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

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- Gallium nitride
- Magnetron sputter epitaxy
- Selective-area growth
- Nanorods
- Lithography
- Focused ion beam
- Nanosphere

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 TiNx 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] 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 TiNx 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 TiNx 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
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 N₂.

Two patterning methods were employed: NSL and FIBL. In both cases a TiNx 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 Titan³ 60–300, operated at 300 kV.

3. Results and discussion

3.1. Growth optimisation 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 non-uniformity 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
similar diameter, but a decreased length. Finally, at 985 °C, the desorption process becomes dominant and no NRs are formed, growth occurring only in the form of small seeds inside the openings.

Fig. 2 shows the temperature dependence upon the dimensional distribution (diameter – Fig. 2a, and length – Fig. 2b) of the GaN NRs. The data was obtained from the measurements performed on the side-view SEM images of the NRs. The sample grown at the lowest temperature, 875 °C, characterized by a self-assembled growth regime, presents the smallest diameters, of around 110 nm, and a length of ~ 310 nm. At 900 °C, the diameter of the NRs increases to an average of 220 nm, as an effect of the mixed self-assembled and selective-area growth regimes. The size of the opening starts influencing the morphology of the NRs, resulting in a larger diameter correlated with shorter and more uniform lengths of around 280 nm. By further increasing the temperature, the NRs selectively grow, only in the designated opening areas. The SAG combined with the characteristic diffusion-induced growth mechanism results in an improved aspect ratio of the NRs, with decreasing diameters and increasing lengths with increasing growth temperature. The average diameters are: 270, 250, 230, and 160 nm, correlated with increasing lengths of 330, 345, 360, and 400 nm, for growth temperatures of, 925, 940, 950, and 965 °C, respectively. By further increasing the growth temperature to 975 °C, desorption of the Ga atoms is enhanced, and the NRs follow the trend of decreasing diameters, to 130 nm, but with decreasing lengths also, to an average value of 330 nm. Due to the high desorption rate at 985 °C, only small nuclei of around 30–40 nm are formed and the openings are not
filled due to the limited supply of material.

3.2. Growth optimization on FIBL-patterned substrates

3.2.1. Milling current effect

The first step in optimizing the FIBL conditions consisted in finding the optimum milling current for patterning. The top-view SEM images of samples grown at 950 °C on substrates patterned with 50, 20, 10, 5, and 2 pA for 50 s milling time are presented in Fig. 3. It can be observed that a high milling current, of 50 pA results in the complete destruction of the mask layer so that NRs grow in a self-assembled mode directly onto the Si substrate. The self-assembled process, combined with the rough substrate surface created by the high milling current, results in a high density of non-uniform, tilted NRs. A decrease in the milling current to 20 and 10 pA induces less damage to the mask layer, so that the proximity effect is less pronounced, and portions of the mask remain unaffected. However, multiple tilted NRs are still formed on the exposed Si areas. At 5 pA, the pattern gets better defined, but the induced substrate damage results in the growth of multiple NRs with diameters smaller than 100 nm. When the milling current is reduced to 2 pA, the pattern is well defined. However, no single NRs are formed, but nanostructures with an average size of 350–400 nm, resulting from
the coalescence of multiple initial NRs.

3.2.2. Milling time and growth temperature effect

To further optimize the FIBL process we tried to find the shortest milling time that would induce a minimum substrate damage and still make it possible to obtain well-defined patterns. As suggested in the previous section, 2 pA current was used and the milling time was varied for: 30, 15, 10, and 5 s. The results can be observed in the SEM images of the NRs grown at 950 °C onto these pre-patterned substrates, presented in Fig. 4a. For 30 s milling time, the coalesced NRs result in the formation of irregular nanostructures, with sizes of 200–300 nm inside the openings. The decrease in milling time to 10–15 s leads to the coalescence of a smaller number of NRs which grow with a higher degree of verticality. Finally, when using 5 s milling time, a combination of single and coalesced NRs can be observed, with average sizes of 100–200 nm.

