MORPHOLOGICAL AND OPTICAL PROPERTIES OF POROUS GALLIUM NITRIDE (GaN) FABRICATED BY PHOTOELECTROCHEMICAL PROCESS

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2015

MORPHOLOGICAL AND OPTICAL PROPERTIES OF POROUS GALLIUM NITRIDE (GaN) FABRICATED BY PHOTOELECTROCHEMICAL PROCESS

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

January 2015

ACKNOWLEDGEMENTS

First of all, I would like to express my special thanks to my main supervisor, Dr. Ng Sha Shiong for his excellent guidance and concern throughout the entire research. Secondly, I would like to acknowledge my co-supervisor, Dr. Yam Fong Kwong, who willing to share his idea and offered me the opportunity to boost and improve my knowledge in the field of porous semiconductor.

I feel greatly thankful to the entire lab assistant and post-graduate students in NOR laboratory for their contribution and support at all the time in my research study. My special thanks also to my team member, Lee Sai Cheong, who willing to spend his precious time in guiding and sharing his knowledge for the simulation study along the project.

Additionally, I'm indebted and thankful to the Ministry of Higher Education of Malaysia for offering me the MybrainSc scholarship to ease my financial burden during my research study. The support from the Ministry of Higher Education of Malaysia Fundamental Research Grant Scheme (FRGS) (Grant No. 203/PFIZIK/6711282) is also greatly appreciated.

Last but not least, I would particularly thanks to my beloved family and friends for giving me the motivation and inspiration to complete my research study.

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LIST OF ABREVIATIONS

Ag	Silver
Al	Aluminium
ATR	Attenuated total reflection
CH_3OH	Methanol
DI	Deionized
EW	Evanescent wave
FESEM	Field-emission scanning electron microscope
GaAs	Gallium arsenide
GaN	Gallium nitride
GaP	Gallium phosphate
$H_2C_2O_4$	Oxalic acid
HF	Hydrofluoric acid
H_2O	Distilled water
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
H_3PO_4	Phosphoric acid
H_2SO_4	Sulphuric acid
InP	Indium phosphate
IPP	Interface phonon polariton
IR-ATR	Infrared attenuated total reflection
IRE	Internal reflecting element
KOH	Potassium hydroxide
$K_2S_2O_8$	Potassium peroxydisulfate
LED	Light emitting diode

LO	Longitudinal optical
NBE	Near band edge
N_2	Nitrogen
PEC	Photoelectrochemical
PL	Photoluminescence
Pt	Platinum
SCR	Space charge region
SEM	Scanning electron microscope
SiO_2	Silicon oxide
SPP	Surface phonon polariton
Ti	Titanium
TO	Transverse optical
UID	Unintentionally doped
UV	Ultra-violet

LIST OF SYMBOLS

θ	Angle of incidence in the medium of incidence
ω	Angular frequency
θ_{c}	Critical angle
m^*	Effective mass
e	Electron charge
ε_∞	High-frequency dielectric constant
m	Independent component
o	Independent component
r	IR reflection coefficient
γ_{LO}	Longitudinal optical phonon damping
ω_{LO}	Longitudinal optical phonon frequency
c_{axis}	Optical axis
$\parallel$	Parallel
$\perp$	Perpendicular
γ_p	Plasma damping constant
ω_p	Plasma frequency
f	Porosity
n	Refractive index
l	Specific layer in multilayer system
N	Total number of layers
γ_{TO}	Transverse optical phonon damping
ω_{TO}	Transverse optical phonon frequency

CIRI-CIRI MORFOLOGI DAN OPTIK GALIUM NITRIDA (GAN) BERLIANG DIFABRIKASI OLEH PROSES FOTOELEKTROKIMIA

ABSTRAK

Kajian mengenai fabrikasi filem nipis GaN berliang melalui proses fotoelektrokimia (PEC) telah dilaporkan. Objektif utama kerja penyelidikan ini adalah untuk mengkaji ciri-ciri morfologi dan optik filem nipis GaN berliang yang difabrikasi. Dua set filem nipis GaN, iaitu GaN terdop yang tidak sengaja (UID) ($<10^{17}$ cm^{-3}) dan GaN terdop silikon (Si) ($1\sim3\times10^{18}$ cm^{-3}), telah digunakan sebagai bahan mentah untuk punaran PEC GaN. Filem nipis GaN berliang yang difabrikasi telah dicirikan oleh mikroskop elektron imbasan pancaran medan (FESEM), spektroskopi fotoluminasi (PL) dan spektroskopi pantulan penuh dikecilkan inframerah (IR-ATR). Kajian mengenai voltan punaran mendedahkan bahawa GaN berliang yang difabrikasi daripada filem nipis GaN UID menghasilkan struktur berliang nipis (sebanyak 0.3 μm) yang bercorak bulatan seragam. Untuk GaN berliang yang difabrikasi daripada filem nipis GaN terdop Si, struktur liang heksagon yang agak seragam telah dihasilkan dalam keseluruhan lapisan terdop (sebanyak 1 μm) pada voltan punaran yang lebih tinggi. Keputusan PL menunjukkan keamatan luminasi struktur GaN yang disediakan daripada filem nipis GaN UID telah dipertingkatkan 4 kali ganda berbanding dengan GaN asas. Walau bagaimanapun, keamatan luminasi turun naik dapat diperhatikan dalam spektrum PL GaN terdop Si. Pengurangan keamatan luminasi untuk GaN terdop Si berliang pada penggunaan voltan yang tinggi disebabkan oleh penyusutan pembawa di dalam struktur berliang. Keputusan IR-ATR menunjukkan polariton fonon permukaan (SPP) sensitif terhadap morfologi permukaan struktur GaN berliang. Keliangan, pembawa bebas dan ketebalan lapisan permukaan adalah faktor utama dalam mengawal frekuensi resonans SPP. Ia didapati bahawa keliangan yang tinggi modulet frekuensi resonans SPP terhadap frekuensi yang lebih rendah manakala ketebalan lapisan permukaan kecil dan pembawa tinggi cenderung untuk mengalih frekuensi resonans SPP terhadap frekuensi yang tinggi. Sepanjang kajian ini, ia menunjukkan bahawa pembawa bebas dalam filem nipis GaN adalah amat penting dalam modulasi ciri-ciri struktur GaN berliang dari segi sifat morfologi dan optik. Disebabkan pengurangan pembawa bebas yang ketara daripada GaN terdop Si tidak dapat dielakkan dalam punaran process, kawalan kedalaman punaran (iaitu, ketebalan berliang di atas lapisan terdop) dalam filem nipis GaN terdop Si berliang diperlukan untuk meningkatkan gerak balas optik dengan ketara.

