

# Synthesis Porous GaN by Using UV-assisted Electrochemical Etching and Its Optical Studies

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# Abstract

The PL of porous GaN sample shows higher intensity with smaller FWHM and red-shifting relative to the as-grown sample. The energy gap for porous GaN sample was smaller compare to the as-grown sample. The SEM surface image of UV-assisted electrochemical etching process is shown a shape and size of pore which was formed on the surface of the GaN, therefore the shape of pores formed was in spherical shape. The size of the pores formed has diameter as small as 85 nm. Two PL peaks were observed in the as-grown and porous GaN sample. For the as-grown GaN, the higher peak was observed at "361.946 nm" and the other at "723.739 nm" which is in UV and red luminescence region respectively. The FWHM is "8.198 nm" at "361.946 nm". For the porous GaN, the higher peak was observed at "364.235 nm" and at "728.039 nm", so their FWHM are "4.244 nm" and "8.926 nm" respectively. The peaks of porous sample were red-shifted at "2.289 nm and 4.30 nm" respectively compare to the peaks of the as-grown GaN. PL intensity of the porous samples was observed to be increased. Raman peaks representative to the wurtzite GaN crystal, namely  $E_2$  (low) at 142.426 cm<sup>-1</sup>,  $E_2$  (high) at 568.771 cm<sup>-1</sup>, and  $A_1$  (LO) at 736.769 cm<sup>-1</sup> were clearly observed.

Keywords: GaN, Porous, Semiconductor, Photo-electrochemical etching

## 1. Introduction

The most interesting property of "III-Nitride" semiconductors is their wide direct band gaps which enable the fabrication of highly efficient optoelectronic device operating in the blue and ultraviolet part of the spectrum. The direct band gap for wurtzite structure of InN, GaN, and AlN are "1.9 eV, 3.4 eV, and 6.2 eV" respectively [H. Sohn et al, 2000]. The "III-Nitride" semiconductors cover a part of the electromagnetic spectrum that is not covered by conventional semiconductor technology. Current semiconductor technology covers the spectrum from infra-red "IR" to green. GaN has a direct band gap of "3.4 eV"; this property makes it the best candidate for devices operating in the blue or UV part of the electromagnetic spectrum [V.S.Y. Lin et al, 1997]. In addition, piezoelectricity is another property of GaN. The piezoelectric properties of GaN can be utilized to fabricate high frequency surface acoustic wave "SAW" devices.

There are many applications for "III-Nitride" semiconductors including blue LED's, efficient full color flat panel displays, blue lasers, UV detectors, and high temperature sensors [P.M. Fauchet et al, (1995)]. Ultraviolet (UV), high brightness, and long-life LEDs are under development to replace incandescent bulbs [L. Beji, 2006]. Full color flat panel displays with low power consumption are desirable for lab-top computers, whose battery life is severely limited by the displays in use today. Blue lasers with their shorter wavelength will permit higher recording densities of all media based on laser technology, including CD-ROM and magneto-optical "MO" disk drives. UV detectors have a variety of military and civil applications and high temperature sensors are desirable under extreme conditions like inside jet engines. The high thermal conductivities of GaN "210 W/m K" and AlN "340 W/m K" make them suitable for high power applications, where the heat generated by these devices must be efficiently dissipated [L. Beji, 2003].

Experimental optical study of low dimensional semiconductor such as nanoporous GaN received enormous attention for the past few years due to its attractive properties which is useful particularly in optoelectronics and sensing devices.

Porous semiconductors show various important optical features compare to normal crystalline semiconductors such as higher intensity of photoluminescence emission, better photoresponce and shift of band gap [H. Hasagawa et al, 2005].

One of the most undesired problems in growing quality GaN is the unintentionally doped GaN. Most material grown so typically range from "10<sup>19</sup>  $10^{16}$ cm<sup>-3</sup>" far had been *n*-type of values in the to [http://en.wikipedia.org/wiki/Gallium nitride]. Unintentionally n-type dopant in GaN is said due to the nitrogen vacancies in it's crystalline since no impurities have so far been observed to account for such a large background carrier concentrations [N.G. Weimann, et al (1998)].

