Selective Area Epitaxy of GaN Stripes With Sub-200 nm Periodicity

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We present growth studies on gallium nitride (GaN) stripes with $\{10\bar{1}1\}$ *side facets grown on c-oriented GaN templates on sapphire. Via plasma enhanced chemical vapor deposition (PECVD), a 20 nm thick* SiO_2 *mask is deposited on top of the templates. Afterwards, a polymethylmethacrylate (PMMA) based resist is patterned with stripes oriented along the GaN a-direction by electron beam (e-beam) lithography. The stripes have a periodicity below 200 nm. The pattern is transferred via fluorine based dry-etching with an inductively coupled plasma (ICP) reactive ion etching (RIE) process. Any remaining resist is removed with oxygen plasma and the samples are cleaned before epitaxy. The influence of e-beam parameters, etching rates, etching agents and etching times on the pattern transfer and subsequent overgrowth is investigated. Semipolar InGaN/GaN quantum wells are deposited on the side facets of the nanostripes.*

1. Introduction

Selective area epitaxy (SAE) of GaN works very well for defect reduction [1, 2]. Even more, by aptly choosing mask patterns and growth conditions, three-dimensional GaN structures — rods, stripes, pyramids — with a high surface to volume ratio as well as non- or semipolar surface facets can be fabricated. These semipolar surface facets on c-oriented templates have great potential for cost-effective light emitters in the green wavelength regime [3]. Reducing them in size allows embedding, resulting in a flat sample surface which enables conventional device processing [4]. Furthermore, the sub-µm sized structures create new potential applications like photonic crystal emitters [5]. For the latter, the periodicity of the GaN nanostructures has to be in the range of the intended emission wavelength. For high refractive index materials, like GaN, periods below 200 nm are necessary for short wavelength emitters. Thus, optical lithography can no longer be used for patterning. Experimentally, the limits of this miniaturization are given by the precision of our growth mask patterning, setting very high requirements for the process control of lithography, dry and wet etching, as well as mask deposition and epitaxy.

2. Experimental

The GaN templates were grown with a horizontal metal organic vapor phase epitaxy (MOVPE) reactor with standard precursors TMAl, TMGa, and high purity ammonia. Purified nitrogen and hydrogen are used as carrier gases. The templates consist of 2 µm unintentionally doped GaN with an oxygen doped nucleation layer [6] on c-oriented sapphire templates. Then, a 20 nm thin layer of SiO_2 is deposited via PECVD and the samples are cleaned with acetone and isopropanol before lithography. For lithography, the samples are coated with a PMMA based resist before a conductive layer of germanium is deposited for better resolution. The electron beam patterning is performed with a Leica EBPG 5 HR. Afterwards, the Ge is removed and the resist is developed. For pattern transfer into the SiO_2 mask, a dry etching process inside an ICP RIE system with a mixed oxygen and carbon tetrafluoride plasma is used. Any remaining resist is removed with a pure O_2 plasma before the samples are either dipped into buffered hydrofluoric acid (HF) or cleaned with sulphuric acid and an aqueous KOH solution. The second epitaxial step to grow the GaN nanostripes uses the additional precursors TEGa and TMIn. The resulting nanostructures are investigated by scanning electron microscopy and photoluminescence (PL) spectroscopy.

3. Electron Beam Lithography Patterning With Sub-200 nm Periodicity

We choose a periodicity of 170 nm, which relates to the wavelength of a violet-blue light emitter inside GaN. The trench openings are intended to be below 100 nm in width to achieve a filling factor of approximately 1:1. There are several aspects to consider for such an undertaking. In the dimension perpendicular to the trenches, the resolution needs to be extremely high, requiring a very small and well focussed electron beam and a very thin resist. Furthermore, the distance between adjacent trenches is equally small, causing proximity effects of scattered electrons and increasing the unintended exposure of the resist between trenches [7, 8]. The length of the trenches, however, is intended to be at least in the milimeter range, with the ultimate goal of running over the whole wafer. This comes with an additional challenge. Previous studies with resist patterns structured by laser interference lithography (LIL) [9] have shown that any irregularities of the patterned mask, like swaying or frayed edges, directly result in inhomogeneities of the nanostripes and the quantum wells (QWs) deposited thereupon. Homogeneous QWs require highly regular masks [10]. Concerning the electron beam lithography, this results in the need for a quasi continuous exposure along the trenches, vastly aggravating the aforementioned proximity effect. Figure 1 illustrates these challenges. Optimal settings, giving results shown in Fig. 1e), were found to be 50 kV acceleration voltage, 280 pA electron current, 500 µC dosis and an aperture of 400.

