III-Nitride Micro and Nano Structures for Solid State Lighting

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EXAMINATION COMMITTEE APPROVAL

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ABSTRACT

*III-Nitride Micro and Nano Structures for Solid State Lighting*

Visible light emitting diodes (LEDs) are widely used in daily consumer electronics systems, such as general lighting, displays, communication, sensing, and also biomedical applications. To mitigate the ever increasing technology demand, there are tremendous on-going efforts in improving material properties and micro-fabrication techniques. In general, visible LEDs are environmentally friendly, robust and reliable light emitters with small device footprint, and are capable of delivering high luminous efficacy.

Typically, LEDs rely on group-III-nitride materials to generate visible light. One of the techniques to generate white light is to coat blue LEDs with yellow phosphor, or ultraviolet (UV) LEDs with red-green-blue (RGB) phosphor. Other scheme relies on combination of RGB LEDs, where high brightness green and blue LEDs are generally grown on robust sapphire substrate. But the current challenges in high threading dislocation density of III-Nitride materials on sapphire or hetero-substrate, phosphor degradation, and bulk-LED mechanical design constraints imposed by the supporting substrate wafer motivate further scientific investigations into strain-engineering, novel reliable phosphor-semiconductor, color-tuning techniques, and transferrable III-nitride vertical LEDs.
The current research presents a significant step towards the utilization of annealed porous GaN as a template for subsequent growth of fully relaxed GaN-based epitaxy materials. In our study, we observed significant compressive strain relaxation of $0.41 \pm 0.04$ GPa in annealed porous GaN fabricated using UV-assisted electroless etching. Moreover, the use of GaN nanoparticles with large wavelength tunability and $10 \mu m$ InGaN microstructures with different indium composition ushers a new way of making reliable phosphor for white light generation. We also investigate the epitaxial lift-off of InGaN LED structures by selectively etching unintentionally doped GaN sacrificial buffer layer. High GaN/InGaN etching selectivity of 100/1 and with GaN lateral etch-rate of 5 $\mu$m/min was achieved using the photo assisted electroless etching process. The kinetics of electron hole transfer in the diffusion limited etching reaction is discussed. Transferred LEDs onto flexible and glass substrates showed ~10 times higher optical power output, 2 times lower series resistance and a lower turn-on voltage than bulk LEDs fabricated from the same wafer. This innovative technique offers a low cost optoelectronic platform for the formation of pixelated red, green and blue (RGB) display on any flexible, transparent or rigid substrates. The technique will also enable new platform for sensing, wearable electronics/optoelectronics and biomedical applications.
ACKNOWLEDGEMENTS

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This dissertation is dedicated to the loving memory of my dear father. It was his undying love that raised me up when I got weary.

Ahmed Ben Slimane
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Thuwal, Saudi Arabia
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# NOMENCLATURE

**Symbols**

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<tbody>
<tr>
<td>λ</td>
<td>Wavelength, m</td>
</tr>
<tr>
<td>h</td>
<td>Planck's Constant, $6.6262 \times 10^{-34}$ Js</td>
</tr>
<tr>
<td>ν</td>
<td>Velocity of light, $3.0 \times 10^8$ m/s</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzman's constant, $1.38 \times 10^{-23}$ J/K</td>
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<tr>
<td>q</td>
<td>Electron charge, $1.6021 \times 10^{-19}$ C</td>
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<tr>
<td>T</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom, $10^{-10}$ m</td>
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<tr>
<td>W</td>
<td>Depletion region, nm</td>
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<tr>
<td>$L_p$</td>
<td>Diffusion length, nm</td>
</tr>
<tr>
<td>e-h</td>
<td>Electron-hole</td>
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<tr>
<td>$E_g$</td>
<td>Energy bandgap, eV</td>
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<tr>
<td>$E_c$</td>
<td>Conduction energy band, eV</td>
</tr>
<tr>
<td>$E_v$</td>
<td>Valence energy band, eV</td>
</tr>
<tr>
<td>$\varepsilon_{xx}$</td>
<td>Compressive strain, GPa</td>
</tr>
<tr>
<td>$K$</td>
<td>Strain coefficient, cm$^{-1}$GPa$^{-1}$</td>
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<tr>
<td>$\omega$</td>
<td>Phonon frequency, cm$^{-1}$</td>
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<tr>
<td>$\varepsilon_{GaN}$</td>
<td>Dielectric permittivity, F/m</td>
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<tr>
<td>$V_{bi}$</td>
<td>built in voltage, V</td>
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<tr>
<td>$N_0$</td>
<td>Dopant density</td>
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**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Bi-PEsC</td>
<td>Back-illumination photo electroless chemical</td>
</tr>
<tr>
<td>CLO</td>
<td>Chemical lift-off</td>
</tr>
<tr>
<td>CPD</td>
<td>Critical point dryer</td>
</tr>
<tr>
<td>D⁰X</td>
<td>Donor-bound exciton peak</td>
</tr>
<tr>
<td>DAP</td>
<td>Donor-acceptor pair</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy-filtered TEM</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>Fx</td>
<td>Free-excitonic peak</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium nitride</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution TEM</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductive coupling plasma</td>
</tr>
<tr>
<td>InGaN</td>
<td>Indium gallium nitride</td>
</tr>
<tr>
<td>InN</td>
<td>Indium nitride</td>
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<tr>
<td>LED</td>
<td>Light emitting device</td>
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<tr>
<td>LLO</td>
<td>Laser lift-off</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid phase epitaxy</td>
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<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
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<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>MQW</td>
<td>Multiple quantum well</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEsC</td>
<td>Photo-electroless-chemical</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>SSL</td>
<td>Solid-state lighting</td>
</tr>
<tr>
<td>RGB</td>
<td>Red-green-blue</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TI-PEsC</td>
<td>Top-illumination photo electroless chemical</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>V\text{GA}</td>
<td>Ga vacancies</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
</tr>
<tr>
<td>WLED</td>
<td>White light emitting devices</td>
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</tbody>
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Figure 6.12 (a) Optical micrograph of the lifted-off cross shape blue LED on Au coated glass substrate (b) blue emission from the lifted-off LED (c) EL spectra of the lifted-off blue LED (d) EL of lifted-off LED on glass and bulk LED (e) I-V characteristics of lifted-off LED and bulk LED (f) L-I characteristics of lifted-off LED and bulk LED.

Figure 7.1 Schematic illustration of pick and place technique of GaN nanowire on LED for extraction coefficient increase by limiting internal reflection.

Figure 7.2 (a) illustration of interconnected micro-LED array on a PDMS substrate (b) illustration of possible application of lifted-off LEDs (spectroscopy characterization of arterial tissue).
1 INTRODUCTION

Group III-nitride based light emitting devices (LEDs) are widely used in many fields ranging from displays to biomedical applications [1]. Nowadays, they became indispensable in the infrastructure of our consumer electronics systems. The history of the development of InGaN-based blue, green and white LEDs began in the 70s, when Pankove et al. discovered the first electroluminescence from GaN metal-insulator-semiconductor diode [2]. Only in the late 80s, the first pn-junction was demonstrated by Amano et al. by enabling conductivity in the p-type GaN [3]. This triggered the development of high-brightness blue LED in 1994 and green LED in 1995, by Nakamura et al., based on InGaN double heterostructures [4, 5]. In 1996, phosphor-based white LED was developed by Nichia Co. by means of blue LED chip coated with yttrium aluminum garnet (YAG) yellow phosphor [6]. To produce high luminous efficient white LEDs, other schemes such as the combination of red-green-blue (RGB) LEDs, have been developed [7, 8]. These bright blue, green and white LEDs are widely used in displays and lighting, and are mainly grown on sapphire substrates.

Enormous efforts have been employed to increase the efficiency of blue and green LEDs. Due to its high melting temperature and its high decomposition pressure bulk single crystal GaN cannot be grown using conventional methods, therefore III-nitride materials are often overgrown on non-native substrates which results in
significant residual strain due to the large lattice mismatch and the large difference in the thermal expansion coefficient between substrates and epitaxy [9, 10]. To reduce the threading dislocation density and residual strain problem, GaN, AlN, and AlInN buffer thin layers have been used, also epitaxial lateral overgrowth (ELOG) and patterned substrate have been employed, however these techniques are time consuming and complicated [11-13]. It was reported that porous GaN semiconductor may accommodate epitaxy strain [14-16], this motivates the development of porous GaN structure for strain and dislocation management beneficial for epitaxial growth.

On the other hand significant applications emerged in white light emitting devices (WLEDs) due to the wide energy spectrum covered by phosphorous material [17]. While phosphor based LEDs are twice as efficient as actual incandescent lamps, they still suffer from poor color rendering index and optical degradation of highly doped blue phosphor materials [18]. This motivates the development of nitride phosphors which offer good material compatibility, high stability, large excitation range (any wavelength lower than the bandgap), and enable a usage lifetime compatible to that of the III-nitride based LED itself. However, most of the proposed preparation methods to make nitride phosphor either require high temperature (like solid-solid reaction) or reduce the luminous efficacy (like chemical co-precipitation) [19]. In contrast, although it is challenging to produce large batches, wet etching offers good morphology control, small particle size and does not require high temperature
processing. This encourages the development of a new material: facile to fabricate, easy to integrate, harnessing the beneficial effect of defects/impurities, and has a tunable broadband emission. The GaN phosphor will be a good candidate for an all III-nitride tunable WLED.

Despite their widespread applications, III-nitride semiconductors are still widely grown on conventional mechanically rigid and chemically stable sapphire substrate, which does not allow easy separation of III-V epitaxial-layers from substrate wafer [20]. Enabling the lift-off and integration of III-nitride layers on LEDs is an attractive alternative to existing low quality phosphor based LEDs [18, 21]. Present advances in pick-and-place technology will enable the transfer of InGaN thin layers for color conversion. Lift-off of LED structures will improve light output efficiency by removing the non-conducting sapphire substrate and transferring the vertical LEDs on a metal. This approach resolves the current crowding and heat dissipation issues facing typical LEDs fabricated on sapphire [22].

Generally, epitaxial lift-off of III-Nitride epi-structures relies on laser lift-off (LLO) and chemical lift-off (CLO) techniques. In this thesis, we will focus on the CLO technique which is based on a wet process of sacrificial layer and have proven to offer a high yield over large area [23]. Currently the existing CLO techniques rely on the regrowth of the III-nitride device structure on extra costly sacrificial layers, such as InGaN/GaN MQW, porous GaN, Si, SiO$_2$ and ZnO [22, 24-26]. The lattice mismatch of these non-conventional layers with the over grown nitride based LED leads to the
formation of various defects that affects the optical and electrical properties [27]. This drives the scientific efforts to develop versatile and high yield post-growth substrate removal or epitaxy lift-off technologies for GaN based devices and structures.

1.1 Motivations

A significant contribution has been made to the development of III-nitride LEDs, but there is still room for improvement. Epitaxial growth of GaN can be addressed and defects can be reduced. By using novel methods to reduce the tensile stress in the overgrown GaN, we can achieve lower dislocation density. Although many groups were using porosity to reduce the stress, to our knowledge, no one used thermal treatment to improve it.

For solid-state lighting (SSL) applications, the generation of white light is generally achieved by: mixing RGB LEDs, stimulating yellow phosphor by blue LED or using RGB phosphor excited by UV LED. GaN nanostructures offer higher stability, better compatibly with III-nitride LEDs, and a higher usage lifetime compared to commercially available phosphor materials. This opens many gaps for exploration to study the GaN NPs emission and to integrate them with UV LEDs. Moreover, their electrical behavior can be investigated. Using these GaN nanostructures as a phosphorous material we can make tunable color-temperature light, such a device is not fully developed and previously uses different driving current for different color LEDs. A systematic investigation into the development of a novel white converted
LED, with a color-temperature that can be adapted to the human preferences, is thus a crucial study that needs to be addressed.

Due to the large refractive index difference between air and III-Nitride material, only 30% of emitted photons are extracted from the LEDs \[28\]. Several methods have been employed to improve extraction such as roughening the surface or depositing nanowire on the top layer. GaN nanoparticles developed in this thesis can be used as scattering source and medium to grade the reflective index step between the device surface and air to enhance the light extraction efficiency.

High brightness III-nitride LEDs are generally grown on sapphire and use unintentionally doped GaN (u-GaN) buffer layer to reduce lattice mismatch. By selectively etching the u-GaN, we can separate the LED structure from the sapphire substrate without integrating costly sacrificial layers that would introduce strain and defects in the epitaxy. The high quality free-standing LED structure can be transferred on flexible substrate for vertical current injection to improve light output efficiency. We can achieve high brightness pixelated inorganic RGB flexible displays by combining green and blue lifted-off LEDs with red LEDs.

### 1.2 Summary of Accomplishments in a Nutshell

- Explained the mechanism kinetics of photoelectroless chemical etching of GaN and the formation of porous structures and GaN nanowires.
• Enhanced strain relieve in the GaN-sapphire template substrate for subsequent epitaxy growth of strain-free GaN-based materials.
• Fabricated GaN nanowires suitable for refractive index engineering.
• Explained the broad emission of GaN in blue region and the large redshift with increasing excitation power in GaN nanoparticles.
• Developed a novel micro-fabrication process to lift-off InGaN microdisks grown on GaN on sapphire substrate.
• Characterized and optically pumped transferred InGaN microdisks on different substrates.
• Demonstrated selective unintentionally-doped-GaN back-illumination PEsC etching in III-Nitride LED structures grown on sapphire.
• Resultant free-standing green and blue LEDs structure were lifted-off and transferred on flexible and transparent substrates.
• Enhanced light output, and decreased turn-on voltage and series resistance by means of vertical current injection in the lifted-off LEDs.

1.3 Thesis Outline

A general overview of the thesis, as well as research objectives, motivations and main achievements are presented in chapter 1. In chapter 2, we will introduce general background information to present basics of LED working principal, III-nitride growth technique, lift-off process and photoelectroless chemical etching (PEsC) mechanism.
In chapter 3 porous GaN and GaN nanowire are fabricated using PEsC etching process. The porous GaN is then annealed to obtain a strain relaxed layer. PL measurements confirmed the Raman results, and a linear relationship between the photon energy and the biaxial strain is derived. On the other hand, fabricated GaN nanowires were transferred on different substrates for optical study. This chapter focuses on the etching mechanism of GaN grown on sapphire using PEsC etching and explains the kinetics of this process. Obtained porous structures are then sonicated to produce GaN nanostructures, which were studied in chapter 4. In this chapter, we study in details GaN nanoparticles with sizes ranging from 10 nm to 100 nm transferred on Si substrates. Power excitation dependent PL emission with large wavelength tunability ~530 meV was observed. This tunability attributed to the localized potential fluctuation and surface state effects, is useful for phosphor semiconductor applications.

