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Pulsed selective epitaxial growth of hexagonal GaN microprisms

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Abstract

Hexagonal GaN microprism structures were fabricated by pulsed selective epitaxial growth (SEG) under conditions that suppressed lateral overgrowth. Unlike previously reported pulsed SEG processes in which the precursor gas flow was modulated by valves, the approach reported here utilizes a flow geometry that produces a significant deposition rate only over the downstream portion of the 2 in wafer, which yields a pulsed deposition process when combined with substrate rotation. Hexagonal GaN microprism structures were grown on a GaN/sapphire substrate with a dielectric (SiO_x) mask of varying thickness (100, 150, and 200 nm) with circular openings ranging from 4 to 20 μm in diameter. Optimal structures were obtained with a SiO_x mask thickness of 200 nm and circular openings of 6 and 8 μm. The vertical growth rate of the hexagonal prism structures was ~50 nm/min, corresponding to the deposition of approximately six GaN bilayers (~1.7 nm) per cycle. This pulsed deposition process has advantages over etching processes for fabricating hexagonal microprisms for optical cavity devices, including elimination of etching damage and formation of crystallographic facets with a high degree of parallelism.

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1. Introduction

Direct-bandgap semiconductor materials such as GaAs, InP, and GaN have been widely utilized for opto-electronic devices. Such devices (e.g. waveguides and diode lasers) often require nearly atomically flat facets for optimal performance. For integrated devices, where cleaving is not an option, selective epitaxy growth (SEG) has advantages over standard etching [1], because it is difficult to achieve vertical, defect-free facets by etching. In addition to crystal facet quality, SEG allows localized control of the growth rate by varying the mask/opening ratio, which is essential

for the growth of three-dimensional waveguides and laser cavity structures [2,3].

In the late 1990s, GaN attracted interest as a semiconductor material for UV/blue photon emission applications, but the lack of an appropriate substrate resulted in GaN films with high defect densities. To circumvent this problem, several SEG techniques have been employed to obtain low defect density GaN epitaxial films through striped patterned openings [4–6]. Furthermore, Akasaka et al. discovered that GaN growth through circular openings resulted in hexagonal microprisms (HMP_r) or hexagonal micropyramids (HMP_y) depending on growth temperature and chamber pressure [7]. As compared to HMP_y structures, the HMP_r structure is more interesting for photonic resonance and stimulated emission due to the vertical prism facets that allow whispering gallery mode resonances with low internal losses [8,9]. However, reports

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of GaN HMPPr structures are few in number, due in part to the narrow growth window [10,11].

Akasaka et al. reported the first GaN HMPPr growth using organometallic vapor phase epitaxy (OMVPE) with a home-built vertical reactor [11]. The optimized HMPPr growth temperature was 1020 °C with a growth rate of $\sim 1 \mu\text{m/h}$, which is two or three times slower than standard film growth rates. Reduced growth temperatures (950–1020 °C) resulted in HMPPr structures with undesirable lateral overgrowth. Further temperature reductions ($< 950 \text{ }^\circ\text{C}$) enhanced the growth rate, exposing $\{1\bar{1}01\}$ inclined planes to form HMPy structures [10]. As an alternative to controlling the deposition and desorption rate of precursor gases via substrate temperature, as suggested by Akasaka et al. [11], pulsed selective epitaxial growth (SEG) was employed in this study. Pulsed SEG has been widely applied to GaAs opto-electronic device fabrication and is effective in preventing lateral overgrowth [12]. The technique is also called pulsed metal-organic epitaxy (PME) or flow-rate modulation epitaxy (FME) [3,12]. The interruption periods during pulsed SEG provide time for precursor or adatom migration, known to be effective for preventing lateral overgrowth [12].

2. Experimental procedures

Flow rates, substrate temperature and reactor geometry in an AIXTRON 200/HT OMVPE reactor were adjusted such that significant GaN growth occurred only over the downstream portion of a stationary 2" substrate (Fig. 1). A 50 nm GaN buffer layer was first deposited on sapphire at 650 °C and 132 mbar with a substrate rotation of 60 rpm followed by epitaxial growth at 1010 °C and 132 mbar without substrate rotation. Precursor gas flows for trimethylgallium (TMGa) and ammonia (NH_3) were 57 $\mu\text{mol/min}$ and 152 mmol/min , respectively. Hydrogen was used as a carrier gas to adjust the total flow rate to 8 slm.

