Enhancing Performance of Porous Si-Doped GaN Based MSM Photodetector Using 50 Hz ACPEC

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Abstract. In this work, we report the formation of porous Si-doped GaN films under a novel alternating current (sine-wave a.c. (50 Hz)) photo-assisted electrochemical etching (ACPEC) conditions. The formation of porous Si-doped GaN by the novel ACPEC is performed in the same electrolyte concentration (4% KOH) used in common dc constant current electrochemical etching process. Ultra-violet (UV) illumination is used to assist in the generation of electron-hole pairs, where etching proceeds through the oxidation and consequently, dissolution of the semiconductor surface. The ac formed porous Si-doped GaN with excellent structural and optical properties. According to the FESEM micrographs, the GaN thin films exhibit a homogeneous nanoporous structures with spatial nano flakes arrangement. The porous layer exhibited a substantial photoluminescence (PL) intensity enhancement with red-shifted band-edge PL peaks associated with the relaxation of compressive stress. The shift of $E_2$(high) to the lower frequency in Raman spectra of the porous GaN films further confirms such a stress relaxation. Electrical characterizations of the MSM photodiodes were carried out by using current-voltage (I-V) measurements indicated that the devices were highly sensitive to ambient light.

1. Introduction
After the discovery of room temperature photoluminescence enhancement from porous GaN by Shelton et al. [1], the structural and optical properties of the porous GaN have been greatly investigated [2-5]. Due to its simple fabrication process, interesting optical properties, research in porous GaN has progressed in wide a range of novel ideas and applications such as gaseous sensor [6, 7], photodetector [8] and chemical sensor [9]. Many other sensing applications based on the large, nanostructure surface area of porous GaN may be imagined.

The photoelectrochemical (PEC) etching method is an attractive technique for preparing porous GaN and producing optical waveguides. With this method, porous layers can easily be prepared over a large area of GaN substrate [10]. Pore morphology can also be controlled by optimizing several parameters, for instance current density, etching time, UV light assistance, and electrolyte concentration. Porous GaN is mostly formed by the constant direct current electrochemical anodization of GaN in a KOH
electrolyte [11, 12]. A common DCPEC process is very sensitive to the electrolyte concentration inside the cell. For example, KOH electrolyte is consumed during the chemical interactions in the pores, and its concentration near to SEI thereby decreases, which negatively affects the etching process. Nitrogen bubbles generated in the pore also decrease the speed of etching, resulting in shallow pores. The solution to this problem is the application of a sinusoidal alternating current. This method leads to the ejection of the gas bubbles and allows fresh KOH molecules to react with GaN substrate, where the KOH concentration at the SEI remains constant.

The goal of this study is to prepare porous GaN by a novel technique, namely by alternating current photo-assisted electrochemical etching (ACPEC) [13, 14]. Results of systematic morphological, structural and surface studies of porous GaN samples are reported.

2. Methodology
The commercial Si-doped GaN film grown by metalorganic chemical vapor deposition (MOCVD) on a two inch diameter sapphire (0001) substrate was used in the formation of porous GaN by the ACPEC etching techniques. The thickness of GaN film is 3 μm with concentration of free electrons of the order of $10^{19}$ cm$^{-3}$ as determined by Hall Effect measurements. The ac etching process was performed at room temperature with a current density of 50 mA/cm$^2$ in 4 % concentration aqueous solution of KOH under in-situ illumination of 500 W ultra-violet for 45, 90 and 120 minutes etch time. After chemical treatment, the samples were carefully rinsed in deionised water and dried in ambient air.

The sample morphology was studied using field emission scanning electron microscope (FESEM) (FEI Nova NanoSEM 450). High resolution X-ray diffraction (HR-XRD) (PANalytical X’pert PRO MRD) was used to assess the crystalline quality of the as-grown and porous samples. The optical properties of the samples were investigated by Raman and photoluminescence spectroscopy (Jobin Yvon HR800UV). The electrical characteristics of the fabricated photodetectors were analyzed at room temperature with a computer-controlled integrated Sourcemeter (Keithly 2400, USA).

