

Deep Ultraviolet-Assisted Photo-Electro-Chemical Wet Etching of N-Type GaN

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ABSTRACT

In this research, room-temperature photo-electro-chemical etching (PEC) of n-type GaN films by using potassium hydroxide (KOH), pH=12.60-12.90, and phosphorus acid (H_3PO_4), pH=1.09-1.39, in a stirred solution under deuterium-lamp illumination was achieved. The process provides anisotropic etching profiles and high etching rates of more than 240 nm/min at moderate light intensities of $\sim 17.3 \text{ mW/cm}^2$ with 237 nm in an H_3PO_4 (pH=1.09) solution. The etching rate and photocurrents are characterized at various concentrations of stirred solutions.

Key Words: photocurrent, photo-electro-chemical etching, GaN, Deuterium lamp

以深紫外線輔助對 N 型氮化鎵做光電化學濕式蝕刻

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摘 要

本文採用光電化學蝕刻的方式，實施了對 n 型氮化鎵半導體材料之濕式蝕刻。提出以波長為 237nm 之深紫外線，光功率密度約為 17.3 mw/cm^2 之氬氣燈為輔助光源，使用 pH=12.6~12.9 之氫氧化鉀 (KOH) 及 pH=1.09~1.39 之磷酸 (H_3PO_4) 做為電解溶液。並獲得了於 pH=1.09 之磷酸電解溶液下，其蝕刻速率大於 240nm/min。本文報導了蝕刻速率及光電流與電解溶液濃度之間的關聯性。

關鍵詞：光電化學蝕刻，氮化鎵，氬氣燈

I. INTRODUCTION

Recently, the wide band gap semiconductor GaN and its ternary alloys with application in high-power or high-frequency optoelectronic devices such as light emitting diodes, lasers, microwave power transistors, AlGaIn/GaN-based high electron mobility transistor (HEMT) with a recess gate, nano-structure light emission device, and UV photo-detectors have been the subject of a vast body of research work. It was reported that the etching technique in GaN includes reactive ion etching (RIE), inductively coupled plasma (ICP), electron cyclotron resonance (ECR) [5, 15]. However, the dry etching generally utilizes a strong physical etch component, which can lead to ion-induced damage on semiconductor and, hence, enhance the leakage current on GaN device. Thus improving the performance of GaN devices from plasma damage is an issue of our work. Wet chemical etching is a low cost, low damage, and selective. But, in past several years, there has few successes in the wet etching of III-V nitrides. AlN can be etched in hot alkaline solutions (about 85°C)[6]. GaN, however, appears to be more resistant upon such a treatment. GaN is insoluble in H₂O acids or bases at room temperature, but dissolves in hot alkali solutions at very low rate [14]. This can be attributed to the exceptional stability at high temperature and under chemical attack in the GaN semiconductor materials.

Photo-electro-chemical (PEC) etching was considered to be an etching with little damage on the fabrication of GaN devices, rather than ion sputtering that inevitably causes surface damage. Minsky et al. [7] have first reported localized electrochemical etching of unintentionally doped n-type GaN layers by using He-Cd laser illuminations (325 nm) and KOH solutions. The dependence of the etch rate and surface morphology on the PEC process conditions was investigated. By controlling the etching parameters, such as electrolyte concentration, illumination intensity, and photocurrent can affect the morphology of etched surface, whisker formation, and etching rate. A detailed description of the PEC system and wet etching process has been reported elsewhere [8, 10, 11].

In this article, the PEC was employed on n-type GaN etching, where the deuterium lamp having deep ultraviolet ($\lambda=237$ nm) of 30 W was used in electrolytes of aqueous KOH or H₃PO₄ with different concentration. To our best knowledge, the deuterium lamp is first used in our study on PEC GaN etching.

II. EXPERIMENTS

An n-type GaN layer was grown on a c-face sapphire substrate by metalorganic-chemical vapor deposition (MOCVD) with a horizontal reactor. Prior to growth, the substrate was

cleaned using organic solvents. Trimethylgallium and ammonia were used as the sources of Ga and N, respectively. Si₂H₆ was employed as an n-type dopant and a 2.5- μm -thick Si-doped GaN film was grown at 1050°C. Hall effect measurements were conducted on the grown n-type GaN sample, which indicated a carrier concentration of $\sim 2 \times 10^{17} \text{ cm}^{-3}$ and a mobility of $\sim 250 \text{ cm}^2/\text{Vs}$ [3,4].