MORPHOLOGICAL AND OPTICAL PROPERTIES OF POROUS GALLIUM NITRIDE (GaN) FABRICATED BY PHOTOELECTROCHEMICAL PROCESS

ABSTRACT

An investigation into the fabrication of porous GaN thin films via photoelectrochemical (PEC) process was reported. The main objective for this research work is to investigate the morphological and optical properties of fabricated porous GaN thin films. Two sets of GaN thin films, namely unintentionally doped (UID) GaN ($<10^{17}$ cm^{-3}) and silicon (Si)-doped GaN ($1\sim3\times10^{18}$ cm^{-3}), were adopted as raw materials for the PEC etching of GaN. The fabricated porous GaN thin films were characterized by field-emission scanning electron (FESEM) microscopy, photoluminescence (PL) spectroscopy, and infrared attenuated total reflection (IR-ATR) spectroscopy. The study of etching voltages revealed that porous GaN fabricated from UID GaN thin films produced a thin porous structure (about 0.3 μm) with uniform circular patterns. For porous GaN fabricated from Si-doped GaN thin film, a relatively homogenous hexagonal pore structure was realized on the entire doped layer (about 1 μm) at higher etching voltage. PL results showed that the luminescence intensity of porous GaN structure prepared from UID GaN thin films was greatly enhanced by more than 4 times compared to as-grown GaN. However, fluctuation of luminescence intensity was observed in the PL spectra of porous GaN prepared from Si-doped GaN thin films. The quenching luminescence intensity of porous Si-doped GaN at higher voltage was attributed to the carrier depletion in the porous structure. IR-ATR results revealed that surface phonon polariton (SPP) is sensitive to the surface morphology of porous GaN structure. The porosity, free carriers and porous layer thickness are the key factors in controlling the SPP resonant frequency. It was found that higher porosity modulated the SPP resonant frequency towards lower frequency while the smaller porous layer thickness and high carriers tended to shift SPP resonant frequency towards higher frequency. Throughout the studies, it showed that free carriers in GaN thin film is paramount importance in modulating the characteristics of porous GaN structure in terms of morphological and optical properties. Due to unavoidable significant reduction of free carriers from Si-doped GaN in the etching process, control of the etching depth (i.e., porous thickness in doped layer) in porous Si-doped GaN thin film was essential to improve the optical responses significantly.

Chapter 1

Introduction

1.1 Introduction

Producing semiconductor materials to the smaller size, range from micron to a few nanometers for the purpose of improving material characteristics in terms of morphology, optical and electrical properties has become a massive and imperative field in the scientific research community. As compared to bulk counterpart, porous semiconductors with larger surface area have been proven to be capable of shifting the band gap energy (Vajpeyi et al., 2006) and altering its optical characteristics (Yam et al., 2007a). It has also been shown that the capability of porous semiconductor in modulating the optical response allows the pore structure achieves greater efficiency in device applications such as sensors (Ramizy et al., 2011b, Yam et al., 2007b), optics (Langa et al., 2005), solid state lighting (Föll et al., 2010) and microelectronic (Arsentyev et al., 2005).

Semiconductor compounds, i.e., gallium nitride (GaN) (Dorp et al., 2009), indium phosphate (InP) (Liu, 2001), gallium phosphate (GaP) (Tjerkstra et al., 2002) and gallium arsenide (GaAs) (Dmitruk et al., 2007) have triggered intense attention for the generation of pore structure. Among the aforementioned semiconductors, wide direct band gap of GaN has demonstrated importance in high power electronics, lasers, and light emitting diode (LED) (Nakamura et al., 2000, Chu et al., 2011). For this reason, focusing surface modification of GaN is especially appealing and thorough study on porous GaN is desirable.

Etching is an essential step in porous fabrication. Generally, it can be categorized into two approaches, namely dry etching and wet etching. Wet etching is the most extensively used approach in producing porous GaN as it requires simple and inexpensive apparatus. More importantly, it induces low etch damage with smooth surface as compared to dry etching (Dorp et al., 2009). Besides of that, wet etching provides high selective etch with respect to the morphological change of GaN semiconductor. The highly selective etching is beneficial for the devices fabrication on smooth surface and can be served as valuable tool for defect evaluation (Zhuang and Edgar, 2005). A multitude of wet etching approaches have been established in the literature such as, chemical etching (Stocker and Schubert, 1998), anodic etching (Nowak et al., 2001), platinum (Pt) assisted electroless etching (Yam and Hassan, 2009), and Photoelectrochemical (PEC) etching (Soh et al., 2013). Details of these fabrication approaches will be discussed in Chapter 2.

