

### Enhanced photoelectrochemical activity of GaN by dry etching into nanopillar array

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Hydrogen is a clean and sustainable energy carrier in the coming future. Various semiconductors have been investigated for their photoelectrochemical and photocatalytic properties [1]. GaN is one of the few materials that can perform water photoelectrolysis without external energy input since the energy band edges straddle the redox potential of water [2]. Surface nanostructuring plays a crucial role on the photoelectrochemical activity of GaN, which enhances the surface area substantially and therefore provides more available active sites for the water oxidation. Moreover, more photocarriers are generated in the depletion region near the electrolyte in case of nanostructures, facilitating carrier separation and carrier migration to the interface.

Recently, nanostructured GaN photoanodes have been demonstrated to have much higher efficiency over planar GaN [3]. (In)GaN nanopillars/wires are commonly synthesized by the epitaxial growth (bottom up approach). However, the photoelectrochemical property of the (In)GaN nanostructured electrodes prepared by etching technology (top down approach) are rarely discussed [4]. In this work we fabricated GaN nanopillars using an economical approach. The surface is roughened from the planar epilayer to the pillar array up to 1.2  $\mu\text{m}$  in height. The effective area is approximately increased by 6 times. The overall solar-to-hydrogen efficiency is increased by 80% from initially 1.5 % (planar GaN) to 2.7 % (1.2  $\mu\text{m}$ -high GaN pillars) in 1 M HCl solution. The influence of the surface nanostructuring on the photoelectrochemical property is investigated.

Single crystalline GaN layer was epitaxially grown on Si (111) substrate by metal organic chemical vapor deposition (MOCVD). The GaN nanopillars were fabricated by dry etching from the epilayer using self-assembled Ni clusters as mask [4]. A 250 nm  $\text{SiO}_2$  layer and 15 nm Ni film were deposited on the GaN epilayer, followed by annealing at 850  $^\circ\text{C}$  in  $\text{N}_2$  environment for 90 seconds to transform the Ni film into the nanoclusters.  $\text{SF}_6$ - and  $\text{Cl}_2$ -based ICP dry etching were applied to etch the  $\text{SiO}_2$  and GaN, respectively. Fig. 1 (a) and (b) shows scanning

electron microscope (SEM) images of 0.8  $\mu\text{m}$ -high GaN pillars in top view and at 45 $^\circ$ , respectively. Fig. 2 (a) plots the photocurrent density vs. bias for the GaN photoanodes before and after nanostructuring under Xe lamp illumination (100  $\text{mW}/\text{cm}^2$ ) in 1 M HCl aqueous solution. The maximum photocurrent density is enhanced from initial 1  $\text{mA}/\text{cm}^2$  (planar GaN) to 2  $\text{mA}/\text{cm}^2$  (1.2  $\mu\text{m}$ -high pillars). Fig. 2 (b) shows the chronoamperometric photocurrent of the planar GaN and GaN pillar electrodes recorded at zero bias vs. the Pt mesh in 1 M HCl solution. The three anodes show high photostability in the presence of  $\text{Cl}^-$  sacrificial reagent. The pillar electrodes show a stronger photoactivity than the planar electrode. The steady-state photocurrent of 1.2  $\mu\text{m}$  high pillars is 80 % higher than the planar GaN. The solar-to-hydrogen conversion efficiency is calculated as 1.5 % (planar GaN), 2.0 % (0.8  $\mu\text{m}$  high pillars), and 2.7 % (1.2  $\mu\text{m}$ - high pillars) in 1 M HCl solution. Therefore we conclude that dry etching of planar GaN into nanopillars is promising to improve the efficiency of photoelectrolysis at limited cost.

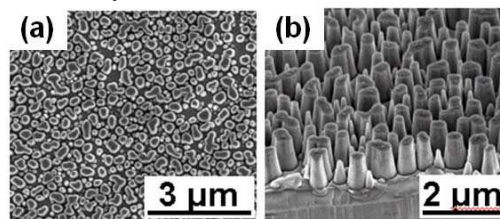


FIG. 1. SEM images of GaN nanopillars of 0.8  $\mu\text{m}$  height (a) at top view and (b) at 45 $^\circ$ .

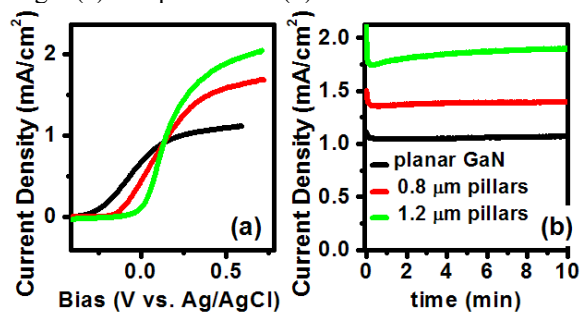


FIG. 2. (a) Photocurrent density-potential responses of GaN pillars and (b) chronoamperometry at zero bias vs. Pt mesh. Both measurement were conducted at Xe lamp illumination (100  $\text{mW}/\text{cm}^2$ ) in 1 M HCl solution.

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