Next, the n-type GaN sample was cleaned by being dipped into a HCl: H₂O = 1:1 solution for 3 min, then a Ti layer (100nm) was deposited by evaporation. The pattern of the metallization was defined by standard metal lift-off techniques. After that, the sample was annealed in N₂ ambient at 850°C for 3 min to form ohmic contacts. The Ti layer was also used as an etch mask.

Fig. 1 shows the experimental apparatus used in this work. A Pt wire was used as cathode and no bias voltage was applied between the sample and Pt cathode. An ampere-meter was used to monitor the current flow within the electrochemical cell and a positive lens was used to converge the light beam. The aperture stop (pinhole) determines the intensity of light reaching the sample.

An unfiltered deuterium lamp provided uniform illumination over the entire surface with an intensity of $\sim 17.3 \text{ mW/cm}^2$ at 237 nm. The electrolyte consists of dilute aqueous solutions of KOH and H₃PO₄ with concentrations ranging from pH=12.60-12.90 to 1.09-1.39, respectively. The solutions were magnetically stirred during the etching. The etch depth and profile of etched samples were characterized by Alpha-step and atomic force microscope (AFM).

III. RESULTS AND DISCUSSION

UV illumination can generate electron-hole pairs on semiconductor surface, which enhance oxidation and reduction

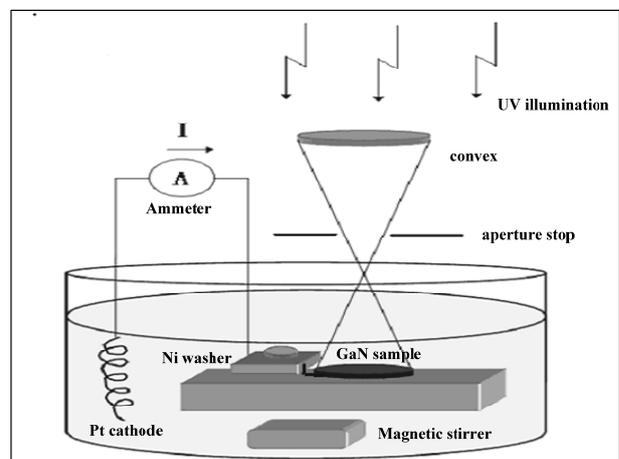
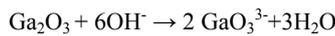
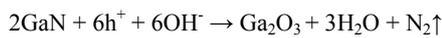
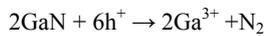


Fig. 1. Schematic of etching apparatus

reactions within an electrochemical cell. Grenko et al. [2] reported that once the electron-hole pairs are generated, then holes are transported to semiconductor surface, weakening the chemical bonds, thus encouraging dissolution, and electrons are swept to the cathode, avoiding subsequent recombination with the holes at the surface. The resultant photocurrent is therefore proportional to the reaction rate of hole-assisted etching at the semiconductor-electrolyte interface. Peng et al. [9] reported that the UV will excite hot carriers at the GaN/electrolyte interface, and excess energy will access the H^+/H_2 and OH/O_2 redox levels in the water and enhance oxidation process. The oxide layer is subsequently dissolved in acids or bases of suitable low concentration.

Youtsey et al. [5] and Rotter et al. [11] proposed the decomposition of GaN is following:



The holes drift to the semiconductor surface, where they oxidize the gallium nitride, thus producing N_2 bubbles, and, hence, Ga_2O_3 was dissolved away. The PEC oxidation of n-type GaN in electrochemical cell with aqueous H_3PO_4 or KOH solutions has similar electrochemical reaction in the PEC etching of n-type GaN [8, 15].

Photocurrent variation with increased etching time is shown in Fig. 2. Approximate exponential decreasing is seen within 20 min, which corresponding to onset of illumination. According to Faraday's law of electrolysis, the photocurrent flowing between anode (GaN sample) and cathode (Pt) is proportional to the reaction rate at the semiconductor/electrolyte interface. We suggest that the total reaction rate is limited by diffusion [8, 12, 15].

