Fabrication of Tapered and Cylindrical GaN Nanowires Using Nanosphere Lithography

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***Abstract*—Nanowires fabricated using the top-down method can offer high uniformity and precise morphology. However, achieving well-controlled dry and wet etching processes is essential to produce large-area uniform nanowires. It is also interesting to have control on their shape, since tapered structures can have favorable light extraction properties, whereas cylindrical shapes are preference for electronics or photodetection. This paper presents a comprehensive study on the fabrication of GaN nanowires using a top-down approach facilitated by nanosphere lithography. We focus on optimizing both dry and wet etching processes to achieve high-aspect-ratio nanowires with controlled shapes. The final wet etching step, critical for shaping the nanowires, was performed with a crystallography-selective method, resulting in nanowires with vertical m-plane facets or tapered structures, depending on the initial diameter of the spheres. This demonstrates the process's adaptability to control nanowire geometry.**

I. Introduction

GaN nanowires have gained significant interest in the field of nanotechnology and materials science due to their exceptional properties and versatile applications. These nanowires exhibit direct band gap, high robustness and chemical stability, making them highly efficient for optoelectronic devices, including light-emitting diodes (LEDs) [1], [2], laser diodes [3], and ultraviolet (UV) photodetectors [4], [5], [6], [7]. Nanowire devices offer lower capacitance, enhanced integration, and excellent spectral selectivity compared to planar devices [8]. The ability to tailor their optical and electronic properties through size, shape, heterostructure and doping adjustments further enhances their appeal for innovative nanoscale device applications.

Two methods can be employed for fabricating vertically aligned nanowires: bottom-up growth (which includes self-assembly, selective area growth, or metal-seeded growth) and top-down fabrication of nanowires from planar layers. Nanowires grown via the bottom-up approach display an almost defect-free structure and enable the combination of different lattice parameters due to surface relaxation through the sidewalls. However, this method also presents drawbacks such as nonuniform doping and defect formation associated with nanowire coalescence [9]. Conversely, the top-down method holds the promise of enhanced uniformity, better nanowire morphology, and better doping control with respect to bottom-up method [10]. To fabricate top-down GaN nanowires, different methods have been employed. For instance electron beam lithography can be used for the definition of the nanowire diameter and periodicity, coupled with additional processes such as dry and wet etching steps [11] or selective area sublimation [12], but the exposure time can be long and it is not easily scalable. Nanosphere lithography has emerged as a promising method for top-down fabrication, because it allows controlling the nanowire diameter and length, and it is scalable [13]. Recently, a novel approach has been developed by da Silva *et al.* [9] in which they reported using polystyrene spheres in combination with a SiO_2 layer to pattern the nanowires employing both dry and wet etching to provide large area thin GaN NWs with an aspect-ratio higher than 30.

In this study, we propose a cost-friendly and reproducible top-down process using nanosphere lithography with SiO_2 as a hard mask, which is applied to GaN samples grown by plasma-assisted molecular beam epitaxy (PAMBE). The dry etching step of the process for nanowire formation has been revised to achieve anisotropic etching, resulting in well-separated nanowires. Moreover, selecting the size of the spheres, it is possible to obtain nanowires either with vertical facets or tapered nanowires.

II. Experimental Procedure

GaN layers were grown using PAMBE on 4-µm-thick non-intentionally-doped (nid) GaN-on-sapphire templates. The nitrogen plasma source was operated at 300 W radio-frequency (RF) power, with 1 sccm N_2 flow rate. The nitrogen-limited growth rate was 0.66 monolayers per second (ML/s). The samples used for dry etching optimization consisted of 600 nm of nid GaN (results shown in Fig. 2). The samples that underwent the complete NW fabrication process consisted of 600 nm GaN:Mg (results shown in Fig. 3 and 4). The sphere shrinking step is performed in a Plassy reactive ion etching (RIE) equipment, whereas the etching of SiO_2 and GaN was performed in an Oxford Plasmalab System100 inductively coupled plasma-reactive ion etching (ICP-RIE) equipment. The samples were examined by scanning electron microscopy (SEM) throughout the complete fabrication process.