Note that numerous etching parameters, including semiconductor types (carrier concentration of raw materials), electrolyte concentration, types of electrolytes, etching voltage, and etching duration, used in porosification greatly affect the resulting surface morphology as well as the optical response of the fabricated porous structure. By accurately controlling and adjusting the appropriate etching parameters, the desired etched feature can be achieved. Through the literature studies, GaN was found to be chemically inert in conventional acid and alkaline aqueous solutions. The strong chemical stability of GaN and the lack of appropriate etching conditions obstruct the development of pores, providing less porous on the GaN surface. As a consequence, it becomes a major challenge for the scientific community and there are plenty of room can be explored to produce porous GaN thin films with more homogenous structure.

Over the last few years, a number of works on the fabrication of porous GaN have been carried out (Hartono et al., 2007, Omar et al., 2009, Park et al., 2009, Zhang et al., 2010). Despite a rapid development in the porosification of GaN thin films, most researches are exclusively pointed to the morphological structure, the impact of etched morphologies of porous GaN on its luminescence response is rarely reported. It is worth mentioning that the different carrier concentration of GaN thin films yield dramatically changes of surface morphologies, which have a direct influence on the luminescence characteristic of porous GaN (Mynbaeva et al., 2001, Vajpeyi et al., 2005, Yam et al., 2007c, Lee et al., 2013). Its luminescence signal can be enhanced or quenched, depending on the raw material properties that employed for porosification.

Besides of the rare investigation in the luminescence response, the optical study of porous GaN using attenuated total reflection (ATR) spectroscopy is yet be reported. There is only one report on the porous III-IV semiconductors (GaAs, InP, and GaP) using ATR technique (Barlas et al., 2012). The authors reported that the surface properties [i.e., surface phonon polariton (SPP) characteristics], porosity and the free carrier concentration of porous materials can be determined via the simulation of ATR spectrum, and this information is greatly beneficial to describe the properties of porous materials upon porosification.

Polariton, namely hybrid (mixed) mode, is the elementary excitation in dipole active material, where the photon coupled with an elementary particle such as phonon, plasmon, exciton, etc (Vasconcelos et al., 2007, Lee et al., 2011). In the case of the infrared (IR) photon couple with an optical photon, the resulting mixed mode is known as phonon polariton. SPP phenomenon arises when the IR photon with transverse magnetic (TM) mode couple to the surface phonon localized near the surface of a polar crystal. The SPP mode travels along a direction perpendicular to the surface normal and its amplitude attenuates exponentially from surface to bulk

(Lee et al., 2011, Albuquerque and Cottam, 2003). Knowledge on the SPP properties is crucial because understanding the behaviour of the coupling effect between the photon and surface phonon, is the basis for the development of several modern devices such as resonant-based sensor and thermo-photovoltaic system (Balin et al., 2009, Huber et al., 2005).

Considering the importance of raw material properties and also the etched morphologies on the optical response (photoluminescence and SPP characteristics) of porous GaN, systematic studies on porous GaN fabrication are carried out. The surface morphology and the optical properties of porous GaN are investigated in detail.

1.2 Research Objectives

The main objectives of this work are:

- To study the effects of etching voltages on the surface morphology and optical properties of porous GaN fabricated from unintentionally doped (UID) GaN via PEC etching.
- To study the effects of etching voltages and etching durations on the surface morphology and optical properties of porous GaN fabricated from Si-doped GaN via PEC etching.
- To determine carrier concentration, porosity, layer thicknesses of porous GaN via ATR spectra with the use of effective medium theory.

1.3 Originality of the research work

In this project, PEC etching of porous GaN with UID GaN and Si-doped GaN as raw materials is reported. For the first time, a variety of morphologies (circular, hexagonal, leaf like-, and honeycomb-like patterns) with uniform surface have been obtained through PEC etching of GaN under various etching voltages. Interestingly, formation of honeycomb-like structure is considered as a new finding because porous GaN with homogenous hexagonal shape has yet been reported in the literature review.

It is worth mentioning that free carrier is the main factor to influence the luminescence efficiency of porous GaN. Control of etched pore depth, notably in Si-doped layer is crucial in modulating the luminescence response. In this work, porous GaN thin films with various pore depths are fabricated. The key parameters for these etching experiments are identified.

ATR is a simple and non-destructive technique that ordinarily used to examine and investigate the optical properties of polymers, organic materials, rubber, powders, surface layer of bulk materials, and thin films. Importantly, none of the work concerning the ATR study on porous GaN with the use of effective medium theory is performed up to now. The investigation of optical properties of porous GaN thin films with the utilization of ATR method is the first time reported in this work. It is found that ATR spectra are very sensitive to the surface layer of porous GaN. Through the model fits of the ATR spectra via the effective medium theory, useful information such as carrier concentration, porosity, and layer thicknesses are successfully extracted. Besides of aforementioned information, surface phonon polariton (SPP) properties of porous GaN thin films are also investigated through ATR analysis.

1.4 Organization of dissertation

The content of this dissertation is divided into 5 chapters. After a brief introduction in this chapter, literature study about various fabrication methods for porous GaN, and the study of ATR characterization in porous semiconductor are provided in Chapter 2.

