

Resonantly enhanced selective photochemical etching of GaN

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Wavelength dependent photochemical etching of GaN films reveals a strong resonant enhancement of the photocurrent at the GaN gap, in close agreement with the excitonic absorption profile of GaN. The corresponding etching rate of GaN strongly correlates with the measured photocurrent. No photocurrent, nor etching is observed for AlGaIn films under same excitation conditions. The method could pave the way to the development of truly selective etching of GaN on AlGaIn for the fabrication of nitride based optoelectronic devices. © 2009 American Institute of Physics.

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Rapid developments in the field of nitride based optoelectronic^{1,2} and electronic devices³⁻⁵ have been largely fueled by the exceptional physical and electrical properties of the nitride material system. The primary stimulation for research into nitride materials comes from their large direct bandgaps and their physical robustness and chemical stability⁶ compared to other semiconducting materials. This same robustness however makes processing of nitride devices exceedingly difficult. Thus, further advances in the fabrication of electronic and optoelectronic devices envisioned for the gallium nitride material system require the development of entirely new processing schemes.

Due to the extreme resistance of the group III nitrides to chemical attack by conventional wet etchants,⁷ etching of nitride films has been carried out almost entirely using dry etching methods.⁸⁻¹¹ However, this technique has two main disadvantages: (i) creation of ion-induced damages and (ii) difficulty to obtain smooth sidewall etches required in many optoelectronic devices.⁷

In recent years, photoelectrochemical (PEC) wet-etching of nitrides¹²⁻¹⁴ has emerged as a promising etching tool for device fabrication, yielding smooth surfaces,^{15,16} and anisotropic etch profiles.^{7,17} Furthermore, highly anisotropic PEC etching and smooth surfaces of *n*-GaN have been demonstrated.¹⁵

In this work, we employ wavelength dependent PEC etching technique to selectively wet-etch GaN films. A sharp resonance is observed in the induced photocurrent when the excitation energy is tuned across the GaN bandgap using tunable frequency-doubled femtosecond pulses. Good agreement is found between measured etch depth and photocurrent. Strong suppression of the photocurrent is observed for excitation below GaN bandgap, producing no etch, and suggesting that the technique can be used to selectively etch films with smaller bandgap than that of the underlying layer.

The experimental setup is shown in Fig. 1(b). The photochemical etching of GaN samples was carried out in an electrochemical cell at room temperature using stirred 0.01 M KOH solution. The electrochemical cell consists of two working electrodes, the anode (GaN film) and the cathode

(platinum electrode) dipped in the electrolyte KOH solution. The electrolyte/GaN interface forms a Schottky contact. Figure 1(a) shows characteristic *I-V* taken under above conditions. When the sample is illuminated with photon energies above GaN bandgap at 300 K, electron-hole pairs are generated in the semiconductor, producing measurable photocurrent seen in Fig. 1(a). The application of a reverse dc bias to the semiconductor further confines the holes at the electrolyte/semiconductor interface, where they participate in the etching process consisting of the Ga oxidation and its oxide dissolution.

The etching experiments were conducted on two samples. A GaN sample which consists of a 4- μm -thick unintentionally doped (mid- 10^{16} cm^{-3}) GaN(0001) film grown on sapphire substrate and an AlGaIn sample consisting of 300 nm of $\text{Al}_{0.32}\text{Ga}_{0.68}\text{N}$ layer on top of 50 nm of Si doped GaN grown over high-resistivity 1- μm -thick GaN(0001)/*c*- Al_2O_3 MOCVD template. The samples were

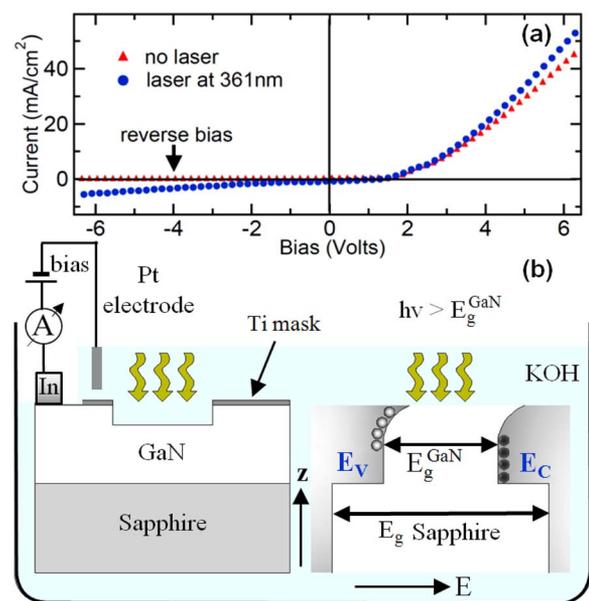


FIG. 1. (Color online) (a) *I-V* curve taken on the sample with and without laser illumination at 361 nm (b) Schematic of the PEC etching setup and the equivalent band diagram of the electrolyte/semiconductor interface.