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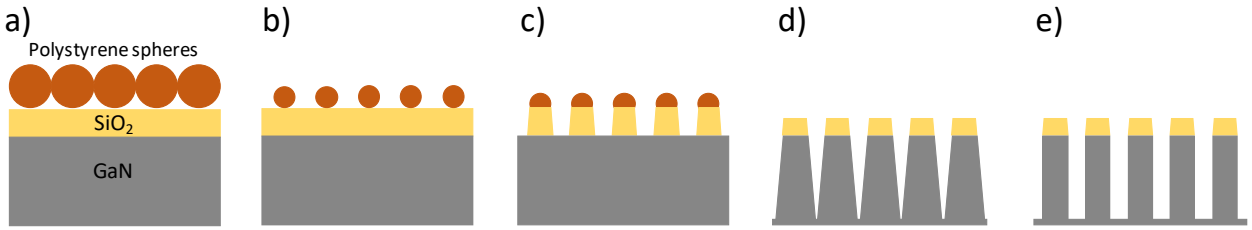

Figure 1. Schematic description of the top-down NW fabrication process a) dispersion of polystyrene spheres on the SiO_2/GaN specimen, b) shrinking the polystyrene spheres, c) etching the SiO_2 layer, d) dry etching of GaN using the patterned geometry, and e) wet etching of GaN nanowires to smooth the sidewalls.

III. Discussion

Our target is to obtain high-aspect-ratio nanowires using a top-down fabrication process, with a pattern generated via nanosphere lithography. For this purpose, we selected polystyrene spheres as the lithographic medium, since we have previously developed a process that uniformly reduces their diameter without deformation, using oxygen plasma in a RIE system [9]. This technique ensures a good separation between spheres, but the selectivity of the GaN etching chemistry is insufficient to use the spheres directly as a mask. Consequently, we need to deposit a SiO_2 layer, whose pattern is defined by the spheres, which serves a hard mask for the etching of GaN. Following this reasoning, this paper describes a nanosphere lithography process that follows the steps depicted in Fig. 1, including a) dispersion of polystyrene spheres on the SiO_2/GaN specimen, b) shrinking the polystyrene spheres to separate them, c) etching the SiO_2 layer, d) dry etching of GaN using the patterned SiO_2 as a mask, and e) wet etching of the GaN rods to obtain nanowires with vertical and smooth sidewalls.

The fabrication protocol started with the deposition of a SiO_2 layer with a thickness of 700 nm, using plasma-enhanced chemical vapor deposition (PECVD). Then, a colloidal solution of polystyrene spheres with a diameter of 1 µm was deposited onto the sample. The spheres, initially provided in an aqueous suspension (2% solids), are highly hydrophobic, leading to a predisposition to clustering [14]. To achieve a homogeneous solution of spheres on the sample surface, the suspension underwent sonication for approximately 30 min. Then, a solution was prepared using water and the sphere suspension at a 2:1 volume ratio. The solution was deposited onto the sample using a drop-casting wet dispersion method with the substrate mounted on a 10° inclined sample holder. A 30 µl droplet of the solution was applied to a specimen with a surface of 5 mm × 5 mm. After dispersion, the sample was left to dry for one hour.

To create some spacing between the spheres, they were etched with oxygen plasma in a RIE system (O_2 flow = 50 sccm, RF power = 100 W, pressure in the chamber = 0.070 mbar) to reach a diameter around 550 nm. Using the shrunk spheres as a mask, the SiO_2 layer was etched in an ICP-RIE system with CF_4/Ar/CH_2F_2 chemistry (20/50/5 sccm, RF power = 500 W, ICP power = 0 W, pressure in the chamber = 12 mTorr).

After the hard mask opening step, the GaN was dry etched using ICP-RIE with a Cl_2-based chemistry. We have evaluated multiple etching protocols, summarized in Table I, aimed at enhancing the verticality of the etched sidewalls. Note that the etching angle (angle between the etched sidewalls and the direction normal to the sample surface) determines the maximum length achievable for the nanowires.

The BC1 recipe in Table I, which uses BCl_3/Cl_2 chemistry, was derived from ref. [9]. Fig. 2a presents an SEM image of a sample after 2 hours of etching, resulting in ≈1.2 µm long GaN pillars, which corresponds to an etching rate of 10 nm/min. Unfortunately, the etching angle is so large that the GaN rods converge at a depth of 1 µm.