Leveraging on previously studied etching process, 400 nm thick InGaN microdisks with 10 µm diameter were lifted-off using the PEsC etching technique. The studied InGaN layer in chapter 5 was epitaxially grown on GaN on sapphire substrate. Combining micro-fabrication techniques and knowhow of electron-hole transfer kinetics in PEsC process, we selectively laterally etched the underlying GaN layer, removed the InGaN layer and transferred it on different substrates, e.g. Si, sapphire, and LED wafers, for optical characterization, heterogeneous integration applications and color conversion LEDs.
We applied similar techniques in chapter 6 to lift-off the LED structure grown on u-GaN buffer layer on sapphire substrate. We discussed the novel carrier diffusion limited selective etching technique of the u-GaN in the back-illuminated PEsC process. LED device characterizations of the lifted-off vertical LEDs showed increase of optical output power, decrease of series resistance and a lower turn on voltage compared to the bulk LEDs.

This new technology offers promising approach for pixelated RGB display formation, and a new integration technology platform for optoelectronic and electronic integrations on any flexible or solid substrates. The outcomes of this work are applicable in sensors, biomedical applications, and flexible optoelectronics devices.

Chapter 7 gives a summary and recommendation for future work of the thesis.
This chapter introduces general background information about working principal of LEDs. Basic knowledge on III-Nitride materials and crystal growth are discussed. In addition, some established lift-off techniques for flexible devices are reviewed and discussed.

2.1 Light Emitting Diodes

The working principal of LEDs is based on semiconductor material doped with impurities to form a typical pn-junction device. Under forward bias, electrons near the p-n junction diffuse to the p-type side where they recombine with holes (see Figure 2.1). The transition of electrons from the conduction energy band to the valence energy band releases energy in the form of photons.

Efficient LEDs rely heavily on semiconductor properties. Semiconductors should have: (i) efficient radiative crystalline structure (ii) direct energy bandgap active layer and (iii) conductive p-type and n-type cladding layer.

(i) It is very important to minimize defects in the LED structures. Defects generally become non-radiative recombination center and trap carriers. Thus grown structures must have similar lattice constant and compatible crystal structure, see Figure 2.2.
(ii) No optical emission is observed in indirect bandgap materials, such as Si and Ge, this is due to the non-radiative recombination of the electron-hole. Thus most commercially available LEDs use III-V semiconductors with direct bandgap properties. The wavelength of the emitted light is inversely proportional to the energy bandgap and can vary from ultraviolet (UV) to infrared (IR).

(iii) Under a forward bias, high densities of electrons and holes are injected from the n-type and p-type cladding layer to the active region. It is very important to have a low resistivity material. For higher carriers’ confinement, some LEDs schemes use p- and n-type heterostructures with compatible crystalline structure with active region layer.

LEDs are widely used in various applications and highly depend on material properties. InGaAsP and InP semiconductors cover wavelengths from 1300 nm to 1550 nm are widely used in optical fiber communication applications [29]. Video and audio remote controllers and local area communication systems used GaAs and AlGaAs semiconductors with wavelengths ranging from 780 nm to 900 nm [30].
Low cost red emitting LEDs for indicator lamp applications used GaAsP semiconductor. For display, indicator and white LEDs, III-nitride materials are generally used to produce visible light [31].

In this thesis, we will focus on the group-III nitrides semiconductors for general lighting, displays, as well as for free-space visible light applications.

2.2 Introduction to group-III nitrides

Fabrication of light emitting devices in solid-state lighting (SSL) relies upon the materials properties. This section describes the material properties of the crystalline III-nitride semiconductors. Gallium nitride (GaN) and indium nitride (InN) are the building blocks of nitride-based optoelectronic devices. They are arranged in a crystalline structure, such as zincblende structure and hexagonal wurtzite structure. A schematic illustration of wurtzite crystal structure by Levrat et al. is depicted in Figure 2.3, [32]. Crystallized atoms are predominately covalently

![Figure 2.2 Schematic representation of grown heteroepitaxial layers (a) strained epitaxy (b) relaxed epitaxy. (c) Schematic representation of different types of point defects that can result from crystal growth.](image)
bounded with two electrons, In and Ga atoms are a group-III elements and have three valence electrons in the outer subshell, while N atoms are a group-V elements and have five valence electrons in the outer subshell.

Efficient LEDs depend on on the semiconductor structure. Compatible materials have to be found, with the same crystal structure, and reduced lattice mismatch. As depicted in Figure 2.2, lattice mismatch, impurities, and vacancy might result in point defects in the overgrown epitaxy, this point defects act as a trap for the light in LEDs. Thus it is important to grow good crystal quality semiconductors. The bandgap of GaN and InN cover a broad visible spectrum ranging from 3.42 eV to 0.64 eV, respectively [31]. Also due to their direct bandgap properties, III-Nitrides are materials of choice for visible LED applications. Figure 2.4, by Shubert et al., shows GaN and InN bandgap versus lattice constant [31]. Combination of binary compounds to generate indium gallium nitride (InGaN) ternary alloys allows the
adjustment of the energy bandgap while maintaining the lattice matching. By varying the In composition in the In$_x$Ga$_{1-x}$N one can obtain efficient blue and green LEDs provided that fundamental requirements are satisfied, such as lattice matching substrate, and reduced defects epitaxy grown layers.

To produce green or blue bright light some LEDs use multiple quantum well (MQW) structures in the active region. Using heterostructures, lower bandgap material such as InGaN can be sandwiched between two larger bandgap GaN layers. This leads to carriers confinement, thus increases the spontaneous emission rate in the active region which is a product of the radiative recombination.

GaN suffers from the lack of lattice and thermal coefficient matched substrates. Despite its large lattice mismatch with GaN, sapphire is the most commercially

\[ \text{Figure 2.4 Bandgap energy versus lattice constant of binary III-nitride semiconductors at room temperature. GaN} \sim 3.42 \text{ eV and InN} \sim 0.64 \text{ eV. From [31].} \]
available substrate. In contrast to SiC, sapphire wafers are considered cost-effective with good thermal and chemical stability, and hence is widely used for the growth of III-Nitride LEDs. As a wide bandgap material, sapphire is transparent to the visible light suitable for back emission [33].

In the later section we shall discuss some techniques for performing epitaxial growth of III-Nitride materials.

2.3 Crystal growth and device processing

In this section we will discuss the fundamental step of GaN crystal growth technology. For efficient LEDs it is necessary to grow high quality single crystal lattice-matched structures. Most used techniques are: liquid phase epitaxy (LPE), metal organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE).

2.3.1 Liquid phase epitaxy

LPE is highly dependent on temperature control. Epitaxial layers are grown at thermal equilibrium for high quality crystal. Single crystal substrate is slid under the bins filled with solution. Temperature is reduced to bring solutions to saturation. To avoid oxidation of the substrate and solutions, the process is kept in a H₂ ambient gas. The dwell time under each melt determines the thickness of the layer. LPE growth is hectic, since most of the composed solutions are prepared by operators and require very accurate scales. Thus nowadays it is easily replaced by MOCVD.
2.3.2 Metal organic chemical vapor deposition

In MOCVD systems, substrate is placed on the reactor which is typically heated by the radio-frequency (RF) induction. Ultrapure gases are then injected into the reactor and controlled with gas valves and manifolds. On the substrate, metal organic materials decompose to produce the epitaxial layer formed of III-V semiconductors. The fabrication of sharp interface and controllable thin layers require low-pressure MOCVD. The growth occurs far from the thermal equilibrium.

2.3.3 Molecular beam epitaxy

MBE growth is generally carried out under ultra-high vacuum (UHV), see Figure 2.5. Heated sources in effusion cells are evaporated and directed to the heated substrate.
Due to the long mean free path of the atoms in the UHV chamber, beams of the evaporated atoms do not interact with each other until they reach the substrate surface where they condense and react with each other to form the epitaxial layer. In addition to the advantage of growing thin high quality single-crystal layer, in-situ observation can be carried out in the MBE to monitor the growth rate.

2.4 Epitaxial lift-off for flexible LEDs

In this section, we will discuss different methods for producing flexible and transferrable light emitting devices. High efficiency III-nitride based LEDs are mainly grown on chemically stable and mechanically hard sapphire substrate, which does not allow easy post-growth substrate separation from the LED structure. Most used techniques for lifting-off GaN-based devices are: LLO and CLO.

LLO is a dry technique that employs a high power KrF excimer laser to dissociate GaN into N\textsubscript{2} gas and gallium droplet. The high intensity laser is directed through the sapphire and aimed at the GaN, as presented in Figure 2.6. This creates a shockwave at the interface, with the side effects of lattice deformation in the active area due to
the high temperature shock wave and a recombination-enhanced defect reaction \[34,35\].

CLO, on the other hand, is a wet-process technique that selectively etches epitaxial sacrificial layers. The demands for high yield and high throughput device lift-off over a large area, have leaded to the development of room temperature CLO techniques \[36\]. Currently, the existing CLO techniques in laboratory scale research rely either on regrowth of III-Nitride devices on sacrificial InGaN MQWs, porous GaN template-substrate, or Si, SiO\(_2\) and ZnO substrates followed by a subsequent exfoliation of the epitaxy layers through mechanical break-off or wet-etching techniques \[22, 24-26, 37\]. Major drawback of these CLO techniques arises from the extra costly epitaxial sacrificial layer, which requires additional growth steps.

Both LLO and CLO techniques introduce high dislocations in the epitaxial layer through thermal-mechanical shock, and etch pits/pores, respectively \[27, 38\]. In this study we shall report on a novel CLO process based on PEsC etching. The mechanism of the PEsC etching is discussed in the next section.

### 2.5 Photo-electroless chemical etching mechanism

PEsC etching mechanism depends on the energy band bending of the semiconductor at the surface with the electrolyte solution \[39\]. Figure 2.7(a) and Figure 2.7(b) shows the energy band diagrams for n-type and p-type GaN in contact with the solution, respectively. For n-type semiconductor the pinned Fermi-level (E\(_f\)) in the
center of the bandgap will cause an upward band bending near the surface. The surface depletion region arises due to the potential difference established by the $E_f$ at equilibrium. At the surface, electrons concentration is then reduced, and holes concentration is increased. When illuminated with high energy UV lights (higher than the bandgap energy ($E_g$) of the semiconductor), electron-hole (e-h) pairs are excited. Within the minority carriers’ diffusion length ($L_p$), photo-generated holes diffuse to the depletion region (W) where they drift towards GaN/electrolyte surface (see Figure 2.7(c)). Confined holes in the potential well at the interface are consumed by the oxidation reaction of the GaN:

$$2\text{GaN(s)} + 6h^+ + 3\text{H}_2\text{O(l)} \rightarrow \text{Ga}_2\text{O}_3\text{(s)} + 6\text{H}^+(l) + \text{N}_2\text{(g)}$$

Electrons migrate to the bulk, where they are collected by a thin Pt layer deposited on the GaN surface prior to etching. From a chemical point of view the absence of
Electrons in bonding orbitals and the presence of holes at the surface in the valence band \( (E_v) \) weakens the lattice bonds, hence increasing the dissolution rate of \( \text{Ga}_2\text{O}_3 \) into aqueous solution after HF attack.

Etching process slowdown (negligible) in compensated semiconductors, e.g. p-type GaN, because of the downward band bending near the surface, minority carriers are swept away to the bulk. As defect vacancies act like deep acceptors causing a decrease in the band bending, in these regions the PEsC etching rate is reduced. This mechanism will help explain the formation of porous GaN and GaN nanowire.

### 2.6 Characterization tools

Optical and structural characterizations were conducted on the fabricated structures.

The surface morphology was investigated by scanning electron microscopy (SEM). For SEM measurements, a focused beam of electrons is directed towards the sample.

![Figure 2.8 Schematic representation of the PL setup. Sample is excited with a laser source emits light, photo-detector collect the emitted light. Monochromator disperse the light. Data are collected by the software.](image)
and scans the surface. Electrons interact with atoms at or near the surface of the sample. Back-scattered electrons reflected back from the elastic interaction are collected by a detector and give information about the morphology and composition.

On the other hand for optical characterization we used photoluminescence (PL) spectroscopy, see Figure 2.8. In PL measurements, a sample is excited with a light source or a laser. A photo-detector is used to detect light emitted from the sample. A monochromator helps to disperse the wavelength. PL provides information about the bandgap of semiconductor as well as many other intrinsic material properties.

The strain in different material was characterized using the Raman spectroscopy, which relies on inelastic scattering. In general a laser interacts with molecular vibrations in the crystalline structure, resulting in a shift of the laser photon energy. This shift gives information about the material strain, molecular polarization and
crystallographic orientation. In this study we will focus on the biaxial strain in the processed material.

Device characterizations were carried out using current versus voltage (I-V), light power versus current injection (L-I), and electroluminescence (EL) built in set-up in the Photonics Lab, see Figure 2.9.
Wide bandgap group III-nitride semiconductors are generally grown on sapphire [40] or SiC [41] substrates. Due to the large lattice and thermal mismatch between III-nitride and these substrates, epitaxial growth of the III-nitride often results in a high dislocation density in the overgrown layer [41]. In addition, despite a partial strain relaxation after the GaN buffer layer growth on sapphire [42], significant residual strain remain in the subsequent growth of III-nitride epitaxy.

To minimize the threading dislocation density and residual strain problem, growing of III-nitride on Al-based III-nitride buffer layers such as AlN [43, 44] and AlInN [45] have been employed. These techniques, however, require complex epitaxy growth processes. It has been suggested that porous semiconductors [46, 47] may serve as a sink for threading dislocations while accommodating epitaxy strain. This motivates the development of porous GaN structure for strain and dislocation management beneficial for epitaxial growth [15, 16]. In spite of the extensive work on porous GaN and annealed bulk GaN, there is no report on the observation of strain reduction resulting from the annealing of porous GaN. Enhancing the strain relief by combining wet etching and annealing is a subject that requires further attention, and hence motivates this investigation. In recent years, while Hartano et al. [48] reported no further strain relaxation after annealing of porous GaN, Vajpeyi et al. [49] observed an increase in compressive strain in annealed porous GaN.
On the other hand, to increase LED efficiency we can: (i) increase the internal quantum efficiency ($\eta_{\text{int}}$), (ii) or increase the light extraction efficiency ($\eta_{\text{ext}}$). Internal quantum efficiency can be increased by improving the LED structure and material properties. Nevertheless, extraction efficiency is low in planar surface III-Nitride based LEDs considering the high refractive index of GaN ($\eta=2.5$) and air ($\eta=1$) [50], the optical critical angle $\theta_c = \sin^{-1}(n_{\text{air}}/n_{\text{GaN}})$ for the light escape cone is about $23^\circ$. Neglecting sidewall emission, only 30% of emitted photons are extracted from the LEDs [28]. Due to the planar surface design light is reflected internally and reabsorbed by the active region or other different layers, unless it escapes through sidewall. Several methods are used to improve the light extraction such as surface roughening or nanowire deposition. Virtually most of the reported techniques to fabricate GaN nanowires use complex deposition techniques [51]. Thus there is still a research gap in finding a novel easy method to fabricate high-density crystalline nanowires on LEDs. These nanowires can also be used in many applications, such as random lasing if quantum confinement and sidewall mirrors provide enough gain, also they can be transferred onto LED surfaces.

In this chapter, we present the development of the PEsC etching process. The etching kinetics based on carrier transport and redox reaction at the semiconductor-electrolyte is described to provide an explanation for the etching mechanism of the porous GaN and GaN nanowires. Porous GaN is annealed for strain relaxation study. High-density nanowires were transferred on different
substrate for optical characterization. The morphology characterization of both structures porous and nanowire were investigated. Applications stemming from these techniques are applicable to the regrowth of high quality crystalline structure on porous GaN using MBE, and increase of the extraction efficiency by transferring GaN nanowires on III-Nitride based LEDs.