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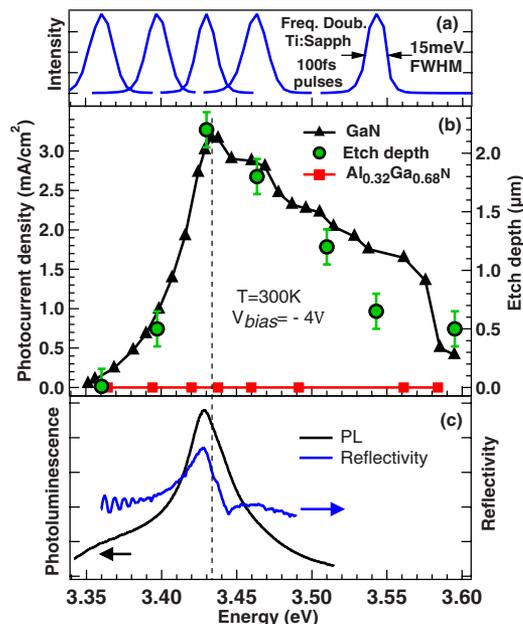


FIG. 2. (Color online) (a) Frequency-doubled, Ti:Sapphire 100 fs pulses with photon energies ranging from 3.3 to 3.6 eV used in PEC etching. (b) Excitation energy dependence of the photocurrent (triangles) during PEC etching of the GaN sample and the corresponding etch depths (circles). The photocurrent under same conditions for the AlGaIn sample is also shown (squares), (c) photoluminescence, and reflectivity spectra at room temperature of the GaN sample.

lithographically patterned into a grid of $40 \times 40 \mu\text{m}^2$ squares with 100 nm thick Ti layer as a mask. The bias was applied through an In contact on the side of the sample and a Pt-electrode dipped inside the electrolyte solution, as shown in Fig. 1(b).

For excitation, we employ a tunable Ti:Sapphire femto-second laser. The 150 fs pulses with tuning range of 670–760 nm are frequency-doubled in a nonlinear beta barium borate (BBO) crystal to yield UV pulses in the range of 3.3–3.6 eV, (i.e., from 100 meV below to 200 meV above the GaN bandgap at room temperature). The illumination with UV pulses, having a spectral full width at half maximum of ~ 15 meV allows the careful study of the etching process dependence on the excitation energy. Typical spectra from UV laser pulses with excitation energies tuned across the GaN bandgap are presented in Fig. 2(a). The resulting photocurrent is measured using a digital multimeter when the sample is reverse biased at -4 V, as shown in Fig. 1(a).

Figure 2(b) shows photocurrent measurements taken on the GaN sample with varying excitation energy, keeping the excitation power density constant at $8.4 \text{ mW}/\text{cm}^2$. We observe a sharp increase in the photocurrent with the onset of GaN absorption at ~ 3.40 eV. For comparison, same measurements have been performed on the AlGaIn sample. As expected, for excitation below AlGaIn bandgap no photocurrent is observed underscoring the fact that no photogenerated carriers are produced. Figure 2(b) also reveals a strong resonance in the photocurrent centered at 3.43 eV. This is attributed to the excitonically enhanced absorption as evidenced from the reflectivity and luminescence data on the same sample shown in Fig. 2(c). The detailed study of reflectivity as a function of temperature clearly shows that the reflectivity spectrum at room temperature is dominated by the A and B excitonic absorption resonances of GaN, separated by a

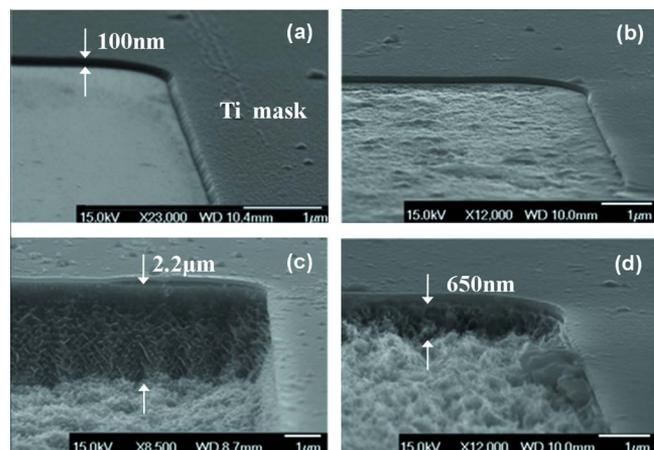


FIG. 3. (Color online) SEM pictures of: (a) Ti patterned GaN sample before the etching, (b) when PEC etched under illumination at 3.36 eV, (c) at 3.43 eV, and (d) at 3.54 eV. All samples were dipped in a KOH solution to remove the residual oxide by-products.

kink in the reflectivity spectrum of Fig. 2(c). The photoluminescence data strongly support the above claim.