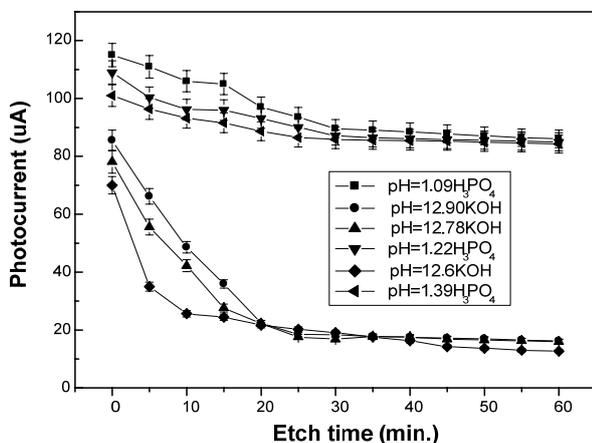
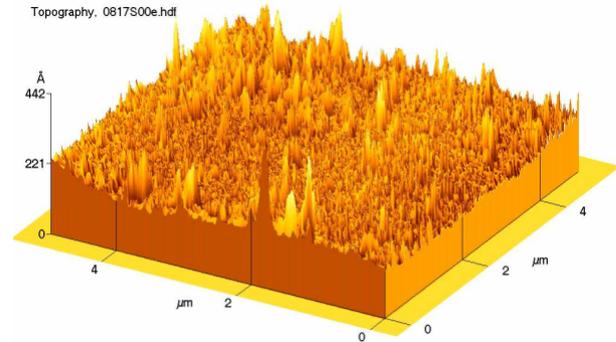


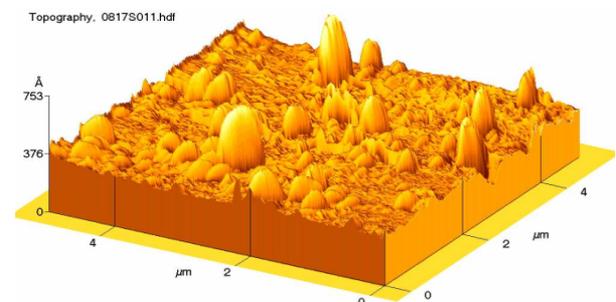
Fig. 2. Plot of time evolution of photocurrent

Fig. 3 and 4 show AFM images of n-type GaN surface etched by KOH (pH=12.90) and H_3PO_4 (pH=1.09) with and without aperture stop, respectively, from these figure, an uniform and smooth etched surface were obtained with root-mean-square (RMS) roughness of 23.7 and 15.2 nm, respectively, for samples with aperture stop. Bardwell et al. [1] reported the RMS surface roughness was 20~29nm on $S_2O_8^{2-}/OH^-$ etching GaN surface. But in our work, the aperture stop was used to uniform the intensity of light, leading to uniform surface. Several groups reported the grain boundary walls are etched more slowly than the center of the crystals. This leads to a hexagonal, rough morphology, as shown in Fig. 3 and Fig. 4. On the photo-assisted etching, a direct chemical reaction also exists. It results in different morphology in bases and acids.

The etched surface is smooth with several whiskers (rode-like) features that are typical for PEC etched GaN. Skriniarova et al. [13, 16] reported whiskers were formed on the sites of threading dislocations with etching selectivity, which is resulting from the electrical activity at dislocations. At these defects, preferential recombination of light induced carriers (electron-hole pairs) occurred and therefore the density

