

## Research paper

# Nonaqueous organic electrolyte for photoelectrochemical etching of gallium nitride surface



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## HIGHLIGHTS

- GaN film can be effectively etched by organic electrolyte.
- The dissolution mechanism of organic electrolyte is proposed to etch GaN.
- The nonaqueous organic electrolyte is first used for GaN etching.

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## ABSTRACT

Nonaqueous organic electrolyte was utilized to etch GaN via photo-electrochemical etching technique. From the point of electrochemical window, the organic electrolyte has wider electrochemical window than conventional aqueous etchants. SEM images show that the pore density is up to  $1.2 \times 10^7$  per square centimeter. The difference of XPS spectra about survey, Ga 3d and N 1s between the non-etched and freshly etched GaN surface can be explained the formation of  $\text{Ga}(\text{BF}_4)_3$ . The proposed dissolution mechanism can be broadly applied for explaining the etching process of nonaqueous etchants under the assist of electric field and strong light.

## 1. Introduction

Gallium nitride (GaN) has attracted significant attention due to its wide applications in LEDs, lasers, microwave amplifiers and high frequency/high power electronics [1]. Etching of GaN is a crucial processing step in device fabrication [2,3]. Plasma-based dry etching techniques tend to generate ion-induced damage of the semiconductor apart from high cost and complex equipment [4]. Wet etching is a promising alternative due to low damage etching, low cost and high output [5]. Etchant is one of vital component in wet etching of GaN and intensively investigated. However, it is noted that the inherently super chemical stability of GaN makes its resistant to traditional etchants [6,7]. Up to now, highly corrosive, extremely toxic acid, or strong bases of aqueous solutions have been recognized to be the efficient etchants for GaN [2,4,8–12].

On the other hand, aqueous etchants are generally low-energy systems and primarily limited to narrow electrochemical stability window for water [13]. Recent study has revealed that organic electrolytes can

be used as a mild etchant for silicon [14]. Compared with aqueous etchants, nonaqueous organic electrolytes have been shown to have wider electrochemical potential window [15]. In theory, nonaqueous organic electrolytes are more effective than conventional aqueous etchant. To the best of our knowledge, nonaqueous organic electrolyte has not been reported as an effective and environment-friendly etchant for GaN etching.

Herein, nonaqueous organic electrolyte has been explored for the first time for etching GaN. The electrolyte consists of ethyl methyl carbonate (EMC) and lithium tetrafluoroborate ( $\text{LiBF}_4$ ). SEM images exhibit the porous structure of etched GaN surface. The difference XPS spectra between the non-etched and etched GaN surface can be interpreted by the dissolution process of organic electrolyte. Nonaqueous organic electrolyte can be used to efficiently fabricate porous GaN. Due to increased surface area-to-volume ratio of obtained porous GaN layer, great enhancements of gas sensing performances and photocurrents intensities are presented compared with the planar thin film [3,16].

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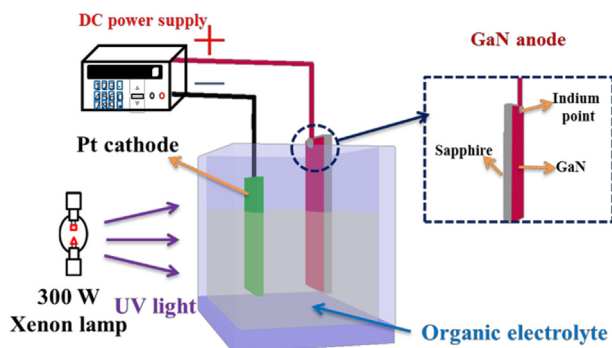


Fig. 1. Schematic diagram of PEC etching device.

## 2. Experimental

Single-crystal n-type GaN (0001) films were grown on sapphires (0001) by hydride vapor phase epitaxy. The 5  $\mu\text{m}$  thick Si-doped GaN layer with carrier concentration of  $4.8 \times 10^{18} \text{ cm}^{-3}$ , which could enhance electron transfer rate in the photoelectrochemical etching process. The GaN films ( $13 \times 3 \text{ mm}$ ) were first cleaned with acetone, ethanol and deionized water, respectively. Then the GaN film was immersed in aqua regia for 30 min to remove surface contamination and rinsed in deionized water. Before etching experiment, GaN chips were blown dry with  $\text{N}_2$ , and indium point was welded onto the front side of GaN to form ohmic contact.

Fig. 1 shows the schematic diagram of PEC etching device. To avoid interference of visible light, the etching device including xenon lamp was placed in a dark box at room temperature. Ultraviolet (UV) illumination was provided by an xenon lamp (Perfect Light, PLS-SXE 300 UV). The GaN film and a platinum plate were used as the anode and cathode, respectively. The M8831 DC power supplied constant etching voltages. An electrolyte of 0.5 M  $\text{LiBF}_4$  was used as etchant, which used EMC as solvent. After etching, GaN film was immersed into 1 M oxalic acid solution for 2 h as surface cleaning-treatment. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

The surface morphology of the GaN was obtained using scanning electron microscopy (SEM, Hitachi S-4800). The surface chemical state of GaN was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI, Thermo Fisher Scientific) with an Al K Alpha X-ray source.

## 3. Results and discussion

Fig. 2a shows SEM images of the surface morphology of etched GaN by the organic electrolyte. Overall, it is clearly seen that the organic electrolyte can effectively fabricate pores. Viewing more closely, as shown in the insets of Fig. 2a, the in-plane porous nanostructure clearly reveals. The in-plane electrically conductive nanostructure takes advantages of the nanowire while eliminating the nano-fabrication obstacles [3]. The pore density is up to  $1.2 \times 10^7$  per square centimeter.

