# INDIUM GALLIUM NITRIDE BASED LIGHT EMITTING DIODE USING PRE-ROUGHENED BACKSIDE (N-FACE) GALLIUM NITRIDE SUBSTRATE

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**by**

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## LIST OF SYMBOLS

| | |
|---|---|
| ° | Degree (angle) |
| $a$ | In-plane lattice constant |
| $aq$ | Aqueous |
| $l$ | Liquid |
| $n$ | Refractive index |
| $s$ | solid |
| $t$ | Thickness |
| $t_b$ | Thickness of quantum barrier |
| $t_w$ | Thickness of quantum well |
| $\omega$-$2\theta$ | Omega-2theta |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| 3D | 3 dimensional |
| AFM | Atomic force microscope |
| $Cp_2Mg$ | Bis(cyclopentadienyl)magnesium |
| DI | Deionization |
| EBL | Electron blocking layer |
| EL | Electroluminescence |
| EQE | External quantum efficiency |
| FWHM | Full width at half-maximum |
| GYE | Green-yellow emissions |
| HVPE | Hydride vapour phase epitaxy |
| IV | Current-voltage |
| LED | Light emitting diode |
| MOCVD | Metal-organic chemical vapour deposition |
| MQWs | Multiquantum wells |
| NBE | Near-band edge |
| NMP | N-Methyl-2-pyrrolidone |
| PL | Photoluminescence |
| PR | Photoresist |
| PSS | Patterned sapphire substrate |
| QB | Quantum barrier |
| QCSE | Quantum-confined stack effect |
| QW | Quantum well |
| rms | Root mean square |
| SEM | Scanning electron microscope |

| | |
|---|---|
| SIMS | Secondary ion mass spectrometry |
| SLs | Superlattices |
| TDD | Threading dislocation density |
| TIR | Total internal reflection |
| WPE | Wall-plug efficiency |
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray diffraction |

# LIST OF APPENDICES

APPENDIX A OPTIMIZATION OF GROWTH CONDITIONS FOR InGaN LEDs ON GaN SUBSTRATE

APPENDIX B GROWTH CONDITIONS OF BASELINE LEDs

APPENDIX C COMPARISON STUDY: InGaN LEDs ON GaN AND ON PSS

**DIOD PEMANCAR CAHAYA BERASASKAN INDIUM GALLIUM NITRIDA MENGGUNAKAN SUBSTRAT GALLIUM NITRIDA BAHAGIAN BELAKANG (MUKA-N) YANG PRA-DIKASARKAN**

## ABSTRAK

Setakat ini, penyelidikan untuk menambahbaik prestasi indium galium nitrida berasaskan diod pemancar cahaya (InGaN LEDs) di atas substrat GaN hanya sedikit disebabkan kos substrat GaN yang tinggi. Oleh itu, prestasi InGaN LEDs di atas substrat GaN lebih rendah berbanding dengan InGaN LEDs di atas substrat nilam walaupun ianya mempunyai ketumpatan kehelan benang yang lebih rendah. Disebabkan itu, Projek ini dijalankan untuk menambahbaik prestasi InGaN LEDs yang ditumbuhkan di atas substrat GaN. Bagi mencapai matlamat ini, tiga buah rangka kerja telah dicadangkan. Pertama, dengan menyisipkan lapisan penutup GaN dalam telaga-kuantum berbilang (MQWs). Kedua, dengan mengasarkan bahagian belakang (muka-N) substrat GaN menggunakan larutan punaran baharu dan menyepuh-lindapkan substrat sebelum proses pengasaran. Ketiga, dengan mengasarkan substrat GaN sebelum pertumbuhan LED. Dengan penambahan lapisan penutup GaN, prestasi LED telah meningkat sebanyak 12% dan homogen kandungan indium di dalam telaga-kuantum InGaN telah terkesan sedikit. Walau bagaimanapun, kelebihan lapisan penutup GaN kelihatan tidak bererti bagi LED yang memancarkan gelombang yang lebih panjang. Ini kerana lebih banyak kecacatan dan kesan polarisasi yang dihasilkan di dalam MQWs dengan kandungan indium yang lebih tinggi. Sementara itu, pengasaran muka-N substrat GaN menggunakan campuran ammonia hidroksida dan hidrogen peroksida ($NH_4OH:H_2O_2$) telah menghasilkan piramid berketumpatan 5.0 × $10^9$ $cm^{-2}$. Dengan mempunyai lebih tinggi ketumpatan piramid heksagon, prestasi bagi

LED dengan punaran $NH_4OH:H_2O_2$ telah bertambahbaik sebanyak 20% berbanding LED dengan punaran kalium hidroksida (KOH). Selanjutnya, pra-penyeluhlindapan oksigen menghasilkan Ga-O pada permukaan LED dan meningkatkan ketumpatan piramid kepada $4.3 \times 10^{10}$ $cm^{-2}$. Hasil ini merupakan antara hasil terbaik yang pernah dilaporkan setakat ini. Kuasa optik untuk LED yang ditumbuhkan di atas substrat GaN yang telah dikasarkan (melalui pra-penyepuhlindapan oksigen) adalah 300% lebih baik berbanding LED tanpa penyeluhlindapan. Akhir sekali, prestasi LED di atas substrat GaN yang pra-dikasarkan adalah 50% lebih tinggi berbanding LED di atas substrat GaN pasca-dikasarkan pada 2 $A/cm^2$. Ini menunjukkan bahawa pra-pengasaran substrat GaN adalah bermanfaat bagi menambahbaik pertumbuhan LED dan meringkaskan proses LED.

## INDIUM GALLIUM NITRIDE BASED LIGHT EMITTING DIODE USING PRE-ROUGHENED BACKSIDE (N-FACE) GALLIUM NITRIDE SUBSTRATE

## ABSTRACT

At this point, there has been little research on improving the performance of indium gallium nitride based light emitting diodes (InGaN LEDs) on GaN substrates due to the high cost of GaN substrates. The performance of InGaN LEDs on GaN substrate is lower to those on sapphire substrates, despite having a lower threading dislocation density. In response to that, this project attempts to improve the performance of InGaN LEDs grown on GaN substrates. To achieve this goal, three frameworks were proposed. Firstly, by introducing GaN cap layer in multiquantum wells (MQWs). Secondly, by roughening backside (N-face) of GaN substrate using new etching solution and annealing the substrate before roughening. Thirdly, by roughening GaN substrate prior to LED growth. By adding a GaN cap layer has led to an increase in LED performance of 12%, and the homogeneous indium content in InGaN quantum wells has had a slightly affected. However, the benefit of the GaN cap layer seemed to be insignificant for the LEDs emitting at longer wavelengths. This is because more defects and polarization effects were generated with higher indium contents. Meanwhile, the roughening N-face GaN substrate using mixture of ammonia hydroxide and hydrogen peroxide ($NH_4OH:H_2O_2$) produced pyramids density of $5.0 \times 10^9$ $cm^{-2}$. By having more hexagonal pyramids density, the performance of the LEDs with $NH_4OH:H_2O_2$ etching improved 20% compared to the LEDs with potassium hydroxide (KOH) etching. Furthermore, the oxygen pre-annealing created more Ga-O on the surface, and hence, increasing the pyramids density up to $4.3 \times 10^{10}$ $cm^{-2}$. The result is among the best

reported result so far. The optical power of LED grown on roughened GaN substrate through the oxygen pre-annealing is 300% better than LED without annealing. Finally, the performance of LED on pre-roughened GaN substrate was 50% higher than LED on post-roughened GaN substrate at 2 A/cm$^2$. This shows that pre-roughening GaN substrate is beneficial for improving the LEDs growth and simplifying the LED process.

