Epitaxial GaN nanotripods: morphology and crystal structure

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Abstract. Abstract. The goal of this work is to study the morphology and crystal structure of novel GaN epitaxial nanostructures (Y-shape nanotripods) grown on silicon (111) by plasma assisted molecular beam epitaxy (PA-MBE). Prior to the nanowire synthesis epitaxial GaN nanoparticles were formed on the Si(111) via nitridation of Ga nanodroplets on Si substrate surface (droplet epitaxy technique). Effect of the seeding layer on further nanostructure growth, GaN/Si heterointerface formation, crystal structure and morphology is studied by use of different microscopic techniques.

1. Introduction

Growth of group-III nitride nanostructures, such as GaN nanowires (NWs), attracts a lot of attention due to their importance both in fundamental research and in development of future optoelectronic nano-scaled devices [1]. Growth of GaN NWs on Si attracts a lot of attention due to several facts. 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]. Another feature of the GaN NWs formation on Si is the self-induced technique. This technique doesn’t involve the substrate surface patterning and catalyst particles use which makes it attractive both from technological and further device application points of view.

Majority of today’s GaN on Si growth technologies inevitably leads to formation of thin silicon nitride (Si\textsubscript{n}N\textsubscript{3}) layer on the substrate surface. In our study we attempted Ga-droplets deposition on the silicon surface. In this report, we will demonstrate that use of the GaN seeding layer prepared by the droplet epitaxy [3,4] can lead to formation of oriented arrays of tripod-shaped nanoparticles (tripods) along with NWs. Previously it was reported, that GaN nanotripods and hexapods can be formed during HVPE on c-plane Al\textsubscript{2}O\textsubscript{3} and PA-MBE [5] on pillar patterned GaN templates [6]. In the papers above, the seeding layers were not used. As far as the authors know, formation of tripod-shaped GaN nanoparticles in PA-MBE on Si deposition process is observed for the first time in our study. It worth to mention, that hexapod shaped nanoparticles were not observed in our work.

2. Experimental

GaN nanostructures were grown by plasma-assisted molecular beam epitaxy (PAMBE) in Veeco GEN-III MBE machine with use of Riber valved RF-plasma nitrogen source (13.56 MHz). Silicon
(111) p-type wafers with a 4° miscut oriented towards (110), cleaned with a Shiraki method were used as substrates. After thermal annealing (10 min @ 950°C) atomically clean Si surface was obtained as confirmed by observation of a 7x7 RHEED reconstruction pattern. Due to the 4° miscut high temperature annealing leads to coalescence of silicon surface steps, i.e. step bunching [7], and ordered step-terrace arrays appear on substrate with average terrace width of ~80 nm.

To monitor the atomic or molecular beam equivalent pressure (BEP) from nitrogen source or effusion cells conventional ion gauge was used. Total nitrogen BEP was in the range of 2.3x10⁻⁷ Torr. To maintain nitrogen-rich (N-rich) conditions Ga source BEP was kept sufficiently small - 1.2x10⁻⁸ Torr. Ga source BEP was kept constant during deposition of the seeding layer and growth process.

In order to obtain direct nucleation of GaN on Si, deposition of the Ga droplet seeding layer was performed prior to ignition of the RF-plasma. In the following stage droplet layer was annealed under the nitrogen activated nitrogen flux up to growth temperature (790-810 °C). After the nitridation further deposition of GaN was carried out.

Ga droplets were formed by exposing the reconstructed Si (111)-(7x7) substrate surface at 200 °C to a Ga molecular beam. Equivalent Ga thickness was estimated by monitoring the Ga-induced surface reconstruction with RHEED. It is known that deposition of 0.3 ML of Ga leads to formation of \( \sqrt{3} \times \sqrt{3} \) -R30° Ga-reconstructed surface [8] and deposition of 0.6 ML leads to formation of 6.3x6.3-Ga induced superstructural phase [9] (1 ML here means 6.81·10¹⁴ atoms/cm², the surface density of the truncated (111) plane of bulk Si) [10]. Seeding layers with equivalent thickness in the range of 0.6-2.5 ML were deposited while monitoring the resulting surface reconstruction in-situ with RHEED. Diffuse semi-circular halos of liquid Ga was observed for the exposition with equivalent thickness more than 1.5 ML. Relatively low substrate temperature and small Ga exposure were chosen to obtain dense arrays of nano-droplets [11].