Chapter 3 presents the fundamental properties of GaN thin film and the physical properties of the raw materials used in the fabrication of porous GaN. The basic principle of PEC approach as well as the operating principle for each of the characterization instruments is also briefly illustrated.

In Chapter 4, details discussion about sample preparation, experimental setup and etching parameters used in this project are given. Besides, a brief description of the theoretical model used for the generation of porous GaN is also included.

Characterization results of porous GaN for each series of the experiments are presented and discussed in Chapter 5. It should be highlighted that one set of experiment (with various etching voltages) is carried out for UID GaN thin films while two sets of experiments (with various etching voltages and etching durations) are performed for Si-doped GaN thin films.

Finally, Chapter 6 concludes all the results obtained in this research work. Some suggestions for future research on the fabrication of porous GaN are proposed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, an overview of the fabrication of porous GaN via wet etching methods will be presented. In addition, part of the reviews will be focused on the ATR characterization of porous semiconductor.

2.2 Overview of the fabrication of porous GaN via wet etching methods

Porous GaN has drawn great deal of interest in the porous semiconductor field owing to its superior mechanical, thermal and chemical stability, making it highly desirable for optical applications. Current development of GaN surface modification is presented via wet etching methods as a result of high selective etched which capable of obtaining the desired etching profile. Basically, wet etching methods can be employed for two purposes (Zhuang and Edgar, 2005, Youtsey and Adesida, 1998, Soh et al., 2013):

1. Established the etching depth with smooth surface (surface patterning)
2. Formed porous structure on material surface (porosification）

Depending on the aim of the study, the use of different etching methods and etching parameters can alter the morphology structure of the GaN materials. In the following contents, etching methods such as chemical etching, anodic etching, Pt-assisted electrochemical etching and PEC etching are elucidated in concise to provide greater understanding on the pore formation of GaN thin films

2.2.1. Chemical etching

Chemical etching is a conventional wet etching method that has been used to study GaN thin films in the early of 1976 (Shintani and Minagawa, 1976). It is a method that completely different with the electrochemical etching as its etching mechanism only involves the reactivity between the sample and the etchant. Fig. 2.1 shows the schematic diagram of chemical etching. Due to high resistive of GaN to the chemical etchant, only several etchants (either aqueous acid or alkaline solutions) are applicable in the chemical etching of GaN. The most common etchants used for the chemical etching are molten phosphoric acid (H_3PO_4) (Shintani and Minagawa, 1976), mixed acid solutions of H_3PO_4 and sulphuric acid (H_2SO_4) (Lu et al., 2004, Weyher et al., 2000), hot hydrochloric acid (HCl) (Hino et al., 2000), molten potassium hydroxide (KOH) (Kozawa et al., 1996), and hot 10-50% KOH in ethylene glycol (Stocker and Schubert, 1998). Researches on chemical etching have also verified that no chemical reaction can occur at room temperature, meaning that GaN cannot be etched with any electrolyte solutions under room temperature. As a result, employment of the elevated temperature for the etchant is essential in the GaN chemical etching. It is usually shown in most of the reported studies that the applied optimal etching temperature can markedly increase the reactivity of the GaN surface with the chemical etchant.

More importantly, it is found that GaN is effective in producing etch pits instead of porous structure with the use of chemical etching. Kozawa et al. (1996) found that the etch pits formed on the GaN surface when molten KOH used as etchant. Stocker and Schubert (1998) also reported that the electrolyte solutions of H_3PO_4, NaOH dissolved in ethylene glycol and KOH dissolved in ethylene glycol were capable of producing dislocation hexagonal etch pits in wurtzite GaN grown on *c*-plane sapphire. They revealed that the optimum temperature applied for the aforementioned experiments were in the range of 90 to 180 ℃. In addition, the distinctive etch pits on the etched GaN surface were observed when GaN thin films subjected to the HCl electrolyte solution at the temperature of 600 ℃ (Hino et al., 2000). Based on the investigation of etched GaN via chemical etching, it is found that the etch pits were usually formed on the defects sites of GaN surface. Consequently, chemical etching has demonstrated to be a promising method for the evaluation of defects in GaN thin films.

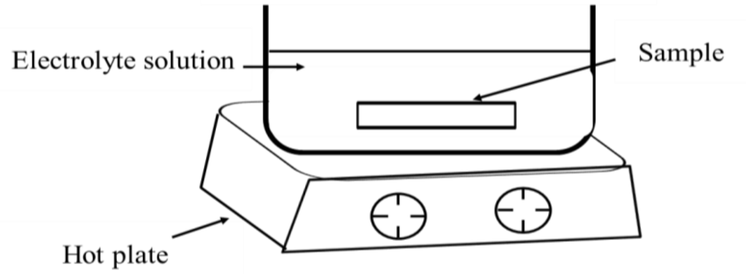

Fig. 2.1 Schematic diagram of chemical etching.

2.2.2. Anodic etching

Anodic etching is a wet etching method that requires external voltage source to etch semiconductor surface into pattern or porous form regardless of the light illumination. In anodic etching, the semiconductor material that intended to be etched and inert electrode are connected simultaneously to the positive and negative terminals of voltage source, respectively. With the application of external biasing, anodic etching is possible to carry out at room temperature in the dark. Hence, it has commonly been utilized to form surface pattern or porous structure in GaN thin films. The schematic diagram of anodic etching is shown in Fig. 2.2. In the following paragraph, several examples of anodic behavior of GaN materials are briefly discussed.