Most of the GaN-based devices realized up to date are deposited by heteroepitaxy, mostly on sapphire " $Al_2O_3$ " or silicon carbite (SiC) substrates. Sapphire features a relatively low cost and it is the most commonly used substrate material for optoelectronic devices. These material have a lattice mismatch of approximately 16%, however it is one of the closest commercially produced lattice type to that of GaN [H. Hasagawa et al, 2005]. The mismatch in the lattice constants and thermal expansion coefficients between the GaN and its substrates gives rise to a high density of dislocations "between  $10^8$  and  $10^{10}$ cm<sup>-2</sup>" and stress, limiting e.g. the electron mobility, doping efficiency and lifetime of devices [M. Dudley et al (2000) and K.E. Miyano et al, 1997].

#### 2. Basic properties of crystalline and nanocrystalline GaN

GaN is one of the III-V compound semiconductors, where Ga is a trivalent element and N is a pentavalent element. The crystal structure of GaN can be in two types, wurtzite and zinc-blende crystal structure. The GaN sample used is the type of wurtzite structure, therefore, in the following, only wurtzite type of GaN will be discussed. In solid, the atoms of Ga and N are bonded to each other by strongly covalent covalent bands. The covalent bonds are formed between tetrahedral "s<sup>1</sup>p<sup>3</sup>"- hybrid orbitals at the angles of "109.5<sup>o</sup>". The equation for the forming of covalent bonds of GaN may be written as following [Hartmut Haug et al (1993)]:

$$Ga (4s^{2}4p^{1}) + N (2s^{2}2p^{3}) \rightarrow Ga (4s^{1}4p^{3})^{+} + N (2s^{1}2p^{3})^{-}$$
(1)

# 2.1 Vibrational property

The atom can undergoes oscillation about that point. Furthermore we assume that all atoms in a plane oscillate together. The planes can move either transverse with respect to each other in two possible ways or longitudinally in one way. For N atoms, there are 2N modes of vibration from the transverse motion and N modes of vibration from the longitudinal motions, thus giving total 3N modes of vibration. The elastic vibrations of a crystal can be considered in the form of elastic wave and we can find the frequency of the elastic wave in term of wave vector and elastic constants [Charles Kittel, (2005)].

## 2.2 Electronic energy band structure

Electrons are restricted to sets of discrete energy levels within atom. Large gaps exist in the energy scale in which no energy states are available. In a similar fashion, electrons in solids are restricted to certain energies and are not allowed at other energies. The different between an electron in an isolated atom and an electron in a solid is that in solid the electron has a range, or band. In a solid, many atoms are brought together and the wave functions of electrons in neighboring atoms overlap, and an electron is not necessarily localized at a particular atom so that the energy levels form essentially continuous bands of energy [Ben G. Streetman (1990)]. One important feature of the band gap of semiconductors is that the value of band gap varies with temperature. For wurtzite structure GaN, the direct band gap value at temperature 300 K is 3.39 eV while at 0K is 3.47 eV.

## 2.3 Properties of nanocrystalline

Following the reduction in dimensions to nanometer size, various changes of properties had been observed, such as the optical, electronic and vibrational properties in nanocrystalline compare to bulk crystalline. In low dimension system, the free charge carriers are confined in different type of confinement systems depend upon the dimensionality of carries confinement. The movement of electrons can be confined in three ways; one directional confinement "quantum well", two directional confinement "quantum wire" and three directional confinement "quantum dot" [M. Jaros (1989)].

## 3. Characterization of GaN semiconductor

#### 3.1 Photoluminescence

In PL characterization, a laser is normally used an excitation source. A variation of frequencies of excitation laser beam will be subjected to the sample of study. Different frequency of laser beam will gives different value of excitation energy to the subjected sample. No absorption will occurred if the energy of subjected laser beam is lesser than the band edge energy gap of the sample. Therefore, the energy of subjected laser beam is equal or more than the energy gap, the sample will absorbs the laser energy and through radiative recombination. The corresponding wavelength at the peak of PL spectra can be used to calculate the band gap energy of the sample [M. Jaros (1989)].

