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The Characterization of Nanostructured GaN Prepared via Low Temperature Photoelectrochemical Etching at Different Etching Period

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***Abstract*— This study investigates the nanostructured GaN prepared via low temperature direct current photoelectrochemical (DCPEC) etching with varying etching durations of 40 min and 55 min. One of the key challenges in optimizing DCPEC is managing the system's thermal stability. Operating at low temperatures is crucial to avoid the excessive heat transfer from the light source, which poses the risk of electrolyte vaporization. Such vaporization can disrupt the delicate balance of the DCPEC process, potentially leading to system instability, inefficient etching, or even failure. This work obtained substantial structural and optical characteristics of nanostructured GaN samples compared to as grown sample. This study ultilized 4% potassium hydroxide (KOH) electrolyte, 30 mA direct current (DC), and 100 W of ultraviolet (UV) light. The FESEM micrographs revealed that the pores have hexagonal shape and ridged structure. The nanostructured samples displayed a significant increase in photoluminescence (PL) intensity and a shift towards longer wavelengths in the band edge PL peaks, which can be attributed to the release of compressive stress. The Full with Half Minimum (FWHM) of the 40 min sample has the lowest value compared to the as grown and 55 min samples for symmetry omega scan, indicating a better crystalline quality of the sample.**

Index Terms*— *etching, GaN, low temperature, optical photoelectrochemical, porous

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I. INTRODUCTION

The unique optical properties of nanostructured semiconductors, as well as their prospective applications in optoelectronics, chemical sensing, and biological sensing, have garnered significant attention in recent years. By altering the level of porosity, it is possible to customise the fabrication of new sensing devices with increased surface area, shifted band gap, enhanced luminescence intensity, and improved photoresponse [1]. The study of nanostructured gallium nitride (GaN) has sparked interest because of its distinctive features that enable its operation in harsh and hazardous environments. In addition, nanostructured GaN has the ability to sink threading dislocations and accommodate strain [2].

The fabrication of nanostructured GaN can be achieved through the utilisation of both dry and wet etching techniques. However, dry etching techniques, such as reactive ion etching (RIE), inductively coupled plasma (ICP), and a combination of the two called inductively coupled plasma reactive ion etching (ICP-RIE), can result in surface damage and do not provide the desired selectivity for morphology, dopant, and composition [3]. The wet etching technique, including photo-assisted electroless etching, direct current photoelectrochemical (DCPEC) etching, and alternating current photoelectrochemical etching (ACPEC), is a cost-effective and sustainable method that does not require the use of hazardous gases, harsh chemicals, or high power consumption. Electroless etching is a technically simple and cost-efficient process that may be applied to both conductive and insulating materials widely [4]. However, this approach makes it extremely difficult to create a uniform pore size and distribution. DCPEC is a widely used etching technique due to its advantages, such as cost-effectiveness and precise control [5−7]. The etching condition or temperature employed during the etching process can influence the formation of nanostructured GaN. Nanostructured GaN can be formed at ambient temperature. Nevertheless, the transfer of heat from the intense UV light used in the etching process tends to increase the temperature of the etching system and transform the electrolyte into vapour. This will lead to a decrease in the volume of the electrolyte, which could affect the creation of the nanostructure. The etching activity and rate will decrease due to the aforementioned difficulties, leading to the uneven and inadequate porosity of the nanostructured GaN.

The objective of this study is to fabricate nanostructured GaN by the process of low temperature DCPEC etching. The findings of a comprehensive analysis on nanostructured GaN samples, including the investigations on their morphology, structure, and optical properties, are presented.

DCPEC etching happens when the electrolyte interacts with the semiconductor at the semiconductor-electrolyte interface (SEI). With the application of direct current, the etching process accelerates due to the movement of electrons.The energy band diagram of the SEI is depicted in Fig. 1 . Electrons flow from the DC source to the Pt wire, which is recognized as one of the most effective counter electrodes in photoelectrochemical (PEC) etching [8]. The Pt wire serves as the counter electrode, facilitating the flow of electrons into the electrolyte. With the assistance of UV light, holes in the valence band become excited into the conduction band above the Fermi level, allowing current to flow throughout the PEC system. Electrons from the GaN surface then react with the KOH electrolyte, initiating the etching process.