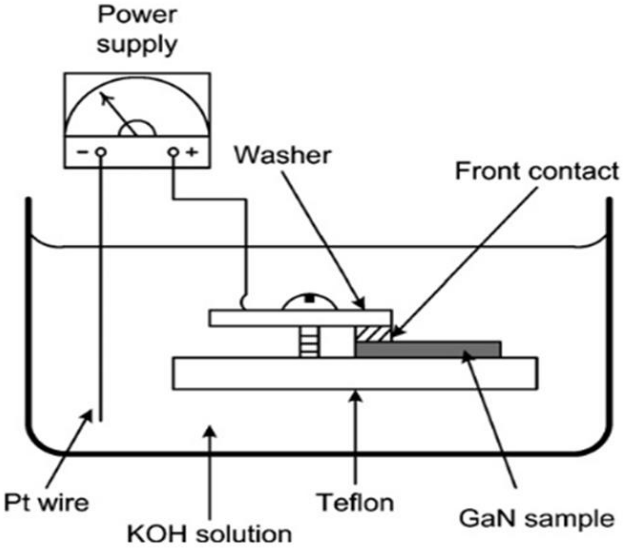

Fig. 2.2 Schematic diagram of anodic etching (Adapted from Yam et al., 2007c).

Pankove (1972) was the earliest research group utilized anodic etching to etch GaN thin films using NaOH electrolyte. Based on the literature reviews, the previous reports on the anodic etching were merely concentrated on the GaN surface patterning (Pankove, 1972, Ohkubo, 1997, Yamamoto et al., 1999, Pakes et al., 2003). More recently, several authors have presented the formation of porous structure in the anodic etched GaN thin films. Schwab et al. (2013) have demonstrated anodic etching of Si-doped GaN thin films under different carrier concentrations and etching voltages with the employment of nitric acid. It was found that by using etching voltage of 15 V, vertically aligned pores was obtained in higher carrier concentration of GaN (2×10^{19} cm^{-3}). Cross-sectional SEM showed that the top surface of GaN was significantly less porous than underlying film, indicating pores were preferentially formed underneath the GaN surface during anodic etching process.

On the other hand, Jang et al. (2013) reported that anodic etching at constant voltage on Si-doped GaN (5×10^{18} cm^{-3}) in oxalic acid solution was capable of producing nanoporous structure. Huang et al. (2013) also performed anodic etching in oxalic acid solution. The authors observed that different porosities of porous GaN could be obtained by varying the etching voltages. The results obtained by Jang et al. and Huang et al. showed the similar morphologies with Schwab et al. where the observation of low porosity was achieved on the top GaN surface. Interestingly, there was a report on the effects of GaN etching to its optical response. According to Lee et al. (2013), the morphology of porous Si-doped GaN was strongly driven by the etching voltage and the carrier concentration. In their optical study, quenching of luminescence efficiency was discovered and the phenomenon could be explained by the depletion of a large portion of GaN crystalline during anodic etching, where the entire doped layer was successfully converted to porous material.

2.2.3. Metal-assisted electroless etching

Metal-assisted electroless etching is another common wet etching method that usually used in the production of porous GaN. In this method, external bias from the power supply or source meter unit could be dispensed with and it requires the aid of UV illumination for porosification. Fig. 2.3 shows the experimental setup of metal-assisted electroless etching. To promote the reactivity of the etchant with GaN surface for the production of porous structure, a few possible ways have been adopted in the metal-electroless etching of GaN, i.e., deposition of Pt metal on GaN surface (Bardwell et al., 2001, Yam et al., 2007a), light illumination on the GaN surface (note that the energy of UV light source must be equal to or greater than the energy band gap of semiconductor to be etched) (Zhuang and Edgar, 2005, Hwang et al., 2004) and the addition of a strong oxidizing agent to the aqueous solution (Vajpeyi et al., 2005, Dorp et al., 2009).

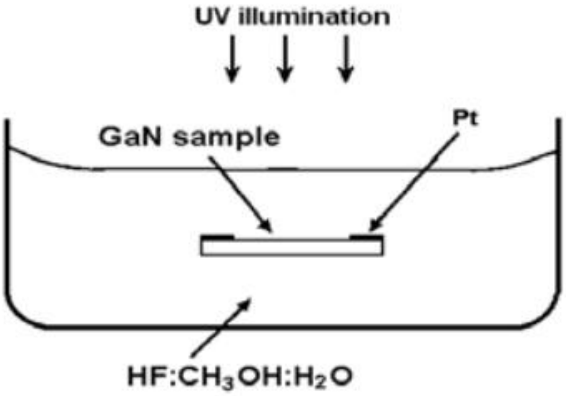

Fig. 2.3 Schematic diagram of metal-assisted electroless etching (Chuah et al., 2009).

A number of studies are well-documented in the literature about the fabrication of porous GaN via metal-electroless etching. In 2001, Bardwell et al. (2001) developed electroless etching on GaN thin films with the combined solution of KOH and potassium peroxydisulfate ($K_2S_2O_8$) under UV illumination. Comparison study between two inert masks (SiO_2 and Pt metals) was employed in this study. Their results proved that Pt metal yielded the highest etch rate, i.e., the etching reaction become rapid when GaN thin film was masked with Pt metal. Besides, the authors found that sonication after the pore formation resulted in the better etched morphology for porous GaN thin films.