3. Results and discussion
Figure 1 shows a top oblique of FESEM images of the samples etched with 50 mA/cm$^2$. Initially, for as grown sample, the structure exhibited a flat and smooth surface as shown by Figure 1(a). Upon the etching process, for the sample etched for 45 min with current density 50 mA/cm$^2$ (Figure 1(b)), FESEM had displayed a surface morphology of GaN thin film with a network of nanoarchitecture of the porous structure. On the other hand, two structural features are present on the GaN surface obtained after 90 min duration etched with a current density of 50 mA/cm$^2$; one is the nanocoral reefs and the other is the sun-flower like nanoporous GaN as apparent in Figure 1(c). At 120 min, layered porous GaN structure can be clearly seen due to the etching process further ensued at underlying layer.

Figure 2 shows a phi-scan for the $(1012)$ planes of a as grown GaN film grown on a sapphire (0001) substrate and Si-doped porous GaN samples etched under current density of ac 50 mA/cm$^2$. From the figure it is clear that the as grown and Si-doped porous GaN samples have the same six-fold azimuthal symmetry with exact match in orientation. Again, this trend is consistent with the wurtzite (hexagonal) crystal structure [15].

The HR-XRD measurements also performed on the symmetric (0002) and asymmetric (10$\bar{1}$2) plane for further confirmed the change of crystalline quality of the Si-doped porous GaN samples which was reflected in the FWHM of the peaks as presented in table 1. Specifically, the defect structure of all Si-doped porous GaN causes significant broadening in both symmetric (0002) and asymmetric (10$\bar{1}$2) rocking curves. This probably indicates that (0002) scan mode only broadened by screw or mixed TD despite the fact that (10$\bar{1}$2) scan mode was broadened by all the TDs [16, 17].
Figure 1. FESEM image of the as grown and Si-doped porous GaN formed under different etching duration with a current density of ac 50 mA/cm$^2$ (a) as grown (b) 45 minutes (c) 90 minutes, and (d) 120 minutes. Inset is the image with higher magnification.

Figure 3 shows the room temperature PL spectra recorded from the nanoflake, nanocoral reefs and sun-flower like nanoporous GaN. The peak position, FWHM, the peak shift and the relative intensity of near band edge PL are given in table 2. The spectra were observed to be slightly broadening toward the low-energy side in the Si-doped porous GaN indicating an incorporation of impurity-induced disorder or surface defect during the etching process [18]. The spectra of the Si-doped porous GaN samples were observed to be slightly red shift of ~ 1 nm (relative to the spectrum of as grown GaN), indicating an reduction in stress [19, 20]. Moreover, the little different in the peak position indicating that the change of porosity has a little influence on the PL peak shift. Similar red shifted PL from porous GaN has been reported before [12, 13, 18]. On the other hand, other researchers claimed that porous GaN samples were observed to be PL blue shifted relative to the as grown sample [4, 21, 22].

The Raman spectra for as grown sample and Si-doped nanoporous GaN were shown in Figure 4 etched under different durations. The scattering intensity is again larger in Si-doped porous GaN than for the as grown sample, and the geometry forbidden TO modes are visible. The increased scattering intensity is, at least partially, because of physical surface roughening, whereas the presence of the geometry forbidden TO modes can be attributed to the increased importance of scattering off of the sidewalls of the Si-doped porous GaN structure. Table 3 compiles the peak position of $E_2$ (high), and $A_1$ (TO) and $E_1$ (TO) forbidden modes obtained from Raman spectra for different samples.

The frequency of the $E_2$ mode in the as grown sample is 569.36 cm$^{-1}$. For the porous samples, the frequency of $E_2$ mode in both 45 min and 90 min are centered at 569.30 cm$^{-1}$, whereas 120 min sample are at 569.26 cm$^{-1}$. As can be seen from the values, there is a small red shift associated with the $E_2$ mode of Si-doped porous GaN indicates the compressive stress relaxation had taken place in these samples. The red shift in the $E_2$ mode was in good agreement with other researchers and have also noted a relaxation in stress in porous [18, 23, 24].
Figure 2. X-ray diffraction phi-scan profiles of as-grown and porous Si-doped GaN samples etched under different durations with a current density of ac 50 mA/cm$^2$ using (1012) plane.

