Effect of Ga seeding layer on formation of epitaxial Y-shaped GaN nanoparticles on silicon

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Abstract. Silicon and aluminium nitrides, commonly used as buffer layers for GaN growth on Si are wide gap insulators, preventing barrier free charge-carrier transport across the heterojunction and limiting the functionality of GaN-on-silicon technology. In this work we explore possibility of direct growth of GaN on Si nano-heterostructures by PA-MBE with use of Ga-nanodroplets as seeds. It is demonstrated that use of seeding layer can result in formation of Y-shaped planar GaN nanoparticles (GaN tripods) along with commonly observed GaN nanowires. Growth mechanism, morphology and structural characterization of GaN/Si nano-heterostructures is discussed.

1. Introduction

Synthesis of group-III nitride nanostructures attracted a lot of attention due to their importance both in fundamental research and potential application in future opto-electronic nano-scaled devices [1]. Geometric confinement and reduced dimension effects, can significantly affect physical properties of nanostructures, as well as promote formation of defect-free hetero-interfaces and provide efficient strain relaxation even on highly mismatched substrates, as it has been demonstrated for epitaxial growth of GaN nanowires on Si [2]. The latter nanostructures are nowadays object of growing interest not only due to high potential of GaN-on-Si technology, but also because of functional GaN/Si heterojunction realization possibility, as it was shown in our previous work [3]. However, majority of today's GaN-on-Si technologies involves formation of silicon nitride or aluminum nitride buffer layer [4], which are wide-gap insulators, prohibiting barrier free charge-carrier transport.

Thus, in this study we investigate possibility of direct growth of GaN/Si (111) nano-heterostructures by plasma-assisted molecular beam epitaxy (PA-MBE) with use of monolayer thick Ga-seeding layer yielding the formation of liquid Ga nano-droplets. Effect of the Ga seeding layer on GaN structures growth and morphology is studied by use of reflection high-energy electron diffraction (RHEED), atomic force (AFM), scanning (SEM) and high-resolution transmission electron microscopy (HRTEM).
2. Experimental

GaN nanostructures were synthesized by PA-MBE in Veeco GEN-III MBE machine with use of Riber valved RF-plasma (13.56 MHz) source of activated nitrogen. To avoid presence of charged species and to increase angular uniformity of nitrogen flux, additional molybdenum aperture plate was installed in front of the source. 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) an atomically clean Si surface was obtained as confirmed by observation of a 7x7 RHEED reconstruction pattern and smooth surface morphology on AFM images. Total nitrogen BEP was in the range of 2.3x10⁻⁷ Torr. To maintain nitrogen-rich (N-rich) conditions Ga beam equivalent pressure (BEP) was kept sufficiently small - 1.2x10⁻⁸ Torr. Ga beam equivalent pressure (BEP) was kept constant during deposition of the seeding layer and growth process. In-growth n-type doping of GaN was done with Si effusion cell.

Structure and morphology of nanoheterostructures were studied with scanning electron microscopy (Zeiss SUPRA 25-30-63) and atomic-force microscopy (Bruker Bioscope Catalyst SPM). High-resolution transmission electron microscopy (HR-TEM) studies were carried out 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 and Discussion

3.1. Seeding layer formation

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 droplet layer was annealed under the nitrogen flow exposure up to growth temperature (790-810 °C) and 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. Such relatively low substrate temperature was chosen to obtain dense arrays of nano-droplets [5]. 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 √3x√3 -R30° Ga-reconstructed surface [6] and deposition of 0.6 ML leads to formation of 6.3x6.3-Ga induced superstructural phase [7] (1 ML here means 6.81 atoms/cm²; the surface density of the truncated (111) plane of bulk Si) [8]. Seeding layers with equivalent thickness in 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. Use of thicker seeding layers was avoided due to risk of eutectic Ga-Si solution formation, unwanted Si substrate doping with Ga atoms and melt-back etching of Si [4].