#### 3.2 Raman spectroscopy

Raman Effect is a type of inelastic scattering with the creation or annihilation of a phonon. In Raman scattering, the incident photon may gives part of its energy to the lattice in the form of phonon "phonon creation" and emerges out with lower energy photon. This interaction is known as Stokes scattering. On the other hand, Anti-Stokes scattering happens when the photon absorbs phonon energy (phonon annihilation) and emerges out as higher energy photon. The Raman Effect comprises a very small fraction, about "1 in 10<sup>7</sup>", of the incident photons [R. Loudon (1964)]. Since the Raman scattering is not very efficient, a high power excitation source such as a laser is normally used. Raman spectroscopy is used to measures the vibrational (phonon) energies of molecules. For a transition to be Raman active there must be a change in polarizability of the molecule which means the polarizability of the molecule must change with the vibrational motion [H. P. Maruska et al (1969)].

#### 4. Nanostructure fabrication

There are several ways can be used to fabricate nanostructure semiconductors. The standard approach for semiconductor nanostructure formation is to use fine crystal growth techniques such as molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE). Various standard etching and metal deposition techniques are used together to fabricate the devices with standard lithography techniques. However, these techniques possess few disadvantages such as high processing cost and complexity of processes. On the other hand, dry and wet etching techniques are more popular methods used in nanostructure fabrication mainly due to its low processing cost and simple experimental procedure and versatility of processes [D. Zhuang, et al (2005)]. Generally, dry etching processes such as reactive ion etching (RIE) can be highly anisotropic, an ideal characteristic for producing vertical profiles. However, due to the strong physical component in dry etching, it has low etch-selectivity between materials and can cause subsurface damage by ion bombardment. In contrast, wet etching, produces negligible damage, can be highly selective, is relatively inexpensive, and can be done with simple equipment.

#### 4.1 UV-assisted electrochemical etching

UV-assisted electrochemical etching is one of the photo-assist electrochemical (PEC) etching techniques and it is also categorized under wet etching techniques. Wet etching of semiconductors involves oxidation of the semiconductor surface and subsequent dissolution of the resulting oxides. Oxidation requires holes that can be supplied either chemically or via an electrochemical circuit in anodic etching, the semiconductor and an inert electrode are attached to the positive and negative terminals of a direct voltage source, respectively. Both electrodes are put inside an electrolyte, e.g. aqueous potassium hydroxide (KOH). The semiconductor is oxidized by removal of bonding electrons (injecting holes) from the surface bonds via an external voltage source. The resulting oxides subsequently dissolve into the electrolyte [D. Zhuang, et al (2005)].

In PEC etching, the supply of holes to the oxidation process is further enhanced by illumination of photons in the etching process. Electron–hole pairs are generated by photons from an illumination source with energy equal to or greater than the band gap energy  $(E_g)$  of the semiconductor. The photogenerated holes assist in the oxidation of the semiconductor surface and the excess electrons are consumed by the reduction reaction on the counter electrode. Increasing the absorption of incident optical radiation with energy greater than band gap energy increases the supply of holes at the surface, thereby enhancing the etch rates.

The GaN oxidation process in the photo-assisted electro-chemical reaction mechanisms was explained in detail as follows [J. W. Seo, et al (2002)]:

$$2\text{GaN}_{(s)} \xrightarrow{h\nu} 2\text{GaN}_{(s)} + 2e^{-} + 2h^{+}$$
(2)

$$2\text{GaN}_{(s)} + 2e^{-} + 2h^{+} \xrightarrow{V} 2\text{GaN}_{(s)} + 2h^{+}$$
(3)

$$2\text{GaN}_{(s)} + 2h^{+} + 3\text{H}_{2}\text{O}_{(l)} \longrightarrow \text{Ga}_{2}\text{O}_{3(s)} + \text{N}_{2(g)} + 3\text{H}_{2(g)}$$

$$\tag{4}$$

The electron-hole pairs are generated on the GaN film by UV illumination as shown in "equation 2". In "equation 3", the photo-generated holes are confined in the potential well formed by biasing at the surface of n-GaN while the extra electrons are swept out to the electrode. The holes accumulated at the surface of n-GaN assist the activation of Ga, and the oxidation reaction in "equation 4" take places.

