm and subsequent thinning in a GATAN precision ion polishing system (PIPS) using Xe ions with an energy of 5 keV under an angle of 5°. The specimens were investigated with a FEI Titan 80/300 microscope equipped with a Cs corrector for the objective lens, a Fischione high angle annular dark field detector (HAADF) and a GATAN post-column imaging filter. For all studies the microscope was operated at 300 kV.

3. Investigation of the nitridated sapphire surface
In a first step, we prepared a TEM specimen from a sample just after the nitridation of the sapphire substrate using the tripod technique. Figure 1 shows a high resolution TEM (HRTEM) micrograph of the specimen exhibiting the formation of islands on top of the substrate due to nitridation. To clarify the composition of the islands, energy filtered TEM (EFTEM) was performed using the K-edges of Al, N, O and C, respectively. From the energy filtered micrographs elemental maps were produced using the three-window technique. Figure 2a and 2b show N and C maps of the sample. In the N-map fluctuations can be observed close to the surface of the sapphire substrate indicating that the islands consist of AlN. The small signal above the N rich regions can be attributed to the presence of a thin layer of glue from the specimen preparation which can be seen from the C-map (Figure 2b). From the high resolution image of the islands we found that the [11-20] direction (the [0001] direction) of the AlN island are perpendicular (parallel) to the surface of the substrate.

4. Investigation of the overgrown sample
In a second step, we investigated the overgrown sample, which was prepared using FIB. Figure 3 shows a STEM micrograph of the structure after the overgrowth. From a first inspection one can see...
that the sapphire substrate is covered by a smooth layer of GaN [10], on which the nanorods are visible. From diffraction patterns we found that the layer was a-plane GaN, as one can expect from growth on r-plane sapphire. The Pt layer on top of the nanorods was deposited during specimen preparation in order to protect the nanorods from ion beam damage. With the 3 window technique elemental maps of Al, Ga and N were produced using the K-edge of Al and N and the L-edge of Ga. Figure 4 shows elemental maps of Ga, Al and N next to each other. In order to inspect closer the interface region between the sapphire and the a-plane GaN the same region was selected from each map and aligned according to the surface of the a-plane GaN layer. The inspection of the interface region in each map shows that a thin layer exists containing Al, Ga and N atoms. This was also done with an O map showing that the O atoms are confined to the sapphire substrate. HRTEM showed that only wurtzite type material is present on top of the sapphire substrate. Therefore, we conclude that the layer consists of wurtzite type AlGaN. In section 3 AlN islands were found at the surface of the sapphire but could not be revealed in the overgrown sample. This could be explained by a dissolution of the AlN islands or by the averaging effect through AlN islands and overgrown a-plane GaN.

Figure 3. STEM micrograph of structure after the overgrowth. On the sapphire substrate an a-plane GaN layer has formed and nanorods are on top of the a-plane GaN. The Pt on top of the nanorods is due to specimen preparation.

Figure 4. Elemental maps of Ga, Al and N. In order to inspect closer the interface region between the sapphire and the a-plane GaN the same region was selected from each map and aligned according to the surface of the a-plane GaN layer (upper dashed line). The inspection of the interface region in each map shows that a thin layer exists containing Al, Ga and N atoms (lower dashed lines). The layer seems to be laterally homogenous.

Figure 5 shows a scanning transmission electron microscopy (STEM) Z-contrast image of the structure. One can clearly distinguish between the sapphire substrate and the a-plane GaN layer on top of the substrate. In between the a-plane GaN and the sapphire substrate, a thin layer exhibiting a lower intensity is visible stemming from the AlGaN layer detected using EFTEM. However, also the HAADF image did not show significant fluctuations within the AlGaN to show the existence of islands at the interface after overgrowth. Figure 5 also shows the nanorods on the a-plane GaN layer, which reduce within the a-plane GaN towards the a-plane GaN/sapphire interface.

The origin of the nanorods appears to be within the a-plane GaN layer, but could also be at the a-plane GaN/sapphire interface as proposed by Aschenbrenner et al. [10]. Due to TEM specimen preparation parts of the nanorods may be truncated in such a way that the origin of the rods is outside of the TEM specimen. To clarify the position of the origin and the faceting of the nanorods STEM tomography and closer investigations of the early stages of the nanorod growth have to be done next. From thickness maps we could show that the darker regions close to the a-plane GaN/sapphire interface are due to voids within the a-plane GaN layer. We further investigated the epitaxial relationship between the
nanorods and the a-plane GaN using selected area electron diffraction (SAD), convergent beam electron diffraction (CBED) and HRTEM. We found that the [1-100] direction of the rods was aligned parallel to the [0001] direction of the a-plane GaN and that the [11-20] directions of both materials were parallel to each other. We applied CBED in order to determine the polarity according to the method proposed by Mader and Recnik [11]. It was found that the growth direction of the rods was the [000-1] direction which was parallel to the [1-100] direction of a-plane GaN. This is in agreement with the common finding that GaN grows N-polar during MBE. Using different dark-field images we also investigated the defect structure in the nanorods. We only found one screw dislocation in one of the rods, suggesting that the defect density is very low. This agrees with the result from photoluminescence [9] where the nanorods showed no yellow luminescence.

Figure 5. STEM Z-contrast image of the structure. The a-plane GaN layer and the nanorods are well distinguished from the sapphire substrate. The nanorods thin towards their origin, which seems to be within the a-plane GaN layer. However, Aschenbrenner et al. [9] proposed that the rods originate on top of the AlN islands. The Z-contrast images did not clearly show where the origin of the rods are, since the rods could be also truncated by specimen preparation and the origin could be outside of the TEM specimen.

5. Conclusion
In summary, we have determined the epitaxial relation between catalyst- and mask free grown GaN nanorods and the surrounding a-plane GaN. The rods exhibited an excellent crystalline quality. However, we could not yet completely clarify the origin of the nanorods.

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