# CHAPTER 1

# INTRODUCTION

Today, light emitting diode (LED) technology has significantly changed the way of our life. In comparison to filament bulbs and fluorescent lamps, LEDs offer higher brightness (light output power), higher luminous efficacy and longer lifetime. Furthermore, LEDs are accepted as energy-saving and environmentally-friendly technology that helps the world to reduce greenhouse gas emissions. In response to this, the Malaysia government has committed to fully utilize LEDs in various lighting applications, which then leads to 50% reduction of energy consumption in the country [1]. Moreover, this effort is in line with one of the initiatives under National Energy Efficiency Action Plan (2016-2025) that aims at improving energy efficiency by minimizing waste towards sustainable nation development [2].

In order to make the LEDs technology reaches at its full potential, it is therefore important that the LEDs are nearly 100% efficient. In the early development of LEDs, zinc selenide (ZnSe) was used as the material to develop blue LEDs. Essentially, blue LEDs are a critical component for producing white LEDs, by partially converting the blue light (which is emitted from the blue LEDs) into yellow light using phosphor. However, ZnSe based LEDs showed only few percent efficiency and shorter lifetime. This is due to the difficulty in obtaining a highly doped p-type, and defects generation during device operation [3,4]. The realization of high efficient white lighting was impossible at that time. In mid-1980s, Shuji Nakamura discovered that high efficient blue LEDs were possible with the use of indium gallium nitride (InGaN) materials. Unlike ZnSe, p-type of GaN materials (that is also one of family members of III-V nitrides) can be achieved by using magnesium doping and thermal annealing [5]. This allows more holes to participate in radiative recombination and thereby increases efficiency. Furthermore, by tuning the indium composition of InGaN, it is possible to develop LEDs emitting in the entire visible spectrum, from ultraviolet to infrared.

To date, sapphire has become the mainstream substrate for InGaN LEDs. However, the LEDs grown on sapphire substrate always suffer from high dislocation density, as well as larger strain and hence, larger bowing effect due to large mismatch of lattice parameters between sapphire and InGaN materials. Despite of tremendous efforts have been done for all these years, the efficiency of the LEDs is still far from unity. At this point, high performance of blue InGaN LEDs grown on patterned sapphire substrates exhibit about 84.3% of external quantum efficiency [6]. Growing the LEDs on GaN substrate has been considered as an ideal route to achieve the efficiency approaching 100%. This is because GaN substrate has nearly perfect lattice-matched substrate with InGaN materials. Nonetheless, GaN substrates are costly, which is about 100 times expensive than sapphire substrate. With advanced growth and fabrication technology nowadays, it is possible that GaN substrate would be affordable in near future. Apart from being a perfect matched substrate for the LEDs, the growth time for the LEDs on GaN substrate can be reduced almost half with respect to the growth time using sapphire substrate. This is because the thick buffer layer in the LEDs growth can be eliminated with the use of GaN substrate.

## 1.1 Challenges in developing InGaN LEDs on GaN substrate

Most light emissions are generated from an active region of an LED, which is constructed by multiquantum wells (MQWs). For visible LEDs, the MQWs consists of alternating layers of InGaN quantum well (QW) and GaN quantum barrier (QB). However, growing high quality of InGaN/GaN MQWs is difficult, especially with higher indium compositions. Commonly, GaN QB is grown at lower growth temperatures between 600 °C and 800 °C. Such temperatures are required to maintain the desirable homogeneous indium in InGaN. However, this condition causes the reduction of ammonia cracking efficiency during GaN QB growth, which then leads to more defects generation in GaN QB. These defects could act as a non-recombination center, which would decrease the performance of the LEDs. There are numerous works, have implemented an additional layer of GaN (always termed as GaN cap layer), which is grown after the GaN QB at higher temperature than GaN QBs [7-9]. It was found that the LED performance has significantly improved without affecting the indium content in InGaN QW. Despite this, the use of the GaN cap layer in MQWs in LEDs on GaN substrate has not been reported. Hence, the effect of the GaN cap layer on the performance of LEDs on GaN substrate is still questionable.

Moreover, the light extraction of LEDs grown on GaN substrate is always lower than LEDs on sapphire substrate. This is mainly due to higher refractive index of GaN substrate ($n$ = 2.4) with respect to air ($n$ = 1). Based on Shell's law, the generated lights can only be extracted when their incidence angle are smaller than the critical angle of GaN, which is 24°. With this small critical angle, only 23.3% of light generated in LED are allowed to extracted to free space [10], while the rest are trapped through total internal reflection effect. In general, the roughening on the backside (N-face) of GaN substrate creates hexagonal pyramids structures, which enable more light scatterings. The light scatterings disrupt the total internal reflection, widening the escape cone for more lights to be extracted to air. So far, works on improving the roughening on the GaN substrate are limited. A higher density of the pyramids are desirable to obtain a high light extraction efficiency [11-14]. The density of hexagonal pyramids on GaN produced by different etching solutions is typically around $10^8$-$10^9$

$cm^{-2}$. Therefore, in order to increase the density of hexagonal pyramids, it is essential to identify a new etching solution and redesign roughening techniques for the backside (N-face) of GaN substrate.

Moreover, backside (N-face) roughening of GaN substrate is commonly performed after LED growth. However, this method could potentially diffuse impurities from the etching solution into the LED structure and degrade the surface quality of the p-GaN of the LED. As a consequence, the voltage of LEDs increases and this limits the overall performance of the LEDs [15-16]. One of the ways to alleviate the problem is to cover the surface of p-GaN with a protective layer like photoresist before roughening. The processing of LEDs can be complicated and time-consuming due to the need for additional steps. In order to simplify the process and not compromise the LEDs' performance, a different approach to roughening the GaN substrate of LEDs is required.