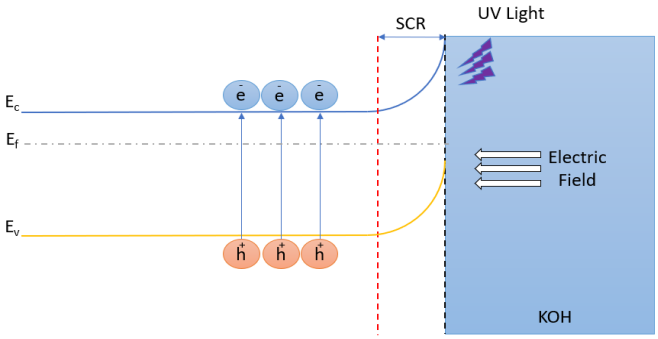

Fig. 1. Energy band diagram of semiconductor electrolyte interface

The excited electrons and holes are separated. The DC current enhances the overall etching process by increasing the number of charge carriers available to drive the etching reaction. These charge carriers are driven to various sites by the applied direct current's electric field. These electrons take part in reduction processes with the electrolyte that cause the semiconductor material to dissolve or etch. The purpose of maintaining a low temperature is to minimize the evaporation of the electrolyte caused by heat transfer from the UV source. When low temperatures are present at the SEI surface, they tend to reduce the recombination rate of electron-hole pairs, thereby slowing down the overall recombination process. As a result, more holes are available to react with the electrolyte, which in turn increases the etching rate.

II. EXPERIMENTAL PROCEDURE

This study utilises unintentionally doped (UID) GaN grown on a sapphire substrate. Subsequently, the material is cleaved into pieces of 1 cm × 1 cm. Due to GaN's potential to react with the air and form native oxide on its surface, it is necessary to perform a thorough surface cleaning. The cleaning procedure consists of immersing the samples in a solution of NH_3: H_2O (1:20) for 5 min, followed by a solution of HF: H_2O (1:50) for 20 sec, and then soaking them in a solution of HNO_3: HCl (1:3) for 5 min. Lastly, the samples are rinsed with deionized (DI) water. Fig. 2 demonstrates the setup of low temperature DCPEC etching on the GaN sample. 100W of ultraviolet light is used as the light source, along with the DC power supply as the current source of the PEC system.

The anode terminal is linked to a metal plate, while the cathode terminal is connected to a platinum (Pt) wire, which functions as the working electrode. The sample is initially wrapped with an aluminium sticker to improve electrical conductivity with the electrolyte. Afterwards, the sample is positioned under the O-ring, which has a diameter of 0.8 cm, while a cooling system operating at a low temperature ranging from 10 °C – 15°C passes beneath the sample. This study used a 4% potassium hydroxide (KOH) electrolyte solution, a DC current of 30 mA, and two different etching durations of 40 min and 55 min.

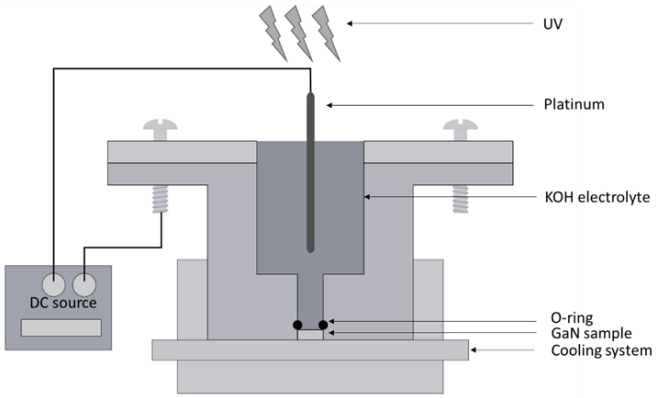

Fig. 2. Schematic diagram of low temperature direct current photoelectrochemical etching of GaN

The surface morphology of the samples was characterised using XHR-FESEM and EDX (FEI Verious 460L). The porosity of the morphology was analyse using ImageJ tools. A High-Resolution X-ray diffraction (HR-XRD) instrument (PANalytical PRO DY 2536) was also used to perform the phase analysis and rocking curve analysis on the samples. The optical properties were analysed using a PL instrument (Horiba LabRAM HR Evolution) model. The laser employed for PL experiments has a wavelength of 325 nm.

III. RESULT AND DISCUSSION

Field emission scanning electron microscopy **(**FESEM) images of the nanostructured GaN samples produced with varying etching durations are shown in Fig 3. Based on FESEM images, as grown sample in Figs 3(a) and 3(b) display a smooth and level surface with less than 1% porosity. The etching for both nanostructured samples was in the early stages. The pores became apparent, and they were fairly small. The 40 min sample's morphology as shown in Fig 3(c) and 3(d) indicates that the etching has only recently begun. It is clear from the darker area surrounding the pores as pointed by the red arrow, that the etching was going to begin in the region. For nanostructured sample, the porosity of the 55 min sample was higher than the 40 min sample which are 4.17% and 1.28%

respectively. When the time duration increases to 55 min, an early development of the ridge shape is seen in the sample. The ridges seem to have formed after the pores merged with each other, which then expose a greater surface area to the etchant. The 55 min sample at high magnification showed that the pores were developing in a hexagonal pattern. It can be noted that the shape of the pores nanostructured GaN produced by electrochemical etching depending on many factors and do not have a uniform shape to each other. The pore shape of GaN appears to form in an elongated, ridged, hexagonal, foam, and honeycomb shape, according to several studies [9−11]. It can be concluded that, the porous formation was found to be influenced by the etching duration where the anodization is occurred. However, prior studies have shown that properly prolonging the etching duration can improve this nanostructured GaN production [12]. Note that there are permissible ranges for etching to occur for each GaN sample with defined parameters; if the etching period is too extended, the GaN thin film will probably be etched away [13].

