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Effect of KOH Concentration on the Properties of Undoped Porous GaN on Sapphire Substrate Prepared by UV assisted Electrochemical Etching

Azzafeerah Mahyuddin[1], Ashraf Rohanim Asari[2], Azrina Arshad[3], Mohd Zaki Mohd Yusoff[4]
[1]Quality Engineering Department, Universiti Kuala Lumpur, Malaysian Institute of Industrial Technology (MITEC), Bandar Seri Alam, Johor, Malaysia
[2]Instrumentation and Control Engineering Department, Universiti Kuala Lumpur, Malaysian Institute of Industrial Technology (MITEC), Bandar Seri Alam, Johor, Malaysia
[3]Quality Engineering Department, Universiti Kuala Lumpur, Malaysian Institute of Industrial Technology (MITEC), Bandar Seri Alam, Johor, Malaysia
[4]Department of Applied Sciences, Universiti Teknologi MARA (UiTM), Permatang Pauh, Penang, Malaysia

ABSTRACT

The main purpose of this work is to investigate the properties of undoped porous GaN fabricated by using cost-effective method named ultra-violet (UV) assisted electrochemical etching by varying electrolyte concentrations. Field Emission Scanning electron microscopy (FESEM), high resolution x-ray diffraction (HRXRD), and Raman scattering are used to characterize the as-grown and porous GaN samples. FESEM results is able to discover the average pore size which has the greatest influence on the electrolyte concentrations. HRXRD measurement shows the porous structure lead to the crystalline quality improvement of GaN epilayer. Further assessment is carried out to study the Raman spectra. It shows that the forbidden mode E1 (TO) was not exist in as-grown GaN sample but appears in the porous samples. Evidence from the studies explains that the quality of the GaN epilayer is able to enhance by the porosity in GaN epilayer.

Key words: GaN, porous, electrochemical, etching, UV.

1. INTRODUCTION

In more recent years, the fabrication of porous semiconductors for the purpose of improving material characteristics has attracted a massive and imperative deal of research interest. As compared to bulk structure, porous semiconductor have been proven to have attractive properties for instance high surface area, band gap energy shift, and abundant luminescence properties. It has also make them promising material in application of optoelectronics, chemical and biochemical sensors [1 - 7]. Additionally, porous semiconductors that is used for substrate is also being as a material that can claimed to reduce the extended defect density when depositing subsequent semiconductor layer [8]. Porous GaN also has been considered to be used as an intermediate layer between GaN layer and the substrate. Porous GaN structure is able to provide stress relaxation of growth template for subsequent III – nitrides layer as compared to as-grown GaN [9]. The reduction of dislocation density of porous GaN layer is also reported in 2017 [10]. At present, there are numerous techniques that have been developed to synthesis porous GaN for instance, dry etching by using anodic alumina templates [11], electroless etching [12-15] and photoelectrochemical etching [16, 17]. Typically, porosification parameters for instance, numerous etching parameters, electrolyte concentration, types of electrolyte, etching voltage, and etching duration greatly affect the surface morphology and the optical characteristics. A precise determination of etching parameters is necessary to ensure the optimum performance of porous structure is achieved for desired application. However, the biggest challenges in developing porous GaN are strong chemical stability of GaN and the lack of appropriate etching conditions. Therefore, it will complicate the researchers to explore the full potential of porous GaN in various application. Indeed, at present, general research in fundamental properties of porous GaN is still in its infancy. Therefore, it is sensible to modify the fabrication techniques that can lead to the new development of porous GaN.

In this study, porous GaN is fabricated by using UV assisted electrochemical etching technique. This technique is chosen since it has remarkable characteristics such as low processing temperature, cost effective, low structural damage, straightforwardness and flexibility process [18]. The effect of potassium hydroxide (KOH) concentration on GaN epilayer were examined by using field electron scanning electron microscopy, high resolution X-ray diffraction, and Raman spectroscopy.

2. EXPERIMENTAL PROCEDURE

The commercial undoped GaN wafer on sapphire (0001) substrate with 2 inches in diameter is cleaved into small pieces with size of 1 cm x 1 cm. Prior to the metallization, the samples are cleaned by considering the following steps; the removal of native oxide in the 1:20 NH4OH:H2O solution for 15 seconds, followed by dipping in 1:50 HF:H2O for 10 seconds. Subsequently, boiling aqua regia (3:1 HCl: HNO3) for 60 seconds is used to chemically etch and clean the wafers. Between the cleaning steps, the samples are rinsed in distilled water. Then, a few narrow stripes of Gold (Au) electrode with thickness of about 6 nm are deposited onto the surface of GaN sample by using Automatic Sputter Coater.

