



Regular article

Fabrication of high aspect ratio gallium nitride nanostructures by photochemical etching for enhanced photocurrent and photoluminescence property

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ABSTRACT

High aspect ratio gallium nitride (GaN) nanostructures were fabricated by photochemical etching using hydrofluoric acid as the etchant. Under the etching time of 20 min, the surface pore density is estimated to be $\sim 5.6 \times 10^9 \text{ cm}^{-2}$, and the aspect ratio of the pore structure is as high as $\sim 10:1$. The biggest photocurrent and strongest photoluminescence intensity of the etched GaN are ~ 3.2 and 9.7 times of that of the as-grown GaN, respectively, which demonstrates high aspect ratio GaN nanostructures have great potential for a series of photoelectric and optical devices.

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Gallium nitride (GaN) has garnered much attention due to its unique physical properties and potential applications in a series of devices such as light emitting diodes, short-wavelength emitters or detectors, high-power and high-frequency electronic devices [1–3]. Etching is an important step in GaN device processing, and the etched GaN layers can be used as the strain-relaxed layers for the overgrowth of III-nitride devices with low dislocation density [4]. In particular, high aspect ratio GaN nanostructures are of great use in the design and fabrication of vertical geometry devices such as sensors and photovoltaic cells because of their advantages of low diffusion barrier and shortened mass and charge transfer pathways, thereby improving the response time of sensors and reducing the electrical resistance of solar cells [5–7]. Compared with dry etching, wet etching has the merits of high selectivity, negligible damage, low cost and simple equipment [8]. However, the super chemical stability makes GaN resistant to traditional chemical etching. Up to now, only electrochemical, photoelectrochemical and metal-assisted chemical etching have been recognized to be the efficient etching methods for GaN [9–11].

The anisotropic nature of electrochemical etching makes it easy to form pores deeper than one micron, but the formed surface pore density is low, leading to the low availability of the deeper pores [12,13]. On the contrary, photoelectrochemical etching can form high-density surface

pores, while it is difficult to realize deep etching [14]. The biggest problem of above electrochemistry-based etching methods is the requirement of electrical contact of GaN, which makes the etching process complicated and impractical. Recently our group demonstrated metal-assisted chemical etching can be used to fabricate special GaN nanostructures like nanoflowers [15] and nanowires [16], whereas the most commonly used metal catalysts are noble metals, it is difficult to remove metal catalysts remaining the pore structure intact [17]. Here in this work, we demonstrate photochemical etching is an effective and efficient vertical etching technique. The enhanced photocurrents and photoluminescence (PL) intensities indicate high aspect ratio porous GaN layers can be significant building blocks for a series of photoelectric and optical devices.

GaN epitaxial wafer was purchased directly from Kyma Technologies, Inc. The detailed physical parameters of the grown GaN layer were as follows. Single crystalline GaN layer was grown on *c*-plane sapphire substrate by hydride vapor phase epitaxy. The Si-doped GaN layer was 5 μm thick with a carrier concentration of $4 \times 10^{18} \text{ cm}^{-3}$, resistivity of $0.02 \Omega\text{-cm}$ and dislocation density of $1 \times 10^9 \text{ cm}^{-2}$. Two-inch GaN wafer was cut into $13 \text{ mm} \times 3 \text{ mm}$ chips. The GaN chips were dipped in aqua regia for 30 min to remove surface contamination. After that, they were rinsed in deionized (DI) water and dried with N_2 prior to use.

Photochemical etching of GaN was implemented by immersing the GaN chip into the etchant under irradiation of 300 W xenon lamp, and the light intensity was 1000 mW/cm^2 . The etchant was 4.6 M HF aqueous solution. The etched GaN chips were rinsed thoroughly in DI

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water and dried with N_2 . The etched GaN was named after the etching time, e.g., GaN-10 is the GaN chip etched for 10 min. The surface morphology of the etched GaN chips was characterized by scanning electron microscopy (SEM, Hitachi S-4800). Raman spectra were recorded using Confocal LabRam HR800 spectrometer operating at the excitation wavelength of 532 nm.