4. Selective Area Epitaxy With Sub-200 nm Periodicity

In a first approach, growth conditions were based on the epitaxy of GaN nanostripes with 250 nm period, described in [11]. First, TMGa with a molar flow of 86 µmol per minute is used to grow a pure GaN stripe with $\{10\bar{1}1\}$ side facets. Then, an InGaN layer with $\approx 5\,\%$ indium is deposited to act as pre-well before a single QW with GaN barriers, followed by a thin GaN cap is grown. However, several specific aspects have to be taken into account for the sub-200 nm stripe masks patterned with electron beam

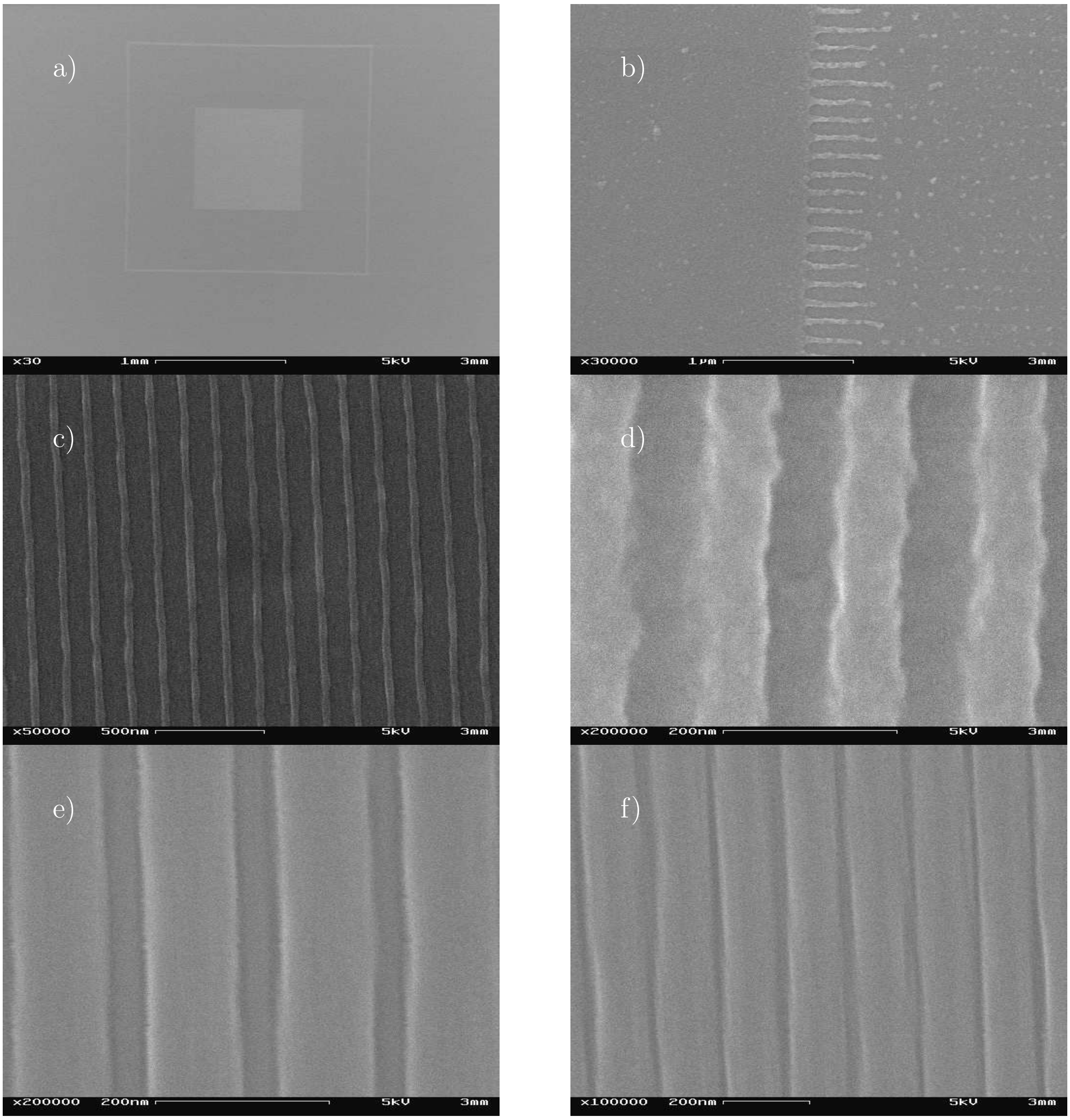

Fig. 1: Optimization steps concerning the e-beam lithography. The overall area is 0.64 mm^2 (a), the proximity of adjacent lines easily leads to overexposure (b), reducing the exposure leads to resist trenches (c), the point by point exposure causes warped, uneven edges (d), reducing the spot size and increasing the number of exposures to have