GaN nanostructures grown on Si(111) by PA-MBE via droplet epitaxy: SEM and HRTEM study

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Abstract. In this report, we demonstrate that the use of GaN seeding layer prepared by droplet epitaxy technique using plasma assisted molecular beam epitaxy (PA-MBE) can lead to the epitaxial stabilization of GaN nanostructures with different lattice orientations. From the high-resolution transmission electron microscopy (HRTEM) studies, it is shown that (111) faceted zinc-blende (ZB) GaN islands act as the fast nucleation sites for the growth of GaN nanowires (NWs) with hexagonal wurtzite (WZ) structure. Further GaN nanostructure morphology depends on lattice orientation of the seeding island. It will be shown that further intergrowth and coalescence of GaN NWs lead to changes in the mutual orientation.

1. Introduction
Growth of group-III nitride nanostructures, such as GaN NWs, attracts a lot of attention due to their importance both in fundamental research and in development of future optoelectronic nano-scaled devices [1]. Small contact area with the substrate, commonly observed for the epitaxial nanostructures, can provide efficient lateral strain relaxation and defect-free NW growth, as it has been demonstrated for GaN NWs [2]. Formation of GaN NWs on Si complies the self-induced growth mechanism. This technique does not involve the substrate surface patterning and catalyst particles use which makes it attractive both from technological and further device application points of view. In this study the Ga-droplets deposition on the silicon surface prior to the NWs growth was used [3,4]. We demonstrate that this technique can lead to synthesis of inclined WZ GaN NWs, formed on (111)-facets of GaN ZB nanoislands.

2. Experimental
GaN nanostructures were grown by PA-MBE using Veeco GEN-III MBE machine equipped with an inductively coupled RF-plasma Riber nitrogen source and group-III material solid source. Silicon (111) p-type wafers with a 4° miscut oriented towards ⟨1-1 0⟩ were cleaned using Shiraki method and used as substrates. Ga droplets were formed using Ga deposition on the reconstructed Si (111)-(7x7) substrate surface at 200°C. The seeding layers had an equivalent thickness in the range of 0.6-2.5 ML controlled in-situ with RHEED by monitoring the Ga-(3x√3)R30° surface reconstruction, corresponding to the 0.3ML of Ga [4]. In the following the droplet layer was exposed under the flux of activated nitrogen and annealed up to GaN growth temperature (790-810°C).
GaN growth was carried out under nitrogen rich growth conditions generally leading to the formation of vertical NWs [5].

Structure and morphology of the synthesized nanoheterostructures were studied with scanning electron microscopy (Zeiss SUPRA 25-30-63) and high-resolution transmission electron microscopy (HRTEM) using a JEOL 2100F microscope (200kV). The samples for HRTEM studies were prepared by standard methods involving ion sputtering at the last stage.

3. Results
Surface morphology of GaN nanostructures grown using 0.6 ML thick seeding layer is presented on SEM image (Fig.1). Cross section view is presented on TEM image (Fig.2 a). Analysis of SEM and TEM images shows the presence of nanostructures with different morphology, namely tripods, vertical and inclined NWs. Closer view of vertical and inclined NWs is presented on (Fig.2 b, c).

**Figure 1.** SEM images of the GaN nanostructures, top view.

HRTEM study of the synthesized structures (see Fig. 2 b) demonstrates the presence of a nanometer-sized (~5nm) nucleation core at the base part of inclined NWs [6]. Close-up view of its central part is presented on Fig.3. Notably, there is no any nucleation particles at the base of vertical NWs (Fig.2 c).

**Figure 2.** HRTEM images of GaN nanostructures, cross section view a) distant view b) pair of inclined NWs protruding from the common seeding particle c) vertical NW
Fast Fourier transform (FFT) analysis of TEM image was used to investigate crystal structure and lattice orientation of GaN nanostructure is presented on the Fig. 3. FFT analysis demonstrates that the crystal structure of the nanostructure core is different from its NW-shaped branches: FFT pattern of the core corresponds to the cubic stacking sequence of the close packed planes, whereas pattern of branches corresponds to the hexagonal structure [7], [8]. FFT images from inclined NWs and their core correspondingly matched with schematic model of reciprocal space nodes (represented with dashed circles) of the hexagonal [11-20] and cubic [1-10] axis zones.

![Figure 3](image)

**Figure 3.** Fast Fourier transform of TEM image of the inclined NWs and common core matched with schematic model of reciprocal space nodes

It can be seen, that ZB core (001) crystalline plane is oriented parallel to the substrate surface (Fig. 3). Apparently, {111} ZB planes serve as nucleation sites for WZ NWs. Therefore, geometrically expected mutual angle between c-axis of coalescing NWs is 109.47°, corresponding to the angle between [111] and [-1-1 1] axis of ZB origin. However, FFT analysis shows that the angle equals ~116°, meaning the formation of energetically favorable grain boundary plane (-1103) instead of the geometrically expected (-3308), which requires a change in the mutual orientation, although there is no visible lattice distortion on FFT image of ZB core.

### 4. Conclusions

In this work growth of GaN NWs on Si (111) substrate by PA-MBE using droplet epitaxy technique was studied. It was found that Ga droplet nitridation leads to formation of epitaxially oriented ZB GaN nanoislands with {001} planes aligned parallel to Si(111). It was shown that during further GaN growth, {111}-facets of GaN nanoislands play a role of nucleation sites for inclined GaN nanocolumns. It was also found that coalescence of the inclined NWs can lead to change in the mutual orientation of NWs and core.
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