



Ph.D. Dissertation

#### Fabrication of high efficiency micro-lightemitting diodes and its application to light-activated gas sensors

#### 고효율 마이크로 엘이디의 제작과 마이크로 엘이디를 응용한 화학저항식 가스 센서

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#### Fabrication of high efficiency micro-lightemitting diodes and its application to light-activated gas sensors

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Abstract

## Fabrication of high efficiency micro-light-emitting diodes and its application to light-activated gas sensors

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A paradigm change in the field of displays has occurred as a result of technological advancement. Demand for low-power technology has increased due to rising global power consumption. In addition, displays are required to be of high resolution, high stability, and small size for various applications, including ultrahigh-definition displays, head-up displays, flexible or wearable displays, augmented reality, virtual reality, and mixed reality displays. Conventional display technologies such as liquid crystal displays (LCD) or organic light-emitting diodes (OLED) are not appropriate for such applications, since LCDs suffer from narrow viewing angles, high energy consumption, and the necessity for backlight units, whereas OLEDs also have narrow viewing angles and low environmental stability. Consequently, as the nextgeneration display technology, micro light-emitting diodes (micro-LEDs have drawn considerable interests from academia and industry. To meet the increasing demands of displays, researchers and companies are focusing on micro-LEDs.

Micro-LED technology has been developing ever since it has been first introduced by professor Jiang in the early 2000's. Many researchers from institutes and companies tried to implement displays using micro-LED technology. A passive matrix display was first attempted, followed by an active matrix display and a full color display using micro-LED. Recently, several companies have released large-area micro-LED TV. Micro-LEDs are utilized not only in displays but also in various fields. Owing to its small configuration and high stability, various studies are being conducted to apply the micro-LEDs in the bio-electronic filed, such as neuron stimulation, or smart contact lens. However, there are still technical issues in realizing micro-LED display. Micro-LEDs are normally fabricated by etching a LED film into micron scale. As the size of each chip decreases, the etching loss increases, affecting the production cost. Moreover, it is found that the dry etching process damages the active layer of the LED, degrading the quantum efficiency of micro-LED devices. Furthermore, conventional transfer processes including laser lift-off or chemical lift-off techniques are costly and time-consuming for micro-LED application. Lastly, emission peak shift induced by quantum confined screening effect (QCSE) also could be a problem for a display device.

In this thesis, sapphire nano-membrane (SNM) technology has been introduced to solve the abovementioned issues. The fabrication process and consequent growth of micro-LEDs on it was investigated. The fabrication of SNM template was carried out through the following process. It started with photolithography to make photoresist (PR) pattern on a sapphire substrate. Then, an amorphous Al<sub>2</sub>O<sub>3</sub> layer with a thickness of 120 nm was deposited by atomic layer deposition. Second photolithography and wet

etching by H<sub>3</sub>PO<sub>4</sub> solution was conducted to make a discrete SNM array. After removal of PR using acetone, the template was annealed at 1100 °C for 2 hours in air to crystallize the amorphous Al<sub>2</sub>O<sub>3</sub> into single crystalline Al<sub>2</sub>O<sub>3</sub> through solid phase epitaxy. Micro-LEDs were grown on the SNM using metal organic vapor deposition (MOCVD). By controlling the space between the nanomembranes, micro-LEDs with various sizes and shapes could be obtained. Micro-LEDs grown on SNM template was in selfpassivated structure and showed enhanced properties including reduced internal strain and threading dislocation density, and enhanced internal quantum efficiency and photoluminescence intensity. The micro-LEDs were transferred to Si substrate using mechanical lift-off at 300 °C and under 10 kgf for eutectic bonding of Au-Sn alloy. The fabricated device showed enhanced leakage current level compared to the dry etched reference sample. Moreover, the micro-LED device grown on SNM showed almost no shift of emission wavelength even though the injection current was increased up to 100 A/cm<sup>2</sup>, while the dry etched reference sample showed significant peak shift. This is because of reduced QCSE screening of our sample, which is owing to the compliant substrate effect of SNM that reduced the internal strain of micro-LEDs grown on it.

Secondly, the crystallization process of SNM was investigated and utilized for novel selective area growth (SAG) of GaN. The crystallization of amorphous alumina to single crystalline sapphire was conducted through solid phase epitaxy (SPE). SPE starts at the interface between the single crystalline and amorphous layer since the activation energy of crystallization at the interface is lower than the random nucleation and growth (RNG) energy at the middle of amorphous layer. In addition to the SNM, homogeneous growth mask for GaN was invented using the energy difference between SPE and RNG, by depositing thick amorphous alumina on a sapphire. Growth of GaN on the sample started before the thick amorphous alumina was completely transformed into single crystalline, resulting in poly crystalline GaN islands instead of GaN film. By selectively depositing the thick amorphous alumina, selective area growth of GaN was accomplished. The selectively grown GaN array showed much faster growth rate compared to the

reference sample since the Ga adatoms were diffused to the exposed growth sites. Moreover, using the principles of crystallization of SNM and SAG of GaN, high efficiency hexagonal GaN array was fabricated. First, hexagonal shaped SNM was fabricated for growth of hexagonal GaN. By controlling thermal treatment time, crystallization of hexagonal SNM was stopped in the middle. Since GaN film was not grown on the region where the crystallization was not complete, selective growth GaN on the single crystalline region was achieved. GaN film grown on the outer hexagonal then grew inside laterally, filling the empty space. After growth of 90 minute, fully grown hexagonal GaN array was achieved. The hexagonal GaN showed reduced strain and TDDs since the threading dislocations were not generated at the laterally grown region.