## 1.2 Novelty of research

Since the cost of GaN substrates is still high at present, there is not much study has been done on improving the performance of InGaN LEDs on GaN substrates. This research intends to fill the gap. The novelty of this work lies on improving the performance of InGaN LEDs by adopting additional high-temperature GaN cap layer in MQWs using GaN substrate for the first time. Moreover, the GaN substrate is being roughened through a new alternative etching solution, which is a mixture of ammonia hydroxide and hydrogen peroxide, and is being annealed prior to roughening. Furthermore, while the roughening of GaN substrate is a common approach to enhance performance of LED, this research introduces a novel roughening technique that involves roughening the GaN substrate before LED growth (pre-roughening). It is worth to note that this method has not been considered so far. Thus, the outcomes from this research provide valuable insight into the development of InGaN LEDs grown on roughened GaN substrates and potentially simplifying the fabrication of LEDs.

## 1.3 Aim and objectives of research

The aim of this research is to improve the performance of visible InGaN LEDs grown on GaN substrate. Hence, the objectives of this research are;

1. To determine the effect of adopting GaN cap layer in multiquantum wells on performance of InGaN LEDs grown on GaN substrate.

2. To identify the etching solutions and pre-annealing ambiences for roughening of the backside (N-face) GaN substrate

3. To evaluate the impact of pre-roughening of the GaN substrate for the InGaN LEDs performance.

## 1.4 Scope of research

The scope of the study has been determined to ensure that the results and discussion fulfill research objective.

Firstly, the research focused on improving the LED performance by adopting 9 nm of GaN cap layer in the MQWs. Two InGaN LEDs on GaN substrate were grown identically, except for the MQWs. First LED was grown with 9 nm of GaN cap layer in MQWs, while second LED without GaN cap layer in MQWs. Both LEDs undergo an identical fabrication and packaging processes. The performance of the LEDs was determine by integrating sphere. Here, the InGaN LEDs were developed with emissions in the range from 409 nm to 524 nm. This is to obtain more comprehensive understanding on the effect of GaN cap layer in MQWs at different LED wavelengths.

Second, this research focused on obtaining a high density of hexagonal pyramids on backside (N-face) of GaN by improving the roughening methods. A few methods were conducted to obtain high density of hexagonal pyramids. The methods involve roughening using various etching solutions and annealing the substrate in different ambiences before roughening (pre-annealing). Only hexagonal pyramids with 6 inclined planes, either with a peak or without a peak are considered when calculating the density of hexagonal pyramids. The influence of hexagonal pyramid density on InGaN LED performance was investigated using an integrating sphere.

Finally, this research focused on the impact of pre-roughening of the GaN substrate on the performance of InGaN LEDs. Two InGaN LEDs on GaN substrate were prepared under identical LED growth and etching conditions. The difference between both LEDs was the roughening of the backside GaN substrate, whether it was done before or after the LED's growth. The performance of both LEDs was assessed and the impact of pre-roughening of the GaN substrate was identified.

## 1.5 Outline of the thesis

This thesis is organized as follows; Chapter 2 describes properties of III-V nitrides materials and reviews published works on improving the performance of InGaN LEDs on GaN substrate from the aspects of epitaxial growth, GaN substrate roughening, and packaging.

Chapter 3 gives details of experiments conducted in this work. This includes growths of InGaN LEDs on GaN substrate using metal-organic chemical vapour deposition (MOCVD) reactor with the variation of parameters like growth temperature, indium composition, and adoption of GaN cap layer in MQWs. Roughening the backside of GaN substrate using different etching solutions, different gas ambience for pre-annealing GaN substrate, and pre-roughening of the GaN substrate were described. Furthermore, this chapter explains characterization measurements for the LEDs in order to evaluate their properties in terms of elemental composition, crystalline quality, surface morphology/topology, electrical characteristic, optical emission, and optical-electrical properties. The fabrication and processing to transform the LEDs epi-wafers into functional devices are also described.

Chapter 4 presents results from series of the growth of InGaN LEDs on GaN substrate and impact of GaN cap layer on performance of InGaN LEDs on GaN substrate. Then, the effect of etching on backside of GaN substrate using different etching solutions and followed by the influence of pre-annealing and impact of pre-roughening of GaN substrate on InGaN LEDs performance.

Chapter 5 concludes the findings of this research. The chapter also proposes several works, which could be as the continuation of the research in future.

# CHAPTER 2

# LITERATURE REVIEW

This chapter begins with discussions on basic properties of III-V nitride materials. The understanding on the materials properties is important in improving epitaxial growths of LEDs based on III-V nitrides. Following that, efforts to develop high performance LEDs using GaN substrate are described. This includes reviewing works on roughening the backside (N-face) of GaN substrate, which beneficial for increasing the performance of the LEDs.

## 2.1 Introduction to III-V nitrides

III-V nitrides are formed by combining atoms from group III (generally; gallium (Ga), indium (In), and aluminium (Al)) with nitrogen atoms from group V. In general, III-V nitrides materials are formed in wurtzite (hexagonal) structure with two lattice constants; that are in-plane (*a*) and out-of-plane (*c*). The atomic arrangement to build up a GaN material, as for an example, is illustrated in Figure 2.1. Each Ga atom is bonded with four N atoms, forming a tetrahedral bonding structure. The stacking sequence for the wurtzite plane (0001) is ABABAB, where the Ga and nitrogen are alternately arranged. The surface in c-plane direction is called Ga-terminated surface, or Ga-face. Meanwhile, the surface on the other side is called N-terminated surface or N-face. As opposed to Ga-face, the surface of N-face is susceptible to chemical reaction. Hence, the roughening of GaN is typically done on N-face of the material. This topic will be discussed in a later section.

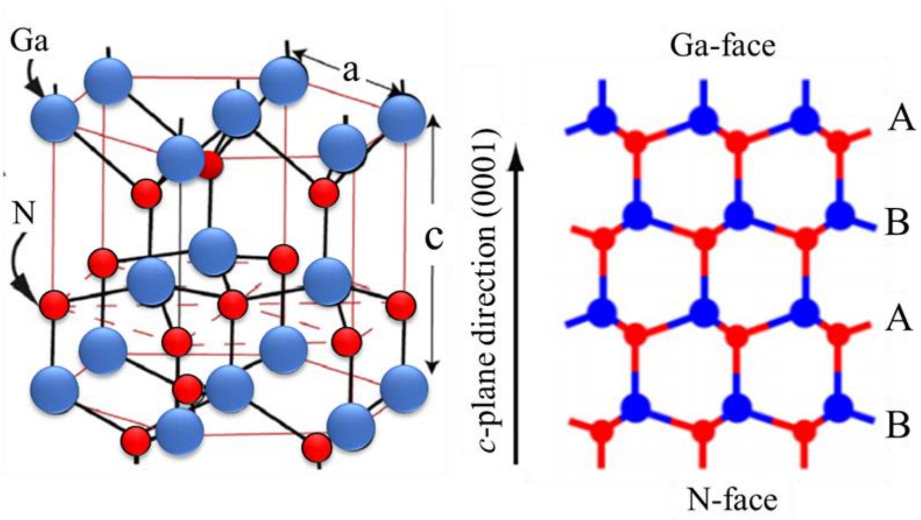


Figure 2.1: Wurtzite structure of a GaN compound. The diagram is modified from [10].