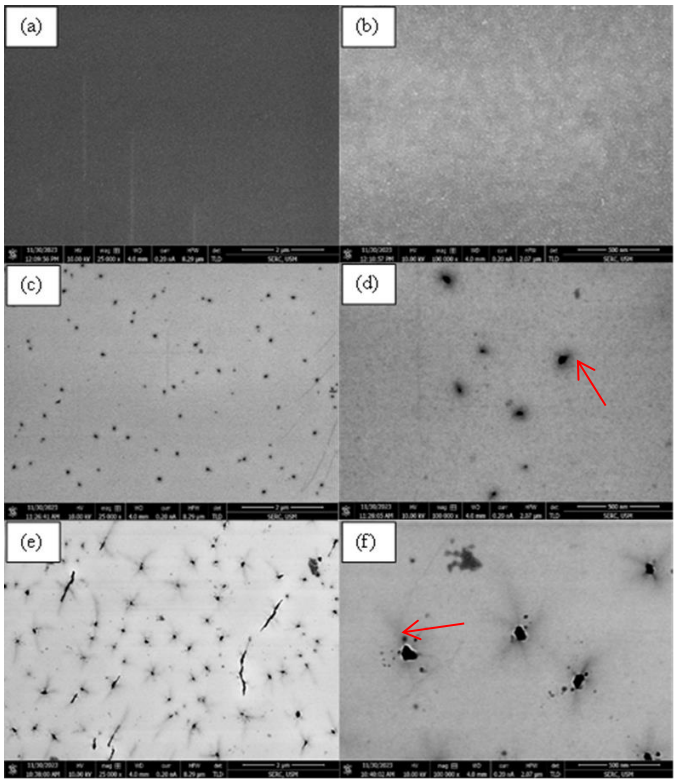

Fig. 3. FESEM images for as grown and nanostructured GaN prepared via low temperature DCPEC at different etching duration: [(a) as grown, (c) 40 min, (e) 55 min] at 2 µm magnification and [(b) as grown (d) 40 min, (f) 55 min] with high magnification at 500 nm.

To comprehensively understand the crystallinity of as grown and nanostructured GaN, HR-XRD analysis was performed. Fig. 4 shows the 2-theta scan of as grown and nanostructured GaN prepared via low temperature DCPEC. There are three (3) peaks shown in the Fig. 4 that indicate the hexagonal phase of GaN oriented in (0002) and (0004), while diffraction peaks are attributed to aluminium oxide (Al_2O_3) which indicate the sapphire substrate. As observed in Fig 4, the peak intensity of the as grown GaN (0002) and (0004) appeared at ~34.60° and ~72.89°, respectively and the sapphire peak appeared at ~41.70°. The 55 min sample has shown a significant change in both GaN (0002) and GaN (0004) in terms of intensity compared to the as grown sample. However, the 40 min sample roughly shows no significant difference in terms of intensity when compared to as grown sample. In comparison to nanostructured GaN samples, the presence of GaN (0002) and (0004) peaks as well as sapphire peaks in all etched samples showed that nanostructured GaN samples retained their epitaxial features and the GaN layer was not completely etched away by DCPEC at low temperature.

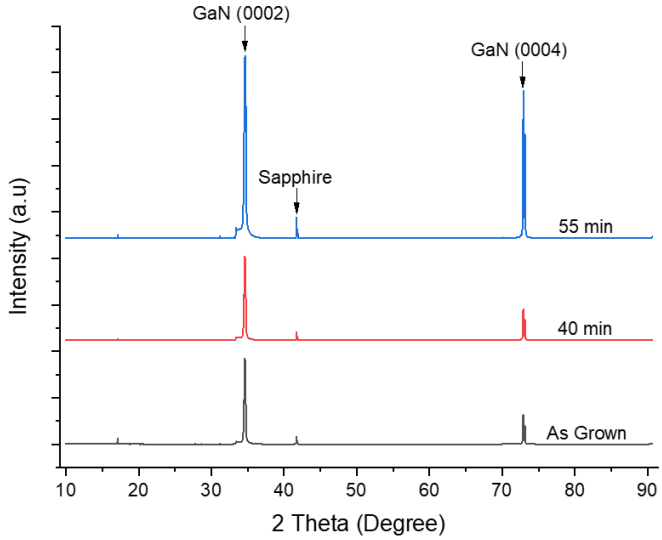

Fig. 4. XRD 2-theta analysis of as grown and nanostructured GaN prepared via low temperature DCPEC.