a quasi continuous exposure gives the optimal result with straight lines which have even edges (e), too low exposure results in narrow trenches with remaining resist at the bottom of the trenches (f).

lithography. A good crystalline quality of the QWs depends on the stripes remaining separate [9] with coaelescence occuring after the QW growth. With the period being reduced by approximately one third, non-embedded (open) nanostripes need one third less growth time or growth rate, as compared to their 250 nm period counterparts. For samples structured via e-beam lithography, however, the area of growth is surrounded

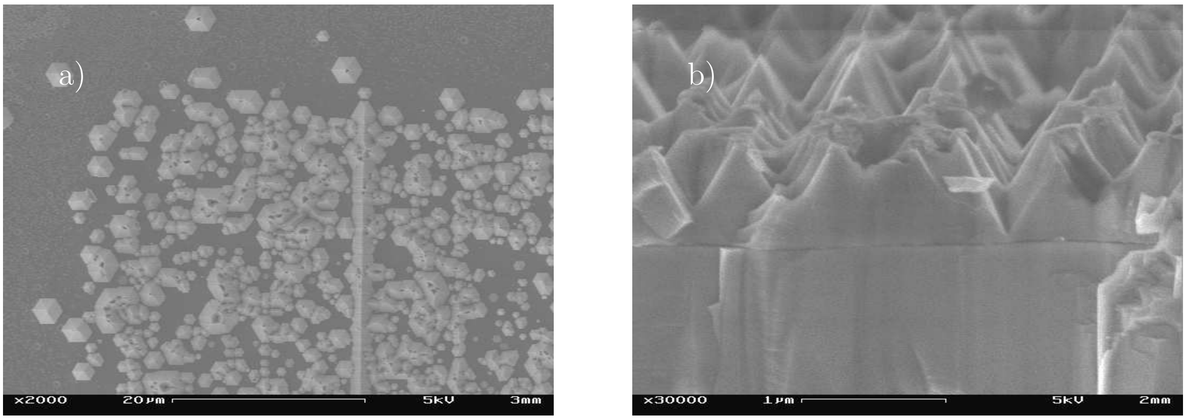

Fig. 2: SAE on templates patterned by electron beam lithography. Insuffcient homogeneity of the trench openings results in chaotic nucleation (a). Even with open trenches, a too high growth rate leads to the merging of neighboring stripes and the regular arrangement with 170 nm period is lost (b).