### 3.1 Experiments

The substrate used in this study consisted of a 30 µm thick Si-doped GaN epitaxy grown on c-plane (0001) sapphire ($\alpha$-Al$_2$O$_3$) substrate with a measured resistivity of less than 0.03 $\Omega$.cm. The estimated dislocation density and measured carrier concentration of the film are $1 \times 10^{8}$ cm$^{-2}$ and $2 \times 10^{18}$ cm$^{-3}$, respectively. Prior to wet
etching in a HF:CH$_3$OH:H$_2$O$_2$ (2:1:2) solution under UV illumination, 10 nm thin strips of platinum (Pt) were sputtered onto the GaN samples at one end of the surface to complete the loop for electron hole exchange between semiconductor and electrolyte [52]. The experiment is illustrated in Figure 3.1.

Room temperature and 77 K PL and Raman measurements were carried out using Jobin Yvon’s LabRAM ARAMIS micro-spectroscopy system. The optical excitation was produced using a Helium-Cadmium (HeCd) laser emitting at 325nm and a diode-pumped solid-state (DPSS) blue laser at 473 nm with a <10μm spot-size. The scanning and transmission electron microscopy (SEM and TEM) investigations were performed using FEI Quanta 600 and FEI Titan G$^2$ 80-300 electron microscopes, respectively.

### 3.2 Porous GaN

The formation of porous GaN originates from dislocations and defects in the surface of the epitaxial layer. In contact with electrolyte, energy band bending is smaller in regions with defect vacancies than in surrounding crystalline epitaxy (see Figure 3.2), surface tension at defect cites enhance the surrounding electric field leading to a faster dissolution rate. Pores nucleate at surface defects by avalanche breakdown, smaller pores coalesce into large pores that preferentially proceed along the crystalline bulk structure. Etching at dislocations regions is much slower, hence pores propagate in a way to avoid dislocations. Favorable etching then proceeds along the (0001) crystallographic direction. Along with the vertical
etching, slower lateral etching proceeds and expands the pores. The Wurtzite hexagonal structure of the GaN limits the pore expansion. Figure 3.3 shows the typical plan-view SEM image of the porous GaN sample (without annealing). The average pore-size is \( \sim 30 \text{ nm} \) for samples etched for 45 min with an average pore density of the order of \( 2 \times 10^{10} \text{ cm}^{-2} \) and the average of the pore side wall is 14 nm, whereas the sample etched for 90 min has both circular-like pores with a size of \( \sim 50 \text{ nm} \), and elongated features with a size \( \sim 100 \text{ nm} \) (not shown here). After annealing using rapid thermal annealing (RTA) process at 400 °C, 600 °C and 800 °C for 1 min in nitrogen ambient at atmospheric pressure, the size and shape of pores was not affected and the pore density remained the same.

In this study, both Raman and PL spectroscopy techniques were employed to study the effect of strain relaxation in the 45 min and 90 min as-etched and annealed porous GaN samples. Since GaN has a smaller in-plane lattice constant (\( a_{\text{GaN}}=3.18\text{Å} \)) compared to the sapphire substrate (\( a_{\text{Al}_2\text{O}_3} =4.76\text{Å} \)), as well as having a large
thermal expansion coefficient, the as-grown GaN was expected to experience residual biaxial or in-plane compressive strain ($\epsilon_{xx} = \epsilon_{yy}$) [53, 54]. Figure 3.4(a) shows Raman spectra of the GaN samples. Consistent with existing literature, both the E$_2$-high and A$_1$-LO modes were observed. The focus will be on the typical phonon frequencies E$_2$-high as they are influenced by the biaxial stress. It is noted that Oh et al. [45] have reported a strain free GaN E$_2$-high peak at 567.7 cm$^{-1}$, which falls between values reported by other groups 568 cm$^{-1}$ and 567.5 cm$^{-1}$ [55, 56]. We adopt here the E$_2$-high peak frequency value of 567.7 cm$^{-1}$ measured by Oh et al. [45] The as-grown GaN has an E$_2$-high peak at 570.0 cm$^{-1}$. It exhibits a blue-shift of about 2.3 cm$^{-1}$ with reference to the strain free value indicating a residual compressive strain. As for, the samples etched for durations of 45 and 90 min showed an E2-high peak close to $\sim$569.5 cm$^{-1}$ (porous / without annealing spectrum

Figure 3.3 SEM image of the porous GaN sample prepared using PEsC etching technique.
in Figure 3.4(a)). Compared to the as-grown, the etched samples show a ~0.5 cm$^{-1}$ red-shift towards the strain free frequencies. It can be deduced that the porous GaN is reducing the biaxial strain as expected.

In the following, the biaxial strain $\varepsilon_{xx}$ is calculated using the linear approximation of the phonon frequency shift $\Delta \omega$ reported by Wagner et al.$[57]$: $\Delta \omega = K\varepsilon_{xx}$.

The linear strain-shift coefficient $K$ can be used to calculate the strain from the Raman shift. A number of strain coefficient values were reported, such as 2.7 cm$^{-1}$GPa$^{-1}$ and 2.9 cm$^{-1}$GPa$^{-1}$ $[55, 58]$. The strain-shift coefficient value of 2.4 cm$^{-1}$GPa$^{-1}$

![Figure 3.4 Plot of: (a) Raman spectra for the as-grown sample, porous GaN, annealed as-grown GaN at 800 °C, and annealed porous GaN at 800 °C etched for 90 min. (b) PL spectra of as-grown GaN, and porous GaN (without annealing)](image-url)
reported by Wagner was adopted in this study [57]. In the as-grown GaN (before etching) the residual strain is estimated to be 0.91 GPa, whereas for the etched samples (45 min and 90 min), the residual strain is around 0.75 GPa.

From the PL measurements, the strain-induced splitting of the valence band dictates biaxial compressive strain ($\varepsilon_{xx} = \varepsilon_{yy}$) would result in the splitting of the valence band with a broadening of the near band edge energy corresponds to the conduction band to heavy-hole transition. As mentioned, the as-grown GaN is expected to experience a compressive strain due to the disparate thermal expansion coefficients and lattice mismatch with sapphire. From the Raman studies, the pore formation in the porous GaN is expected to reduce the biaxial compressive strain. Therefore, porous GaN results in a reduction of bandgap from high bandgap energies (as-grown GaN) towards lower bandgap energies (relaxed GaN). This is evident in Figure 3.4(b) where the peak PL energy for the porous samples (etched for 45 min and 90 min) red-shifted by $\Delta E \approx 9$ meV (corresponding to wavelength shift $\Delta \lambda \approx 1$ nm) as compared to the as-grown sample. The peak energies are plotted in Figure 3.5.

The annealing effect on biaxial strain in GaN using PL and Raman spectroscopies is further investigated. As expected, the annealing of the as-grown GaN reduces the biaxial strain. In fact, The $E_2$-high peak of the annealed samples at 400 °C, 600 °C and 800 °C all shifted to $\sim 569.4$ cm$^{-1}$ (purple dotted line in Figure 3.4(a)). Thus using the linear strain coefficient, the residual compressive strain is around 0.7 GPa for the
annealed samples. Moreover, the observed peak PL of the as-grown bulk GaN (Figure 3.5, as-grown and without annealing) experiences a redshift of \(\approx 10 \pm 1\) meV at annealing temperatures of 400 °C, 600 °C and 800 °C. This effect is attributed to the increase in the a-plane lattice constant (parallel to the interface), which is consistent with our PL and Raman observations. Annealing is used also to relieve the residual strain distribution in the bulk GaN epitaxy [59].

For the annealing of porous GaN prepared using wet etching, we note that Hartono et al. [48] reported a pore size of up to 250 nm with no further relaxation after annealing, and a total Raman shift of \(\Delta \omega = 0.7\) cm\(^{-1}\) was measured. On the other hand Vajpeyi et al. [49] showed a study on thermal annealing of nanoporous GaN with a
redshift in Raman phonon peak leading to an increase in compressive stress due to a reduction in pore density.

In contrast to other reported work, when the strain relaxation benefits of PEsC etching and RTA is combined, a Raman E\textsubscript{2}-high peak shift to 569 cm\textsuperscript{-1} is observed (see Figure 3.4(a)). The phonon frequency difference between the annealed porous GaN and the strain free GaN (567.7 cm\textsuperscript{-1}) is reduced by ~1.3 cm\textsuperscript{-1}, corresponds to a reduction in compressive strain of ~0.5 GPa. It is noted that, compared to the as-grown GaN, the annealed porous GaN experienced a red-shift in the phonon frequency peak of ~1 cm\textsuperscript{-1}, this shift is higher than the one experienced after GaN etching (0.5 cm\textsuperscript{-1}), bulk GaN annealing (0.6 cm\textsuperscript{-1}) and the annealed porous GaN reported by Hartono et al. [48] (0.7 cm\textsuperscript{-1}). Thus the annealing of porous GaN leads to a larger biaxial strain relaxation.

Comparing the obtained results with other reported works [48, 49], the relative large degree of strain relief in these samples is attributed to the small pore wall (average thickness of 14 nm) resulting from the pore size (i.e.,~50nm) and large pore density (i.e., ~2×10\textsuperscript{10} cm\textsuperscript{-2}). It is noted that the pore size in Hartano et al. [12] ranges from 20 to 250nm with a pore density ~1.2×10\textsuperscript{10} cm\textsuperscript{-2}, also the average pore size in Vajpeyi et al. [49] is about 70 nm with an average pore density of ~4.2×10\textsuperscript{9} cm\textsuperscript{-2}. The thinner pore wall and larger pore density allow high degree of atomic diffusion in all dimensions during annealing, hence, leading to a large degree of strain relaxation.
Also, a large peak PL redshift of ~26 meV (~2.5 nm) from that of the as-grown is observed, with the maximum PL redshift occurred for 90 min etched porous GaN when subjected to annealing temperatures of 600 °C and 800 °C. This is close to the PL energy of 3.396 eV (365.6 nm) reported by Oh et al. [45] in strain-free GaN grown on the AlInN interlayer.

The reason for the limited residual strain relieve in the as-grown bulk GaN after RTA is due to the thermal mismatch between sapphire substrate and bulk GaN. In the case of porous GaN, the nanostructure has more room to retain its lattice constant after wet etching and annealing as there are less lateral or sidewall lattice compliances/restrictions. Hence, porous GaN can retain a lower strain condition after RTA compared to the bulk GaN, as evident in PL and Raman results.

Figure 3.6 A linear fitting of the PL peak energy versus the corresponding biaxial strain.
A relationship between the bandgap and biaxial strain in the GaN were also established to guide the annealing process. In Figure 3.5, the PL peak shifts are attributed to residual strain relief. Figure 3.6 shows the PL peak positions versus the residual strain of (from right towards left) as-grown GaN, 90 min as-etched porous GaN, annealed GaN at 800 °C, annealed porous GaN and strain free GaN. By fitting the data, a linear approximation expressing the PL bandgap in terms of biaxial strain is obtained: \( E_g = 3.396 + 0.03 \epsilon_{xx} \) (eV)

The linear coefficient value obtained in this study is consistent with references [60, 61].

### 3.3 GaN Nanowire

GaN nanowires (NWs) are formed along with porous structures. As detailed previously, pores proceed along the vertical (0001) crystallographic direction in the epitaxial layer with a slower rate at dislocations sites, leaving behind NWs like

*Figure 3.7 SEM images showing different stage of NWs formation (a) Pores proceed to etch vertically to the surface (b) nanowire start to nucleate (c) vertical nanowire are left behind as etching continue downward*
structures. The diameter \( d \) of the etched NWs relies on the depletion region \( W \) within the semiconductor:

\[
W = \sqrt{\frac{2\varepsilon_{\text{GaN}} V_{\text{bi}}}{q N_D}}
\]

Where \( \varepsilon_{\text{GaN}} \) is the dielectric permittivity of GaN, \( V_{\text{bi}} \) is the built-in voltage, \( q \) is the electron charge and \( N_D \) is the dopant density. If \( d > W \) holes drift to the surface and electrons transfer to the bulk, hence GaN on the surface with electrolyte dissolve into aqueous solution. When \( d < W \) the energy band bending flatten and generated electron-hole recombine, therefore GaN nanowire become more resistant to PEsC etching. SEM images in Figure 3.8 show etched GaN nanowire using PEsC etching process at different duration. These NWs have an average diameter of 35 nm, with a length varying from \( \sim 300 \text{ nm} \) (etching duration = 45 min) to \( \sim 1300 \text{ nm} \) (etching duration = 90 min).

At a later time, longer NWs start to cluster and collapse (see Figure 3.9(a)), covering the surface with a wool like structure. The length of these NWs varies between 1 \( \mu \text{m} \) and 20 \( \mu \text{m} \). High resolution transmission electron microscopy (TEM) shows GaN...

\(\text{Figure 3.8 Cross-section view of as etched GaN nanowire for a duration of (a) 45 min (b) 60 min and (c) 90 min.}\)
NW with nano-crystallite structures surrounded with amorphous structure (see Figure 3.9(b)). These nanocrystallites represented in the inset of Figure 3.9(b) are smaller than 10 nm, their corresponding calculated Fast Fourier Transform (FFT) patterns presented as an inset in Figure 3.9(c). The interval of closest interplanar distance is 0.25 nm, which corresponds to the crystal plane (1 0 0) of GaN, in accordance with the suggested vertical etching mechanism. The amorphous structure surrounding these nanocrystallites originated from the oxidation of the GaN and dangling bonds on the surface after PEsC etching. The electron energy loss spectroscopy (EELS) analysis revealed the oxygen amount to be about 14 at.%. The spatial distributions of all three constituent elements, namely Ga, N, and O, are determined and acquired using the energy-filtered TEM (EFTEM) technique (see Figure 3.9(c)). It can be noticed from Figure 3.9(c) that the O map (green) is mostly present in the surrounding of nanocrystallites which is in agreement with results obtained from HR-TEM.
The morphology of these NWs is different from the ones prepared using vapor-liquid-solid (VLS) method. Typically VLS-grown GaN NWs have triangular cross-sections, straight vertical direction to the surface, smooth and are tipped with a catalyst particle (Au or Pd) [51]. However, in this study NWs are twisted and bent in different directions. This is due to the mechanism of formation of the PEsC etched NWs originating from dislocations sites.

Figure 3.10 shows PL spectra at room temperature of the as-grown GaN and the as-etched GaN NWs excited with a UV laser source (325 nm). In the as-grown GaN the energy photon peak is observed at the UV region, 3.421 eV, attributed to the free-excitonic peak (FX). The full width at half maximum (FWHM) of the as-grown sample is 42 meV, smaller than the FWHM of the as-etched sample which is 46 meV. This slight broadening of the FWHM in the as-etched is expected due to the
inhomogeneous distribution of the crystalline structure in the NWs. The as-etched GaN NW sample exhibits a peak PL photon energy at 3.412 eV, which is red-shifted by 9 meV compared to the as-grown. Typically this redshift might be attributed to the relaxation of the strain in the crystalline structure. It is believed that the distribution of NWs over the porous structure may affect the PL measurement, which was very well detailed in the previous section 3.2. The thinner pore wall and larger pore density of the porous structure allow high degree of atomic diffusion in all dimensions, leading to a large degree of strain relaxation (Figure 3.4(b)).