It is well accepted that III-V nitride materials have been indispensable materials in LEDs development. In comparison to other traditional semiconductor materials like silicon (Si), III-arsenides and II-phosphides, III-V nitrides materials have wider direct energy bandgap. By adjusting the indium and aluminium compositions in the AlInGaN material, the energy bandgap and hence, emission energy of a III-V nitrides LED can be varied from 0.64 eV (InN) to 6.0 eV (AlN). This is shown in Figure 2.2. The energy bandgap of the InGaN and AlGaN materials with corresponding In and Al compositions can be expressed using Vegard's law, as follows [17,18],

$$E_g^{InGaN\ or\ AlGaN} = E_g^{InN\ or\ AlN}\, x + E_g^{GaN}\,(1 - x) - bx\,(1 - x) \qquad (2.1)$$

where $x$ is indium composition in InGaN or aluminium composition in AlGaN. $E_g^{InN}$, $E_g^{GaN}$ and $E_g^{AlN}$ are the energy bandgap of InN (0.64 eV), GaN (3.42 eV), and AlN (6.0 eV), respectively. Meanwhile, $b$ is the bowing parameter of InGaN and AlGaN with a value of 1.3 eV [19] and 0.8 eV [20], respectively. From Figure 2.2, it can be seen that only lattice constant of $a$ is shown. Typically, lattice constant of $a$ is more significant in determining the material quality of III-V nitrides than lattice constant of *c* [21,22]. With respect to GaN, the in-plane (*a*) lattice mismatch for InN is 10% [23], while for AlN is 2.4% [24]. Meanwhile, the mismatch will be larger with respect to sapphire (16%) [25], which is a common substrate for nitrides. The larger the mismatch, the higher is strain and defects generations. This indicates that growing nitrides LEDs (operating in visible spectrum) on GaN substrate is more preferable than foreign substrate like sapphire.

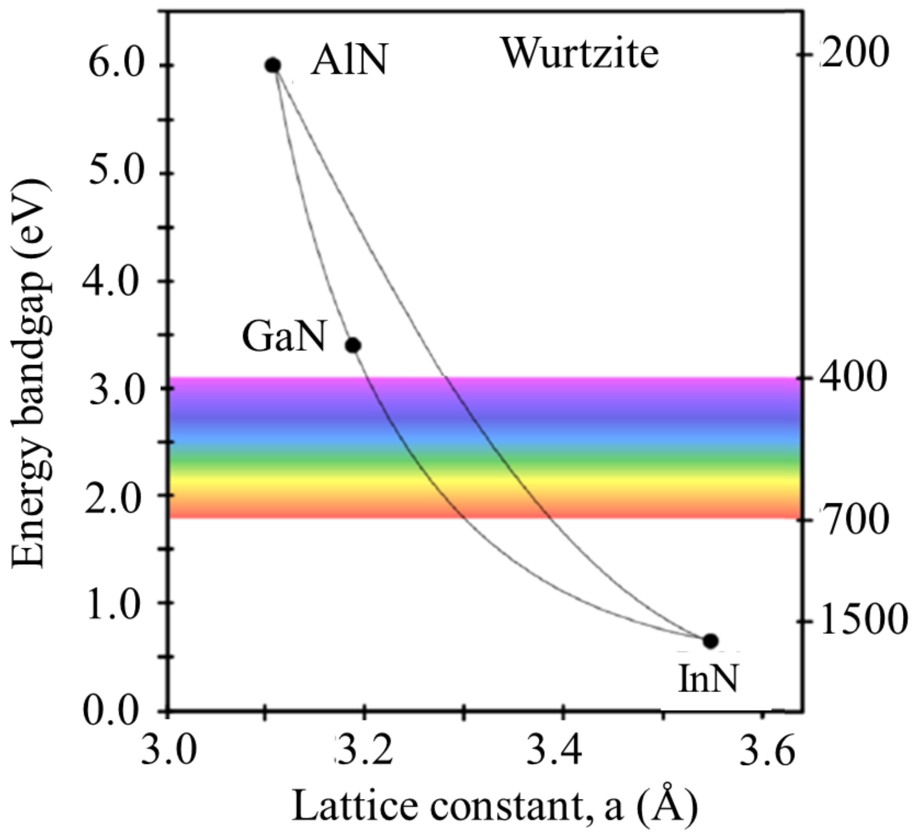


Figure 2.2: Energy bandgap as a function lattice constant, a of III-V nitride materials. The graph is taken from [26].

## 2.2 Growth of III-V nitrides materials for LEDs

III-V nitride materials do not exist in nature. High quality III-V nitride materials are typically formed via atom-by-atom technique using hydride vapour phase epitaxy (HVPE), molecular-beam epitaxy (MBE), and metal-organic chemical vapour deposition (MOCVD) techniques. In general, HVPE has higher growth rate than MOCVD and MBE. For this reason, HVPE is suitable for growing bulk nitrides, for example free-standing GaN substrate. However, HVPE is not preferable for growing thin films. In order to produce high quality thin films, the growth rate needs to be precisely controlled. MBE has a relatively low growth rate, which is suitable for thin films growth. Since MBE growth is performed under ultra-high vacuum ($10^{-8}$-$10^{-12}$ Torr), MBE is considered by many as a complex and costly technique. On the other hand, MOCVD is widely used in mass productions for growing III-V nitrides LEDs since it does not require the ultra-high vacuum, while its growth rate can be controlled precisely. In fact, MOCVD growth can be performed in atmospheric pressure. Even so, there is a concern that MOCVD is using hazardous sources/precursor for growing the nitrides materials. With advanced gas handling safety and gas purification system nowadays, the issue can be addressed properly.