In order to investigate the effect of pulsed SEG on patterned GaN epitaxy, GaN films with SiO_x masks were prepared by standard optical lithography and lift-off processes. Circular photoresist mesas of varying diameter (4–20 μm) were defined on three 1 cm \times 1 cm GaN/sapphire samples, followed by e-beam evaporation of SiO_2 pellets to fabricate SiO_x masks with varying thickness (100, 150, and 200 nm). Subsequent photoresist removal exposed the GaN film through circular windows in the SiO_x mask. The completed mask consisted of an array of circular openings of varying diameter with center to center spacing of 500 μm . The samples were then placed on the perimeter of a SiC-coated graphite "satellite" that was rotated between 25 and 60 rpm, which caused the samples to experience a periodic presence and absence of precursor gases. The effects of circular opening size and SiO_x mask thickness on GaN morphology were investigated by conducting simultaneous GaN growth (10 min) on three samples with varying SiO_x thickness. The GaN growth morphology

was subsequently characterized with a Hitachi S4800 field emission scanning electron microscope (SEM), a Digital Instruments Multimode atomic force microscope (AFM), and a PANalytical X'pert Pro MRD high-resolution X-ray diffractometer.

3. Results and discussion

Fig. 1 shows the resultant GaN coverage of a 2" sapphire wafer when the satellite was not rotated except during the 50 nm buffer layer growth period. Three distinct GaN growth regimes were observed by SEM and X-ray diffraction (XRD). The areal coverage for these GaN regimes can be varied by up to 10% when the chamber pressure is decreased or increased by ± 50 mbar, respectively.

XRD analysis indicated no detectable GaN in region A, indicating that even the thin buffer layer (50 nm) re-evaporated during high temperature growth. On the other hand, region C demonstrated smooth GaN epitaxy. The RMS roughness of the epitaxial film within region C was less than 3 nm as measured by AFM over a 1 $\mu\text{m} \times$ 1 μm scan area. Region B showed behavior intermediate to regions A and C, with GaN growth consisting of rough surfaces and hillocks. These results indicate that the precursor gas concentrations were monotonically increasing from gas inlet point to gas exhaust over the satellite.

When a GaN/sapphire sample (1 cm \times 1 cm) with a patterned SiO_x mask was placed in region C of Fig. 1(a), GaN growth without rotation yielded significant GaN growth along mask edges closer to the precursor gas inlet nozzles (Fig. 2). Similar to other epitaxial lateral overgrowth (ELO) results [4,13,14], the GaN grew laterally with vertical facets, partially covering the SiO_x mask film. There are several GaN islands on the downstream sides of the patterns; these features may be attributed to local turbulence in the gas flow. Based on these observations, a continuous supply of precursor gases results in substantial lateral overgrowth. Prior work on GaN has shown that the lateral overgrowth that occurs during continuous growth can be effectively suppressed by using valve-modulated SEG [15]. Thus, the resulting epitaxial growth features will resemble the mask patterns [3,12]. Note that the pulsed SEG approach in this study provides pulsed flow of both gases (TMG and NH_3), whereas conventional valve-modulated pulsed SEG provides continuous gas flow of NH_3 and pulsed gas flow of TMG (Fig. 3) [3]. Compared to valve-modulated pulsed SEG, the pulsed SEG process described here involves relatively long rise and fall periods (represented as τ in Fig. 3(b)).

The optimized satellite rotation rates for hexagonal microprism (HMPPr) GaN structures was found to be 30 ± 5 rpm. Assuming a satellite rotation speed of 30 rpm, a sample is exposed to a precursor supply (region C) for approximately 0.9 s, an interruption time (region A) of 0.7 s, and a rise/fall time (region B) of about 0.2 s. These parameters provide a growth/interruption ratio of ~ 1.6 , which is comparable to optimized GaAs pulsed-SEG [3].