Photocurrent measurements were performed by a CHI 660D electrochemical workstation using a three-electrode cell. The GaN chip, platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. The electrolyte was 1 M NaOH aqueous solution. A 300 W xenon lamp was used as the light source. PL measurements were carried out by a Princeton Instruments SP2500i spectrometer operating at the excitation wavelength of 325 nm.

Fig. 1 shows the top-view and cross-sectional SEM images of the etched GaN. After etching for 10 min, the surface of GaN-10 becomes rough, but there are only few pores formed on the surface (Fig. 1a). The cross-sectional view shown in Fig. 1b exhibits zigzag structure, and the etching depth is ~ 77 nm. After etching for 20 min, the surface of GaN-20 shows porous structure (Fig. 1c). The pore diameter is between 38 and 108 nm, and the pore density is estimated to be $5.6 \times 10^9 \text{ cm}^{-2}$. The cross-sectional view (Fig. 1d) exhibits vertical pore structure, and the pore depth is ~ 577 nm. The increase of the pore depth is much larger than that of the pore size, which indicates the etching rate in the vertical direction is larger than that in the lateral direction. Based on the analysis of the generating way and movement of holes in the etching process, the reasons why uniform high aspect ratio pore structure is formed by photochemical etching rather than electrochemical and photoelectrochemical etching are as follows. In electrochemical etching process, holes are supplied by Zener tunneling and avalanche breakdown under strong applied electric field, which mainly occurs in the defect sites, so the formed surface pores are not uniform [13]. In photochemical and photoelectrochemical etching processes, holes are generated by the excitation of electrons from the valence band via above band-gap light irradiation. Under the photoelectrochemical condition, the generated holes are continually migrated and consumed at the interface of solid-liquid via the driving force of electric field, in this case, deep etching cannot be realized because holes aggregate and stay at the interface throughout the whole etching process [14]. On the contrary, under the photochemical condition, the etching proceeds along the direction of light irradiation to form deep etching, and the vertical etching stops until the light cannot touch the bottom of pores. After etching for 30 min, the pore size of GaN-30 is between 50 and 105 nm, and the

pore density is estimated to be $6.0 \times 10^9 \text{ cm}^{-2}$ (Fig. 1e). However, the pore depth (~ 308 nm) of GaN-30 shown in Fig. 1f is smaller than that of GaN-20, which suggests the top surface has been etched away. As the etching depth increases, the vertical etching rate decreases due to the following two reasons. On one hand, the light intensity falling on the already formed pores is weakened as the etching proceeds. On the other hand, the supply of the etchant into the deeper pores is more difficult. So the etching rate of the lateral direction becomes larger than that of the vertical direction, leading to the decrease of the pore depth. After etching for 40 min, the pore size of GaN-40 is between 60 and 273 nm, and the pore density is estimated to be $3.2 \times 10^9 \text{ cm}^{-2}$ (Fig. 1g). As the etching proceeds, several small pores turn into one big pore leading to the increase of pore size and the decrease of pore density. From the view of cross-section (Fig. 1h), monodisperse vertical GaN nanowires are formed, and the length of these nanowires is ~ 500 nm. The reason why vertical GaN nanowires are formed is that the pore walls between adjacent pores are etched away.