Increasing the ICP power should result in a higher reactive ion flux, potentially facilitating more anisotropic etching, whereas increasing the RF power should lead to higher etching rate [15]. Hence, we adjusted the CB1 recipe by increasing both the RF and ICP power settings (recipe CB2 in Table I). Fig. 2b depicts the outcome of the new recipe after 10 min of etching. Despite the anticipated increase in etching rate (65 nm/min), the etching angle was comparable or even larger than the one in Fig. 2a.

In a new effort to improve the sidewall verticality, we decided to change the etching chemistry to pure Cl_2, using the C1 recipe in Table I. The SEM image in Fig. 2c, after 10 min of etching with this recipe, reveal a negligible GaN etching rate. However, by augmenting the ICP power to 990 W (as per recipe C2 in Table I), we achieved substantial etching rates of 300 nm/min, as depicted in Fig. 2d following 10 min of etching.

These experiments demonstrate the efficacy of using pure Cl_2 for deep etching of GaN, facilitating high etch rates, while maintaining small etching angles. This conclusion aligns with the observations of Jaloustre *et al.* [16], reinforcing the

TABLE I. ICP-RIE recipes applied in this study.

Recipe	Chemistry	Flow Ratio (sccm)	RF Power (W)	ICP Power (W)	Pressure (mTorr)	Temperature (°C)
BC1	BCl_3/Cl_2	30/10	30	100	10	20
BC2	BCl_3/Cl_2	30/10	300	1000	10	20
C1	Cl_2	80	100	400	8	20
C2	Cl_2	80	100	990	8	20

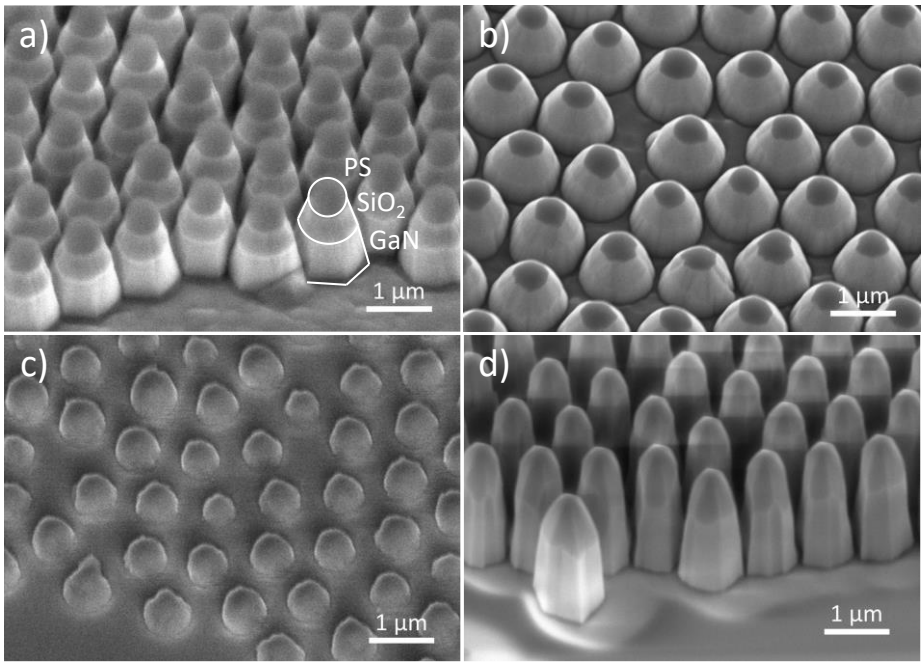

Figure 2. SEM images of GaN dry etching study after using different ICP-RIE recipes a) BC1, b) BC2, c) C1, and d) C2 (All images are tilted with 30°).

preference for pure Cl_2 over BCl_3/Cl_2 in applications requiring deep etching of GaN.