Figure 1. AFM images (900x900 nm) of the Ga nanodroplet layer with equivalent thickness of 1.6 ML deposited at 200 °C (a) before and (b) after nitridation.

Surface morphology of the Ga droplet layer with 1.2 ML equivalent thickness deposited on vicinal Si (111) is presented on AFM image in Figure 1 (a). As it can be seen from AFM images high temperature annealing of vicinal silicon surface leads to coalescence of surface steps, i.e. step bunching, and ordered step-terrace arrays with average terrace width of ~80 nm appear on the substrate surface.
Ga droplets are located at the surface steps edges and have a height about 2-3 nm, average distance between droplets is 100 nm, lateral resolution is limited by AFM tip size.

Surface morphology obtained after nitridation of Ga droplet layer with equivalent thickness of 1.2 ML is presented on AFM image in figure 1 (b). Comparing figure 1 (a) with figure 1 (b) we deduce that nitridated GaN nanoislands are also located at the surface step edges, but do not longer take spherical shape and present ring-like morphology with a 0.5-1 nm thick pit in the ring center. After nitridation islands possess decreased height (1-2 nm) and increased surface density comparing with Ga nanodroplets. Similar nanoring morphology can be obtained during droplet-epitaxy of GaAs [9] and related to localized III-V growth at the Ga-droplet edge. Surface morphology of the nitridated layer did not change after etching with the hydrochloric acid (HCl) aqueous solution, which confirms that there was no metallic Ga or eutectic Si-Ga solution on the surface after sample nitridation in our experiments.

### 3.2. Structure and morphology of Y-shaped GaN nanoparticles (GaN tripods)

Surface morphology of GaN/Si nanoheterostructures grown with use of seeding layer are presented on the SEM images shown in figure 2. It was found that use of nanodroplet seeding layer can result in formation of oriented Y-shaped (tripod) GaN nanoparticle arrays. As can be seen from top- and side-view SEM images (figure 2 (a) and (b)) Y-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 Y-shaped ones. Unfortunately, nanoparticle faceting cannot be resolved by means of AFM or SEM. In our case growth of vertical GaN nanowires are also observed, and as will be shown further, surface densities for both NWs and Y-shaped nanoparticles strongly depend on equivalent thickness of the seeding layer and growth parameters and as a consequence can be controlled. According to analysis of SEM images Y-shaped nanoparticles demonstrate several preferential in-plane orientations corresponding to alignment of the nanoparticle branches along the <110> and <112> directions in Si. Nanoparticles orientations are indicated in figure 2 (a) with colored solid Y-marks. Crystal rotational twinning corresponding to 180° rotations around normal to the Si substrate are indicated with dashed Y-marks. Mosaic spread of in-plane orientation in the range of ±5° is observed. According to the [10] similar tripod shaped nanoparticles were observed during hydride vapour phase epitaxy (HVPE) of GaN on sapphire (0001) substrates. The authors suggest that 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 [10].

**Figure 2.** (a) Top and (b) side view (45°) SEM images of GaN/Si nanoheterostructure surface; (c) and (d) HRTEM images of a single branched GaN nanoparticle.

More detailed analysis of crystal structure and morphology of the Y-shaped nanoparticles was performed with HRTEM. Cross-section images of the single branched GaN nanoparticle are presented in figure 2 (c) and (d). Presence of thin (~0.6 nm) amorphous layer at the heterointerface between GaN nanoparticle and silicon substrate can be clearly seen on HRTEM images. According to the transmission
electron microscopy microdiffraction (not presented here) nanoparticles have a hexagonal wurtzite GaN crystal structure. GaN c-planes (0001) can be seen on close-up image in figure 2 (d). Estimated angle between silicon (111) and GaN (0001) planes is around 72.8° which is close to value of the angle between (0001) and (11̅21) planes of GaN (72.92°) [10]. There is no any visible presence of the ZB-phase acting as a seed on the obtained HRTEM images. This can be related with small size of the core and sample preparation procedure. Linear contrast features at the HRTEM image (figure 2 (c)) 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 polype. On the other hand, visible planar defects can be caused by polarity inversion at domain boundaries.