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. **GaN tripod-shaped nanostructure**

It is well known that deposition of GaN on Si (111) substrate in N-rich conditions usually lead to formation of vertical GaN NWs [2]. Our growth series revealed that use of nano-droplet seeding layer can result in formation of well oriented tripod-shaped GaN nanoparticles grown along with NWs on Si (111) substrate. SEM images of the obtained structures are presented in Fig. 1. According to the literature [5,6] tripod and hexapod formation were observed under the certain conditions, and transition between GaN nanocolumn axial growth and tripod formation can be observed [6] while in our research both NWs and tripods growth can occur simultaneously and surface densities for both NWs and nanotripods strongly depend on equivalent thickness of the seeding layer and growth parameters. As can be seen from top view SEM images (Fig. 1) tripod-shaped nanoparticles have planar structure and are formed with three equally sized elongated branches lying at an angle of 120° to each other. Single and double branched V-shaped GaN nanoparticles can be found along with the tripod-shaped ones. According to [5] GaN tripod growth is related with the formation of nanoparticle in the zinc blende (ZB) phase and further nucleation and growth of the wurtzite (WZ) nanorods on the \{111\} facets of the ZB core. We assume that in our case formation of small ZB nanoparticles occurs during the seeding layer growth in droplet epitaxy process.

According to analysis of SEM images tripod-shaped nanoparticles demonstrate several preferential in-plane orientations which correspond to alignment of the nanoparticle branches along with the \(<\overline{1}10>\) and \(<\overline{1}1\overline{2}>\) directions of Si. The approximate particle orientation is determined by comparing the directions of branches and wafer primary flat (or cleavage direction). Crystal rotational
twinning corresponding to 180° rotations around normal to the Si substrate and mosaic spread of in-plane orientation in the range of ±5° are observed. In-situ registered RHEED pattern shows six-fold symmetry corresponding to the twinned wurtzite structure.

Figure 1. Top SEM images of tripod-shaped GaN on Si substrate

More detailed analysis of crystal structure and morphology of the tripod-shaped nanoparticles was performed with HRTEM. As can be seen from the cross-section TEM-images (Fig. 2 a) direct Si-GaN heterointerface cannot be obtained: a thin (~1.5nm) amorphous layer is observed at the heterointerface. Formation of the SiNₓ layer under the nanostructures takes place most probably during the seeding layer formation: redistribution of the Ga species from the droplets and subsequent exposure of the silicon surface to the nitrogen flux. Another process leading to the substrate surface nitridation is volume diffusion of nitrogen atoms from the GaN into the Si surface layer [15].

Figure 2. TEM images of the synthesized nanostructures: a) vertical NW, b) inclined NW, c) HRTEM of the bottom part of inclined NW

According to the RHEED and HRTEM nanoparticles have a hexagonal wurtzite GaN crystal structure. GaN c-planes (0001) can be seen on close-up image in Fig. 2 (c). Linear contrast features at the HRTEM image (Fig. 2 (b)) are related to planar defects perpendicular to the (0001) direction, in particular, stacking faults in the hexagonal lattice caused by disorder in stacking sequence and monolayer-thick inclusions of zinc-blende GaN polytype.

In Fig. 2 one can find TEM (b) and close-up HRTEM (c) images of inclined nanocolumns which are forming the branches of nanotripod. According to the HRTEM image (Fig. 2 c) zinc-blende phase can be found in the central part of the tripod-shaped island.

We assume, that zinc-blende GaN nanoparticle can be formed during seeding layer formation by droplet layer epitaxy. It is known [18-19], that low temperature and excess Ga can lead to the
nucleation of zinc-blende GaN islands. After formation lateral \{111\} facets of the zinc-blende nanoislands play role of nucleation sites and formation of inclined nanocolumns and nanotripods islands occurs.

4. **Conclusions**

Tripod-shaped nanoparticles (nanotripods) were grown on silicon (111) PA-MBE with use of seeding layer prepared by droplet epitaxy. Nanotripods demonstrate several preferential in-plane orientations with twinning corresponding to 90° and 180° rotations around normal to the Si substrate. The direct Si-GaN heterointerface without SiN\(_x\) layer under the nanostructures cannot be obtained even with use of Ga-droplet seeding layer. GaN nanoparticles forming the seeding layer crystallizes in zinc-blende phase and acts as a seed for further growth of inclined NWs or tripod-shaped nanoparticles which are crystallized in hexagonal wurtzite GaN crystal structure.

**Acknowledgements**

This work was supported by the Russian Foundation for Basic Research (grants 16-32-00560, 15-02-06839), Council for grants of the Russian Federation President (grant MK-3632.2017.2), grants 16.2593.2017/4.6, 16.2593.2017/8.9 of the Ministry of Education and Science of the Russian Federation and Leading universities of the Russian Federation grant 074U01.

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