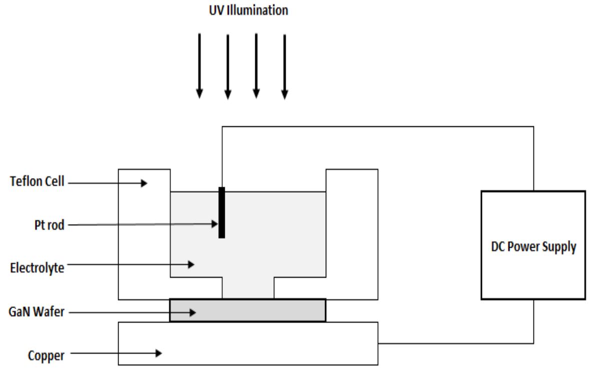


Figure 1: Photo electrochemical etching techniques.

The porous GaN samples are synthesized by employing photo electrochemical etching method as presented in Figure 1. Aqueous potassium hydroxide (KOH) is used as an electrolyte known as etchant solution for this method. The experimental set-up is conducted by using a Teflon etching cell. A GaN sample is mounted on the cell and has act as an anode (working electrode). Meanwhile, Pt wire acts as counter electrode and is connected to cathode (negative terminal) of the power supply. Then, the samples are placed in KOH electrolyte to start the etching process for 15 minutes under 400 W of UV lamp. UV illumination is important to enhance the etching process. The concentration of KOH electrolyte is varied for 5%, and 10%, respectively. Constant current density of 0.15 A mm-2 is applied. After the etching process, the samples are rinsed with deionized water and they have leave dried in ambient air.

The surface morphology of the samples is observed by using field emission scanning electron microscopy (FESEM) (Hitachi sub8020). The information of the crystal structure and properties of as-grown GaN and porous GaN samples is carried out by considering high resolution X-ray diffraction (HR-XRD) measurements (Panalytical X'Pert PW3040). The optical characteristics of the porous samples are investigated by using the Raman spectroscopy (HORIBA XploRA Plus system) at room temperature.

3. RESULTS AND DISCUSSIONS

FESEM measurement is applied to characterize the surface morphologies of undoped porous GaN thin films. During photo electrochemical etching, illumination of UV light induce the generation of electron – hole pair which assisted the oxidation process at the GaN epilayer surface. Thus, the resultant produces from the oxidation process will be dissolved in KOH electrolytes. Figure 2(a) reveals the topography FESEM photographs of the as-grown and porous GaN samples fabricated under various KOH concentration. The inset figures show high magnification of porous structures. The KOH concentration during photo electrochemical etching has huge impact on the morphologies of porous structure formed. Figure 2(b) represents 5% KOH sample. It clearly explains that, there are a lot of tiny pores with some rifts start to form and appear along the grain boundaries, suggesting the etching process was in the early phase. The results obtained agreed with previous work that had been carried out by Ko et. al [19]. At the beginning process of etching, weak atomic bonding at the interface between grains, known as defective region are started to be etched by the KOH electrolyte. Apparently, the increase of pore sizes are found in sample etched in 10% KOH as shown in Figure 2(c). A higher magnification of FESEM image reveals that pores structure with hexagonal features are obtained. FESEM images discovered that the average pore size are about 150 nm and 350 nm for 5% KOH and 10% KOH, respectively. The increase of pore sizes with high KOH concentration can be explained by the increase in etching rate of Ga and N components. Therefore, it can be concluded that the defective region in GaN epilayer which contains weaken atomics bonding are highly attacked by high concentration of KOH electrolyte. From FESEM images as well, it can be perceived that the pores on GaN surface is not uniformly distributed. This trend is also in general agreement with other researchers and interestingly the porous GaN is not result in the same surface morphology [20 – 23].