In Figure 3.11 NWs were transferred on a Si substrate to evaluate their optical properties and avoid confusion with optical emission from porous layer. PL spectra obtained at 77K with an excitation laser at 325 nm shows a typical UV peak photon energy at 3.47 eV of the as-grown GaN attributed to the donor-bound exciton peak.
(D°X), this energy peak blue-shifted compared to the PL obtained at room temperature. The typical blue shift arises from the thermal excitation of the carriers leading to the band gap dependence described by Varshni’s equation [62]. The small hump at 3.40 eV attributed to oxygen impurities originated from Al₂O₃, i.e. the oxygen impurity related donor-to-valence band transitions as reported by Chung et al.[63, 64]. The FWHM of the as-grown PL spectrum at 77k is 19 meV, smaller than the FWHM of the single NW which is 26 meV. The broadening indicates the contribution of amorphous structure and porosity in the nanowire PL emission. These results confirm the TEM observation, in Figure 3.9(c), and the influence of etching process on NWs structure leading to the oxidation of the surface. It was expected that the freestanding GaN NW will experience a strain relief, thus the PL peak should red-shift compared to the as-grown. But the slight blue-shift observed in Figure 3.11 suggests that there is quantum confinement in the NW. The quantum confinement effect dictates that the characteristic size of the crystalline material should be less than the Bohr radius of the free exciton of bulk GaN, which is around 11 nm [65]. The TEM of the 20 nm wide GaN NW (see Figure 3.9(b)) shows nanocrystallite structure surrounded by amorphous layers, these nanocrystallites are smaller than 10 nm, therefore smaller than the Bohr radius. The change in the structure is further confirmed in the EFTEM image (see Figure 3.9(c)) indicating the possible blue shift in the PL peak energy due to the quantum confinement of the GaN nanocrystallite structure.
Time-resolved PL measurements on individually dispersed nanowires in ethanol are studied at room temperature. Figure 3.12 shows the temporal decay of PL for dispersed GaN NWs prepared by electroless etching for 240 min etching time. Although the curve was fit to a single-exponential decay for best fitting results nevertheless, PL decay processes with decay time >9 ns were evident in these nanowires. Such decay time, slower than the 2 ns PL decay time and carrier lifetime observed in high-quality bulk GaN with threading dislocation densities at or below 10^6 cm^{-2} reported by Schlager et al [66, 67] on GaN NWs grown by catalyst-free, confirms the inhomogeneity present in the GaN NWs causing defect trap states for carriers.
3.4 Summary Notes

In summary, we demonstrated and explained the etching mechanism of PEsC process to fabricate strain relaxed porous GaN and high density GaN nanowires. Biaxial compressive strain relief is obtained after annealing of porous GaN. A linear relationship between the PL emission energy and the biaxial strain is derived, with a linear coefficient of $30 \pm 2 \text{ meV}$. We attributed the large degree of strain relaxation to the small pore wall and the large pore density. GaN nanowires were fabricated and transferred on different substrates for morphological and optical study, these GaN nanowires can be printed onto a LED surfaces to increase extraction efficiency. Porous layer is effective in relieving strain in the GaN-sapphire template substrate for subsequent epitaxy growth of strain-free GaN-based materials.
4 TUNABLE GAN NANOPARTICLES

Optical properties of GaN nanostructures are of great current interest because of the potential application in solid-state lighting (SSL) [68, 69]. In n-type GaN, UV peak at ~3.42eV usually dominates the PL spectrum [70]. The blue luminescence at 2.7-3eV peak energy has been extensively studied, this peak dominates due to optically active defects and impurities [71]. Although such defects can be destructive in a device, a well-engineered inorganic nanoparticle-approach can offer many advantages [72]. Despite enormous efforts in studying the GaN defect related emissions [71], there is still a research gap in explaining the origins of PL shift with optical power injection [73]. The localized potential fluctuations within the GaN matrix introduced by the Ga vacancies (V_{Ga}) and impurities are considered in explaining the PL shifts [74]. Reschikov et al. observed a blue shift with increasing power due to the potential fluctuation in bulk p-type GaN [75]. On the other hand, in nanostructures having a large specific area, the surface states effect became significant in influencing the carrier recombination mechanism [76]. However, to our knowledge, large PL redshift with increasing excitation power was not reported and require further investigations.

In this chapter, we demonstrated the fabrication of group-III nitride-based nanoparticle (NP) using photoelectroless chemical (PEsC) etching method and explained the switch-over in optical emission mechanism from defect-dominated to
bulk dominated PL transitions. The resultant GaN NPs are chemically stable, simple to fabricate, easy to integrate, and, most importantly, offer tunable broadband emission. We studied the emission mechanism of such novel GaN NPs, which showed controllable redshift of $\sim 80$ nm ($\sim 600$ meV) with increased optical excitation power. The tunability feature renders these nanoparticles a good candidate for further development of tunable-color-temperature III-N-phosphor-based white LEDs, essential for matching room lighting with human circadian rhythms[77].

4.1 Set-up

Similar to chapter 3, the substrate used consisted of a 30 µm thick Si-doped GaN epitaxy grown on c-plane (0001) sapphire ($\alpha$-Al$_2$O$_3$) substrate with a measured resistivity of less than 0.03 Ω.cm. The estimated dislocation density and measured carrier concentration of the film are $1 \times 10^8$ cm$^{-2}$ and $2 \times 10^{18}$ cm$^{-3}$, respectively. Prior to wet etching in a HF:CH$_3$OH:H$_2$O$_2$ (2:1:2) solution under UV illumination, 10 nm thin strips of Pt were sputtered onto the GaN samples at one end of the surface to complete the loop for electron hole exchange between semiconductor and electrolyte [52]. The resultant nanostructures were later transferred onto a Si wafer for subsequent room temperature and 77 K PL measurements using Jobin Yvon’s LabRAM ARAMIS micro-photoluminescence ($\mu$PL) spectroscopy system. The optical excitation was produced using a HeCd laser emitting at 325nm with a <10µm spot-
size. The SEM and TEM investigations were performed using FEI Quanta 600 and FEI Titan G² 80-300 electron microscopes, respectively.

4.2 Large Photoluminescence red-shift

Figure 4.1(a) shows the SEM image of the GaN NPs on a Si substrate in the form of grain-like structure having NPs with sizes ranging from 10nm to 100nm. Using high resolution TEM (HRTEM) (Figure 4.1(b)), we observed adjoining single-crystal GaN NPs with each particle surrounded by amorphous-like boundary. The electron energy loss spectroscopy (EELS) analysis revealed the oxygen amount about 20 atomic %. The spatial distributions of all three constituent elements, namely Ga, N, and O, are determined and acquired using the EFTEM technique (see in Figure 4.1(c)). It can be noticed from Figure 4.1(c) that the O map (blue) is mostly present in the surrounding of NPs which is in agreement with results obtained from EELS. The presence of oxygen in the nanoparticle can be explained by the finite surface oxidation of GaN simply due to large specific surface.

In order to understand the difference in the emission mechanism of as-grown GaN epitaxy and the as-fabricated NPs, we studied the normalized μPL spectra at 77K. Figure 4.2(a) shows disparate emission characteristics of GaN in both GaN epitaxy and NPs. In the as-grown GaN epitaxy, we clearly observe the existence of one relatively sharp peak at the UV region, 3.479 eV (~356 nm) with a full-width at half-maximum (FWHM) of 13 meV, which is attributed to the donor-bound exciton peak ($D^0X$) [70]. The small hump at 3.484eV is assigned to the free-excitonic peak (FX).
We attribute the small PL peak $I_{ox}$ at 3.4eV mainly reported from oxygen impurities originated from $\text{Al}_2\text{O}_3$, *i.e.* the oxygen impurity related donor-to-valence band transitions as reported by Chung *et al.*[63, 64]. The donor-acceptor pair (DAP) peak at 3.308 eV has its longitudinal optical (LO) phonon peak at lower photon energy.

The $\mu$PL spectrum of the GaN NPs presents $\sim$110 meV redshift that could be attributed to the relaxation of the compressive strain [72], but foremost, we observe a relatively strong/prominent increase of the DAP and $I_{ox}$ peak intensities. In the n-type GaN DAP transitions, these acceptor-like sites have been reported by a number of authors to originate from Ga vacancies ($V_{\text{Ga}}$) [78, 79]. The GaN NPs underwent chemical etching, thus resulting in an increase of oxygen and vacancies sites at the surface due to the competition between the formation and dissolution of $\text{Ga}_x\text{O}_y$ (Figure 4.1(c)). This explains the increase in the emission intensity of DAP peaks.

Figure 4.1 (a) SEM image of the NPs prepared using PEsC etching technique, and (b) TEM image of NPs. (c) Overlaid elemental maps of Ga, N, and O in red, green and blue, respectively, acquired by means of Energy Filtered TEM.
Figure 4.2 (a) Normalized 77K μPL emission spectra of as-grown 30 μm GaN epitaxy and GaN NPs cluster with semi-log scale. (b) Normalized room temperature μPL emission spectra of as-grown GaN (dash line), and GaN NPs (solid line) cluster excited with increasing laser power (0.08, 0.8, 2, 4, 8 kW/cm²). (c) The peak PL photon energy (black squares) and the FWHM (blue triangles) dependence over the excitation power.

The power dependent PL measurement was performed on the NPs. Figure 4.2(b) shows a typical room temperature μPL emission spectrum of the as-grown GaN excited at 0.08 kW/cm² together with the excitation power dependent μPL emission spectrum of the GaN NPs. Compared to the 77K PL, we observe in the room temperature PL of the as-grown a quenching of D⁰X peak while the FX emission
became dominant at 3.42 eV (~362 nm). The broadening in the lower photon energy due to the oxygen impurity is still observable whereas the DAP peak disappeared. Most importantly, room temperature PL of GaN NPs excited at 0.08 kW/cm² exhibits a luminescence peak centered at 3.353eV (369nm) which is red-shifted by 69 meV compared to the as-grown sample. As the excitation power increases from 0.08 kW/cm² to 8 kW/cm², we observe an approximate linear decrease of the peak PL photon energy with a total span of 530 meV (Figure 4.2(c)). We investigated several spots in the as-grown GaN bulk epitaxy but no shift with increasing excitation power was observed. Besides the redshift, the measured FWHM shows a direct dependence over the excitation power as it increases from 120 meV (~13 nm) at 0.08 kW/cm² to 263 meV (~40 nm) at 8 kW/cm² (Figure 4.2(c)). Such a wide FWHM is twice as large as the measured FWHM of the peak from the as-grown GaN bulk epitaxy where the linewidth broadening at the same power density is 42 meV (~4.5 nm). This FWHM widening indicates a contribution of inhomogeneous broadening in the clusters of NPs.

For clarity, we turn to another dispersed GaN NPs whose PL spectra are also distinguished with a dominance of the impurity and oxygen related peaks over the FX peak with increasing the temperature (Figure 4.3(a)). For comparison Figure 4.3(b) shows the semi-log scale PL of these NP cluster at 77K, it confirms our previous observation where the DAP and I_{ox} peaks increase with respect to that of the as-grown GaN epitaxy (see Figure 4.2(a)).
In the following discussion, we investigate the large redshift and linewidth broadening in PL emission redshift and broadening of the NPs triggered by the increase of the power density. It is generally accepted that several processes can cause this shift, namely (a) bandgap renormalization\cite{80}, (b) changes in the DAP\cite{81}, (c) impurity band formation\cite{71}, and (d) surface states and/or the potential distribution in the crystal\cite{82, 83}.

(a) In bandgap renormalization, the formation of ionization and electron hole plasma leads to the bandgap narrowing\cite{81}. Calculations specific to our material and experimental conditions, based on the empirical relation $\Delta E = kn^{1/3}$ reported by Lee et al\cite{80}, where $k$ is the band gap renormalization coefficient ($k \approx 10^{-8}$ eV.cm), $E$ is the band gap energy and $n$ is the carrier density predict a bandgap narrowing in
the order of 20 meV. This prediction is inconsistent with our experimental measurements, specifically considering the large redshift measured, so bandgap renormalization can be safely neglected as a plausible cause.

(b) Due to the Coulomb interaction, transitions related to DAP blue-shift with increasing excitation intensity. In fact, the photon energy ($h\nu$) is inversely proportional to the distance, $r$, between neutral acceptors and donors, i.e. $h\nu \propto 1/r$. With increasing excitation power, the distance decreases and as a consequence, the photon energy blue-shifts by a few meV[81]. In our case, conversely, a significant redshift is observed and, hence, we might ignore the blue-shift caused by the Coulomb interaction in these transitions.

(c) The GaN used in this study is n-doped and has a carrier density of $2\times10^{18}$ cm$^{-3}$, thus the redshift might be due to the presence of impurity band generated from doping concentrations [71].
(d) The potential fluctuations model, on the other hand, explains this large redshift in the PL with increasing excitation power. It is known that the crystalline orientation distortions cause effective bandgap dispersion, and thus creates lateral potential fluctuations. Vacancies, impurities, dangling bonds, strain and structural defects, all introduce these fluctuations\cite{82,83}. In our case, the material underwent chemical electroless etching from which a different structural shape and strain in the NPs arises\cite{84}. This coalescence of the NPs induces the formation of boundary dislocations and, additionally, the preferential etching increases the impurity and vacancy defects concentration\cite{84}.

The bandgap dispersion in NPs creates local potential minima where carriers recombine\cite{85} (Figure 4.4). Upon low excitation power, non-equilibrium electrons and holes are generated and move towards the conduction band minima and valence band maxima, respectively. While in the as-grown GaN, at room temperature, FX transitions are intense. After etching, acceptor-like sites are created in the surface and a small redshift is induced due to the increase of donor-to-valence band and DAP transitions. When we increase the excitation power, more electrons get excited in the conduction band inducing an electric field screening effect and band flattening in the fluctuated potential bands. As a consequence of these effects, the carrier life time is longer and excited carriers have more time to reach lower energy localized states (Figure 4.4). Electrons overcome the lowered potential barriers (presented by the small red arrow in Figure 4.5) and get trapped in the
deep localized potential minima, where the blue luminescence is stronger. This can be understood if we recall that the wave function of electrons in these local minima is relatively quite spatially extended, and thus can easily overlap with the wave function of holes bound in the acceptor-like sites, increasing the probability of such a transition. There may exist many lower energy states and donor trap sites, this recombination would increase the emission line-width.