Vajpeyi et al. (2005) also introduced the fabrication of porous GaN thin films via Pt-assisted electroless etching. GaN thin films were chemically etched with the solution of methanol (CH_3OH): hydrofluoric acid (HF): hydrogen peroxide (H_2O_2) (1:4:1). SEM results revealed that smaller and larger pores were obtained in porous GaN etched under an hour. With the employment of longer etching duration (2 hours), elongated branched pores were dominated. Their optical study proved that

GaN with stronger luminescence signal was obtained upon the formation of porous structure. Apart from that, Yam et al. (2007a) have shown the etched characteristic of porous GaN generated via Pt-assisted electroless etching. They claimed that, no pores were observed in the etching of 15 minutes. When the etching time increased up to 60 minutes, ridges with circular pores were produced. Enhanced emission peak of porous GaN with respect to as-grown GaN has been showed in the optical study of Yam et al. (2007a). It indicated that PL intensity gradually increased with the increment of etching durations.

2.2.4. Photoelectrochemical (PEC) etching

Photoelectrochemical (PEC) etching is a modification of anodic etching, which utilizes electrolyte, external potential (power supply, source meter unit, potentiostat) as well as UV light source in the etching process. The experimental setup of PEC etching is schematically shown in Fig. 2.4. Unlike electroless etching, the addition of oxidizing agent can be eliminated in the PEC etching of the semiconductor materials. With the assistance of both UV light source and external potential, it is possible to enhance the etch rate and the etched characteristics. Due to this reason, PEC etching has been widely explored in the fabrication of porous GaN thin films.

Recent breakthroughs by PEC etching have produced distinctive surface morphologies in GaN thin films, depending on the employed etching conditions. There has been reported that the etched features of porous GaN have a strong effect on its optical properties, which would enhance or quench the luminescence response of porous GaN. Raw material of GaN thin films (doping characteristic) is especially an important parameter for the fabrication of porous GaN thin films, its carrier concentration not only influences the surface morphologies, but also the optical response of porous GaN. The literature information on PEC etching of GaN using different raw materials is provided in subsequence paragraph.

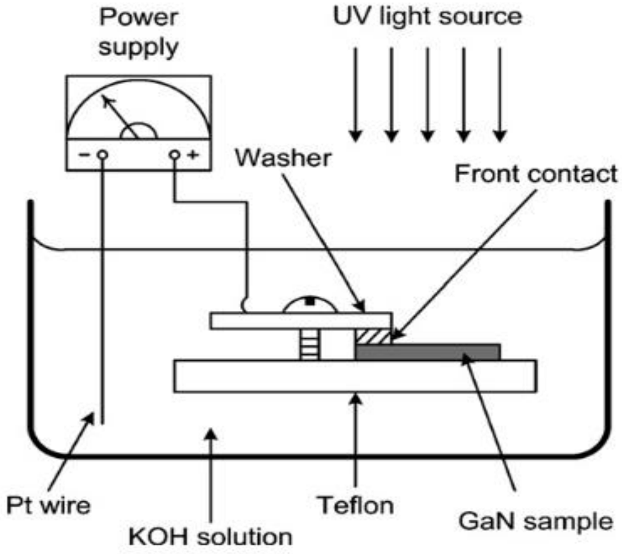

Fig. 2.4 Schematic diagram of PEC etching (Yam et al., 2007c).

Yam et al. (2007b) have demonstrated the effects of electrolyte concentration and etching voltage on the morphologies of porous GaN fabricated from unintentionally doped (UID) GaN. SEM result revealed that PEC etching of UID GaN produced porous structure with different shapes, i.e., circular and elongated shapes. Through their optical analysis, enhancement of PL intensity has found in the porous structure and the observed enhancement was due to the high surface area upon the etching process. Other authors such as Omar et al (2009) and Al-Heuseen et al (2010) also observed the enhancement of PL intensity for their porous samples fabricated through PEC etching of UID GaN. The authors noted the amplification of PL emission could be ascribed by a strong extraction of the light scattering from surface and the sidewall of porous structure.

Vajpey et al (2007) performed PEC etching on doped GaN with different carrier concentrations. The carrier concentrations of GaN samples were varied from 1×10^{16} to 1×10^{19} cm^{-3}. They have shown that doping characteristics strongly affect its surface morphology. It was found that fewer pores were formed in porous GaN obtained from low doped sample which due to its low conductivity that hindered the electrochemical reaction. PL characterization from this study showed that porous GaN prepared from heavily Si-doped GaN possessed highest emission peak, which is probably due to the combined effects of Si-doping and pore size. A significant enhancement of luminescence signal of porous Si-doped GaN with respect to as-grown GaN has also been reported by Hartono et al. (2007). They performed PEC etching using 2 M NaOH solution with the current concentrations varied from 5 to 25 mA/cm^2 for 30-60 minutes. The carrier concentrations of GaN samples used for the anodization were 8×10^{17} - 5×10^{18} cm^{-3}. By obtaining the optimum etching conditions, the authors have produced uniform pores with higher pore density.

Although the observation of luminescence enhancement has been reported in most of the PEC etching of porous GaN, quenching of emission peak, however, also happened in the certain case. It should be highlighted that the decrement of PL intensity was mostly observed in the porous structure fabricated from Si-doped GaN. A more extended study on the quenching of the luminescence behavior of porous GaN was performed by Mynbaeva et al. (2001). They found the emission peak became weaker as a result of the increment of the resistivity of GaN upon PEC etching. The authors believed that the quenching effect was related to the reduction of carrier concentration upon porosification. Apparently, optical luminescence in porous GaN thin films could be enhanced or decreased, depending on the raw materials as well as the etching conditions. However, besides of Mynbaeva et al.

