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Site-controlled growth of GaN nanorod arrays by magnetron sputter epitaxy

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ABSTRACT

Catalyst-free GaN nanorod regular arrays have been realized by reactive magnetron sputter epitaxy. Two nanolithographic methods, nanosphere lithography (NSL) and focused ion beam lithography (FIBL), were applied to pattern Si substrates with TiN_x masks. The growth temperature was optimized for achieving selectivity and well-faceted nanorods grown onto the NSL-patterned substrates. With increasing temperature from 875 to 985 °C, we observe different growth behaviors and associate them with selective insensitive, diffusion-dominated, and desorption-dominated zones. To further achieve site-specific and diameter control, these growth parameters were transferred onto FIBL-patterned substrates. Further investigation into the FIBL process through tailoring of milling current and time in combination with varying nanorod growth temperature, suggests that minimization of mask and substrate damage is the key to attain uniform, well-defined, single, and straight nanorods. Destruction of the mask results in selective area growth failure, while damage of the substrate surface promotes inclined nanorods grown into the openings, owning to random oriented nucleation.

1. Introduction

Gallium nitride (GaN) is a direct bandgap semiconductor, with technologically relevant properties such as: high thermal stability (when compared to common semiconductors), high electric breakdown field, and chemical inertness [1]. Due to this, it is already a well-established semiconductor used in solid-state lighting devices, [2,3] and in high-temperature as well as high-power operation electronic applications [4–6].

GaN nanorods (NRs) combine the intrinsic properties of the GaN material with distinctive features induced by the reduced dimension and the NR geometry like: increased photon extraction efficiency, high crystal quality and strain relaxation [7,8]. The NRs fabrication processes include: self-assembled (SA), [9] catalyst-induced, [10] and selective-area growth (SAG) [11]. SA processes are characterised by a random growth of NRs leading to non-uniform properties and hindering device processing [12,13]. This can be overcome by SAG of NRs, using pre-patterned substrates by lithographic methods such as: photolithography, [14] electron-beam lithography, [15] focused ion beam lithography (FIBL), [16] nanoimprint lithography [17] or nanosphere lithography (NSL) [11]. The usage of mask layers, limits the growth to specific areas, resulting in ordered NR arrays with controllable sizes, shapes, positions, and densities.

The dominating techniques used for the epitaxial growth of GaN NRs are metal-organic chemical vapor deposition [18–20] and molecular-beam epitaxy [21–23]. However, magnetron sputter epitaxy (MSE) of GaN and related alloys, has gained momentum in recent years [24–26]. MSE is a versatile, industrially-mature method, and a series of high-quality structures which include SA [27] and SAG [11] NRs, and thin films [28] have been reported.

In this paper we demonstrate the growth of GaN NR arrays on Si substrates pre-patterned by two techniques: NSL and FIBL, employing TiN_x mask layers. GaN NRs were grown by reactive MSE onto these patterned substrates. A temperature-dependent series was grown onto NSL-patterned substrates in order to attain the optimum growth conditions to achieve selectivity and well-defined morphology. NSL is a simple, fast and cheap method that offers the possibility of obtaining size-uniform NRs. However, it does not offer the control on the size, position or density. To circumvent this, we transferred the growth parameters onto FIBL-patterned substrates. FIBL enables accurate control of position and size of the openings that are prepared in the mask layer, enabling the growth of uniform, well-defined NR arrays. For this, the optimum patterning conditions were tested for obtaining well-defined openings in the TiN_x mask and for minimizing substrate damage. FIBL optimization included tailoring of the milling current (2–50 pA) and milling time (5–50 s). Low milling currents are necessary to avoid damage to the whole mask layer. A minimum ion beam induced substrate damage is achieved at low currents of 2 pA and short milling

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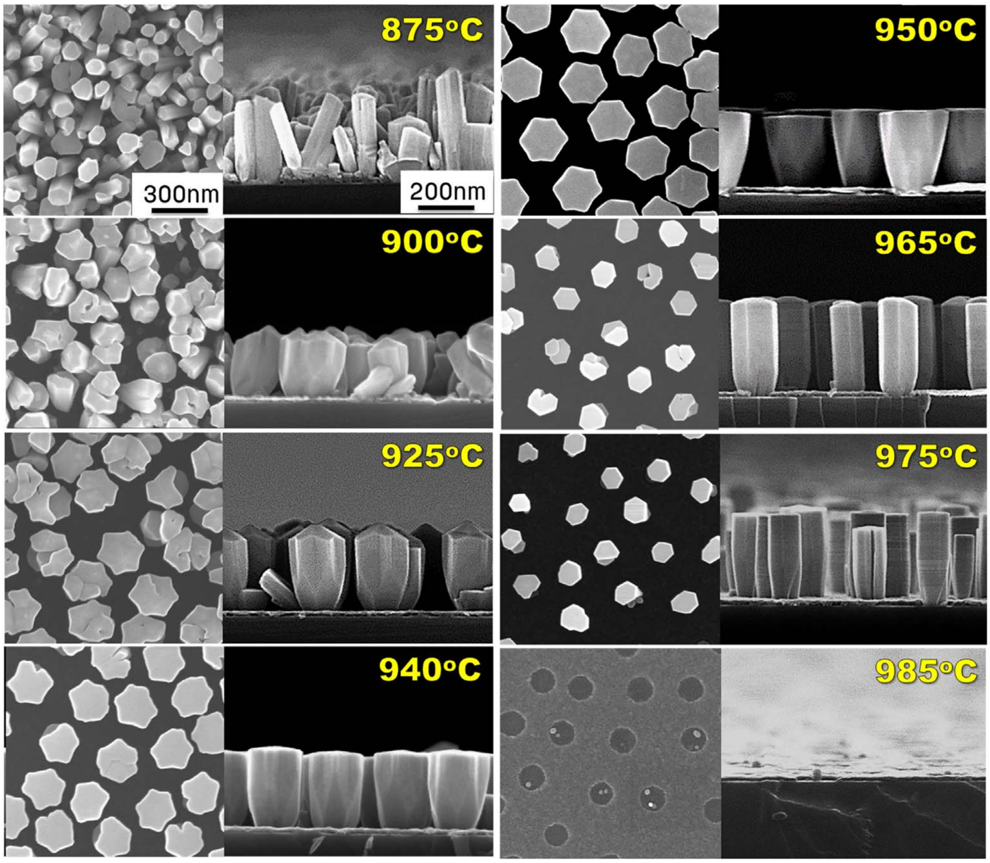