Furthermore, due to the extremely high surface to volume ratio of the produced NPs

Figure 4.5 Schematic representation of potential fluctuation and surface states caused by defects and band distortion. (a) Bulk GaN, (b) NP thoroughly depleted at low excitation power/low temperature, and (c) NP with high carrier concentration at high excitation power/high temperature has a surface depletion region with small width. Arrows indicate recombination of free electrons and bound holes.
paired with localized potential fluctuation, surface states cannot be neglected. The n-type GaN NPs have surface defects, thus we have band bending in these regions (Figure 4.5). The creation of surface depletion will change the emission in the GaN NPs. The calculated width of the depletion region in our case is $W \approx 24 \text{nm}$, given by[86]:

$$W = \sqrt{\frac{2\varepsilon_{\text{GaN}} V_{\text{bi}}}{q N_d}}.$$  

Where $\varepsilon_{\text{GaN}}$ is the static dielectric constant of GaN, $V_{\text{bi}}$ the potential at the boundary, $q$ the electronic charge, and $N_d$ the donor density. For NP with a width $d < 2W$, the NP will be totally depleted. $V_{\text{Ga}}$ centers acting like acceptor sites will be depleted from holes and we have FX transitions dominating. If $d > 2W$, both depletion region and non-depletion region can exist. Furthermore, by increasing excitation power or temperature, the depletion region decreases and Fermi level increases. Thus, holes populate the acceptor like sites in the depletion region and electrons populate donor states, therefore, we have an increase of DAP and donor-like oxygen states acceptor-like $V_{\text{Ga}}$ states. This leads to the visible blue emission at higher excitation power. In Figure 4.5(c), the depletion region is a collective representation of trap-states due to sharp edges within a NP, and across different NPs with size inhomogeneity evident in Figure 4.1. The sharp edges and/or smaller NP sizes enhance oxidation, and therefore increase the density-of-states and carrier capture cross section of carrier traps, i.e. localize states. In addition, the smaller the NP, the higher the conduction band minima of the local potential fluctuation. The LO phonon enhancement is due to indirect transition from the silicon donor states to the valence band maxima of the local potential fluctuation, confirms the PL peak broadening.
The emission yield, wavelength tunability, and FWHM of our NPs can be modified by controlling the size and inhomogeneity of the nanoparticles. We expect to see a significant improvement in quantum yield of the GaN NPs with further process optimization and post-processing treatments through, for example, annealing and surface passivation.

4.4 Summary Notes

In summary, GaN nanoparticles with size dispersion between 10nm to 100nm have been fabricated using the PEsC method. A large emission wavelength tunability of ~530 meV has been observed from the nanoparticles. We demonstrated that the localized potential fluctuation and surface state effects are responsible of such shift. These fabricated oxide encapsulated GaN nanoparticles can be used as phosphor for the tunable color-temperature white LED application.
5 INGAN MICRODISKS

Thin layer wide bandgap III-nitride semiconductors have attracted much attention for the fabrication of visible optoelectronic devices [87]. Heterogeneous integration and flexible application of these single crystalline structures is highly appealing [88]. Most significant challenges to epitaxially lift-off InGaN nano-layers rely on the selective lateral wet etching process. Existing selective wet etching techniques rely on regrowth of nano-layers on sacrificial layers such as Si, SiO\textsubscript{2} and AlAs [89, 90]. However, high quality single crystalline InGaN nano-layers are mainly grown on chemically inert GaN buffer epitaxy on sapphire substrate [5]. Bandgap selective etching of InGaN/GaN multiple quantum wells (MQWs) and GaN/AlGaN QWs has been achieved [91]. In this context high lateral selective etching of lattice matched GaN layer grown on sapphire offers an attractive alternative. This technique will further improve the crystalline quality of the overgrown InGaN layer and reduce its generated defect. Also it will inherit the advantages stemming from matured substrate platform and growth technique, get rid of the extra costly InGaN/GaN QW sacrificial layer, and benefit of commercially available template substrates. In addition, the reuse of sapphire substrate can also be facilitated [92].

The most striking application of InGaN-based LEDs is white LEDs. There are three major methods to generate white light emitting devices (WLEDs): (1) the combination of RGB LEDs [8]; (2) the use of high brightness blue LED for exciting
yellow phosphor [93]; (3) the use of UV LED for exciting RGB phosphor [94, 95]. While RGB LEDs provide high efficiency and improved color rendering, the integration of three-color LED in a single package poses fabrication challenges. The combination of blue LED with yellow phosphor as well as the combination of UV LED with RGB phosphor has the advantages of small footprint and large wavelength emission [17]. However, phosphor-based WLEDs suffer from poor color rendering index and/or optical degradation [96]. The optical degradation is associated with the reliability of RGB or yellow phosphor and still constitutes a significant research gap in tunable color-temperature [18]. This gap arises as humans naturally react to the changes in color temperature throughout the day with low color temperature near dawn and higher color temperature during the day. Currently used phosphors are generated from highly doped materials, having poor blue light emission and low luminous efficiency [96, 97].

In recent years, much research has been devoted to the development of rare earth doped III-V compound semiconductor based phosphors including GaN-based semiconductors [98, 99]. GaN and InGaN based phosphors have advantages over other types of phosphors in term of high quantum efficiency, excitation spectrum well matched to LED emission wavelengths and linewidths, fast photoluminescence lifetime, large tunability of excitation and emission wavelength, and high thermal stability. To date, most of the available methods for making nitride phosphor either require high temperature (like solid-solid reaction) or reduce the luminous efficacy
(like chemical co-precipitation) [19]. This PEsC lift-off method offers many advantages, such as the use of In composition to tune colors [27].

In this chapter we investigate the novel process technology to achieve high lateral selective etching of GaN using PEsC bandgap wet etching technique. The PEsC etching of the underlying large band gap GaN epitaxy through carrier transfer mechanism enables the lift-off of the overgrown InGaN nano-layer. The diffusion and transfer kinetics of the carriers during the PEsC etching is further discussed. Using this novel method, free-standing InGaN micro-disks have been successfully lifted-off and transferred to different substrates for optical pumping. The resultant InGaN layer offer good material compatibility with III-V LEDs, high chemical stability, large excitation range, and a life-time compatible to that of the GaN-based LEDs. The micro-disks are simple to fabricate, easy to integrate, and, most importantly, offer tunable emission rendering them a good candidate for pixelated RGB displays. Pick and place technique can bring forth new optoelectronic device schemes applicable to flexible devices and Inorganic laser phosphor display.

5.1 InGaN etching

5.1.1 Experiments

400 nm undoped In$_x$Ga$_{1-x}$N epitaxy was grown on 4 µm thick unintentionally doped GaN, on c-plane sapphire ($\alpha$-Al$_2$O$_3$) substrate, to investigate the etching mechanism. The estimated dislocation density of the top InGaN layer is $1 \times 10^8$ cm$^{-2}$ and
measured carrier concentration of the sacrificial GaN layer is \(5 \times 10^{17}\) cm\(^{-3}\). The as-grown In\(_x\)Ga\(_{1-x}\)N with x=0.2, x=0.3 and x=0.4 grown by MOCVD and have PL emission in the visible spectrum (see Figure 5.1). Pt was sputtered on both sides of the diced sample followed by PEsC etching.

Room temperature and 77 K PL and Raman measurements were carried out using Jobin Yvon’s LabRAM ARAMIS micro-spectroscopy system. The optical excitation was produced using a Helium-Cadmium (HeCd) laser emitting at 325nm and a diode-pumped solid-state (DPSS) blue laser at 473 nm with a <10μm spot-size. The SEM investigations were performed using FEI Quanta 600 electron microscopes.

Figure 5.1 Room temperature PL of the as-grown In\(_x\)Ga\(_{1-x}\)N on GaN, with x=0.2, x=0.3 and x=0.4
5.1.2 Porous and InGaN nanowhiskers

The PEsC etching mechanism depends on the slight upward energy band bending of the semiconductor at the surface with the electrolyte [39]. When illuminated with high energy UV lights electron-hole (e-h) pairs are excited. At the surface, electrons concentration is reduced, and holes concentration is increased. Within the minority carrier diffusion length ($L_p$), photo-generated holes diffuse to the semiconductor skin depth depletion region ($W$) where they drift towards semiconductor/electrolyte surface. Confined holes in the potential well at the interface are consumed by the oxidation reaction of the GaN. Electrons migrate to the bulk, where they are collected by a thin Pt layer deposited on the GaN surface prior to etching. From a chemical point of view the absence of electrons in bonding orbitals and the presence of holes at the surface in the valence band ($E_v$) weakens

![SEM images](image-url)

*Figure 5.2 (a) SEM image of $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ sample after 20 min of PEsC etching, showing nanowhiskers on the surface (b) SEM image of $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ sample after 20 min of PEsC etching, showing nanoporous structure.*
the lattice bonds, hence increasing the dissolution rate of (In)Ga$_2$O$_3$ in the HF-based aqueous solution.

Similar to the GaN, the etching of the InGaN layer results in formation of porous structure originating from dislocations and defects in the surface of the epitaxial layer. In contact with electrolyte, energy band bending is smaller in regions with defect vacancies than in surrounding crystalline epitaxy, pores formed at the surface coalesces and proceed vertically following the crystalline structure. SEM picture in Figure 5.2(a) shows In$_{0.2}$Ga$_{0.8}$N sample etched for 20 min, we notice the formation of InGaN nanowhiskers on the surface, these nanowhiskers coalesce due to the capillary forces in the wet solution. The formation mechanism of these whiskers is similar to the porous structure described in chapter 3. Due to the higher In composition in the second sample, we observe the formation of porous structure in Figure 5.2(b) for same etching duration, 20 min. by increasing In composition the resistivity increases slowing down the etching rate, which is highly dependent on carriers transport [41].

### 5.1.3 Optical characterization

In order to understand the emission mechanism of the as-grown and the as-etched In$_x$Ga$_{1-x}$N semiconductor, we investigated the PL spectra at room temperature. Figure 5.3(a) shows emission characteristics of the epilayer with In composition $x=0.2$. In the as-grown In$_{0.2}$Ga$_{0.8}$N layer we observe a wavelength peak at 470 nm,
with surrounding peaks due to the interference in the thin InGaN epilayer confined between the GaN and air. In Figure 5.3(a), the spectrum of the as-etched sample is red-shifted by 5 nm. The red-shift can be attributed to the strain relaxation in the top layer as explained in chapter 3. The stronger peak at 506 nm might be explained by the stronger interference due to the thinner InGaN layer after etching. Consistent with our results, a comparison between the as-grown Raman phonon peak and the as-etched Raman phonon peak, in Figure 5.3(c), shows a large shift of 20 cm$^{-2}$ of the...
A1(LO) modes, it is noted that this mode is strongly related to the In composition [100]. The Raman results confirm the reduction of the In composition in the epilayer due to the etching and formation of whiskers, therefore explains the observed large shift. E2(high) modes influenced by the GaN layer have smaller peak intensity in the as-grown than in the as-etched InGaN semiconductor. This might be explained by the etching of the top layer that revealed the GaN epitaxy, thus increasing the peak count. PL and Raman spectra were also collected for higher In composition x=0.4 (see Figure 5.3(b)&(d)), we observed a small peak wavelength red-shift, 3nm, of the as-etched sample compared to the as-grown InGaN. Consistent with our SEM results in Figure 5.2, at higher In composition the etching rate decreases, resulting in a smaller strain relaxation. The strain relaxation is observed in the Raman spectra where A1(LO) modes of the as-etched sample shifted by 1 cm⁻¹.

It is noted that peak PL wavelength of the as-grown samples in Figure 5.3 are different from PL spectra in Figure 5.1. This is due to the non-uniform MOCVD growth of InGaN layer over the 2 inch substrate. In fact due to the temperature variation in the wafer holder during growth, it is noticeable that the resultant wafers have color changes and variations from dark in the center to clear colors on the edge. As we dice small samples for our process (1cm x 1cm), results obtained from two different samples and from the same wafer might present some discrepancy.
5.1.4 Sonicated porous InGaN platelets

Figure 5.4(a) shows SEM picture of the PEsC etched In$_{0.3}$Ga$_{0.7}$N layer on GaN after Ar bombardment. Due to the ion channeling in the epitaxial layer after reactive ion etching (RIE), micro-cracks appear on the thin In$_{0.3}$Ga$_{0.7}$N epilayer (Figure 5.4(b)), these micro-cracks permit the HF solution to reach the GaN underlayer. After PEsC etching, we notice the formation of porous GaN and GaN nanowires. The porosity reduce the sticking coefficient of the GaN to the InGaN, thus the InGaN experience a sheer peeling force. The sample is then submerged in an isopropanol (IPA) solution and sonicated for 30 min at room temperature. Using the centrifuge, platelets sonicated in IPA are collected in the bottom of the recipient. The porous InGaN micro-layers are then transferred on a Si substrate for optical characterization.

Figure 5.5(a) shows the PL spectra of the as-grown In$_{0.3}$Ga$_{0.7}$N layer and the porous In$_{0.3}$Ga$_{0.7}$N platelets transferred on Si substrate after RIE and PEsC etching. These platelets are ~160 nm thick with rough porous surface due to the HF attack.
Nanowires are also observed on the SEM picture in Figure 5.5(b), these nanowires might originate from the etched GaN. PL emission of the as-grown In$_{0.3}$Ga$_{0.7}$N layer presents a peak PL wavelength at 540 nm with small periodic humps surrounding it, these peaks can be explained by the interference in the In$_{0.3}$Ga$_{0.7}$N thin layer on top of the GaN layer. The PL peak wavelength of the platelets transferred on the Si substrate is red-shifted by 10 nm, this is due to the strain relaxation in the thin peeled-off layer and due to the etching of the InGaN. Also we noticed a broadening of the FWHM due to the inhomogeneity of the surface composition after PEsC etching and defects generated from RIE bombardment.

Results obtained from this sonication process are satisfying and offer some transferrable InGaN microstructures. But the etching process affects the crystallinity of the InGaN layer, where porosity and defects in the thin layer act as light traps,
therefore these platelets might not be a good candidate for optically pumped structure and inorganic transferrable micro-phosphors.

In the next section we will discuss a novel lift-off technique of InGaN microdisks after selective lateral etching of GaN layer for better crystal quality of free-standing InGaN semiconductor.

5.2 Lateral GaN PESC selective etching

5.2.1 Experiments

To investigate the selective etching of GaN we used the same structure in 5.1.1. 400 nm undoped In$_x$Ga$_{1-x}$N epitaxy grown on 4 µm thick unintentionally doped GaN, on c-plane sapphire (α-Al$_2$O$_3$) substrate. Microcolumns, with 10 µm diameter, and height ranging from 200 nm to 1 µm, were fabricated using standard photolithography technique followed by inductively coupled plasma (ICP) etching process (lithography mask used is presented in Appendix-Figure A.1). A 10 nm thick

Figure 5.6 Schematic illustration of InGaN microdisks lift-off process (a) InGaN on GaN on Sapphire (b) ICP dry to define microcolumns, GaN layer is revealed, Pt layer is sputtered around the microcolumns (c) Sample is submerged in UV solution and illuminated with UV light (d) microdisks picked with a flat PDMS.
Pt layer was sputtered onto the surface followed by a metal lift-off step to define the Pt electrode such that the top surface of microcolumns was left uncoated. The Pt served as a cathode during the electroless-chemical etching to complete the electron–hole exchange loop between semiconductor and electrolyte. The wet electrochemical etching was performed by immersing the sample in a HF/CH₃OH/H₂O₂ (2:1:2) solution with UV illumination from the top surface. The selective etching process of the GaN for lift-off of the InGaN microdisks is described in the next section. Experiments are illustrated in Figure 5.6. The resultant micro-structures were later transferred onto different substrates for subsequent room temperature PL measurements using Jobin Yvon’s LabRAM ARAMIS. The scanning electron microscopy (SEM) investigations were performed using a FEI Quanta 600.