Following the dry etching process, which transformed the GaN layer into 2 µm long rods, the samples underwent wet etching at 65°C in AZ400K developer (KOH-based developer from AZ Electronic Materials USA Corp.). Fig. 3a shows that after 10 min of wet etching, the formation of nanowires with a diameter of approximately 200 nm is already evident. Additional etching steps reveal non-uniform etching of the nanowires (Figs. 3b and 3c). Furthermore, the nanowire geometry transitions from cylindrical to conical reminds the report of Kazanowska *et al.* [17] of tapered GaN nanowires resulting from crystallographic wet etching using phosphoric acid. This process was found to be crystallographically sensitive in nature, with semipolar planes exposed rather than nonpolar planes. To our knowledge, a nanowire geometry with sharp tips has not been previously reported when using KOH as a wet etchant, which is known to expose m-{10−10} facets [18], [19], [20], [21]. Note that these GaN nanowires with sharp tips could find utility in scanning probe microscopy or field emission devices.

To obtain cylindrical nanowires with controlled height, we need to adapt the process to spheres with a larger diameter. Therefore, polystyrene spheres with a diameter of 2 µm were dispersed and etched under the same oxygen plasma conditions (RIE with O_2 flow = 50 sccm, RF power = 100 W, pressure in the chamber = 0.070 mbar) until their diameter reduces to approximately 1.35 µm, with a pitch size of 600 nm. Following the SiO_2 etching (ICP-RIE with $CF_4/Ar/CH_2F_2$ 20/50/5 sccm, RF power = 500 W, ICP power = 0 W, pressure in the chamber = 12 mTorr), GaN was etched using the C2 recipe in Table I, to obtain 2 µm long rods, which were subsequently wet etched. Fig. 4 illustrates the evolution of the sidewall facets during wet etching. The areas damaged during dry etching are quickly eliminated, as observed in Fig. 4a which shows the state of the sample after 10 min of etching. After 30 min (Fig. 4b), the vertical m-{10−10} facets start to appear at the upper portion of the structures, whereas the lower section exhibits nanofacets, mostly c-(0001) and m-{10−10} planes. Further increasing the etching time (Fig. 4c), the vertical facets become larger and the presence of (0001) nanofacets is restricted to the region closer to substrate. For longer etching time (Fig. 4d), the nanowires present a cylindrical shape with vertical sidewalls and a flat top facet. Once such a profile is obtained, the rate of decrease in nanowire diameter depends on the etching time.

Let us remind here that the process began with a shrunk-sphere diameter of 1.35 µm. After wet etching for 10 min, the top-facet diameter reduces to 1 µm due to the rapid elimination of the material damaged during the ICP-RIE process. From there, the evolution of the diameter of the top facet as a function of the etching time is given in Fig. 4e. In a

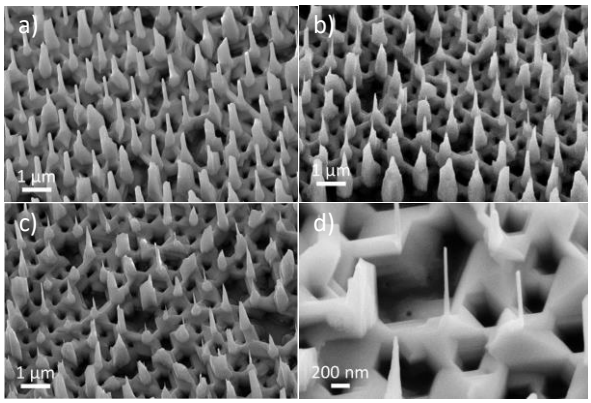

Figure 3. SEM images of wet etching study with 1 µm spheres in AZ400 solution for a) 10 min, b) 12 min, c) 14, and d) 17 min. (All images are tilted with 30°).