The oxidation reaction in "equation 4" is in agreement with the interpretation of [Li et al, (2002)] who performed etching in aqueous KOH solutions. According to "Li et al, (2002)", the hydroxide ion "OH<sup>-</sup>" is first adsorbed on the sample surface and subsequently react with Ga atoms following the reaction [D. Zhuang, et al, (2005)]:

$$2GaN + 3H_2O \xrightarrow{KOH} Ga_2O_3 + 2NH_3$$
(5)

The "equation 5" is a simplified equation of oxidation reaction of GaN compare to the oxidation reaction in "equation 4". The KOH electrolyte here works as a catalyst and is also a solvent for the resulting  $Ga_2O_3$ .

## 5. Sample preparation

The UV assisted electrochemical etching set up is shown in "figure 1". In this technique, silver "Ag" was first deposited at one corner of the GaN surface for front contact by using thermal evaporator. The silver coated area is then contacted with copper washer and tightened with a bolt. In the anodic etching process, platinum is used as electrode, the GaN sample was connected by a copper wire to power supply and biased positive. The fabrication conditions were 30 minutes etching duration, 10V applied voltage and KOH electrolyte concentration of 1.0% and the sample illuminated with ultra-violet "UV" light source with "500 W".

## 6. Results and Discussion

The SEM surface image of the untreated as-grown GaN shows in "figure 2" that is smooth surface. No pores or any significant surface defects. The smooth surface is shown the single-crystallite layer of GaN deposited on sapphire substrate. However, some relatively dark spots were observed all over the surface of as-grown GaN. These dark regions may be the micro-defects of the as-grown GaN. The oxidation rate of GaN depends mainly on the photo-generated holes supply rate. Thus the larger pores formed may be attributes to higher holes concentration at that surface area. Although the movement of holes in semiconductor was predicted to be random, but since the etching rate depends solely on the parameters of the etching process (the applied voltage and illumination of UV lights were constant through out the etching process), the different etching rate at different concentration of holes through out the surface of GaN. It is believed that the concentration of holes through out the semiconductor surface area may be selective where holes may be more concentrated at certain area such as at the micro-defect area. Since the movement of holes in semiconductors is uncertain, so it is difficult to conclude that the holes concentration is higher at defect areas. However, it is known that the surface etching pattering has relation with the defects in the semiconductors.

The SEM surface image of UV-assisted electrochemical etching process is shown a shape and size of pore which was formed on the surface of the GaN as shown in "figure 3", therefore the shape of pores formed was in spherical shape. The size of the pores formed has diameter as small as 85 nm.

The room temperature PL spectra of as-grown and porous GaN samples were illustrated in "figure 4". The peak position, Full Width at Half Maximum (FWHM), peak shift and the peak intensity of the PL are summarized are shown in "table 1". The energy band gap,  $E_g$  was calculated based on  $E_g = hc/\lambda$ , where c and  $\lambda$  are speed of the nature light and selected wavelength, respectively. The wavelengths were obtained from the peak positions of near band edge of PL. Two PL peaks were observed in the as-grown and porous GaN sample. For the as-grown GaN, the higher peak was observed at "361.946 nm" and the other at "723.739 nm" which is in UV and red luminescence region respectively. The FWHM is "8.198 nm" at "361.946 nm". For the porous GaN, the higher peak was observed at "364.235 nm" and at "728.039 nm", so their FWHM are "4.244 nm" and "8.926 nm" respectively. The peaks of porous sample were red-shifted at "2.289 nm and 4.30 nm" respectively compare to the peaks of the as-grown GaN. PL intensity of the porous samples was observed to be increased. The intensity of emitted lights is proportional to the number of photons emitted. This means that the number of photons emission is much higher for porous GaN than as-grown GaN. The amplification of porosity-induced PL intensity could be explained by the extraction of strong PL by light scattering from the sidewalls of the GaN crystallites. Since the surface area per unit volume is higher in porous GaN, the larger surface area of porous GaN provide much more exposure of GaN molecules to the illumination of PL excitation lights. This would results higher number of electrons to take part in the excitation and recombination process in porous GaN compares to the smaller surface area of as-grown GaN. As a result, the number of emitted photon due to radiative recombination process is higher in porous GaN.