Previous PEC etching experiments by other groups have not revealed such excitonically enhanced photocurrent measurement, mainly owing to the fact that excitation sources typically used in those experiments were either He–Cd lasers at 325 nm (Refs. 12 and 18) or filtered¹³ and unfiltered⁷ broadband excitation sources, such as xenon or Hg arc lamps. The tunable spectrally narrow and intense laser source of this study is a key factor for our findings.

To confirm that the photochemical etch rate is proportional to the photocurrent we performed several etching runs at various excitation energies, keeping the same excitation power density and exposure time. Following the etch, the samples were dipped in a concentrated KOH solution to remove the residual oxide by-products and were then characterized by scanning electron microscope (SEM). Their etch depths were analyzed by alpha step profilometer. In Fig. 3, a series of SEM images are presented corresponding to excitation at selected excitation energies across the GaN bandgap: (a) before the etch, (b) at 3.36 eV, (c) at 3.43 eV, and (d) at 3.54 eV. Before the etch, a smooth GaN surface is seen, patterned with the 100 nm thick Ti mask. The Ti mask serves multiple purposes. First, it allows an assessment of the etch anisotropy and second it provides precise reference for the determination of the etch depth. As expected, negligible etch rates are seen in Fig. 3(b) for excitation below the GaN bandgap. The small roughness is attributed to etching caused by the photogenerated carriers in the absorption tail and to the small spectral broadening of the excitation pulse. Excitation at the photocurrent peak, exploiting resonantly enhanced excitonic absorption, resulted in an etch depth of $2.2 \mu\text{m}$ with relatively sharp sidewalls. The resonant behavior is further confirmed in Fig. 3(d), where excitation at higher energy, yields smaller etch depth. The extracted etch depths in Fig. 2(b) are recorded for several excitation energies, as shown in Fig. 2(a). The resulting etch depths follow nicely the measured photocurrent profile. Small discrepancies between etch depths and photocurrent profile for excitation at higher energies could result from particular surface morphology during etch, affecting the intensity of the penetrated light at the etch front and modifying slightly the etch rates.

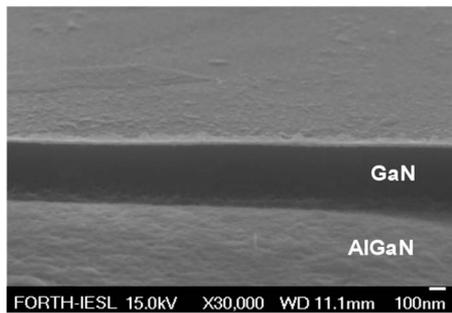


FIG. 4. SEM picture following selective PEC etching of GaN on $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ showing sharp sidewalls and smooth etched surface. The 350 nm sidewall which is independent of etch time proves the bandgap selective nature of the etching process.

The above results suggest that PEC etching under resonant excitation at the GaN exciton energy is by far more efficient compared to the excitation by broadband lamp source. In addition, it opens exciting possibilities to exploit the bandgap selective nature of PEC etching, as a tool to achieve a truly selective etching technique for fabrication of optoelectronic devices that require smooth optical quality surfaces. Indeed PEC experiments on the AlGaIn sample with excitation at 3.43 eV revealed no etching at all.

An inevitable consequence of the PEC etching process is the creation of oxide by-products at the semiconductor surface. Several methods have been proposed in the literature as possible techniques for oxide removal¹⁹ based on concentrated HCl or KOH solutions. Under certain etching conditions, the etched surface has the ability to self-clean, often seen as an oscillation of the photocurrent due to the buildup and gradual dissolution of the oxide layer.²⁰ This behavior is confirmed in our experiments since dipping the etched samples in a concentrated KOH solution did not alter the depth nor the roughness of the etched surface.

Interestingly, the development of bandgap selective PEC etching technique will lift the necessity to perform oxide removal since it would be possible to obtain smooth surfaces by simply allowing a long enough exposure to obtain a clean etched surface, without causing damage to the underlying higher bandgap semiconductor layer.

Such bandgap selective PEC etching has been verified by performing experiments on a third sample using excitation centered at 3.40 eV to selectively etch GaN over AlGaIn. The Ti patterned sample consisted of a 350 nm thick GaN layer grown over 100 nm thick $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ on a GaN *c*- Al_2O_3 template. The etch depth is found to be independent of exposure time. The PEC etch process stops naturally as the etch front reaches the GaN/ $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ interface, resulting in a sharp 350 nm sidewall shown in Fig. 4. It also shows that the underlying etched surface is smooth and requires no

oxide removal procedure. Our results show that such bandgap selective etching technique could have important advantages in processing of nitride materials.

In conclusion, we demonstrate strong dependence of the PEC etching photocurrent on the excitation energy marked by sharp resonant excitonically enhanced absorption in GaN. The corresponding etching rates are consistent with the photocurrent measurement on the same sample. The demonstrated selective etching of GaN on AlGaIn suggests that the technique could be used as a fundamental tool for processing nitride semiconductors. This could have particular advantages for the fabrication of optoelectronic devices that require optical flatness.

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