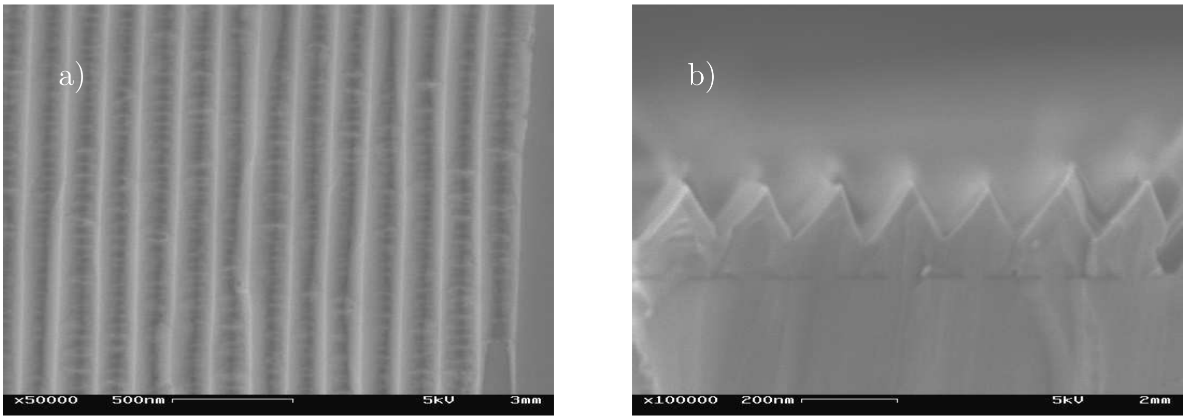

Fig. 3: Using extremely low material supply, homogeneous nanostripes could be realized. Top view shows slight deviations (a). In cross-section view, the homogenous size of the stripes and remarkably narrow ridges can be observed (b).

by vast masked areas where no growth occurs. Precursors diffuse from the completely masked area to the area where the mask is partly open [12], thereby immensely increasing the growth rate. Furthermore, it is critical to achieve homogeneously opened trenches by careful etching of the SiO_2 and sufficient exposure/development of the resist. Otherwise, nucleation will happen randomly. As soon as clusters are generated, stripe growth is no longer possible. More information on the effects of partly patterned masks can be found in [13]. Figure 2 shows the effects of inhomogenious trench openings and too high growth rate. The growth rate was drastically reduced — equivalent to ≈ 1 nm/min for unmasked templates — by using only TEGa instead of TMGa for the GaN growth and we were able to produce GaN nanostripes with QWs on semipolar $\{10\bar{1}1\}$ side facets on most of the patterned area, see Fig. 3. The top view reveals slight deviations, especially at the regions of beginning coalescence. The ridges are extremely sharp, well below 10 nm in width. Cross-section images reveal a mask opening of 50 nm and that the mask has been overgrown by 60 nm. The exact position of the QWs is not visible and would necessitate transmission electron microscopy measurements.

4.1 Quantum well luminescence

For this first successful experiment, the QW emission is detuned from its intended blue wavelength. Figure 4 shows the PL spectrum recorded at 300 K. The sample was excited with a HeCd laser emitting at 325 nm, the spectrum was recorded with a monochromator with 300 lines/mm grating and an electrically cooled charge-coupled device (CCD). The excitation spot has a diameter of ≈ 100 µm, so it averages over a relatively large area, compared to the stripes dimensions. The overall emission is broad but bright and exhibits several sharp resonances which can be attributed to guided modes being extracted due to the growth mask acting as photonic crystal [5].

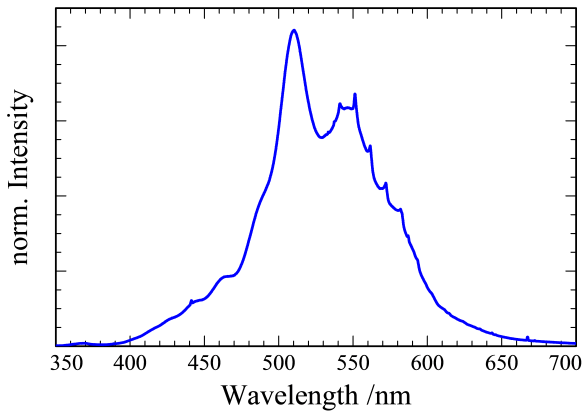

Fig. 4: PL spectrum taken at 300 K. The QW emits at 520 nm. At longer wavelengths, we observe sharp resonances related to the growth mask acting as photonic crystal.

5. Conclusion

Considerable optimization resulted in the realization of regular and homogeneous resist stripes with periodicities of 170 nm and a trench width below 100 nm. These patterns could be transferred to 20 nm thin SiO_2 layers acting as growth mask for SAE. InGaN/GaN nanostripes with triangular cross-sections and semipolar $\{10\bar{1}1\}$ side facets were presented and show QW luminescence, proving that sub-200 nm periodic GaN nanostripes for photonic crystal LEDs and distributed feedback laser diodes are feasible.

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