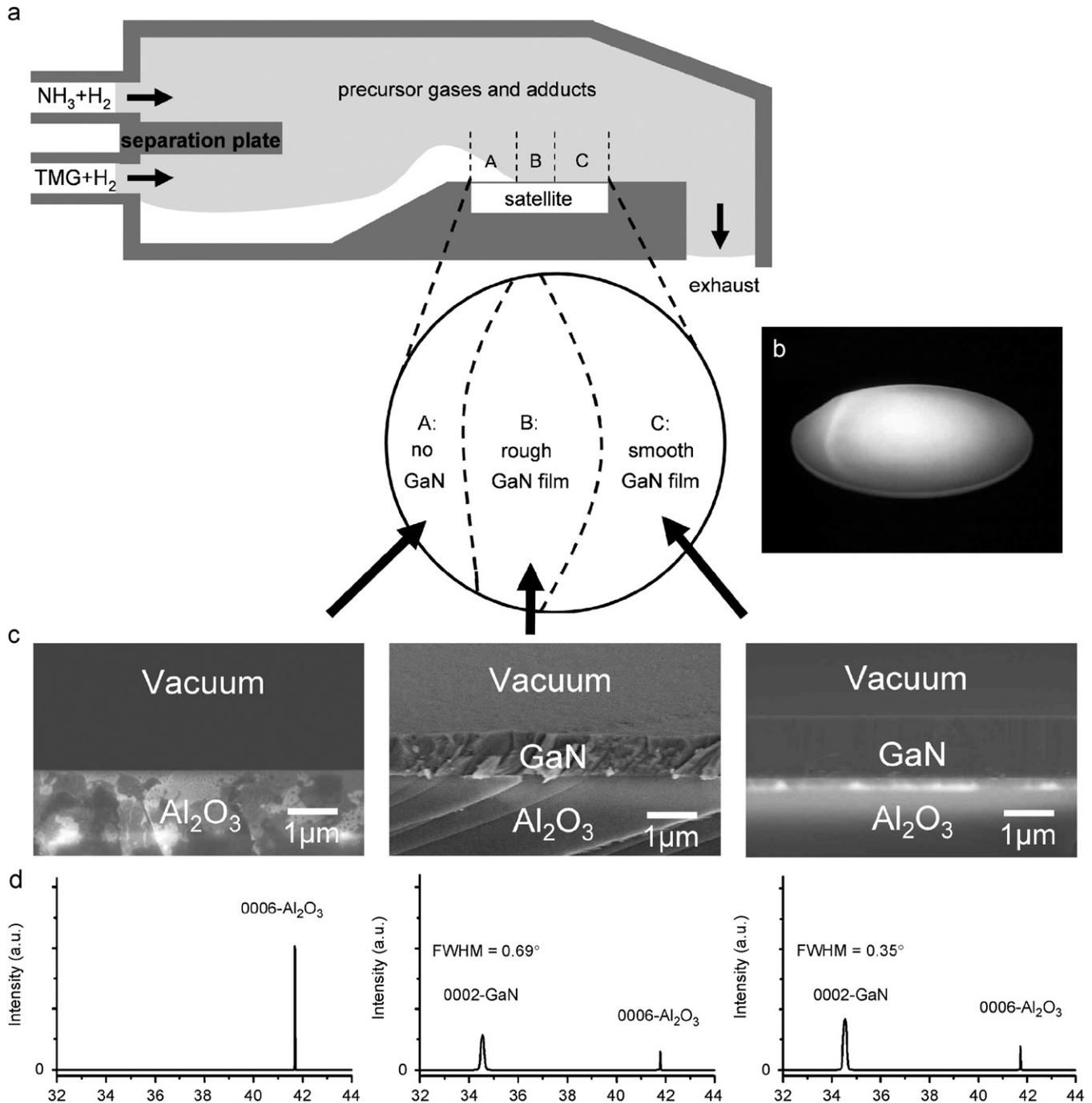


Fig. 1. (a) Schematic of the OMVPE reactor, showing approximate location of precursor gases and adducts and (b) optical photograph of a 2" sapphire wafer with three distinct GaN growth regions. (c) FESEM cross-section images from three regions and (d) the corresponding HRXRD $2\theta-\omega$ scans along with FWHM values from ω rocking curves.

Rotation speeds greater than 35 rpm resulted in increasing lateral overgrowth and the development of HMPy with exposed $\{1\bar{1}01\}$ planes. Rotation speeds lower than 25 rpm were not possible with the OMVPE system used for this study.