The distribution of pore diameter is showed in Fig. 2b. The pore size is between 50 nm and 130 nm and the average value is 86 nm. Fig. 2c shows the cross-sectional image of the etched GaN. The etching rate is calculated to be 9 nm/min. In addition, the morphologies of the porous GaN were dependent on both the UV density (Fig. S1) and the applied voltage (Fig. S2). The results indicated that the pore sizes increases, when the UV density is increased. With increasing of the applied voltages from 10 to 30 V, the pore size of etched GaN increases from 37.5 nm to 245.5 nm. For  $U_{\text{etch}} = 10$  and 15 V, the density of the surface pores is  $3.2 \times 10^6$  and  $1.2 \times 10^7 \text{ cm}^{-2}$ , respectively.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.08.064>.

In order to analyze the difference in chemical composition between non-etched and etched GaN surface, the XPS spectra of survey, Ga 3d and N 1s were showed in Fig. 3. Fig. 3a and b showed the survey-scan spectrums of non-etched GaN surface and etched sample from 0 to 500 eV. As shown in Fig. 3a, the survey-scan spectrums of non-etched GaN recorded the peaks at Ga 3d (19.9 eV), Ga 3p (106.0 eV), Ga 3s (162.4 eV), N 1s (397.0 eV) and  $\text{GaL}_{3\text{M}_{45}\text{M}_{45}}$  (418.3 eV) [17,18]. Meanwhile, Fig. 3b clearly illustrated the survey-scan spectrums of etched GaN, which also recorded Ga 3d (20.0 eV), Ga 3p (106.2 eV), Ga 3s (162.7 eV), N 1s (397.3 eV) and  $\text{GaL}_{3\text{M}_{45}\text{M}_{45}}$  (418.5 eV). Apart from the above five peak numbers, the survey spectrum of the etched GaN surface has another peak number at 285.0 eV. The survey spectrum of the etched GaN surface is also larger than that of the non-etched GaN surface. As shown in Fig. 3c, the Ga 3d spectra of the non-etched GaN surface could be fitted with four symmetric components with different chemical shifts corresponding to Ga bonding to nitrogen [4,19]:  $\text{Ga}_\text{N}$  (BE = 19.6 eV) [20], Ga bonding to oxygen:  $\text{Ga}_{\text{Ox}}$  (BE = 20.3 eV) [17], Ga bonding to N–H:  $\text{Ga}_{\text{H-N}}$  (BE = 18.9 eV) [21], and metalGa (BE = 17.8 eV) [18]. Fig. 3d showed that the Ga 3d spectrum of the etched GaN surface could also be divided into four components at  $\text{Ga}_\text{N}$  (BE = 21.1 eV), Ga bonding to oxygen:  $\text{Ga}_{\text{Ox}}$  (BE = 21.8 eV), Ga bonding to N–H:  $\text{Ga}_{\text{H-N}}$  (BE = 19.4 eV), and metalGa (BE = 19.3 eV). Compared with Fig. 3c and d, the binding energies of four gallium components obtained from the etched GaN surface are larger than that of the non-etched GaN surface, which means the outer electron density of gallium species on the etched GaN surface is lower than that on the non-etched GaN surface. The shift indicates that the crystal lattice of GaN surface is destroyed by organic electrolyte. In a word, positive shift of Ga 3d in XPS spectra is because of the damaged crystal lattice of GaN and decreased outer electron density of Ga. Fig. 3e clearly showed that the N 1s spectrum of the non-etched GaN surface could be fitted with two components including  $\text{N}_{\text{Ga}}$  (395.5 eV) [20] and a Ga LMM Auger electron with satellites [18]. Except for the components of  $\text{N}_{\text{Ga}}$  and Ga LMM Auger electron with satellites, the N 1s spectrum (Fig. 3f) of the etched GaN surface has another component at 399.7 eV, which can be regarded to belong to the bonding of  $\text{BF}_4^-$  with a Ga site on the freshly etched GaN surface. The result infers that  $\text{BF}_4^-$  has intensely electrostatic attraction with holes at the interface, therefore, the triple bonds with Ga and N are weakened by formation of  $\text{Ga}(\text{BF}_4)_3$ . The survey spectrum (Fig. 3b) of the etched GaN surface has another component at

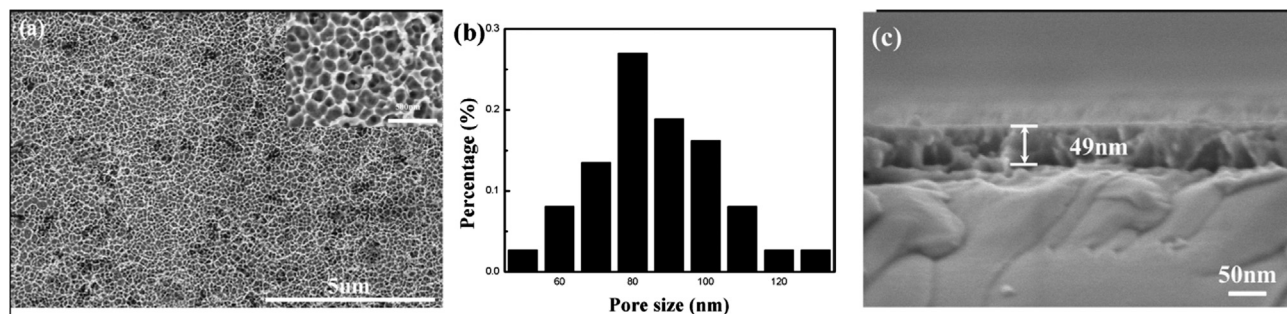


Fig. 2. (a) Top-view SEM image of etched GaN. (b) Pore size distribution histograms of porous GaN. (c) Cross-sectional SEM image of etched GaN.

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