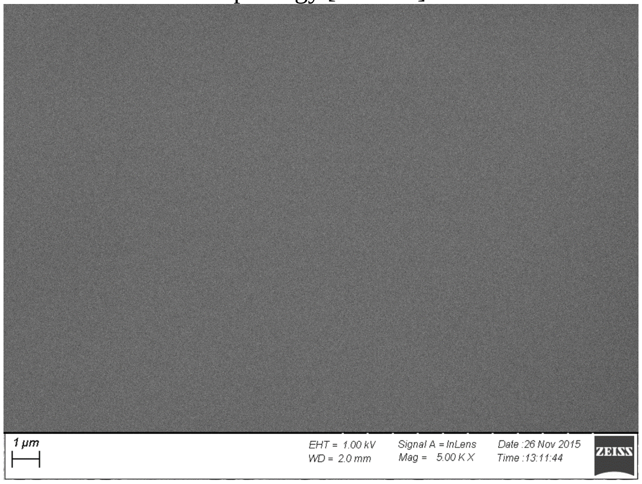
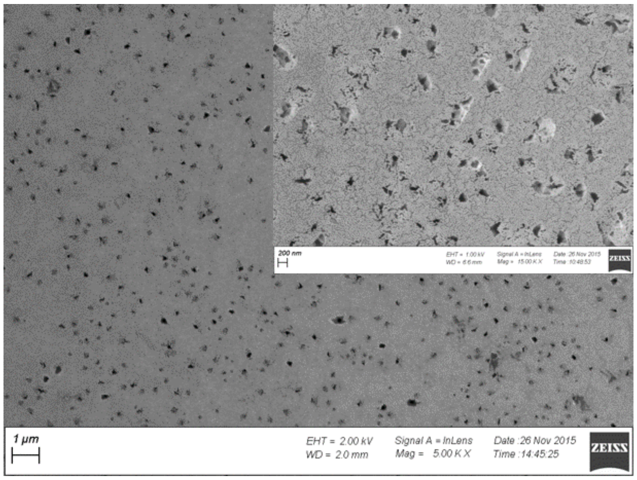
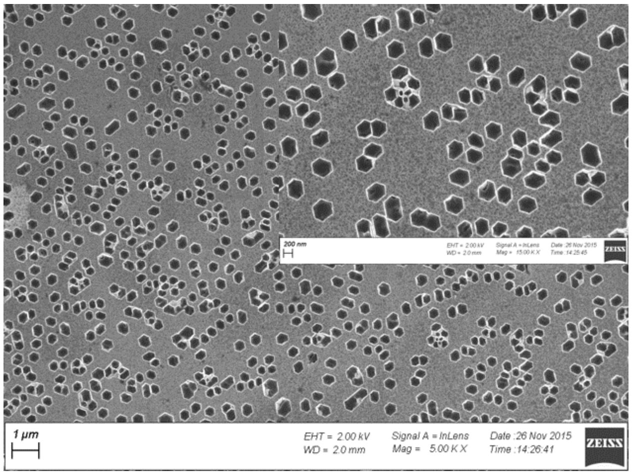


Figure 2: Top-view FESEM photographs of; (a) as-grown GaN and porous GaN prepared by UV assisted electrochemical etching with KOH concentration of, (b) 5%, and (c) 10%, respectively. Insets displayed the photograph with greater magnification.



(b)



(c)

The results for HR-XRD as a function of KOH concentration for porous GaN are depicted in Figure 3. As can be seen, GaN of (0002) and (0004) orientation peaks are observed at 34.5o and 72.0°, respectively for non-porous sample. The peak at 41.7° is ascribed as (0006) plane of the sapphire substrate. In view of the results obtained, all samples showed GaN peak is still observable and not completely etched away during the etching process. Therefore, it reveals the porous GaN retained its epitaxial feature.

The ω-scan plot of rocking curve (RC) measurement at symmetric (0002) of the samples for influences of KOH concentration is depicted in Figure 4. The quality of the crystal structure for GaN can be predicted by full width at half maximum (FWHM) values. In view of the results obtained, as comparison between as-grown and porous GaN epilayer, samples with porous structure show reductions of FWHM values as KOH concentration increases. This represents the decrease of FWHM as a result of a decrease in dislocation density of GaN epilayer [24].

The screw plus mix dislocation density is assessed by incorporating the RC data based on the following equation [25]:

$$N_{screw+mix} = \frac{\beta^2_{(0002)}}{4.35xb_c^2} \qquad \text{(eq.1)}$$

where is the FWHM values (which converted into radian), is estimated to be 0.5185 nm which named as Burger vector of the screw (c-type) threading dislocation [26]. The value of FWHM and calculated screw plus mix dislocation density are depicted in Table 1.

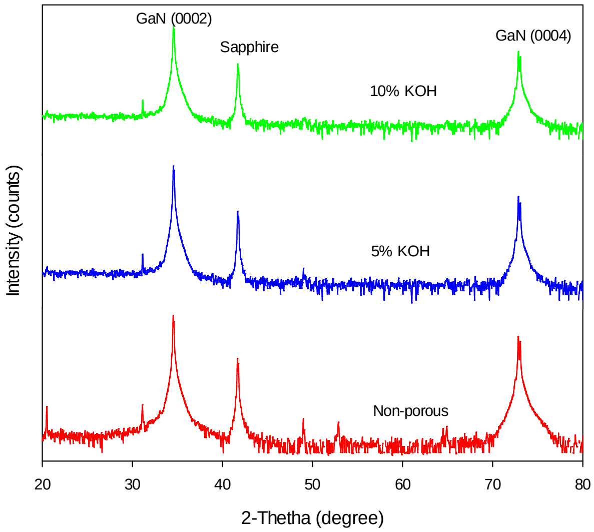


Figure 3: The HR-XRD graph of the non-porous sample and porous GaN samples etched under KOH concentrations of 5% and 10%, respectively.