Fig. 2 shows the Raman spectra of the as-grown and etched GaN, measured in the $z(x, \text{unpolarized})\bar{z}$ where x is in the plane direction (perpendicular to the c -axis of the hexagonal crystal). Under this configuration the $E_1(\text{TO})$ is forbidden, this explains its absence. Apart from the signal of sapphire substrate, the Raman spectrum of the as-grown GaN shown in Fig. 2a exhibits phonon mode $E_2(\text{high})$ and small peaks of $E_2(\text{low})$, $A_1(\text{TO})$ and $A_1(\text{LO})$. All spectra of the etched GaN also only have the above four peaks, which demonstrates the optical property of the etched GaN is unchanged compared to that of the as-grown GaN. This result also suggests photochemical etching is a very mild etching method compared to electrochemical etching [14]. To further verify the change of the crystal structure before and after etching, the precise peak positions of $E_2(\text{high})$ of the as-grown and etched GaN are shown in Fig. 2b. The full width at half-maximum value of $E_2(\text{high})$ peaks of the etched GaN is smaller than that of the as-grown GaN, which indicates the improvement of the crystal structure after etching [18]. In addition, for GaN, $E_2(\text{high})$ phonon frequency is only affected by stress. A decrease of the $E_2(\text{high})$ phonon frequency with respect to strained GaN indicates the relaxation of compressive stress, whereas an increase points to the relaxation of tensile stress [19]. The $E_2(\text{high})$ phonon frequency of GaN-30 and GaN-40 decreases compared to that of GaN-10 and GaN-20. That is because, as the etching time increases, the increasing vertical porosity leads to the compressive stress relaxation [20]. So the GaN-30 and GaN-40 layers can be used as strain-relaxed layers for the overgrowth of III-nitride devices.

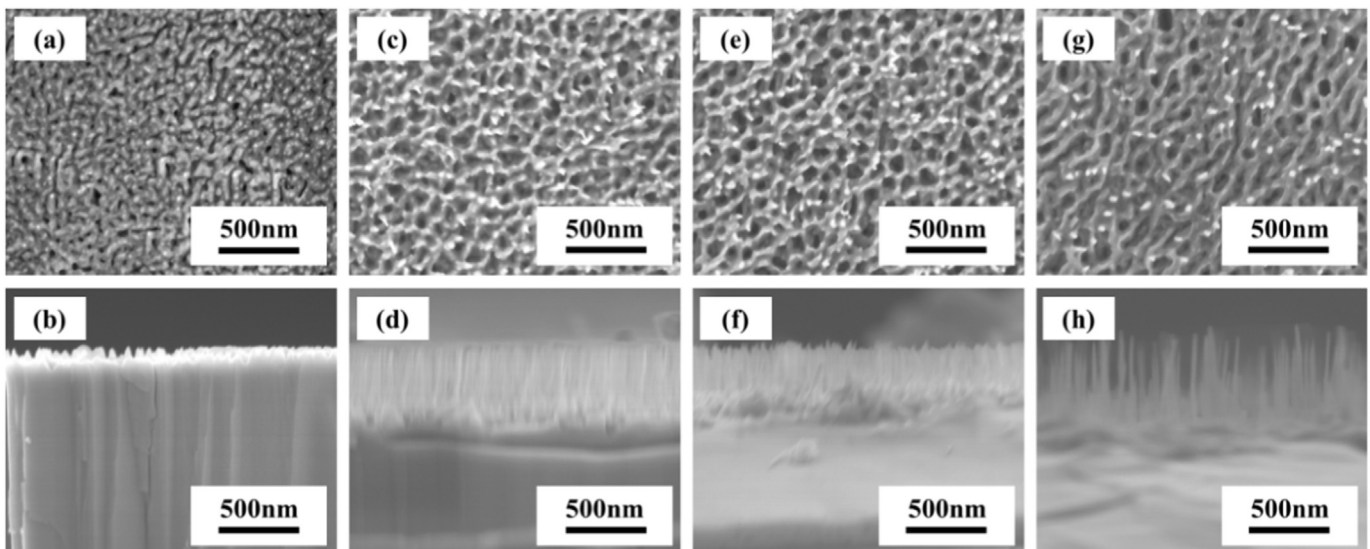


Fig. 1. Top-view and cross-sectional SEM images of the etched GaN under different etching time. (a–b) 10 min, (c–d) 20 min, (e–f) 30 min and (g–h) 40 min.

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