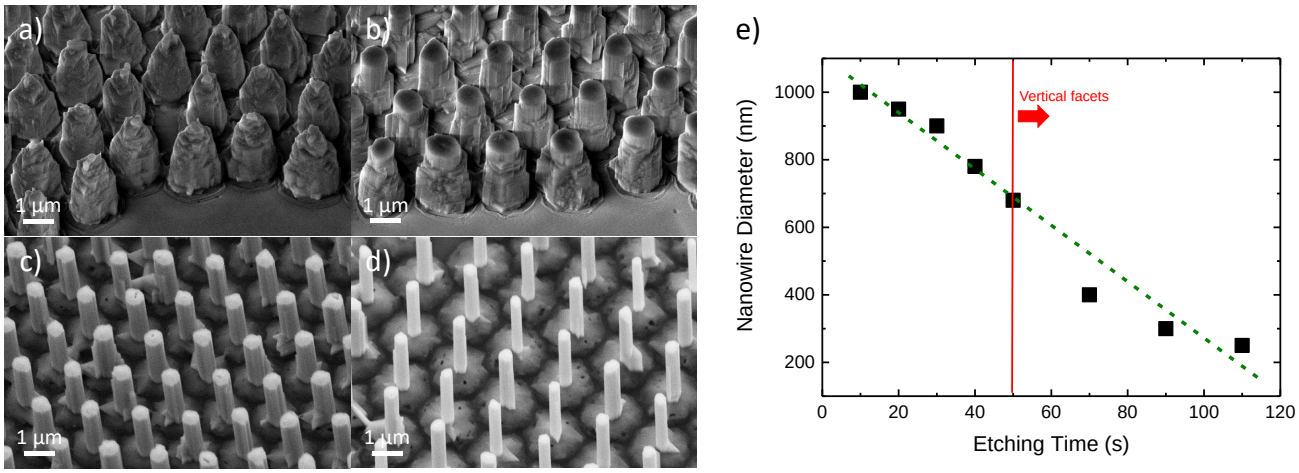

Figure 4. SEM images of the wet etching study with 2 µm spheres in AZ400 solution for a) 10 min, b) 30 min, c) 50 min, d) 90 min (All images are tilted 30°). e) Nanowire diameter as a function of the wet etching time. The dashed line represents the linear behavior.

first approximation, after the first 10 min, the diameter decreases linearly with time. The vertical m-plane facets get fully exposed after 50 min, when the top facet diameter is around 700 nm.

The process is schematically described in Fig. 5 for the two tested sphere diameters. This evolution explains the tapered geometry of the nanowires fabricated using 1 µm spheres, Fig. 5a. In that situation, the sphere diameter was approximately 550 nm after oxygen plasma etching, and after 10 minutes of wet etching, the diameter of the nanowire top facet had decreased to 200 nm. In the case of 2 µm spheres, Fig. 5b, the diameter reduced from 1.35 µm to 1 µm. This implies a difference of 350 nm between the diameter of the shrunk spheres and that of the nanowire top facet after 10 min of wet etching, regardless of the initial sphere diameter. In the case of the small spheres, with only 200 nm as initial point for the top facet, the nanowires will start losing height before attaining the point that leads to fully vertical facets. This diminishment occurs because the top facet's size is insufficient to prevent lateral etching. Therefore, inclined facets appear at the nanowire tip can subsequently be further etched. As a result, we obtain a tapered structure instead of a cylindrical shape and lose nanowire height reducing the aspect ratio of the fabricated structures.

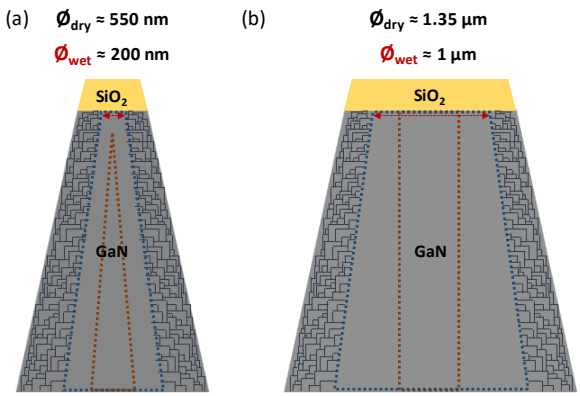

Figure 5. Schematic description of wet etching profile of samples prepared with a) 1 µm spheres and b) 2 µm spheres. Orange dashed lines illustrate the final shape of the nanowires.

IV. Conclusion

In conclusion, we have successfully developed a top-down process for the fabrication of GaN nanowires, using nanosphere lithography. Our results indicate a clear preference for employing pure Cl_2 chemistry over BCl_3-Cl_2 mixtures for the deep etching of GaN via ICP-RIE, a critical step that ensures the production of well-separated nanowires with high aspect ratios. The final crystallographic-selective wet etching step facilitates the formation of vertical nanowires with m-plane facets or tapered structures, depending on the initial diameter of the spheres. In summary, we demonstrate that the use polystyrene spheres with SiO_2 as a mask, coupled with meticulous adjustments in dry and wet etching steps, renders the top-down GaN nanowire fabrication process more reliable and allows controlling the nanowire shape.

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