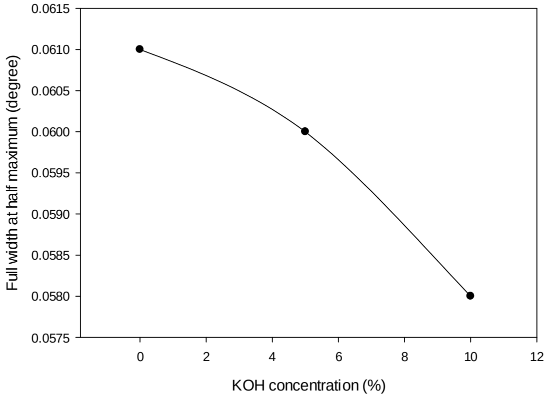


Figure 4: Dependency of full width at half maximum (FWHM) from rocking curve measurement for GaN epilayer etched at different KOH concentrations.

From Table 1, it can be seen that the value of dislocation density are decreased as the KOH concentration increased relative to as-grown GaN sample. Similar findings are also reported by several groups [21, 27]. The results are in similar covenant with the FESEM measurements as defective region at the grain boundaries are highly etched at higher KOH concentration. The reduction of FWHM and value of dislocation density indicate that porous GaN is significantly enhanced the quality of GaN and this structure would be promising material for electronic applications.

Table 1: The FWHM of (0002) and dislocation density of different samples measured by HRXRD.

Sample	FWHM (^{o})	Dislocation density (cm^{-2})
Non - porous	0.061	9.70 x 10^{11}
5% KOH	0.060	9.38 x 10^{11}
10% KOH	0.058	8.76 x 10^{11}

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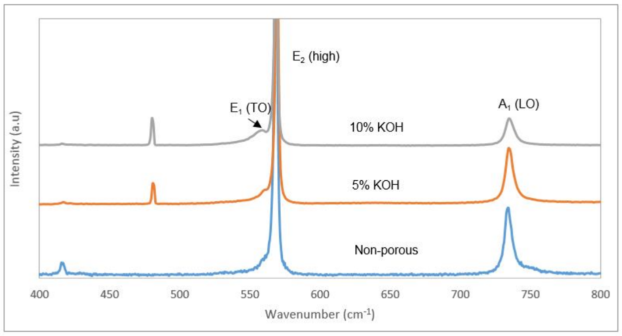

Figure 5: Raman graph of as-grown GaN and porous GaN samples etched under KOH concentrations of 5% and 10%, respectively

For assessing GaN microscopic disorder, Raman scattering is used to monitor internal stress in the GaN epilayer. The measurement is conducted by measuring the frequency, polarization characteristics and broadening of the Raman active phonons. Room temperature of Raman spectra of all the samples are presented in Figure 5. Comparison between Raman spectra of as-grown GaN and porous GaN reveals that formation of porous structure has a tendency to influence the E2 (high) peak. This peak in porous samples are experiential frequency shift to lower mode relative to the as-grown GaN sample. This is caused by stress relaxation of porous samples. It should be highlighted that for Raman selection rules, only two allowed phonon modes in this scattering geometry which are E2 (high) and A1 (LO). The spectra are dominated by strong E2 (TO) and A1 (LO) phonons near 568 cm-1 and 734 cm- 1, which are in agreement with Raman selection rules for wurtzite GaN. From the raman spectra, the forbidden mode E1 (TO) is absent in as-grown sample but present in the porous samples. This peak is found to be stronger with the higher KOH concentration. Yam et. al stated that the existence of the forbidden peaks in the porous GaN has direct relation towards its optical properties [1]. This is believed to occur due to the crystal disordering in the films. Therefore the increase of scattering from the sidewalls of the porous structure possibly will change the light polarization. This represents the increase of pore density as a result of stronger scattering effect. Thus, the obtained results show that porous structure might enhance the optical properties of GaN and could be promising material for optical device applications. This trend is also in general agreement with other researchers [1, 3, 21] and consistent with the results obtained from FESEM and HRXRD measurements as previously discussed.

4. CONCLUSION

In summary, this work is devoted to assess the properties of undoped porous GaN. This is performed by using UV assisted electrochemical etching method in order to assess the effect of KOH electrolyte concentration on the porous structures. FESEM measurement shows that the average pore size of porous GaN increases with KOH concentration. The increase of FWHM values from HRXRD measurement is obtained for porous samples suggest the dislocation density in as-grown GaN is diminished. Raman spectra shows that the absence of forbidden E1 (TO) mode in the as-grown sample is observed in porous samples. The results obtained from this study have laid an important platform in which the porous structure might influence various properties of the material.

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