5.2.2 InGaN Microdisks

For the lift-off of In₀.₃Ga₀.₇N epilayer, PEsC process is used to laterally etch the GaN sacrificial layer. Similar etching to the previous section 5.1 is employed; however, dry etching is used to reach the sacrificial layer, after defining micro-columns using lithography step. In this section, we will discuss the etching mechanism dependence on the ICP etch depth of the etched micro-columns. As depicted in Figure 5.7(b), in the case where GaN layer is not exposed during the etching of micro-columns, electrons from the InGaN microdisks diffuse towards the Pt layer surrounding the microstructure (choice of Pt placement is discussed in section 5.2.3). In this case, PEsC etching resulted in whiskers and porous structure on the InGaN microdisks.
which are not desirable, similar results are observed in section 5.1 and Figure 5.2(a). In order to preserve the top InGaN layer, one has to prevent electron transport in the InGaN layer towards the Pt layer. Figure 5.7(c) depict the schematic implementation of electron within the InGaN layer by means of ICP etching into the undoped GaN layer thereby forming a natural electron blocking through the conduction band offset as well as a resistive route through the undoped layer. The experiments are further elaborated in the following paragraph.

In Figure 5.8(b), the 2 min ICP etching formed a depth ~400 nm exposing the underlying GaN, in addition to the top InGaN layer. During the subsequent 20 min PEsC wet etching process, with UV light illuminated, the photogenerated holes diffused and drifted through the depletion region to the exposed InGaN and GaN

Figure 5.7 PEsC etching mechanism model: (a) Photogenerated electrons (e⁻) and holes (h⁺) in the depletion region and band bending at n-type semiconductor-electrolyte interface (b) skin depth light absorption causing electron-hole pairs generation and diffusion in the InGaN material leading to redox reaction occurring at the semiconductor-electrolyte interface when pre-patterned InGaN micro-columns are formed on planar GaN, (c) skin depth absorption resulted in electron-hole pairs generation and diffusion on the exposed GaN surface, and incomplete conduction loop for the InGaN material due to the more insulating GaN. This enhances GaN etching while InGaN etching only occurs at the perimeters for the case of pre-patterned InGaN/GaN microcolumns (see inset in Figure 5.8(a)).
surfaces. On the other hand, the photogenerated electrons diffused to the Pt surface. Both conduction band offset and high resistivity GaN \[41\] prevents photogenerated electrons within InGaN from conducting through the GaN to the Pt layer thereby preventing fast etching process on the InGaN surface, this results in a high etch selectivity of GaN over InGaN. In Figure 5.8(c), by increasing the etch time to 5 min to achieve an etch depth of 1 µm, a faster lateral GaN wet etching is achieved, indicated GaN depth dependent PEsC wet etching due to a larger GaN surface exposing to HF solution easing the transport of chemical species. In Figure 5.8(b), after PEsC etching we observed the formation of porous GaN membrane surrounding the microcolumns \[101\]. As the GaN PEsC wet etching proceeds, the porous GaN regions formed underneath the InGaN layer, propagate inward from the perimeter of the micro-columns. The porous GaN formed voids that enhance HF
solution reaction through capillary effect whereby both inward and downward etching continues towards the sapphire substrate (see Figure 5.8(c)). After 40 min of etching, the entire GaN layer under the 10 µm disks is consumed, and the InGaN layer is then only supported by porous nanowires. This process is highly selective as the etch rate in the InGaN layer is negligible compared to GaN (etch rate of ~200 nm/min). After PEsC, the sample is dried using a critical point drier (CPD) method to prevent the InGaN layer from permanently sticking to the substrate permanently. The formation of InGaN microdisks are then complete and ready to be transported onto a flat flexible PDMS (Polydimethylsiloxane) [102] or silicon handler substrate.

5.2.3 Pt deposition

In the PEsC reaction, Pt deposited prior to the etching process acts like a cathode in the electrochemical reaction. Photo generated electrons migrate to the bulk, where they are collected by the thin Pt layer. The role of the placement of the metal is studied in this section.

For higher lift-off yield we studied 3 schemes presented in Figure 5.9. Stripes of thin Pt layer were deposited on both sides of the sample (Figure 5.9(a)) and used for etching GaN and InGaN epilayer in chapter 3 and 4, for studying porosity and nanowire formation this scheme was more suitable. In fact Pt acts as a catalyst in the etching reaction and observation of higher etching rate closer to the Pt layer helped understand better the mechanism and pore evolution. For single epilayer in
contact with electrolyte and with Pt layer on top, the semiconductor surface is uniform therefore electron hole loop is satisfied and carriers transport is faster nearby the deposited metal. After ICP etching and revealing of GaN layer, electrons generated at both surfaces InGaN and GaN compete to participate in the PEsc reaction. Micro-columns closer to the Pt have a higher under layer etching rate, leading to a low lift-off yield of InGaN microdisks (Figure 5.10(a)).

Pt deposited in a 500 µm x 500 µm rectangular disposition defined by a photoresist lift-off process covers most of the microcolumns (Figure 5.9(a)). In this process, most of the light generated from the top of the sample is absorbed and reflected by the Pt layer. Although the lift-off yield is higher than in the stripes scheme (Figure 5.10(b)), the etching rate is slower and non-repeatable results present some discrepancy.

Figure 5.9 (a) Pt stripes deposited on both sides of the sample, (b) rectangular Pt layer coating semiconductor columns after lithography deposition (c) Pt layer deposited on the microcolumns followed by metal lift-off such that microcolumns are left uncoated.
After ICP etching, a thin layer of the used photoresist mask is left on top of the microcolumns. We directly coat the sample with the metal layer and use sonication in acetone to lift-off the Pt covering the InGaN regions (Figure 5.9(c)). In this scheme Pt is surrounding the microcolumns, thus allowing the electrons generated on the GaN surface to migrate faster to the deposited Pt, whereas electrons generated at the InGaN layer are blocked by the higher bandgap GaN under-layer. Hence we selectively etch the GaN over the InGaN. Higher yield free-standing InGaN microdisks are observed using this process Figure 5.10(c). Results are more repeatable and easier to perform (fewer steps).

5.2.4 InGaN Microdisks transfer

Pick-and-place technique was used to transfer InGaN microdisks onto different substrates. A flat PDMS stamp was made by mixing 10:1 (Sylgard 184:Dow Corning) and cured at 90 °C. The kinetics of the transfer printing is governed by the adhesion of the elastomeric stamp [102]. After PEsC etching, InGaN microdisks on the laterally etched porous GaN layer were peeled off using the rubber stamp, by
putting the flat PDMS in contact with donor sample and manually stripping it in a fast movement. Subsequently, microdisks were deposited on different substrates by means of gravitational potential and adhesion energy hysteresis, by putting the stamp with microdisks in contact with the receiving surface, then removing the PDMS slowly.

**Figure 5.11** shows µPL emission spectra of transferred micro disks on PDMS. The high intensity peak PL wavelength at 569 nm from the In$_{0.3}$Ga$_{0.7}$N microdisks confirms the good quality of the lifted-off microdisks. In **Figure 5.11(b)** µPL measurements, performed on microdisks lifted-off from diced sample from the center of the wafer and diced samples from the edge of the wafer, show the PL shift due to the In incorporation variation along the wafer, this variation is caused by the MOCVD growth and temperature disparity along the wafer during InGaN growth.
Flexible substrate can be used to study the strain and mechanical stretch of the microdisks and InGaN layer (see Figure 5.12(d)). Other potential application can be the integration of the thin semiconductor layer in the stamp or the epoxy dome for phosphorous applications.

Microdisks were later transferred on Si substrate using sonication Figure 5.12(a) and on LEDs using pick-and-place technique Figure 5.12(c). Figure 5.12(a) shows
the room temperature µPL spectra of the lifted-off InGaN microdisks transferred on Si substrate and on blue LED substrate. Blue LED excited with 325 nm laser emits at 463 nm which excites the InGaN layers and generate the green emission at 580 nm. In Figure 5.12(c) the emission spectra of the InGaN microdisks optically pumped by the blue LED is an excellent proof-of concept implementation of InGaN thin layer conformal phosphor on LED.

5.3 ZnO on InGaN

ICP etching defined microstructures with 500 µm diameter and 400 nm depth in the InGaN sample grown on GaN on sapphire substrate. Prior to PEsC etching, Pt was deposited on both sides of the sample. The lithography mask deposited for the dry etching was thin such that Ar bombardment can reach the InGaN layer through the photoresist. The ICP etching resulted in cracking of the top InGaN layer, and ion channeling through the epilayer helped the wet etching process to etch the underlaying GaN layer. The cracked InGaN layer is then partially lifted-off Figure 5.13(a).

We then deposited ZnO using atomic layer deposition (ALD) on the top surface which led to the self-rolling up of the InGaN top layer forming a scroll tube (see Figure 5.13(b)). This might be explained by the sheer force applied to the partially lifted-off InGaN layer after PEsC etching enhanced with the deposition of the strained ZnO layer. The differential deformation caused by the etching mechanism is called strain and expressed as change in length per unit length. Deposition process
of ZnO thin film on the InGaN layer causes strain in the upper layer due to the thermal and lattice mismatch. Debonding of the thin film tends to appear at the edge of the patterned features (see Figure 5.13(c)). The rolling up of the film is caused by the non-zero force applied at the edge of the layer. Many applications can stem from this process such as quantum confinement of scroll tubes formed by ZnO/InGaN QWs.

5.4 Summary Notes

In summary, we describe and demonstrate high GaN/InGaN etching selectivity of 100/1 and lateral GaN etching of 5 µm/min using PEsC etching. Thin InGaN layer
were grown on GaN on sapphire with different In composition. Free-standing 10 µm InGaN microdisks, with different colors, were fabricated using dry etching process to reveal and selectively etch the sacrificial GaN layer. The proposed model for etching process mechanism unveils the reason for high etching selectivity of undoped GaN over InGaN. Lifted-off InGaN microdisks were optically characterized and transferred on blue LEDs for optical pumping. This process offers promising approach for pixelated RGB InGaN phosphor material, and a new integration platform for heterogeneous inorganic nano-membranes applications.
6 FLEXIBLE GAN-BASED LEDS

The existing technology for growing epitaxial structures for high efficiency GaN-based LEDs on conventional substrates (sapphire and silicon carbide), which are chemically inert and mechanically hard, does not allow substrates to be easily removed through substrate polishing so that the epi-structure of the LED device can be integrated onto alternate substrates [5, 103]. Transferring the LED epi-structure onto flexible substrates for the fabrication of vertical conduction LEDs is highly attractive alternative to existing rigid devices, enabling non-conventional functionalities and applications in optoelectronics and biomedical applications [104-108]. Another fundamental advantage of vertical conduction LEDs is the full area coverage of p- and n-contact metals solving issues in the conventional lateral LED design such as current crowding, heat dissipation and low light extraction efficiency [22]. This drives the scientific effort to develop versatile and high yield post-growth substrate removal or epitaxy lift-off technologies for GaN based devices and structures [1, 101, 109-111].

Leveraging on existing knowledge on lift-off technologies for compound semiconductors such as InGaP/AlGaInP structures [112], two main methods for producing free-standing III-Nitride LEDs have been developed [113, 114]. There are (i) laser lift-off (LLO) and (ii) chemical lift-off (CLO). LLO is a dry technique that employs a high power excimer laser to dissociate GaN into N₂ gas and gallium
droplet [113], with the side effects of lattice deformation in the active area due to the high temperature shock wave and a recombination-enhanced defect reaction [34]. CLO on the other hand is a wet-process technique that selectively etches epitaxial sacrificial layers. The demands for high yield and high throughput device lift-off over a large area, have leaded to the development of room temperature CLO techniques [23]. Currently, the existing CLO techniques in laboratory scale research rely either on regrowth of III-Nitride devices on sacrificial InGaN MQWs [24], porous GaN template-substrate, or Si, SiO₂ and ZnO substrates followed by a subsequent exfoliation of the epitaxy layers through mechanical break-off or wet-etching techniques [22, 25, 26]. Both LLO and CLO techniques introduce high dislocations in the epitaxial layer through thermal-mechanical shock, and etch pits/pores, respectively [27, 38]. Innovation in CLO-based epitaxial transfer technique is required to separate GaN LEDs from the sapphire substrate with high controllable (selective) etching and reduced defect regenerations for III-Nitride devices.

In this paper, we report on a novel process technology to achieve these goals by means of simultaneous bandgap selective and doping-selective CLO based on backside-illumination photoelectroless chemical etching (BI-PEsC) process in addition to the conventional bandgap selective top-illumination photoelectroless chemical etching (TI-PEsC) process. The BI-PEsC enables PEsC wet etching of underlying large banggap nitride materials through limited carriers diffusion
allowing lateral etching of the undoped sacrificial GaN or the undoped GaN buffer layer. A model based on the carrier transport kinetics in addition to the PEsC processes of: (i) redox reaction at the semiconductor-electrolyte interface, and (ii) electron conduction at the metal-semiconductor interface is described to provide an explanation for the innovative selective etching mechanism of unintentionally doped GaN to lift-off thin InGaN layer overgrown on sapphire, which inherited the advantages stemming from matured substrate platform and growth technique; thus ensuring the retention of epitaxial quality without nucleating new threading dislocation density compared to the LLO technique. Without resorting to research in new substrate platform development for the purpose of epitaxial transfer, the technique can be readily employed without new investment in costly equipment and foundry infrastructure in depositing sacrificial layers, e.g. ZnO, that are not existence in commercially available template substrates. In addition, the reuse of sapphire substrate can also be facilitated [92].

Using this novel method, free-standing GaN-based LEDs have been successfully lifted-off and transferred to gold-coated polydimethylsiloxane (PDMS) and glass substrates; the fabricated vertical conduction LED possess excellent optical and electrical characteristics: ~10 times increase in light output compared to the bulk LEDs, and decrease in the turn on voltage as well as the series resistance. This approach greatly increases heat dissipation since the active region is close to the metal contact, enables truly vertical carrier injection and increases the sidewalls
extraction efficiency. The outcomes are applicable to flexible optoelectronics for biomedical applications, bendable displays and on chip 3D integration.

6.1 GaN/InGaN Quantum Well microstructures

6.1.1 Experiments

![Figure 6.1](image)

*Figure 6.1 (a) Schematic illustration of the MBE grown blue LED for QW lift-off (b) holes generated after UV illumination are confined in the depletion region, higher confinement in the n⁺-GaN layer compared to the GaN and u-GaN*

The structure studied in this section consists of MBE grown blue LED: 360 nm thick undoped GaN grown over a buffer layer on sapphire substrate, 360 nm heavily doped n⁺ GaN, 540 n-type GaN, 80 nm InGaN/GaN MQW, and 180 nm p-type GaN (see Figure 6.1(a)).