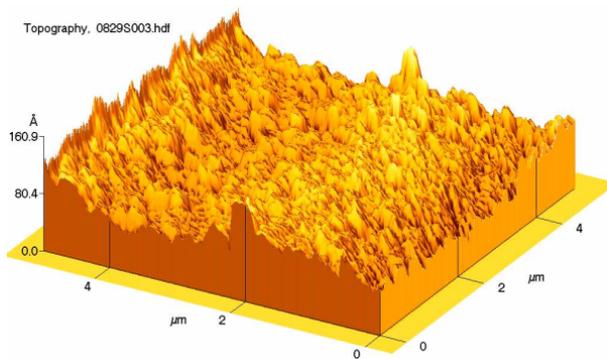


(a) with aperture stop, 0.7 μm etch depth, 60 min etch time, roughness 23.7nm

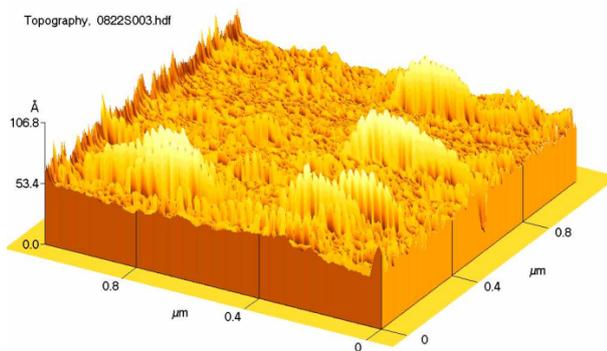


(b) without aperture stop, 0.67 μm etch depth, 60 min etch time, roughness 45.7nm

Fig. 3. AFM images of GaN surface etched by KOH, pH=12.90



(a) with aperture stop, 1.83 μm etch depth, 60 min etch time, roughness 15.1 nm



(b) without aperture stop, 1.71 μm etch depth, 60 min etch time, roughness 33.8 nm.

Fig. 4. AFM images of GaN surface etched by H₃PO₄, pH=1.09

of holes available for etching reaction is reduced.

Fig. 5 shows the GaN etch rate in our work. The etch rate gradually decrease due to the decrease in photocurrent within 15 min. We believe the oxide dissolution rate equals to the oxidation rate of underlying n-type GaN film, the photocurrent levels out within 43–60 min, as shown in Fig. 2.

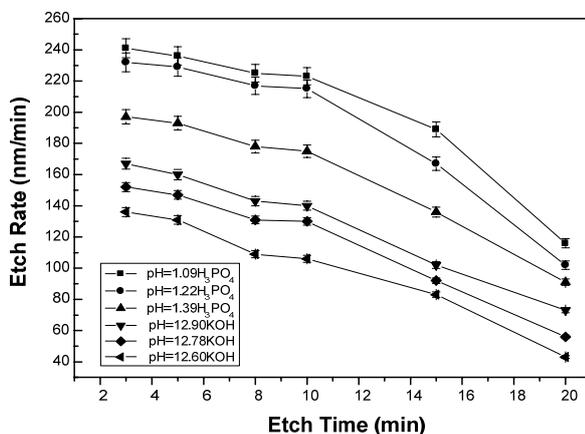


Fig. 5. Etch rate of our samples

Peng et al. reported a peak etch rate of 125 and 90 nm/min in H₃PO₄ and KOH solution at pH=0.75 and 14.25, respectively, with an illumination of 253.7 nm Hg light source [1]. In this work, we observe a peak etch rate of 241 and 167 nm/min in H₃PO₄ and KOH solution at pH=1.09 and 12.90, respectively. This behavior can be attributed to absorption in the GaN/electrolyte interface or GaN surface, because penetration depth is very short for wavelength of 237 nm. Thus, majority photons are absorbed in the GaN/electrolyte interface where photocurrent is generated. We suggest the absorption coefficient is large at the GaN/electrolyte interface by using deuterium lamp light source, corresponding to the total quantum efficiency in excess of those using Hg lamp light source. The etch rate in H₃PO₄ solution is larger than that in KOH solution. Because the amounts of photo-generated electro-hole pair are sufficiently large in H₃PO₄ solution, as shown in Fig.2. In addition, several groups reported that oxide growth rates in KOH solution are larger than that in H₃PO₄ solution [11, 12].

IV. CONCLUSION

In this paper, we use a positive lens as a light beam to converge and enhance photocurrent. The process provides highly etch rates >240 nm/min at moderate light intensities of ~17.3 mW/cm² @237 nm by deuterium lamp in H₃PO₄ solution. The etch rate and photocurrent are characterized at various concentration of stirred solutions. A uniform and rather smooth etched surface was obtained with a RMS roughness 15.1 nm in stirred solution (H₃PO₄, pH=1.09) at room temperature.