The Raman spectra of the both as-grown and porous GaN exhibit phonon mode  $E_2$  (high),  $A_1$  (LO),  $E_2$  (low) and an additional peak which are shown in "figure 5, (a), (b)". However,  $A_1$  (TO) phonon mode only observed in the porous GaN. All the phonon modes in porous GaN observed to be shifted to lower frequency relative to the as-grown GaN with the exception of the additional peak which remain the same. On the other hand, the Raman intensity of porous sample was found to be decreased except the additional peak. "Table 2" compiles all the peak position of the observed phonon mode together with its intensity. Three allowed Raman peaks representative to the wurtzite GaN crystal, namely  $E_2$  (low) at "142.426 cm<sup>-1</sup>",  $E_2$  (high) at "568.771 cm<sup>-1</sup>", and  $A_1$  (LO) at "736.769 cm<sup>-1</sup>" were clearly observed. In addition, a peak from the sapphire substrate was also seen at "415.971 cm<sup>-1</sup>". All the phonon mode peak positions of the as-grown GaN observed in our Raman study is in good agreement compare with the value obtained It should be noted that all the GaN samples above were grown on sapphire and the entire phonon mode values are in cm<sup>-1</sup>. For porous GaN, all the peaks of  $E_2$  (low),  $E_2$  (high), and  $A_1$  (LO) were observed to be shifted to lower frequency compare to the as-grown GaN. However, the peak attributed to sapphire was observed to be at the same position "415.971 cm<sup>-1</sup>" for both as-grown GaN and porous GaN but with higher intensity for porous GaN. The same peak position for both samples shows that the sapphire substrate was not subjected to the chemical etching process. The higher intensity observed for

porous GaN may be due to reduction of GaN thickness in the dissolution process during etching. With lower thickness of GaN in porous GaN, the argon ion laser beam may penetrate deeper to sapphire, hence higher intensity of Raman scattering. The red shifting in Raman spectral has further confirmed the compressive stress relaxation in porous GaN compare to as-grown GaN. It is interesting to note that the forbidden modes  $A_1$  (TO) were present in our Raman spectral. The forbidden modes, i.e.  $A_1$ (TO) and  $E_1$ (TO) were absent in the as-grown sample but present in some of the etched samples. The forbidden peaks in the porous samples shows that the porosity, indeed, could change the optical properties of the material, this could be ascribed to the crystal disordering in the films, in which the increase of the scattering from the sidewalls of the porous structure eventually may change the light polarization.

Finally, it is hoped with better understanding of the optical properties of GaN, the potential of GaN semiconductor in optoelectronics devices can be fully utilized. The optical properties of the stress-free GaN, porous GaN and as-grown GaN can be compared and leads to a more understanding on the influence of residual stress in GaN on its optical properties.

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# Table 1. PL spectra peaks position

	As-Gro	wn GaN	Porous GaN		
	Peak 1	Peak 2	Peak 1	Peak 2	
Peak position (nm)	361.946	723.739	364.235	728.039	
Energy, $E_g$ (eV)	3.425	1.713	3.404	1.703	
Peak intensity, (a.u)	3297.19	540.005	57206	6193	
Relative intensity	1.00	1.00	17.34	11.47	
FWHM (nm)	8.198	-	4.244	8.926	
Peak shift (nm)	-	-	2.289	4.30	

# Table 2. The phonon modes detected in the Raman spectra

Sample	As-grown GaN		Porous GaN			
Phononmode	Peak position (cm <sup>-1</sup> )	Intensity (a.u)	Peak position (cm <sup>-1</sup> )	Intensity (a.u)	Peak shift (cm <sup>-1</sup> )	
E2(high)	568.771	5094	567.1750	2284.2	-1.596	
A <sub>l</sub> (TO)	-	-	536.7740	767	-	
A <sub>1</sub> (LO)	736.769	859	713.126	421.8	-23.643	
E2(low)	142.426	286	143.5590	247.4	-1.133	
Additional peak	415.971	205	415.971	303.4	0	



Figure 1. The electrochemical etching set up







Figure 3. SEM surface images of porous GaN



Figure 4. Room temperature PL spectra of the as-grown and porous GaN







Figure 5. Raman spectra of (a) as-grown GaN (b) porous GaN