## 2.3 Development of InGaN LEDs on GaN substrate

At present, sapphire and silicon substrates have become the mainstream substrate in InGaN LEDs manufacturing. However, the lattice mismatch between the nitrides layers of the LEDs and foreign substrates like sapphire substrate and silicon substrate is ~ 16% and 17%, respectively [25]. This leads to high threading dislocation density (TDD) and large strain in the LEDs. When the threading dislocation reaches the active region or known as MQWs of the LEDs, non-radiative recombination centres are created [27]. These centres trap lights generated from the MQWs, thereby reducing the performance of the LEDs. To date, the average of TDD for InGaN LEDs grown on sapphire substrate an silicon substrate is around $10^8$-$10^9$ $cm^{-3}$ [28]. So far, many growth approaches have been proposed to reduce the TDD. One of the most effective ways to reduce the TDD is by adopting epitaxial lateral overgrowth (ELOG) in the LEDs growth. Commonly, ELOG consists of a silicon nitride ($Si_3N_4$) or silicon oxide ($SiO_2$) stripe-mask-patterned on the substrate, which can be deposited via chemical vapour deposition technique. Then, the mask-patterned is transferred on the substrate through photolithography and this is followed by an plasma etching process to open the $Si_3N_4$ or $SiO_2$ mask layer. Ji et. al. [29] reported that by adopting ELOG in the growth of an InGaN LED, the TDD can be reduced as low as 3 x $10^5$ $cm^{-2}$, which is almost similar value for a reported InGaN LED grown on GaN substrate [30,31]. Moreover, the indium incorporation in the MQWs of the LED improved due to the strain relaxation by the ELOG. As mentioned above, ELOG requires additional steps and growth interruption, which lead to complication and prolong duration for the LEDs growth.

An ideal route to reduce the TDD and strain in InGaN LEDs is by growing the LEDs on GaN substrates. This is called homoepitaxy. The GaN substrate is nearly lattice-matched to the InGaN LEDs. At this point, the highest external quantum efficiency (EQE) of InGaN LEDs grown on GaN substrate is 73% [32]. However, there is limited information available about the epitaxy structure of this LED. The majority of research shows that EQE of InGaN LEDs on c-plane GaN substrate is below 40%, as depicted in Figure 2.3. The majority of reported works for InGaN LEDs on foreign substrates have an EQE of over 40%. Although semipolar GaN substrate is used to lessen spontaneous polarization in LEDs, the LED performance is still lower than those of InGaN LEDs on foreign substrates. Due to limited research and the higher cost of GaN substrate, there has been little progress in improving the performance of InGaN LEDs on GaN substrate.

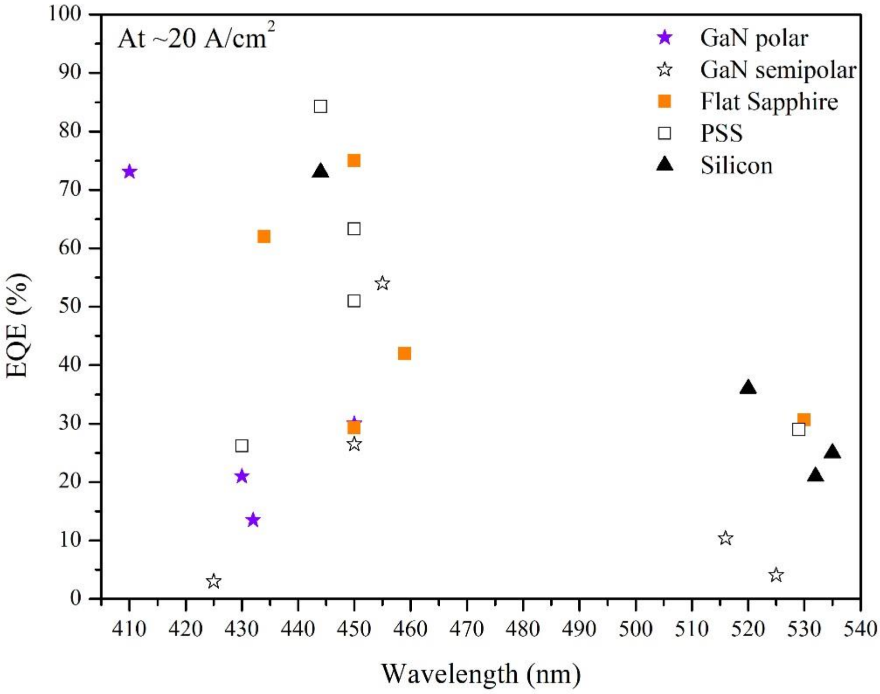


Figure 2.3: The external quantum efficiency (EQE) of InGaN LEDs grown on different substrates as a function of emission wavelength of LEDs adapted from [6,9,14,32-41].

Even though the EQE of InGaN LEDs on GaN substrates is lower compared to InGaN LEDs on sapphire substrates, several studies have indicated that the droop efficiency of InGaN LEDs on GaN substrate is always better than that of LEDs on sapphire substrate [42-44]. The droop efficiency can be calculated using the following equation:

$$Droop_{eff} = \frac{EQE_{peak} - EQE_{100\ Acm^{-2}}}{EQE_{peak}} \times 100\% \qquad (2.2)$$

where the $EQE_{peak}$ and $EQE_{100Acm^{-2}}$ represent the EQE maximum and the EQE at current density of 100 A/cm$^2$. A recent report by Tsai et al. [42] inferred that ultra-low TDD and high thermal conductivity with the use of GaN substrate, helped to improve the droop efficiency. Furthermore, Cao et. al. [43] suggested GaN substrate allows good heat dissipation and current spreading to InGaN LED. This is due to the fact that thermal conductivity of GaN is 220 W/mK [45], while sapphire is 46 W/mK [46]. Table 2.1 summarizes the reported droop efficiency of InGaN LEDs grown on sapphire and on GaN substrate. The results indicate that InGaN LEDs grown on GaN substrates have a clear advantage for applications that require high performance at higher current densities, such as high-power LED lighting (spotlights).

Table 2.1: Droop efficiency of InGaN LEDs grown on sapphire and on GaN substrates.

| Reference | Wavelength (nm) | Droop efficiency (%) | |
|---|---|---|---|
| | | On sapphire | On GaN |
| Tsai et al. [42] | 400 | 20 | 3 |
| Chao et al. [44] | 445 | 44 | 28 |
| Cao et al. [43] | 465 | 57 | 20 |

### 2.3.1 Development of multiquantum wells of InGaN LEDs

The selection of substrate is not the sole problem with InGaN LEDs. As can be seen in Figure 2.3, the performance of LEDs decreases when the wavelength increases for all substrates. This is due to growing high quality of InGaN/GaN MQWs is challenging, especially with longer wavelength (higher indium compositions). Most light emissions are generated from MQWs. For visible LEDs, the MQWs consist of alternating layers of InGaN QW and GaN QB. Commonly, higher growth temperatures above 1000 °C are required to maintain the quality of GaN layer. By increasing the growth temperature, the efficiency of ammonia cracking, as a mean to produce N-radicals, increased. This subsequently suppressed the nitrogen vacancies and carbon impurity and hence, improving the GaN. Such defects could act as a non-recombination centre which would decrease the performance of the LEDs [27].