Omega scan also has been conducted in this section via HR-XRD for (0002) symmetry. The summarization of peak position, peak intensity and FHWM of all sample were tabulated in Table I. All samples exhibit peaks at the ~17°, but they differ in terms of peak intensity and Full Width at Half Maximum (FWHM). As FWHM, 40 min sample have the lowest value which is 215.86 sec compared to as grown and 55 min which are 219.52 sec and 219.75 sec respectively. Lower FWHM value indicates better crystallinity of the sample [14].

TABLE I. THE PEAK POSITION, PEAK INTENSITY, AND FWHM OF XRD ANALYSIS

Sample	Peak position	Peak intensity (a.u)	FWHM (sec)
As Grown	17.6127	3.52 E5	219.52
40 min	17.3147	2.89 E5	215.86
55 min	17.5754	2.73 E5	219.75

a.u = aubitary unit, sec = second

PL spectra obtained from nanostructured GaN prepared via low temperature DCPEC etched at different etching durations is shown in Fig 5. For comparison, the PL spectrum of the as grown GaN epilayer was also presented. A PL line shape shows

a small broadening toward the low energy side. The slight broadening relative to the as grown GaN epilayer emission could be due to incorporation of impurity-induced disorder or surface defects during DCPEC [15]. Table II provides an overview of the peak position, peak shift (in comparison to as grown GaN), and relative intensity.

It was found that the nanostructured sample's spectrum was red-shifted in comparison to as grown. The relaxation of the compressive stress in the nanostructured samples was also attributed to the red shift. Similar red-shifted PL from nanostructured GaN has been reported before [15−16]. On the other hand, the nanostructured GaN showed a notable increase in PL intensity as compared to the as grown GaN.

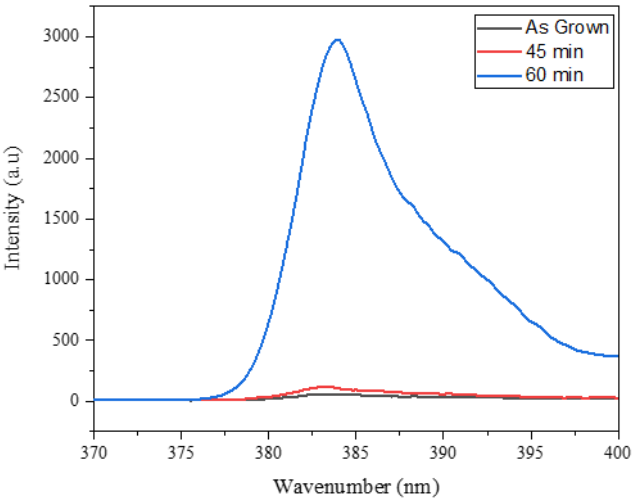

Fig 5. PL spectra of nanostructured GaN prepared via low temperature DCPEC etched at different etching durations.

When comparing the 55 min sample to the as grown GaN, the PL intensity was almost 36 times higher. Due to the nanostructured GaN's greater surface area observed in FESEM images, GaN molecules are exposed to PL excitation light significantly more. Conclusively, nanostructured GaN prepared via low temperature direct current PEC etching can alter the peak position and peak intensity compared to as grown sample.

TABLE II. THE PEAK POSITION, PEAK SHIFT, AND RELATIVE INTENSITY OF PL ANALYSIS

Sample	Peak Position (nm)	Peak shift	Relative intensity
As Grown	383.41	-	1.00
40 min	383.64	0.23	1.89
55 min	384.10	0.69	36.37

IV. CONCLUSION

Conclusively, a modified practical and cost effective DCPEC etching into low temperature innovation was proven to be an effective technique to form nanostructured GaN. GaN fabricated using low temperature direct current exhibits alterations in both peak position and peak intensity in XRD as well as PL when compared to the as grown sample. FESEM pictures indicated that varying the period of etching had a major effect on the nanostructured morphology which DCPEC at low temperature able to alter the level of porosity and enhance the surface area of the nanostructured GaN. PL measurements indicated that the peaks at the band edge of all nanostructured samples exhibited a red shift. Varying the etching duration has the potential to significantly influence the characteristics of a wide range of devices, such as UV photodetectors. By controlling this parameter, specific material properties can be tailored, which enhances the performance and functionality of these devices across various applications.

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