After 10 min of growth at 30 rpm, the height of GaN HMPs with 6 μm diameter was 510 nm, corresponding to a vertical growth rate of ~ 1.7 nm/growth cycle. Thus, each growth and interruption cycle allows six bilayers of GaN deposition in the $\langle 0001 \rangle$ direction. HMPs with 8 and

10 μm diameters had heights of approximately 500 and 482 nm, respectively, indicating a minimal dependence of growth rate on opening diameter.

The effect of SiO_x opening size and SiO_x mask thickness on GaN growth morphology is shown in the SEM images of Fig. 4. Pseudo-cylindrical structures were obtained under the conditions of Regime I while hexagonal prism structures developed in Regime II. The general trend is that increasing mask thickness and decreasing opening size lead to sharper faceting of the hexagonal structures. Optimal

conditions for HMPr structure fabrication are mask thickness/opening size combinations of 150 nm/6 μm, 200 nm/6 μm, and 200 nm/8 μm, for the range of mask thicknesses and opening sites investigated in this study. Fig. 5(a) shows an optimal HMPr structure with a corresponding side view (Fig. 5c). The dislocation densities

in the HMPr structures were not measured for the present study, but dislocation reduction will be critical for future fabrication of GaN-based HMPr light-emitting diodes and lasers. Ongoing work is focused on fabricating low dislocation density HMPr structures on high quality GaN substrates obtained by epitaxial lateral overgrowth.

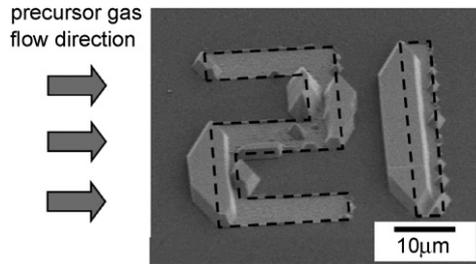


Fig. 2. SEM image of laterally overgrown GaN structure. The lateral overgrowth was dominant on the sides closest to the gas nozzle. Dashed lines represent original SiO_x mask opening.

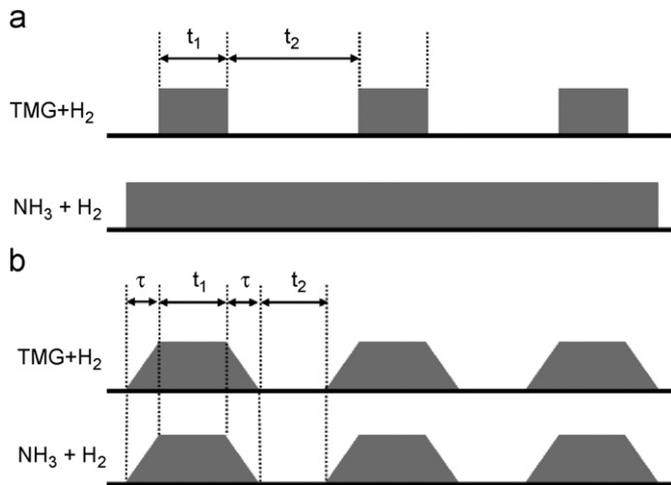


Fig. 3. Flow sequence of TMG and NH₃ for (a) valve-modulated pulsed SEG and (b) pulsed SEG in this study.

The vertical growth rate, normal to the (0001) plane, under pulsed-SEG was six GaN bilayers per growth cycle, which is more than one order of magnitude lower than that of epitaxial films or HMPy. One possible explanation for the slow vertical growth is the periodic interruption cycle, which enhances the reevaporation of atoms from incomplete bilayers. In addition, the interruption cycle assists stabilization of the {1 $\bar{1}$ 00} planes by promoting migration of adatoms from the side walls to the (0001) facet [10]. In the case of lateral growth, the lateral dimensions are restricted by the SiO_x mask boundary, which results in a hexagonal prism shape with stabilized {1 $\bar{1}$ 00} planes. The relationship between the morphology (hexagonal prism or pseudo-cylinder) versus the mask thickness and opening size is not yet fully understood. However, results from continuous (Fig. 2) and interrupted gas supply (Fig. 4) cases imply that interruption periods have a significant role in preventing lateral growth and balancing deposition and reevaporation.