Unlike GaN, growth of InGaN is rather challenging, especially with higher indium (In) compositions. In order to develop LEDs with longer emission wavelengths, the InGaN QWs should be grown with higher In compositions. High quality InGaN can be obtained at higher growth temperatures. However, in real experiments, this is not practical as InN has relatively high vapour pressure than GaN. Therefore, InGaN is typically grown at lower temperatures than GaN, of around 650-850 ℃ [47]. Figure 2.4 shows indium composition of InGaN as a function of growth temperature, as reported in [47]. Apparently, the In composition in the InGaN is higher at lower temperatures. As discussed, growing an InGaN layer at a lower temperature is not only degrading the material quality of the layer, but also leads to reduction of ammonia cracking efficiency.

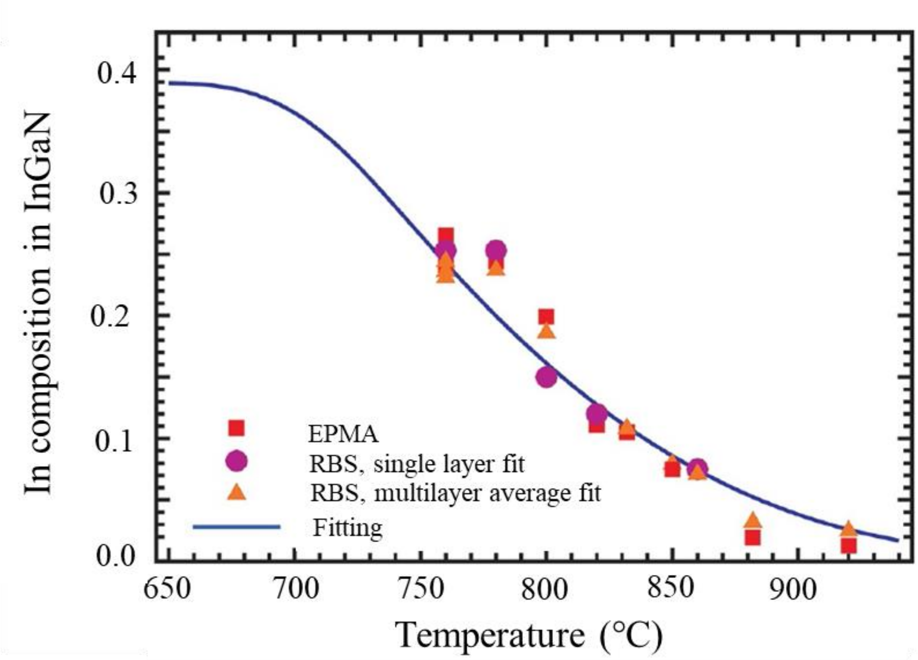


Figure 2.4: Indium composition of InGaN as a function of growth temperature of MOCVD. The diagram was modified from [47].

To address the issue with regard to the ammonia cracking inefficiency at lower growth temperatures, high ammonia flow rate and high V/III ratio were proposed, as an attempt to increase the nitrogen radicals [48,49]. Despite of that, this approach is not suitable for growing thin InGaN layers. As mentioned above, thin InGaN layers are important for visible LEDs, which serve as QWs of the LEDs. Since the thickness of the InGaN QWs is only 2-3 nm, the In from the QWs can be easily etched by hydrogen radicals, which are also resulted from the ammonia cracking. This has been proved by Yang et. al. [50], which found that higher ammonia flow rates generated more hydrogen radicals, leading to In etching. Subsequently, the etching caused fluctuations of thickness and indium composition in the InGaN QWs. These fluctuations contribute to a serious problem to the LEDs performance, in term of uniformity and purity of the emission wavelength. Moreover, the hydrogen radicals could etch the GaN QBs of the LEDs [51]. In standard visible LEDs, GaN QBs (grown with slight thicker than InGaN QWs) are grown alternatively with InGaN QWs to form MQWs structure, which is known as the active region of the LEDs. As found in [51], the presence of hydrogen gas during the growth of the GaN QBs resulted in defects.

Alternatively, Leem et al. [52] proposed that the quality of a MQWs of the LED could be improved by increasing the growth temperature of the GaN QBs. By increasing growth temperatures of QBs, the defects such as point defects [53,54] impurities [55] and complexes [53] that act as non-radiative recombination centers in MQWs are reduced. This leads to increase in InGaN LEDs performance. However, there is possibility for the indium to decompose from the InGaN QWs [56] when the growth temperatures of GaN QBs increase. Wang et al. [57] modified MQWs growth conditions by applying dual-temperature of GaN QB. First layer of GaN QB was grown at similar growth temperature with InGaN QW. This layer is used to prevent indium from desorption during high-temperature growth. The second layer of GaN QB (always termed as GaN cap layer) was grown at a higher growth temperature than InGaN QWs. It was found by optimizing thickness of low-temperature GaN QBs [9] and growth temperature of GaN cap layer, the performance of LED was increased and the indium decomposition can be minimized. Moreover, Zheng et al. [58] found low-temperature GaN QBs with a thickness of 3 nm can effectively prevent indium from desorption during high-temperature growth. Table 2.2 presents the reported performance of InGaN LEDs on sapphire substrate (at 20 $A/cm^2$) using different MQWs structures.

Nonetheless, the adoption of the GaN cap layer in MQWs of visible LEDs is not widely demonstrated, especially the LEDs grown on GaN substrate. Hence, the significance of the cap layer in the LEDs development is still questionable. This research intends to fill in the gap by adopting the GaN cap in MQWs of InGaN LEDs grown on GaN substrate. The results will provide an insight on the significance of adopting the cap layer in MQWs on performance of the InGaN LEDs grown on GaN substrate.