Fig. 1. Top- and side-view SEM images of GaN NRs grown on NSL-patterned Si substrates at different temperatures. The figures have the same scale.

times. Longer milling times induce extensive substrate damage as observed by scanning transmission electron microscopy (STEM) and energy-dispersive x-ray spectroscopy (EDX). The resulted rough substrate surface conducts to the growth of multiple, tilted NRs inside one opening. Growth temperature optimization was also performed. At lower growth temperatures (950 °C) nanostructures resulted from the coalescence of multiple, tilted, and irregular NRs are observed. The tilting of the NRs is reduced when increasing the growth temperature to 980 °C resulting in hexagonal, mostly single, straight NRs with uniform sizes and controlled position.

2. Experimental details

The growth of GaN NRs was performed by direct current-MSE in an ultrahigh vacuum chamber with a base pressure of 1.33×10^{-6} Pa. A liquid Ga (99.99999% pure) target, placed in a stainless-steel crucible is used as a sputtering target. Details may be found elsewhere [29]. The NRs deposition on the pre-patterned Si(001) substrates was optimized by changing the growth temperature in the interval 875–985 °C. The working pressure was kept constant at 2.67 Pa N_2.

Two patterning methods were employed: NSL and FIBL. In both cases a TiN_x layer was employed as a mask layer with thicknesses of 20 nm and 6 nm for the NSL- and FIBL-patterned substrates respectively. Details about the NSL process can be found in our previous work [11]. FIBL was performed using a Carl Zeiss Cross-Beam 1540 EsB system. A 30 keV Ga^+ ion beam was used for patterning. The milling current (2–50 pA) and milling time (5–50 s) were tailored in order to achieve the optimum patterning conditions. The sample surface was tilted 54° from the horizontal and placed at 5 mm working distance.

Sample morphologies were characterized in side- and plan-view with a Zeiss Leo 1550 field-emission gun scanning electron microscope (SEM), operated at 10 kV. Microstructural and elemental analysis were performed by STEM and energy-dispersive x-ray spectroscopy (STEM-EDX) using the double-corrected Linköping FEI Titan^3 60–300, operated at 300 kV.

3. Results and discussion

3.1. Growth optimization on NSL-patterned substrates

To study the temperature effect on the morphology of the GaN NRs and achieve the optimum growth conditions, a temperature-dependent growth series was prepared. Fig. 1 presents the top- and side-view SEM images of GaN NRs grown on NSL-patterned Si substrates at 875, 900, 925, 940, 950, 965, 975, and 985 °C. As it can be seen, the increase in temperature results in improved selectivity of the SAG GaN NRs. At temperatures of 875 °C and lower, selectivity is not achieved, and NRs randomly grow both on the mask and inside the openings. The NRs grown at these temperatures are characterized by accentuated size nonuniformity and a large deviation from verticality is observed in the case of the NRs that nucleate onto the mask layer. Increasing the growth temperature to 900 °C leads to a tendency to grown only inside the openings, however, growth on the mask is still visible. The improved selectivity results also in a smaller NR length variation. The NRs have the tendency to develop a pencil-shaped top and are highly coalesced. At 925 °C selectivity is achieved, and the side-view SEM shows faceted NRs that grow inside the openings and the coalescence is reduced. When the growth temperature is raised further, selectivity is maintained and the NRs shape becomes better defined with an improved aspect ratio. Starting from 940 °C the NRs develop a flat top-shape and better defined hexagonal cross-section. The sizes of the samples grown at 925, 940, and 950 °C are similar. At 965 °C, the correlated increased diffusion length conducts to a reduced growth along semipolar direction and *c*-axis growth becomes the dominant growth direction after less than 100 nm height. By further increasing the growth temperature to 975 °C, desorption of the Ga atoms is enhanced, and the NRs have a