Table 1. The diffraction peak positions and lattice constants of the as-grown and Si-doped porous GaN samples measured by HR-XRD.

| Sample   | (0002) Peak (°) | FWHM (arcsec) | (1012) Peak (°) | FWHM (arcsec) | c (Å)  | a (Å)  | c/a ratio |
|----------|-----------------|----------------|-----------------|----------------|--------|--------|-----------|
| As grown | 17.676          | 298.8          | 24.073          | 334.8          | 5.0739 | 3.2656 | 1.5537    |
| 45 min   | 17.411          | 298.8          | 24.123          | 374.8          | 5.1487 | 3.1951 | 1.6114    |
| 90 min   | 17.298          | 306.0          | 24.056          | 360.0          | 5.1812 | 3.1900 | 1.6242    |
| 120 min  | 17.357          | 295.2          | 24.066          | 360.0          | 5.1642 | 3.1993 | 1.6142    |

The current-voltage (I-V) characteristics in porous Si-doped GaN etched with a current density of 50 mA/cm$^2$ for 90 min etching duration were studied. For comparative study, a reference MSM photodetector was also fabricated on the as grown Si-doped GaN sample from the same wafer using same processing tools and under identical parameters. A comparison between electrical characteristics
of porous Si-doped GaN is shown in Figure 5. The results indicate the effect of combinational etching on the I-V characteristics of MSM photodetectors measured in the dark ($I_d$) and under illumination ($I_p$).

![Figure 3](image1.png)

**Figure 3.** The near band edge PL spectra of the samples etched under different durations with a current density of ac 50 mA/cm² measured at room temperature: (a) Full spectra, and (b) The observed near band edge luminescence.

**Table 2.** The peak position, FWHM, peak shift and relative intensity of near band edge PL of samples.

| Sample  | Peak position (nm) | $E_g$ (eV) | FWHM (nm) | Peak shift (nm) | Relative intensity |
|---------|--------------------|------------|-----------|-----------------|-------------------|
| As grown| 362.82             | 3.417      | 6.38      | -               | 1.00              |
| 45 min  | 363.55             | 3.410      | 6.61      | 0.73            | 1.68              |
| 90 min  | 363.81             | 3.408      | 6.61      | 0.99            | 1.05              |
| 120 min | 363.45             | 3.411      | 6.48      | 0.63            | 1.11              |

The dark current porous Si-doped GaN sample was lower than as grown sample due to high surface resistivity. The high surface porosity of porous Si-doped GaN sample enhanced the resistivity of this sample and thus decrease the dark current values. Despite its high surface resistivity, the porous Si-doped GaN sample showed a tremendous response upon its exposure to photon by producing significant free carriers for the enhanced current conduction. The degree of change in the current for the porous Si-doped GaN sample was the highest among all the samples due to it had the highest porosity.
Figure 4. The Raman spectra of the samples etched under different durations with a current density of ac 50 mA/cm$^2$. Inset is the observed shift for $E_2$ (high) from porous film.

Table 3. Peaks position, position of $E_2$ (high), $A_1$ (TO) and $E_1$ (TO) of different samples obtained from Raman spectra.

| Sample  | $E_2$ (high) peak position (cm$^{-1}$) | $A_1$ (TO) intensity (arb. unit) | $A_1$ (TO) peak shift (cm$^{-1}$) | $E_1$ (TO) peak position (cm$^{-1}$) |
|---------|--------------------------------------|----------------------------------|----------------------------------|-------------------------------------|
| As grown| 569.36                               | 222.24                           | -                                | -                                   |
| 45 min  | 569.30                               | 542.41                           | 0.06                             | -                                   |
| 90 min  | 569.30                               | 1077.30                          | 0.06                             | 560.00                              |
| 120 min | 569.26                               | 747.80                           | 0.10                             | 539.51                              | 560.85                              |
Figure 5. I-V characteristics of fabricated MSM photodetectors on as grown and porous Si-doped GaN samples etched with a current density of ac 50 mA/cm$^2$ for 90 min etching duration under dark ($I_d$) and under light illumination ($I_p$).

4. Summary
In summary, a novel, simple and cost-effective alternating current PEC etching was demonstrated to be an effective technique for the formation of nano-porous GaN with excellent properties. According to FESEM images, the etching duration has significant impact on the size of the pores. The obtained results hint at the possibility to prepare high quality nano-porous GaN layers with tunable stress. We strongly believe that further refinements of the sine-wave ac electrochemical processing technologies will enhance their role in semiconductor nanotechnology and nanoelectronics in the near future.

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