Table 2.2: The performance of InGaN LEDs on sapphire substrate using different multiquantum wells structures. Values which were not provided by the literature are left empty.

| Method | Growth temperature | | Wavelength (nm) | Voltage (V) | EQE (%) | Droop efficiency (%) | Ref. |
|---|---|---|---|---|---|---|---|
| | QW | GaN cap | | | | | |
| Without high-temperature GaN QB | 770 | - | 447 | 3.28 | 46 | 21 | [8] |
| High-temperature GaN QB | 770 | 840 | 449 | 3.44 | 49 | 20 | |
| Without high-temperature GaN QB | 800 | - | 550 | 4.0 | 5 | 0 | |
| High-temperature GaN QB | 800 | 875 | 550 | 3.5 | 22 | 40 | [41] |
| High-temperature GaN QB and AlGaN cap layer | 800 | 875 | 529 | 3.5 | 29 | 77 | |
| High-temperature GaN QB | 802 | 950 | 535 | - | 25 | - | [9] |
| High-temperature GaN QB | 800 | 920 | 455 | - | 82 | - | [59] |

### 2.4 Development of InGaN LEDs on roughened GaN substrate

On the other hand, the light extraction efficiency (LEE) of LEDs grown on GaN substrate is always lower than LEDs on sapphire substrate. A simulation work by Kuritzky [60] found that the LEE of InGaN LED on sapphire substrate was 30.5%, while the LED on GaN substrate was only 23.3%. Majority of the generated light loss occurred in the GaN substrate, which was 35.2%. The difference of refractive index between GaN (*n* = 2.4) and air (*n* = 1.0) is large, hence promoting a narrow escape cone of 24°. Hence, only 23.3% of the generated light from MQWs active region of LEDs to be extracted to air [10]. The remaining lights suffer from total internal reflection, which are bounced back in the LEDs. This leads to more loss of light along with longer optical path length, as illustrated in Figure 2.5(a). Hence, poor light extraction is expected.

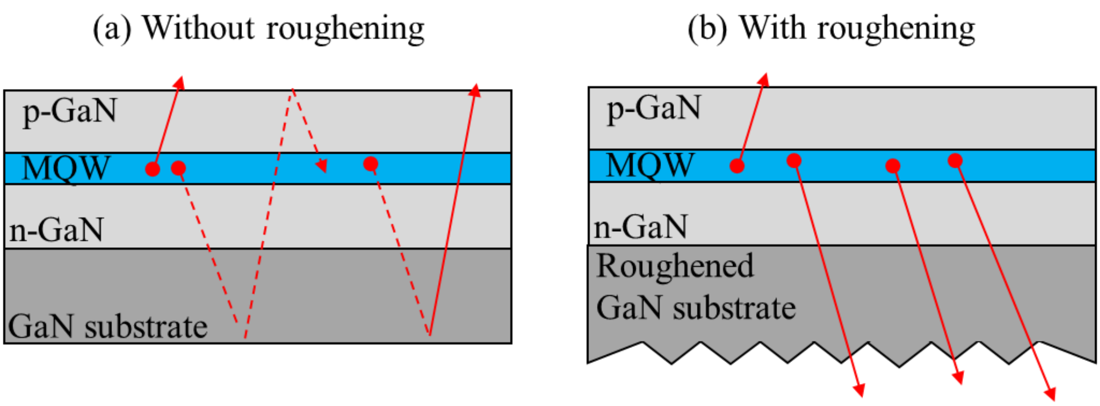


Figure 2.5: Light extraction for an InGaN LED (a) without and (b) with roughening on backside of GaN substrate.

One of ways to address this problem is by roughening the backside of the GaN substrate, which has been proved to increase the LEE [11,60,61]. A simulation work by Kuritzky et. al. [60] found that an LED on roughened GaN substrate showed a LEE of 58%, which was more than two times higher than an LED on non-roughened GaN substrate with LEE of 23.3%. This indicates that with the roughened GaN substrate (typically with hexagonal pyramids), the light extraction can be increased through light scattering effects, as shown in Figure 2.5(b). Thus far, numerous studies have been done to optimize the hexagonal pyramids in terms of their shape, angle, size and density. A small angle of pyramids (between 30° to 50°) and higher density of the pyramids are desirable to obtain a high light extraction efficiency, as reported by [11-13].

Roughening of backside of GaN can be done through etching; either by dry etching or by wet etching [36,62,63]. Dry etching or physical etching is conducted using reactive gases or plasma. Inductively coupled plasma (ICP) or reactive-ion (RIE) machines are widely used for the dry etching. Through dry etching, the shape, size, and density of the patterns can be precisely controlled. However, dry etching involves additional steps like photolithography process. Furthermore, Kim et al. [64] reported that bombardments by reactive gases or plasma via dry etching damaged the surface. If this occurs on an LED on GaN substrate, the voltage of the LED would increase, thereby, reducing the LED efficiency, reliability and lifetime [65].

### 2.4.1 Roughening of InGaN LEDs using wet etching

Alternatively, wet etching or chemical etching is a simple technique and does not require the photolithography. In fact, its etching mechanism is considered softer than dry etching. In general, the process of wet etching starts with the formation of oxides on the surface and subsequently, the dissolution of the oxides by the etchant. In the case for GaN etching, hydroxide ions ($OH^-$) from water or etching solutions are adsorbed on the surface. Consequently, the ions react with Ga atoms to form gallium oxides ($Ga_2O_3$) on the surface. These oxide compounds are then dissolved by the etchant. The formation of the $Ga_2O_3$ compounds during the etching can be expressed by Equation 2.3 [66].

$$2GaN + 3H_2O \xrightarrow{\text{catalyst (e.g KOH, } NH_4OH)} Ga_2O_3 + 2NH_2 \tag{2.3}$$

Numerous studies have found that the crystalline quality of GaN material strongly influences the etching behaviour. This is because poor crystals consist of a large number of defects (weak bond), which are easier to remove during the etching. Another factor that influences the etching behaviour is the GaN polarity. In comparison to N-face, Ga-face of GaN is highly resistant to chemicals [66]. This is due to a large repulsive force between incoming $OH^-$ and three occupied dangling bonds of nitrogen, which prohibit $OH^-$ from approaching to Ga atoms to form oxidation on the surface. Meanwhile, N-face has only one dangling bond of nitrogen, which is accessible to form the $Ga_2O_3$ compounds. Figure 2.6 shows the etching mechanism on N-face GaN.

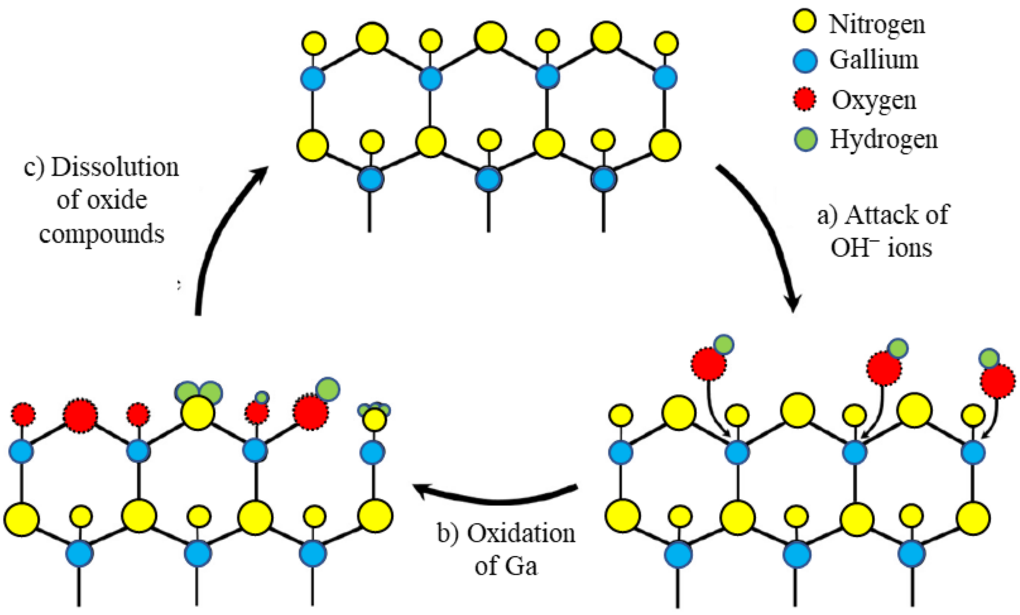


Figure 2.6: Mechanism of etching on N-face GaN [67].