3.3. The role of growth parameters on surface density and morphology of GaN/Si nanoheterostructures

3.3.1. Role of the seeding layer thickness. As was reported previously [12], [13] and according to our studies there is no direct correlation between surface density of the nanoislands of the seeding layer and density of the synthesized GaN nanoparticles. But despite that fact, it has been found that the effective thickness of the seeding layer significantly affects further GaN growth. Thus nitridated Ga-droplets are not acting as nucleation centres, but affect surface diffusion processes. For instance, at specific growth conditions (substrate temperature of 800° C and Ga BEP of 1x10⁻⁸ Torr) use of a seeding layer with an equivalent thickness less than 0.6 ML results in formation of vertical arrays of GaN NWs with low surface density (~1 µm⁻²) – nucleation and growth of Y-shaped nanoparticles are absent. For the seeding layers thicker than 0.8 ML the growth of Y-shaped nanoparticles appears. With an increase of the seeding layer equivalent thickness the surface density of the Y-shaped particles and NWs increases. It has been found that use of the seeding layer with an equivalent thickness of more than 2.4 ML, leads to formation of two-dimensional compact layer which significantly alters further growth of GaN.

Figure 3. (a),(b), (c) Top view SEM images (WxH: 660x740 nm) of GaN/Si nanoheterostructures grown at different Ga fluxes, (d) size and aspect ratio dependence on the Ga flux.

Figure 4. Top view SEM images (WxH: 2x1.5 µm) of GaN/Si nanoheterostructure surface grown at different substrate temperatures (a) 790° C, (b) 800° C, (c) 810° C.
3.3.2. Role of III- V fluxes ratio. As will be shown further N-rich growth conditions lead to Y-shaped particle branches elongation in the similar way as it affects growth of GaN nanowires [2]. Typical surface morphology of GaN/Si nanoheterostructures grown at different Ga BEP (1, 1.5, 2 × 10⁻⁸ Torr) is presented in figures 3 (a), (b) and (c). In general, increase of the Ga flux and excess of Ga leads to increase of the nucleation centers density, stimulates radial growth rate – and subsequently increases surface density of GaN nanoparticles with decrease in their dimensions (see graph in figure 3 d)). It was found that aspect ratio (relation between the length along the c-axis and width – lateral size of the c-plane) for the Y-shaped nanoparticles and NWs decreases with increase of Ga flow and can vary in the range of 2 to 1 and 3.5 to 2 respectively - see inset in figure 3 (d). Formation of coalescent two-dimensional compact layer occurs in case of Ga BEP larger than 2 × 10⁻⁸ Torr.

3.3.3. Influence of growth temperature. It is found that due to small values of the group III- and V-elements fluxes, growth of GaN nanostructures occurs only in a narrow temperature window. The SEM images of the GaN/Si heterostructures surface morphology grown at 790, 800 and 810° C are shown in figures 4 (a), (b), (c) respectively. It can be seen that at temperatures above 805° C, nucleation of Y-shaped nanoparticles can be suppressed almost completely, leaving only NWs on the surface. On the other hand, at a substrate temperature of 790° C and below, the surface density of the Y-shaped nanoparticles becomes so high that they begin to coalesce and form a continuous layer.

4. Conclusions
Formation of epitaxial arrays of Y-shaped GaN nanoparticles on Si (111) by PA-MBE is observed for the first time. Surface density, size and aspect ratio of the structures can be controlled by choosing the growth temperature and group III-, V- fluxes and the equivalent thickness of the seeding layer. It is shown that nucleation can be completely suppressed in favor of the NWs or Y-shaped GaN nanoparticles by choosing the appropriate growth conditions. Epitaxial relations for the Y-shaped nanoparticles are found - the (1121) plane of GaN is parallel to the (111) plane of the silicon substrate, <1126> direction of Ga can be aligned along the <110> and <112> silicon directions with a ±5° mosaic spread.

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