The mask layer used in the case of FIBL-patterned samples (6 nm) is thinner than that in the NSL case (20 nm). This allows an increase in growth temperature, since we can grow SA GaN NRs on Si substrates at temperatures up to 1000 °C [27]. The same series of samples, but deposited at 980 °C is presented in Fig. 4b. In this case, when using 30 s milling time, fewer NRs form inside the openings and we can observe the presence of single NRs also. Most of the openings contain 2–3 NRs that coalesce. This tendency is increasingly accentuated for shorter milling times, and mostly single NRs are obtained with a diameter of around 150 nm. Some of the NRs grow tilted and hexagonal faceting appears. Finally, the sample milled for 5 s presents a better morphology, featuring single hexagonal NRs of around 100 nm diameter and with improved verticality.

3.3. Compositional and structural characterization

3.3.1. Multiple nanorods

A thin TiNx mask layer was used in both cases. For the NSL-patterned samples, the growth temperature (in the range 875–985 °C) affects the morphology of the NRs. At lower temperatures, selectivity is not achieved and NRs randomly nucleate on both the mask layer and inside the openings. The increase in temperature results in improved selectivity of the SAG GaN NRs. Starting from 925 °C, the NRs develop strictly inside one opening. Softer milling conditions with low current and short time, improves the smoothness of the opening areas. These conditions, correlated with an optimum growth temperature, conduct to the formation of single, uniform, and vertical NRs which develop exclusively inside the opening areas.

3.3.2. Single nanorods

Fig. 7a shows the SEM image of the TEM lamella prepared by FIB from the sample grown at 980 °C onto the 5 s milled substrate, confirming the formation of single, straight and uniform NRs. The pattern consisted of 100 nm wide openings, spaced 500 nm distance from each other. These characteristics are maintained, resulting in ~550 nm long NRs with diameters in the range of 115–125 nm. The initial growth of one NR, starting at the interface was analyzed by STEM-EDX (Fig. 7b). The maps confirm the selective formation of a single GaN NR in the TiNx mask opening. The Si map, does not show extensive ion beam-induced substrate damage, but a smooth interface resulting in the formation of a single, straight NR.

This investigation of the FIBL process suggests that minimization of mask and substrate damage is a significant key for growing uniform and well-defined NR arrays. Ion beam-induced damage of the substrate surface promotes a random oriented nucleation of the NRs and results in the growth of multiple, tilted NRs inside one opening. Softer milling conditions with low current and short time, improves the smoothness of the substrate surface. These conditions, correlated with an optimum growth temperature, conduct to the formation of single, uniform, and vertical NRs which develop exclusively inside the opening areas.

4. Conclusions

We report on the selective-area growth of GaN NRs by reactive MSE. The controlled growth was achieved by employing Si substrates, pre-patterned by NSL and FIBL. A thin TiNx mask layer was used in both cases. For the NSL-patterned samples, the growth temperature (in the range 875–985 °C) effect upon the morphology of the NRs was studied. At lower temperatures, selectivity is not achieved and NRs randomly nucleate on both the mask layer and inside the openings. The increase in temperature results in improved selectivity of the SAG GaN NRs. Starting from 925 °C, the NRs develop strictly inside the openings. At higher growth temperatures, NRs with an improved aspect ratio are obtained, exhibiting reduced diameters and increased lengths. This trend is terminated at 985 °C, when the process is governed by desorption and no NRs growth occurs. The growth conditions were transferred on FIBL-patterned substrates, which offers better control on the NRs sizes and positions. The tailoring of the milling current and milling time during the FIBL process, helped to attain the optimum patterning conditions which resulted in the growth of straight, single NRs inside the pre-defined openings. High milling currents and long milling times induce ion beam damage in the substrate. The rough surface resulted in these conditions, leads to the growth of multiple, tilted NRs inside one opening. Finally, by reducing the substrate damage to the minimum with low milling currents and short milling times, the high growth temperature resulted in well-defined, single, uniform, and straight NRs.
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