(2001), there is no relevant study report on the discovery of optical quenching in porous GaN thin films via PEC etching. As a result, investigation of porous GaN fabrication on its optical response with different carrier concentrations is highly demanded in this work.

2.3 Attenuated total reflection (ATR) study of porous semiconductor

Optical characterization such as attenuated total reflection (ATR) has generated considerable research interest on the thin films (Ng et al., 2008), surface layer of bulk materials (Lee et al., 2011b, Torri et al., 2000) as well as porous materials (Dmitruk et al., 2010, Barlas et al., 2012). It is a non-destructive technique and commonly used to examine the surface properties of the particular materials. With the employment of the effective medium theory, one can describe the properties of surface mode and useful information can be extracted through the simulation of the ATR spectrum. Indeed, by qualitatively fitted the theoretical spectrum with its experimental spectrum, information such as surface phonon polariton (SPP), layer thicknesses, porosity, and carrier concentration could be attained.

Early reports on ATR study have been devoted to the thin film and bulk materials. For instances, Torri (2000) investigated the SPP mode of bulk GaN. Ng et al (2008) carried out the study of the SPP mode in wurtzite GaN thin films grown on sapphire substrate. Lee et al. (2011) studied the SPP characteristic of bulk wurtzite ZnO crystal. In recent years, particular attention has been focused on the porous structure materials. Both Dmitnuk et al. (2010) and Barlas et al. (2013) have performed ATR study in porous gallium arsenide GaAs, gallium phosphate GaP, and indium phosphate InP.

SPP mode is very sensitive to the properties of the surface layer (Lee et al., 2011a) and the porosity of porous materials. By substituting the proper surface thickness and porosity, approximate theoretical ATR spectrum can be generated. Our recent studies reported that porosity of porous GaN has great influence on its SPP resonant frequency. Evidently, ATR analysis can be generally utilized for the characterization of the optical properties of the fabricated porous structure. By performing the appropriate theoretical models in the simulation of ATR spectra, understanding of the optical characteristic in the particular porous materials might be improved.

2.4 Summary

Through the literature studies, it is found that various etching approaches can be implemented for the fabrication of porous GaN thin films. The summary of the literature reviews on the pore generation of GaN via different etching methods is tabulated in Table 2.1. The studies of ATR analysis in the thin films and porous materials have been illustrated and some useful information can be extracted with the aid of the theoretical simulation. Note that majority of the research studies have only been concentrated on the morphological properties of porous GaN. Yet, the study on the optical properties of porous GaN is not well-established. In this work, a clearer picture on the influence of surface morphologies on the optical properties of porous GaN is presented.

Table 2.1: Summary of the literature reviews on the porous GaN fabrication (etching methods, types of materials, etching conditions)

Method	Types of GaN (carrier concentration in cm^{-3})	Etching conditions					*Remarks	#Ref.
		Etching time (min)	Etching voltage (V)	Current density (mA/cm^2)	Electrolyte	Types of light source		
Chemical etching	GaN	10	-	-	KOH:H_2O 1:10	-	-Formation of etch pits on GaN surface.	1
Anodic etching	Si-doped GaN 5×10^{18}	30	15	-	0.2 M oxalic acid	-	-Formation of pores with diameter of 20-30 nm.	2
Anodic etching	Si-doped GaN 2.1×10^{19}	45	-	75	CH_3CH_2OH +HF (5:1)	-	-Anodic etching induced pores with different sizes.	3
Anodic etching	Si-doped GaN 2×10^{19}	-	10,15, and 20	-	0.3 M oxalic acid	-	-Porous GaN exhibits two porous layers. -Low porosity layer on top GaN while high porosity layer underlying the top surface.	4
Anodic etching	Highly doped single crystal GaN	30	-	13	Dilute HF (30%)	-	-10 µm porous GaN layer was observed. -Porous GaN exhibited two distinctive pore distributions.	5

Table 2.1 Continue…

Method	Types of GaN (carrier concentration in cm^{-3})	Etching conditions					*Remarks	#Ref.
		Etching time (min)	Etching voltage (V)	Current density (mA/cm^2)	Electrolyte	Types of light source		
Anodic etching	Si-doped GaN 8×10^{18}	10	40,50, and 70	-	0.3 M oxalic acid	-	-Formation of residual irregular sidewalls. -Only doped GaN layer was etched, p-type and undoped GaN remained impervious to attack by anodic etching.	6
Anodic etching	Si-doped GaN 2.5×10^{18}	3	30	-	0.3 M oxalic acid	-	-Coral-like porous GaN. -**Emission efficiency (PL) decrease** due to the removal of large portion of GaN crystalline.	7
Metal-assisted electroless etching	GaN	-	-	-	KOH + K2S2O8	500 W Hg arc lamp	-Pt mask and heavily doped GaN yielded highest etch rate. -The etch rate of GaN near the mask was higher, resulted in rough morphology of porous GaN.	8