ICP etching process was used to define micro-structures with depth of ~ 1 µm to reveal the heavily doped n⁺ GaN. The size of these micro-structures was varied to study the lift-off mechanism. Prior to wet etching Pt layer was deposited on the
surface followed by metal lift-off step to define the metal such that the top surface of semiconductor microstructures was left uncoated. The Pt served as a catalyst in the PEsC reaction, electrons migrate to the cathode layer were they complete the electron-hole exchange loop between semiconductor and electrolyte. The wet electrochemical etching was performed by immersing the sample in a HF/CH$_3$OH/H$_2$O$_2$ (2:1:2) solution with UV illumination from the top surface. The etching process is described in the next section. The SEM investigations were performed using a FEI Quanta 600.

6.1.2 Quantum Well microstructures lift-off

PEsC etching can be defect-selective [115], dopant selective [39], and band gap selective [24]. It is highly dominated by carriers transport in the semiconductor and at the interface with the electrolyte. Sacrificial layer can therefore be prepared by designed doping profiles. The sacrificial layer in this structure is the heavily doped GaN layer (n$^+$-GaN). After ICP dry etching, sacrificial layer is in contact with the HF solution and exposed to the etching. Holes accumulate at the surface charge region at the interface with the electrolyte, were the band bending with n$^+$-GaN surface is higher than the n-GaN surface (see Figure 6.1(b)). Better confinement of the holes enhances the dissolution rate of the semiconductor. Thus it is expected that the lateral etching rate of n$^+$-GaN is higher than the n-GaN.
From SEM images obtained after PEsC etching, we noticed unexpected results, Figure 6.2. For etching duration of 5 min microdisks peel off and start rolling up, this is due to the strain on the edges of the film caused by the lattice mismatch between GaN and InGaN, thus the upper layer (p-GaN) is lifted-off, Figure 6.2(a). The QW is etched away; this is due to the high electron hole confinement in this region. We tried to modify the etching such that we revealed the u-GaN after ICP dry etching. In this case Pt is in contact with the u-GaN layer. For an etching duration of 5 min we noticed that the u-GaN begin to etch while other layers remained intact, Figure 6.2(c). For longer etching duration of 15 min the n-GaN, n+-GaN and QWs are etched, Figure 6.2(d). This is explained by the placement of the Pt layer, in contact
with u-GaN electrons generated at the surface are sunk and transferred to the metal, thus allowing the etching of the undoped layer. We believe that the doping concentration difference between the heavily doped layer and the Si doped layer is not very important such that using this process we have higher selective etching of the n⁺-GaN layer.

In the next section we will discuss a novel method to selectively etch the u-GaN and use the n-GaN for electrical contact for flexible application.

6.2 Green LED lift-off

6.2.1 Set-up

The MOCVD grown green LED structure under study consists of 1.8 µm thick undoped-GaN grown over a buffer layer on sapphire substrate, 3 µm n-type GaN, 50 nm n-type Al₀.₁Ga₀.₉N hole blocking layer (HBL), 50 nm n-type GaN, 200nm
InGaN/GaN MQWs, 50 nm p-type Al$_{0.1}$Ga$_{0.9}$N electron blocking layer (EBL), 600 nm p-type GaN (Figure 6.3(a)). The surface of the structure is intentionally roughened to increase the light extraction efficiency. For electrical contacts, p-metal contacts consisting of Ni/Au (5 nm/5 nm) layers were deposited on p-GaN prior to dry etching and annealed at 550 °C. Similar ICP etching process was used to define cross-structures with depth of ~ 5 µm to reveal the undoped-GaN. After sputtering of the Pt layer, top-side illumination PEsC (TI-PFsC) and backside illumination PEsC (BI-PFsC) were applied for comparison (Figure 6.3(b) and Figure 6.3(c), respectively). After lift-off, LEDs were transferred onto a gold-coated plastic substrate (PDMS) and glass substrate (SiO$_2$). For comparison, the bulk LED was fabricated with the same growth conditions and the same structure without lift-off, the ICP etching revealed the n-GaN layer for n-contact (1.4 µm thick LEDs). Device
characterizations were performed on the transferred LEDs and bulk LED. I-V measurements was performed using Keithley 2400, Newport power meter 2936-C model to get the L-I characteristics, and Ocean Optics QE65000 was used to measure the emission spectrum of the device.

6.2.2 Topside-illumination PEsC etching

For the green LED device etching, a similar top-illumination PEsC (TI-PEsC) process was used. It is noted that the TI-PEsC process etches each layer at different rates. For the p-type GaN, due to the downward energy bend bending at the interface between the p-GaN and the electrolyte, accumulation of holes near the depletion region is reduced, and thus p-GaN etching is negligible [39]. However, unlike single bulk InGaN layer presented in chapter 5, a strong internal electric field (piezoelectric field) causes carrier confinement in the active MQW region, and hence the etching rate would be greatly enhanced in the MQW region [24]. As the etching

![Figure 6.5 Schematic illustration of the 2 steps TI-PEsC etching, (a) a first mesa structure is dry etched to reveal the n-GaN layer, (b) then protected with a photoresist (PR) layer or Perylene, (c) a second dry etching is performed to reveal the u-GaN and a Pt layer is deposited, (d) finally PEsC etching is performed with mask on the structure to protect top layers from HF etching.](image-url)
depends heavily on the carrier confinement, and doping concentration, it is expected that etch rate of undoped GaN reduces accordingly. Furthermore, the photogenerated carriers is greatly enhanced and accumulated in the active region since the UV light is illuminated from the top (Figure 6.3(b)). As expected, a PEsC process for the LED device structure resulted in a fast etch rate of the MQW (200 nm/min) and n-GaN (200 nm/min) layers compared to the p-GaN (<1 nm/min) and undoped-GaN layers (negligible due to negligible photons absorption) (see Figure 6.4(a)). The device will obviously fail to function in this case.

Another scheme was exploited, illustrated in Figure 6.5, were in two steps the LED structure was dry etched first to reveal the n-GaN and coat it with a photoresist mask or a Perylene mask then in the second step dry etch a larger structure to reveal the u-GaN. The objective was to use polymer based layers to protect QW and n-GaN sidewall from etching. Nevertheless, after UV illumination at 750 W under the mercury arc lamp, PEsC process etched the n-GaN and QWs similar to the previous.
scheme. It is believed that the polymer mask couldn’t withstand the heat and HF attack.

The next section will discuss the novel process to solve the etching and lift-off of the green LED while preserving the good quality of n-GaN and QWs.

### 6.2.3 Backside-illumination PEsC etching

Typically, when illuminated from the back, electron-hole diffusion is limited (carrier diffusion length is ~300 nm, highly dependent on the doping concentration), and most of the UV photons get absorbed in the first few micro-meters of the undoped GaN buffer layer [116, 117], rendering carriers unable to reach the semiconductor/electrolyte interface, therefore no etching occurs. BI-PEsC etching has been attempted on several samples with thick undoped-GaN and n-GaN layers without significant etching of the top surfaces, due to the diffusion limited etching regime and absorption of UV light by GaN layer. Unlike existing wavelength filtering
method utilizing a large-bandgap on small-bandgap nitride material structure, *e.g.* GaN-on-InGaN, or \( \text{In}_y\text{Ga}_{1-y}\text{N}-\text{on-In}_x\text{Ga}_{1-x}\text{N} \) where \( y < x \), to selectively etch the small bandgap underlying material [24], the presented etching method break this limitation by enabling etching of undoped large bandgap material instead. The novelty of the current investigation lies in the process capability in selectively etching the undoped GaN, leaving behind the complete functional LED device structure by illuminating the UV light from the back substrate.

In this process, ICP dry etching was used to vertically etch the 60µm x 60µm cross shape alignment features, exposing the undoped-GaN layer to the HF solution, followed by deposition of a 10 nm Pt layer using metal-lift-off process. During PEsC etching process, the sample was submerged in the HF solution and UV light was illuminated from the back substrate, as illustrated in Figure 6.6. The ICP etching exposed u-GaN to the HF solution rendering electron-holes able to reach the semiconductor-electrolyte interface, thus participate in the etching process (See Figure 6.3(c)). Figure 6.7(a) shows a typical SEM image of the LED structure after BI-PEsC, in which the undoped-GaN structure is fully etched while the LED epitaxy is left un-etched. It is noted that if the process is left to proceed for duration longer than 12 min, the entire LED structure will eventually start to get etched. However, the high selectivity allows one to optimize the process for achieving high process yield (Figure 6.7(c)).
The lifted-off green LEDs were then transferred onto 12 pairs of SiNX/SiOx Distributed Bragg reflector (DBR) mirror grown by ALD on sapphire substrate with reflectivity of 0.98 at wavelengths between 520 nm and 560 nm, and optically pumped using a blue laser emitting at 473 nm. The PL emission from the LEDs on DBR increased by 7x compared to the ones transferred on PDMS (see Figure 6.8). The increase in PL emission intensity, obviously, is a result of the increase of reflectivity of spontaneous photons from the back plane of the device. Our result indicates that integration of high reflectivity DBRs for high efficiency vertical light

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Figure 6.8 (a) Room temperature PL spectra of the lifted-off LEDs on PDMS with and without a bottom DBR (b) Image of the micro LEDs on DBR under blue laser excitation, bright green light emitted (c) Reflectivity of DBRs fabricated using ALD with different pairs number, by courtesy of M. Sharizal.
emitting devices and to form high-Q cavity for vertical cavity surface emitting lasers (VCSELs) is possible using this approach.

### 6.2.4 Device level characterization

In Figure 6.9(d) the EL spectrum of the proof-of-concept chemical lift-off LEDs shows a typical green LED peak wavelength around 520 nm, the blue shift with increasing current injection is due to the band filling. The EL peak of the lifted-off LEDs is blue shifted by ~10 nm compared to the bulk LED (Figure 6.9(e)), this can be explained by the strain relaxation in the freestanding LEDs [40]. Figure 6.9(f) shows the measured V-I characteristics of the cross-structure LEDs on Au/glass substrate. Flexible lifted-off LEDs have a lower series resistance compared to the bulk LEDs due to the current injection flow (see Figure 6.10). Additionally, we observed a very significant decrease in the turn-on voltage from ~10 V to ~6 V, likely due to formation of improved Ohmic contact between the lifted off LED with the gold layer on PDMS, a lower series resistance and the reduced polarization in the active region [118]. It is noted that, the Ohmic contact is non-uniform due to the roughened p-GaN surface. Further improvement of the LED fabrication process could increase the performance of our lifted-off device.
Heat dissipation was also expected to decrease in the freestanding micro-LEDs due to the current spreading in the transferred devices on gold surface [22]. The deposited Au layer on the PDMS and glass wafer acts as a heat sink that can improve the micro-LED performance. With better heat dissipation, the lift-off LED can

Figure 6.9 (a) lifted-off 60µm x 60 µm cross shape alignment feature of the green LEDs mesas transferred onto PDMS and held on a finger-tip, (b) Optical image of the green LEDs on PDMS (c) Electrically pumped lifted-off LEDs on PDMS (d) electroluminescence (EL) spectra of lifted-off LEDs at different current injections (e) EL spectra of lifted-off green LEDs and bulk green LED (f) I-V characteristics of lifted-off LEDs and bulk LED (g) L-I characteristics of lifted-off LEDs and bulk LED.
withstanding higher current injection. L-I characteristics confirm our previous results (see Figure 6.9(f)). At small current injection the bulk LED output power was higher than the lifted-off LED, while at higher injection current (700 µA), the lifted-off LED has 10 times higher output power due to heat generation and current crowding effect in the bulk LED. The sidewall roughness of the lifted-off LEDs after BI-PEsC help to enhance the extraction efficiency leading to higher emitting intensity, moreover narrow escape cones for sidewall light extraction due to the flat surfaces in the bulk LED limit the output light intensity.

6.3 Blue LED lift-off
The MOCVD grown blue LED structure under study consists of 1.8 µm thick undoped-GaN grown over a buffer layer on sapphire substrate, 3 µm n-type GaN, 50 nm n-type Al$_{0.1}$Ga$_{0.9}$N HBL, 50 nm n-type GaN, 300nm InGaN/GaN MQW, 50 nm p-type Al$_{0.1}$Ga$_{0.9}$N EBL, 150 nm p-type GaN, and 1 nm n-type GaN for tunnel junction at p-contact. For electrical contacts, p-metal contacts consisting of Ni/Au (5 nm/5 nm) layers were deposited on p-GaN prior to dry etching. Similar ICP etching to reveal the u-GaN was carried on, followed by Pt deposition and BI-PEsC etching. After lift-off, LEDs were transferred onto a gold-coated plastic substrate (PDMS) and glass substrate ($\text{SiO}_2$). For comparison, the bulk LED was fabricated with the same growth conditions and the same structure without lift-off, the ICP etching revealed the n-GaN layer for n-contact (1.4 µm thick LEDs).
Similar to the previous device structure, revealed u-GaN exposed to BI-PESC process is etched away, leaving behind nanowires and fragile nanoporous structures under LED layers (see Figure 6.11(a)). After CPD the LED is lifted-off and ready for

Figure 6.12 (a) Optical micrograph of the lifted-off cross shape blue LED on Au coated glass substrate (b) blue emission from the lifted-off LED (c) EL spectra of the lifted-off blue LED (d) EL of lifted-off LED on glass and bulk LED (e) I-V characteristics of lifted-off LED and bulk LED (f) L-I characteristics of lifted-off LED and bulk LED
transfer. We put the glass substrate coated with Au layer in contact with the lifted-off LED, and then remove it slowly (see Figure 6.11(b)). The picked up free-standing LED is then electrically probed for device characterization.

To complete the proof of concept demonstration of the lift-off process using PEsC etching, we fabricated a lifted-off blue LED with similar structure. Figure 6.12(a) shows a micrograph of the cross shape structure LED placed on Au coated glass substrate. The lifted-off blue LED EL emission is presented in Figure 6.12(c), and shows a typical blue LED peak wavelength emission around 447 nm. The blue shift with increasing current injection (Figure 6.12(c)) is due to the band filling and quantum confinement stark effect. When compared to the bulk LED, the EL peak of the lifted-off LEDs is red-shifted by ~8 nm (Figure 6.12(d)), it is believed that this shift is due to the relaxation of the biaxial strain or the local heating [40]. Figure 6.12(e) shows the measured V-I characteristics of the cross-structure blue LEDs on Au/glass substrate. Due to the vertical current injection and the reduced path of current flow, the series resistance in the lifted-off blue LED is reduced compared to the bulk LED. Additionally, we observed a very significant decrease in the turn-on voltage from ~3.9 V to ~2.7 V, likely due to formation of improved Ohmic contact between the lifted off LED with the gold layer on PDMS, a lower series resistance and the reduced polarization in the active region [118]. It is noted that, the turn voltage for the blue LED is much lower than in the green LED, this can be explained by the uniform surface at p-contact in the blue device and the rough
surface in the green contact, as explained previously the non-uniform Ohmic contact increases the turn on voltage.

Further improvement of the device parameters can be observed in the L-I curve in Figure 6.12(f). As explained previously, heat dissipation is decreases in the freestanding micro-LEDs due to the current spreading in the transferred devices on gold surface [22]. The deposited Au layer on glass wafer serves as a heat sink that can improve the micro-LED performance. With better heat dissipation, the lift-off LED can withstand higher current injection. As shown in Figure 6.12(f), at higher injection current (3 mA), the lifted-off LED has a higher output power due to heat generation and current crowding effect in the bulk LED. The small sidewall roughness of the lifted-off blue LEDs after BI-PEsC observed in the SEM in Figure 6.11(a) helps to enhance the extraction efficiency leading to higher emitting intensity, moreover narrow escape cones for sidewall light extraction due to the flat surfaces in the bulk LED limit the output light intensity.