In addition to HMPrs grown at 1020 °C/132 mbar, hexagonal pyramid structures (HMPy) were grown at reduced substrate temperature (950 °C) and increased chamber pressure (250 mbar). Fig. 5 shows SEM images of an HMPr and an HMPy with identical growth times, but different growth conditions. The HMPy growth rate was ~10 times faster than that of the HMPr; however, no lateral overgrowth was observed in either structure (refer to the circular SiO_x mask pattern in Fig. 5(a); the SiO_x mask was removed in Fig. 5(b)). With respect to the sharpness of facets in HMPy structures, mask thickness/opening size combinations of 200 nm/4 μm and 200 nm/6 μm yielded

opening size / SiO _x thickness	4 μm	6 μm	8 μm	10 μm	20 μm
100 nm					
150 nm					
200 nm					

Regime I (rows 100 nm and 150 nm)

Regime II (rows 150 nm and 200 nm)

10 μm scale bar

Fig. 4. SEM images showing the dependence of morphology on the diameter of the circular opening and on the SiO_x mask thickness. All three samples with different mask film thicknesses were grown by OMVPE simultaneously. The rough surface for the 20 μm opening size and 100 nm SiO_x opening suggests multiple nucleation sites for this particular geometry.

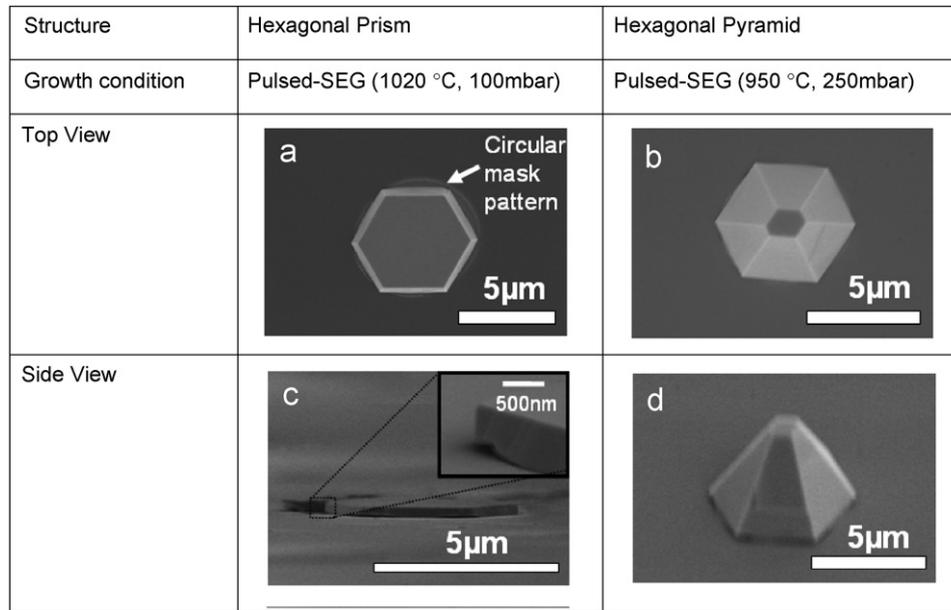


Fig. 5. SEM images of HMPr with 6 μm diameter in top view (a) and side view (c). The inset in (c) shows the magnified vertical prism facet. SEG images of HMPy with 6 μm diameter in top view (b) and side view (d). Both structures were grown for 10 min with 200 nm SiO_x mask thickness.

superior results for a growth temperature of 950 °C and a total pressure of 250 mbar.

4. Conclusion

Highly ordered HMPr GaN structures without lateral overgrowth were grown using a pulsed SEG technique. Instead of turning on and off precursor gas valves, similar results were obtained by combining satellite rotation with an inhomogeneous precursor gas distribution. Satellite rotation caused the samples to sequentially enter regions of varying precursor gas concentrations, effectively pulsing the precursor gases. This approach may be more practical than conventional valve-modulated SEG as there is no stress on valves.

The pulsed SEG in this study was effective in preventing lateral overgrowth and enhancing vertical facet development. The effect of SiO_x mask thickness and circular opening size on morphology was determined, with a general trend of thicker masks (~ 200 nm) and smaller openings ($\leq 8 \mu\text{m}$) leading to more well-defined hexagonal prisms. The combination of a practical pulsing technique with the superior faceted structures induced by SEG is expected to facilitate the demonstration of manufacturable whispering gallery mode cavity structures for resonant-cavity light-emitting diodes and low-threshold lasers.

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