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REFERENCES

- Bardwell, J. A., J. B. Webb, H. Tang, J. Fraser and S. Moisa (2001) Ultraviolet photoenhanced wet etching of GaN in K₂S₂O₈ solution. *Journal of Applied Physics*, 89(7), 4142-4149.
- Grenko, J. A., C. L. Reynolds, Jr., R. Schlessler, J. J. Hren, K. Bachmann and Z. Sitar(2004) Nanoscale GaN whiskers fabricated by photoelectrochemical etching. *Journal of Applied Physics*, 96(9), 5185-5188.
- Hwang, J. D., G. H. Yang, W. T. Chang, C. C. Lin, R. W. Chuang and S. J. Chang (2005) A novel transparent ohmic contact of indium tin oxide ton-type GaN. *Microelectron Engineering*, 77, 71-75.
- Hwang, J. D., G. H. Yang, Y. Y. Yang and P. C. Yao (2005)

- Nitride-Based UV metal-insulator-semiconductor photodetector with liquid-phase-deposition oxide. *Japanese Journal of Applied Physics*, 44(11), 7913-7915.
5. Hwang, Z. H., J. M. Hwang, H. L. Hwang and W. H. Hung (2004) Electrodeless wet etching of GaN assisted with chopped ultraviolet light. *Applied Physics Letters*, 84(19), 3759-3761.
 6. Mileham, J. R., S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, R. J. Shul and S. P. Kicoyne (1996) A: Vacuum surfaces and films. *Journal of Vacuum Science & Technology*, 14(3), 836-839
 7. Minsky, M. S., M. White and E. L. Hu (1996) Room-temperature photoenhanced wet etching of GaN. *Applied Physics Letters*, 68(11), 1531-1533.
 8. Peng, L. H., C. W. Chuang, J. K. Ho, C. N. Huang and C. Y. Chen (1998) Deep ultraviolet enhanced wet chemical etching of gallium nitride. *Applied Physics Letters*, 72(8), 939-941.
 9. Peng, L. H., C. H. Liao, Y. C. Hsu, C. S. Jong, C. N. Huang, J. K. Ho, C. C. Chiu and C. Y. Chen (2000) Photoenhanced wet oxidation of gallium nitride. *Applied Physics Letters*, 76(4), 511-513.
 10. Riedl, T., F. Hitzel, A. Hangleiter, S. Miller, A. Weimar, G. Brüderl, A. Lell and V. Härle (2003) Revealing the defect structure in laterally overgrown GaN stripes utilizing photoelectrochemical etching techniques. *Japanese Journal of Applied Physics Part 1*, 42(6A), 3381-3382.
 11. Rotter, T., D. Mistele, J. Stemmer, F. Fedler, J. Aderhold, J. Graul, V. Schwegler, C. Kirchner, M. Kamp and M. Heuken (2000) Photoinduced oxide film formation on n-type GaN surfaces using alkaline solutions. *Applied Physics Letters*, 76(26), 3923-3925.
 12. Seo, J. W., C. S. Oh, H. S. Jeong, J. W. Yang, K. Y. Lim, C. J. Yoon and H. J. Lee (2002) Bias-assisted photoelectrochemical oxidation of n-GaN in H₂O. *Applied Physics Letters*, 81(6), 1029-1031.
 13. Skriniarova', J., A. Hart, H. P. Bochem, A. Fox and P. Kordos (2002) Photoenhanced wet chemical etching of n⁺-doped GaN. *Materials Science and Engineering*, B91-92, 298-302.
 14. Strite, S. and H. Morkoc (1992) GaN, AlN, and InN: A review. *Journal Vacuum Science Technology*, B 10, 1237-1241.
 15. Youtsey, C., I. Adesida and G. Bulman (1997) Highly anisotropic photoenhanced wet etching of n-type GaN. *Applied Physics Letters*, 71(15), 2151-2153.
 16. Youtsey, C., I. Adesida and G. Bulman (1998) Gallium nitride whiskers formed by selective photoenhanced wet etching of dislocations. *Applied Physics Letters*, 73(6), 797-799.

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