### 6.4 Summary Notes

In summary, this chapter demonstrated and explained the highly selective etching mechanism of a novel technique based on back-illumination PEsC (BI-PEsC) of undoped GaN for lifting off green LEDs and blue LEDs grown on sapphire substrate. This is achieved without resorting to growing lattice-mismatched InGaN sacrificial layer (a purely bandgap selective process), while still able to selectively etch undoped GaN over n-doped GaN contact layer (bandgap and doping selective
process), which has not been demonstrated to date, thereby preserving crystal quality, achieving full device functionality, and simplifying batch device processing. The proposed model for etching process mechanism unveils the reason for high etching selectivity of undoped GaN over n-GaN and InGaN. Free-standing 60µm x 60 µm cross shape blue and green LEDs were fabricated after selective etching of undoped GaN. LED device characterizations of the lifted-off LEDs showed ~10 times increase of optical output power, 2 times decrease of series resistance and a lower turn on voltage than the bulk LEDs. With this new technology LEDs are no more constraints by their bulky substrate wafers and no longer confined rigidly in conventional epitaxial matrix but can be transferred to a variety of substrates. This could bring forth new optoelectronics device configurations such as pixelated RGB display formation on flexible transparent substrates. This technique is also applicable in biotechnology systems and wearable electronics.
7 CONCLUSIONS AND OUTLOOK

7.1 Conclusions

A model describing the mechanism kinetics was presented to explain the process of PEsC etching. Using this technology we demonstrated the fabrication of strain relaxed porous GaN for subsequent growth of fully relaxed GaN epitaxy materials. After annealing of the porous structure we observed a significant strain relaxation of 0.41 ± 0.04 GPa. A linear relationship between the PL photon energy and the biaxial strain is derived. Strain releaved porous GaN is an attractive alternative for regrowth on lattice mismatched non-native substrates.

Using PEsC etching we fabricated GaN nanowires with lengths ranging from nm scale to 20 µm. These nanowires were transferred on different substrates. PL and morphological results confirmed the oxidation and the formation of amorphous structure on the nanowires; this led to the formation of nanocrystallites which are responsible of quantum confinement. GaN nanowires are compatible with existing III-nitride based LEDs, using pick-and-place technique or ink jet we can coat the surface of LEDs with nanowires to increase the extraction efficiency.

GaN nanoparticles with size dispersion between 10nm to 100nm have been fabricated using the PEsC etching method. The power dependent PL showed a large emission wavelength tunability of ~530 meV from the nanoparticles. Morphological results showed oxidation on the surface resulting from the etching. We demonstrated that this
large tunability is due to the localized potential fluctuation, surface effects and heating. These fabricated oxide encapsulated GaN nanoparticles can be used as phosphor for the tunable color-temperature white LED application.

Leveraging on our etching knowledge of GaN, we applied the PEsC etching on InGaN layer grown on GaN on sapphire. To separate the InGaN layer from the substrate, micro-fabrication was necessary to define 10 μm columns in order to reveal the GaN. High GaN/InGaN etching selectivity of 100/1 and lateral GaN etching of 5 μm/min was achieved using this PEsC etching technique. We explained the electron-hole transfer mechanism in details during the etching process and the bandgap selectivity. Free standing InGaN microdisks with different indium compositions were fabricated. Optical characterizations unveiled the strain relaxation of the lifted-off InGaN microdisks and the broad spectrum coverage. Microdisks were then transferred on blue LEDs for optical pumping. This process offers promising approach for pixelated RGB InGaN phosphor material, and a new integration platform for heterogeneous inorganic nanomembranes applications.

In the last part, we demonstrated the novel epitaxy lift-off technique to separate III-nitride structure grown on sapphire substrate simply by selectively etching the unintentionally doped GaN buffer layer. Back-illumination PEsC etching was performed taking advantage of the diffusion limited process to selectively etch the u-GaN sacrificial layer. Free standing 60μm x 60 μm cross shape high brightness blue and green LEDs were fabricated and transferred on flexible transparent
substrate and a glass substrate. Device characterization of the transferred vertical LEDs showed improvement when compared to the bulk lateral LEDs. We observed increase of optical output power, and decrease of series resistance and turn on voltage; we related this improvement to the extraction efficiency by roughening the sidewalls, the current crowding, and heat dissipation. This promising etching technique is achieved without resorting to growth of additional non-conventional sacrificial layer, while still able to selectively etch u-GaN over n-GaN, thereby preserving crystal quality, and simplifying batch device processing. This new technology offers promising approach for pixelated RGB display formation, and a new integration technology platform for optoelectronic and electronic integrations on any flexible or solid substrates. In addition, this technique will also enable many new applications for sensors, wearable electronics/optoelectronics and biomedical applications.

### 7.2 Outlook and Applications

In this work, we presented novel techniques to transfer III-Nitride semiconductor micro and nano structures onto different substrates. These techniques are expected to impact many diverse applications including: (i) crystal regrowth of relaxed GaN epitaxy on porous structure, (ii) printed nanostructures on LED flat surface for increased light efficiency and tunable color temperature, (iii) phototherapy, spectroscopy, sensors and biomedical applications such as blood oxygenation,
accelerated healing, and highly localized photodynamic drug delivery, and (iv) flexible RGB display.

(i) Having studied the biaxial strain relaxation in the PEsC etched porous GaN layer after annealing, it would be interesting to study the regrowth of the GaN layer on this relaxed porous structure. High quality GaN based optical devices can be overgrown using MBE and MOCVD. The overgrown layer is expected to replicate the underlying strain but also the dislocation sites might reduce and coalesce [119]. It is noted that the preparation of such substrate is important, extra sonication steps might be needed to have a more homogenous porous layer. Also a better uniform light illumination during the PEsC etching can improve the morphological porous distribution on the sample. In addition, it might be interesting to explore the effect of annealing on the processed porous GaN under different ambient gases.
(ii) High-throughput ink-jet printing technique has proven to be very useful in flexible electronic organic-devices [120]. Considering the properties of the process high density GaN NPs and NWs (e.g. material compatibility with III-nitride based LEDs, chemical stability, longer lifetime compared to organic materials, wide bandgap, high carrier mobility and small footstep) it would be interesting to study the optical properties of transferred nano structures on different substrates, as depicted in Figure 7.1. Ink-jet printing techniques could be used to transfer these particles on large area flat surface LEDs for extraction efficiency study. Also, GaN NPs could be embedded in the epoxy dome or in a PDMS layer on top of the LED for tunable color temperature device to replace the blue phosphor. In addition, the biocompatibility of the GaN has opened up the possibility for biotechnology application [121]. These nanowires can be integrated in metal-oxide field-effect-transistors (MOFET) for DNA sensing [122].
(iii) In addition, the nontoxicity and chemical robustness of III-nitride materials render it a suitable material for biomedical applications [1]. Future application of lifted-off micro-LEDs can be used in in-situ optical mapping of tissue, tumors and cardiovascular disorders [123, 124]. Also spectroscopy characterization of arterial tissue represents other possibilities [125]. The selective etching of u-GaN led to the separation of good quality device structure, this is useful in many other diverse applications such as sensors which require high brightness LEDs. Vertical transferred III-nitride structures can also be used as photo-detectors if driven under reverse bias. It might be interesting to fabricate simple structures (with electron blocking layers), and transfer them onto flexible substrate, co-integrate LEDs and photo-detectors on the same substrate simple by driving the first one under forward bias and the second one under reverse bias. The fabrication process can be improved to have an array of LEDs on flexible PDMS substrate, by: (1) mechanical stamping to remove the lifted-off structures from the sapphire substrate, (2) transferring them onto flexible surface covered with a n-contact mesh, (3) coating with photoresist epoxy, (4) and defining opening of the p-contact using lithography step and metal deposition. As depicted on the illustration in Figure 7.2, the array of LEDs and photo-detectors can be placed facing each other in artery for blood discrepancy level detection.

(iv) The novel epitaxial lift-off technique presented in this work can achieve higher efficiency compared to organic LEDs and LEDs lifted-off using LLO technique or
sacrificial foreign substrate. We already observed lower turn-on voltage in lifted-off blue LED compared to the bulk and green LED, this is due to the blue LED flat p-type surface. Further improvement of the lifted-off green LED by improving the fabrication process, including thermal annealing of p- and n- contact, improving the carrier transport in the contact layer using tunneling junctions, flattening the p-type surface for better Ohmic contact and controlled roughening of sidewalls after etching to increase extraction efficiency, could greatly enhance the lifted-off green LED efficiency. Using selective pick and place techniques with an automated printing machine, we can obtain interconnected arrays of green and blue micro-LEDs on the same substrate, combined with the existing technology to lift-off red AlInGaP LEDs [112], we can obtain pixelated RGB display and next generation wearable tattoos.
APPENDICES

A.1 Processing scheme for InGaN microdisks:

This process and its results are described in section 5.2:

**Dry etching:**

1. Grow thin InGaN layer on GaN on sapphire.
2. Clean the InGaN wafer (sonication in acetone for 5 min, sonication in isopropyl alcohol (IPA) for 5 min).
3. Spin-coat photoresist (PR) (ECL3027, 1750 rpm, 60 sec) and soft-bake at 100°C for 1 min.
4. Expose with 365 nm optical lithography through chromium mask for 200 mJ. (Define columns- see Figure A.1).
5. Develop in AZ726 for 60 sec.
6. Etch with ICP-RIE (10 mTorr, Ar 3 sccm, Cl₂ 15 sccm, RF 100W, ICP 500W) vary time between 1min to 5min is needed to expose the GaN (sacrificial layer) underneath the InGaN layer. Etch rate is ~ 200 nm.

**Pt deposition:**

7. Plasma-sputter coat 10 nm of Pt (20 mA, 1 min).

**PES etching:**

8. Sonication in Acetone for 1 min to remove photoresist and lift-off Pt on the micro-columns, then rinse with IPA.
9. Submerge the sample in HF/CH₃OH/H₂O₂ (2:1:2), such that illumination is directed towards the InGaN from the top.
10. Illuminate with Mercury lamp at 750W for 10 min to 20 min (depends on the size of the micro-columns).
11. Very fast remove the sample from the HF solution and transfer to an IPA solution.
12. Dry the sample using the CPD.
Lift-off:

13. Lift-off using a flat PDMS stamp formed by mixing base: curing agent 10:1, followed by thermal annealing at 100°C for 2 hrs.
14. Manually bring the PDMS stamp in contact with the under etched LED structure.
15. Remove very fast the laminated PDMS such that the LEDs are peeled from the sapphire substrate and inked to the flexible substrate.

*Figure A.1 Mask used in step number 4 to define 10 µm microcolumns*
A.2 Processing scheme for LED lift-off using polymer to protect sidewalls from HF attack:

This process and its results are described in section 6.2.2:

Dry etching:

1. Clean the LED wafer (sonication in acetone for 5 min, sonication in isopropyl alcohol (IPA) for 5 min).
2. Spin-coat photoresist (PR) (ECL3027, 1750 rpm, 60 sec) and soft-bake at 100°C for 1 min.
3. Expose with 365 nm optical lithography through chromium mask for 200 mJ. (Define internal columns- see Figure A.2).
4. Develop in AZ726 for 60 sec.
5. Etch with ICP-RIE (10 mTorr, Ar 3 sccm, Cl2 15 sccm, RF 100W, ICP 500W) for 2 min to reveal the n-GaN. Etch rate is ~ 200 nm.
6. Sonication in Acetone for 1 min to remove photoresist, then rinse with IPA.

Second dry etching:

7. Deposit 2 µm of perylyne to protect the sidewalls.
8. Spin-coat photoresist (PR) (ECL3027, 1750 rpm, 60 sec) and soft-bake at 100°C for 1 min.
9. Expose with 365 nm optical lithography through chromium mask for 200 mJ. (Define external columns- see Figure A.2).
10. Develop in AZ726 for 60 sec.
11. Etch with ICP-RIE (10 mTorr, Ar 3 sccm, Cl2 15 sccm, RF 100W, ICP 500W) for more than 10 min to reveal the u-GaN. Etch rate is ~ 200 nm.

Pt deposition:

12. Plasma-sputter coat 10 nm of Pt (20 mA, 1 min).

PEsC etching:

13. Submerge the sample in HF/CH₃OH/H₂O₂ (2:1:2), such that illumination is directed towards the p-type from the top.
14. Illuminate with Mercury lamp at 750W for 10 min to 20 min (depends on the size of the micro-columns).

*Figure A.2 Green mask used first to define internal circles for lithography step, after etching the microcolumns a second mask (red) defines the external circle that will protect the sidewalls from HF etching*
A.3 Processing scheme for flexible green and blue LED:

This process and its results are described in chapter 6:

Dry etching:

1. Clean a green or blue LED wafer (sonication in acetone for 5 min, sonication in isopropyl alcohol (IPA) for 5 min).
2. Deposit 5 nm/5 nm of Ni/Au by electron beam evaporation.
3. Anneal at 550°C in atmospheric ambient environment.
4. Deposit 1 µm of SiO$_2$ using PECVD.
5. Spin-coat photoresist (PR) (ECL3027, 1750 rpm, 60 sec) and soft-bake at 100°C for 1 min.
6. Expose with 365 nm optical lithography through chromium mask for 200mJ. (Define cross-structure—See Figure A.3).
7. Develop in AZ726 for 60 sec.
8. Etch with ICP-RIE (10 mTorr, Ar 3 sccm, Cl$_2$ 15 sccm, RF 100W, ICP 500W) more than 20 min is needed to expose the u-GaN (sacrificial layer) underneath the LED structure. Etch rate is ~ 200 nm.
9. Sonication in Acetone for 1 min to remove photoresist, then rinse with IPA.

Pt deposition:

10. Plasma-sputter coat 10 nm of Pt (20 mA, 1 min).

PEsC etching:

11. Submerge the sample upside-down in HF/CH$_3$OH/H$_2$O$_2$ (2:1:2).
12. Illuminate with Mercury lamp at 750W for 10 min.
13. Very fast remove the sample from the HF solution and transfer to an IPA solution.
14. Dry the sample using the CPD.

Lift-off:

15. Lift-off using a flat PDMS stamp formed by mixing base: curing agent 10:1, followed by thermal annealing at 100°C for 2 hrs.
16. Transfer to 100 nm Au mesh on plastic sample.
17. Manually bring the PDMS stamp in contact with the under etched LED structure.
18. Remove very fast the laminated PDMS such that the LEDs are peeled from the sapphire substrate and inked to the flexible substrate.

Figure A.3 Mask used in step number 4 to define microLED structures in a plus sign shape 60 µm × 60 µm
A.4 Schematic illustration of light escape cone in different LED schemes

Figure A.4 Schematic illustration of (a) light escape cone in bulk LED semiconductor, (b) mesa structure in LED semiconductor, sidewall emission, and (c) Nanowire on top of the p-type surface increase the extraction efficiency by increasing the escape cones for light.
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