Therefore, the roughening on GaN substrates has been widely applied on N-face (backside) of the substrates [68,69]. At this point, various etching techniques have been proposed for improving the roughening, which results in a high density of the hexagonal pyramids. Potassium hydroxide (KOH) solution has been commonly used as the etching solution for the GaN roughening. Figure 2.7 shows a reported hexagonal pyramids formed after roughening on the backside (N-face) of a GaN substrate by KOH etching [70]. As reported by Fu et al. [15], the hexagonal pyramids on a GaN substrate increased the optical power of the overgrown LED by 21%, as compared to the LED grown on non-roughened GaN substrate. Meanwhile, Cich et al. [32] found that the EQE of an LED can be achieved up to 73% by using a roughened GaN substrate.

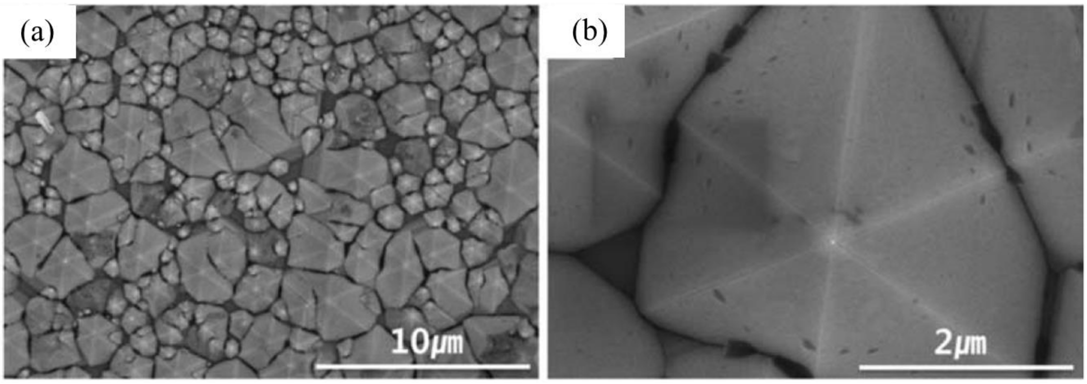


Figure 2.7: Hexagonal pyramids formed on N-face GaN after KOH etching with (a) a small magnification and (b) a high magnification [70].

Nonetheless, KOH is an aggressive etching solution. Hence, KOH etching always results in poor repeatability and controllability in forming the pyramids on the N-face GaN [40]. As report by Jeong et. al. [71], prolonged KOH etching tended to destroy the pyramids, and this eventually reduced the density of the pyramids. It is important to obtain a high density of hexagonal pyramids in order to achieve a high

LEE of an LED. Guo et. al. [72] attempted to address the issue by adding hydrogen peroxide ($H_2O_2$) as an oxidizing agent in KOH etching. They found the size of the pyramids became smaller, and correspondingly, the density of the pyramid increased. Table 2.3 provides an overview of the various roughening conditions for N-face GaN and their impact on LED performance. Even though roughening with KOH and other etching solutions has been done extensively, the density of pyramids on N-face GaN is still below $5 \times 10^9$ $cm^{-2}$. Therefore, a new etching solution and approaches is needed to increase the density of pyramids on N-face GaN.

So far, ammonia hydroxide ($NH_4OH$) solution has been widely used as an etching solution for etching GaAs material [73,74]. However, for GaN, $NH_4OH$ solution is commonly used as a cleaning agent to remove oxides and impurities on the surface prior to epitaxial growth. There is a lack of demonstration of using $NH_4OH$ as an etching solution for roughening N-face GaN. As reported by Sohal et. al, [75], the oxides can be dissolved in $NH_4OH$. However, this solution is still insufficient to promote etching activity. As mentioned previously, the etching of GaN is strongly influenced by the formation of $Ga_2O_3$ compounds. By adding an oxidizing agent like $H_2O_2$ in $NH_4OH$ solution, more formation of the $Ga_2O_3$ compounds would be expected and this resulted in higher hexagonal pyramids density [72,76]. Further increase in the $Ga_2O_3$ compounds could be obtained by annealing the substrate in oxygen-containing ambiences, prior to the roughening. Thus far, there is no work has considered to use a mixture of $NH_4OH$ and $H_2O_2$ with pre-annealing in oxygen containing ambiences for GaN roughening.

Table 2.3: Overview of the roughening condition of N-face GaN, pyramid density, external quantum efficiency (EQE) and optical power (OP) of InGaN LEDs. Values which were not provided by the literature are left empty.

| Reference | Roughening condition | Pyramid density | LED performance | LED improvement (%) |
|---|---|---|---|---|
| Hwang et al. [36] | Without roughening (after substrate removal) | $5.4 \times 10^{8}$ cm$^{-2}$ | EQE = 10% | 40 |
| | 1 M KOH, 75 °C, 25 min | $1.0 \times 10^{9}$ cm$^{-2}$ | EQE = 14% | |
| Fu et al. [15] | Without roughening | | OP = 13.2 mW | 93 |
| | 2 M KOH, 80 °C, 10 min | $2.0 \times 10^{9}$ cm$^{-2}$ | OP = 25.6 mW | |
| Jeong et al. [71] | 5 M KOH, 80 °C, 10 min | $3.2 \times 10^{7}$ cm$^{-2}$ | OP = 2.2 mW | 36 |
| | AZ300MF, 60 °C, 110 min | $1.0 \times 10^{8}$ cm$^{-2}$ | OP = 3.0 mW | |
| Guo et al. [72] | 1 wt% KOH, 70 °C, 60 min | $5.6 \times 10^{6}$ cm$^{-2}$ | | |
| | 1 wt% KOH with 10 wt% $H_2O_2$ | $2.0 \times 10^{7}$ cm$^{-2}$ | | |

*OP = Optical Power