Table 2.1 Continue…

Method	Types of GaN (carrier concentration in cm^{-3})	Etching conditions					*Remarks	#Ref.
		Etching time (min)	Etching voltage (V)	Current density (mA/cm^2)	Electrolyte	Types of light source		
Pt-assisted electroless etching	Si-doped GaN 1.2×10^{18}	60 and 120	-	20	CH_3OH: HF:H_2O_2 (1:4:1)	350 W UV lamp	-Porous GaN etched under an hour showed smaller and larger pores while elongated branched pores were observed for porous GaN etched under 2 hours. -**PL enhancement** was observed, i.e., deeper pores induced stronger PL intensity .	9
Pt-assisted electroless etching	UID GaN 3×10^{16}	10-60	-	-	CH_3OH: HF:H_2O_2 (1:2:1), (1:2:2)	Hg lamp	-Small pores with ridge/ trench structure were formed. -Longer etching duration (60 min) was able to extend the pores all the way to GaN-sapphire interface.	10
Pt-assisted electroless		15, 30, 60, and 90	-	-	CH_3OH: HF:H_2O_2 (1:4:1)		-Ridges with circular pores were formed. -**Increment of PL intensity** was observed for porous GaN sample.	11

Table 2.1 Continue…

Method	Types of GaN (carrier concentration in cm^{-3})	Etching conditions					*Remarks	#Ref.
		Etching time (min)	Etching voltage (V)	Current density (mA/cm^2)	Electrolyte	Types of light source		
PEC etching	UID GaN 2.3×10^{17}	15 and 45	10, 15, and 20	-	KOH (0.2, 0.5, 1, and 2 wt %)	500 W UV lamp	-Spherical, elongated, triangular and squarish type of pores were observed -Formation of pores led to the **enhancement of PL Intensity**.	12
PEC etching	UID GaN 1×10^{17}	20	-	5, 10, and 20	HF:H_2O (2:1)	~4 W UV lamp	-Formation of nanoporous GaN. -Higher current density applied in porosification showed **stronger PL intensity**.	13
PEC etching	Si-doped GaN 1×10^{18}-1×10^{19}	60	-	40	HF:H_2O (2:1)	350 UV lamp	-Heavily doped GaN showed more porous than low doped GaN. -The **PL intensity** of heavily doped GaN was **higher** than low doped GaN.	14

Table 2.1 Continue…

Method	Types of GaN (carrier concentration in cm^{-3})	Etching conditions					*Remarks	#Ref.
		Etching time (min)	Etching voltage (V)	Current density (mA/cm^2)	Electrolyte	Types of light source		
PEC etching	Si-doped GaN 8×10^{17}-5×10^{18}	30-60	-	5-25	2 M NaOH	400 W UV lamp	-Current density of 20 mA/cm^2 produced well layered porous structure. -**Significant enhancement in PL intensity** was observed for porous structure.	15
PEC etching	Si- doped GaN 10^{18}	90		25	0.66M HF & 2M KOH	UV lamp	-Different electrolyte solution produced different network of pores, i.e., nanopillars and hexagonal features.	16
PEC etching	Si-doped GaN 5×10^{18}	-	-	5-25	Aqueous HF	200 W mercury lamp	-**Quenching of PL intensity** due to the decrease of carrier concentration in porous GaN sample	17
Anodic etching + PEC etching	Si-doped GaN 3×10^{18} to 2×10^{19}	-	2- 40	-	0.3M oxalic acid	UVP UVL-18 EL lamp	-Formation of nucleation layer after anodic etching. -Removal of nucleation layer can be achieved by subsequent PEC etching.	18

#References:

1. (Zhao et al., 2006)
2. (Jang et al., 2013)
3. (Ramizy et al., 2011a)
4. (Huang et al., 2013)
5. (Gautier et al., 2013)
6. (Park et al., 2009)
7. (Lee et al., 2013)
8. (Bardwell et al., 2001)
9. (Vajpeyi et al., 2005)
10. (Díaz et al., 2002)
11. (Yam et al., 2007a)
12. (Yam et al., 2007c)
13. (Al-heuseen et al., 2010)
14. (Vajpeyi et al., 2007)
15. (Hartono et al., 2007)
16. (Soh et al., 2013)
17. (Mynbaeva et al., 2001)
18. (Schwab et al., 2013)

CHAPTER 3

MATERIALS AND INSTRUMENTATIONS

3.1 Introduction

A clear understanding on the material used for the fabrication is critically important. This chapter is first presented the fundamental properties of GaN thin film. Next, the physical properties of the materials used for the fabrication of porous GaN are given. The basic principle of the photo-assisted electrochemical etching and the principle operations of characterization instruments are also introduced.

3.2 Fundamental properties of GaN

GaN is an III-V compound semiconductor with wide direct band gap energy of about 3.4 eV. GaN can crystallize in two common crystal structures (Zeng et al., 1999, Lei et al., 1991), e.g., wurtzite and zinc blende polytypes. This wide band gap of GaN naturally possesses the hexagonal wurtzite crystal structure at room temperature with the lattice constants, a = 0.3189 nm and c = 0.5185 nm (Quay, 2008). In wurtzite structure, the growth is generally found along the c-axis. Fig. 3.1 shows the schematic diagram of wurtzite structure of GaN.

With the large band gap energy, GaN has emerged as a material of interest for optoelectronic devices operating in the blue or ultraviolet spectral ranges (Nguyen et al., 2010). Due to its high thermal conductivity (Asnin and Pollak, 1999), GaN is suitable for high power application under the harsh environmental condition. Also, GaN exhibits strong piezoelectric characteristic. This property is the driving force for the GaN material towards the application of surface acoustic wave devices (Lee et al., 2001) and pressure sensing devices (Pearton et al., 2004).