For the application of micro-LEDs, light activated chemoresistive gas sensor was selected. Chemoresistive gas sensor is one type of gas sensor which detects the change of resistance according to the reaction with the target gas. Conventional gas sensors required external heater for activation of

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sensing material with the target gas, which induced complicated structure and high production cost of the device. To overcome the disadvantages of the conventional gas sensors, light activated gas sensors are investigated. Using the light activation principle with micro-LEDs, the device with lower power consumption can be fabricated with lower production cost. For such purpose, micro-LED platform for gas sensor application was fabricated with interdigitated electrodes (IDEs) on the micro-LEDs. SnO<sub>2</sub> nanoparticle was chosen for sensing material since it showed good responsibility and stability with high selectivity by metal doping or decorating. SnO<sub>2</sub> nanoparticle solution was drop casted on the micro-LED platform and sensing property to NO<sub>2</sub> was tested using gas sensing system. With increasing the light intensity, base resistance of the samples were decreased due to increased photogenerated electron-hole pairs. However, the response of the SnO<sub>2</sub> nanoparticle was reduced due to increased recombination of electron-hole pairs. Optimal value of light intensity was chosen considering the base resistance and response of the gas sensor. Under optimal light intensity, various gas sensing properties

including reliability, linearity, and detection limit was analyzed. Under blue light illumination, the sample showed constant base resistance and responsibility after 4 repeating pulses of NO<sub>2</sub>. In addition, the sampled showed a linear increase in response with an increase in the gas concentration. From the linear relation of the response and gas concentration, detection limit of the  $SnO_2$ nanoparticle sample was calculated to be 2.71 ppt, meaning that the sample can detect the NO<sub>2</sub> gas with such low value.

**Keywords:** Epitaxial growth, Micro-LED, Gallium nitride, Solid phase epitaxy, Metal-organic chemical vapor deposition, Gas sensor, Metal oxide, Nanoparticle

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#### **Chapter 1. Introduction**

#### 1.1 Micro-light-emitting diodes

With technological advancement, displays are required to be applied various technologies, including ultra-high-definition displays, head-up displays, flexible or wearable displays, augmented reality, virtual reality, and mixed reality displays.<sup>[1,2]</sup> For such purpose, each pixel that constituting the display should have extremley small configuration with high efficiency and stability. Conventional displays such as liquid crystal displays (LCDs) or organic light-emitting diodes (OLED) are not appropriate, as LCDs suffer from narrow viewing angles, high energy consumption, and the necessity for backlight units<sup>[3,4]</sup> whereas OLEDs also have narrow viewing angles and low environmental stability.<sup>[4]</sup> Micro-light-emitting diodes (Micro-LEDs) have been attracting interest of researchers from academics<sup>[5,6]</sup> and industries<sup>[7,8]</sup> with its extremely small size and superior properties over other displays. Micro-LEDs exhibit higher light extraction efficiency, better current spreading, and

lower self-heating effect than even conventional LEDs.<sup>[9-11]</sup> In addition, micro-LEDs possess other advantages, including a short response time, low power consumption, and high visible light communication performance<sup>[12–14]</sup> from an electrical point of view. They also have a limited wavelength shift, a minimal efficiency drop in high voltage applications, and high brightness and contrast in terms of the photoelectric aspect. Most importantly, owing to their inorganic nature, micro-LEDs have an extremely long lifetime of over 10 years and superior environmental stability compared with other technologies. The outstanding performance parameters of micro-LEDs over other displays are organized in Table 1.

First introduced by professor Jiang,<sup>[15,16]</sup> many studies were conducted to implement micro-LED displays as shown in **Figure 1.1**. The majority of research efforts were directed toward developing passive and active matrix displays, and ultimately, fullcolor displays. Recent studies have shown interests in achieving high quantum efficiency micro-LED and massive transferring the micro-LED chips onto backplane. In this thesis, obstacles that hinder the realization of micro-LED display will be discussed. Those include an increase in kerf loss, a decreased in quantum efficiency, time-consuming transfer technology, and emission wavelength shift with injection currents. To overcome the abovementioned issues, we proposed a novel growth template for micro-LED, called sapphire nano-membrane (SNM). Sapphire nano-membrane is an ultra-thin 3D structure created on a sapphire substrate. Using the SNM, a discrete array of micro-LED could be grown by metal organic chemical vapor deposition (MOCVD). A detailed fabrication method of SNM and growth of micro-LED on it will be discussed in Chapter 2 in this paper. Moreover, crystallization mechanism of SNM and growth behavior of GaN on it will be explained in Chapter 3.

In addition to the display technologies, micro-LEDs can be employed in a variety of applications owing to their superior properties mentioned above such as high stability and low power consumption, in addition to being extremely small. The possible applications include neuron stimulators<sup>[17–19]</sup> optical cochlear implants,<sup>[20,21]</sup> optoelectronic tweezers,<sup>[22,23]</sup> and mask-free

lithography.<sup>[24]</sup> In this thesis, light activated chemorerirtive gas sensor based on micro-LED platform will be introduced. Chemoresistive gas sensor is a type of gas sensor based on semiconducting materials such as metal oxides or 2-dimensional materials. The device operates by sensing a change in resistance according to a reaction with gas molecules. For activation of sensing material, conventional gas sensors used thermal activation technique. However, the thermal heating system required complex device structure and high operating temperature, which hindered the miniaturization and portability. The light-activated gas sensor, on the other hand, is regarded as a next-generation technology since it is produced easily, is highly mobile, and consumes very little power. A detailed fabrication method of micro-LED gas sensor platform and its gas sensing properties will be discussed in Chapter 4.

	LCD	OLED	Micro-LED
Energy consumption	Medium	Medium	Low
Pixel density	Up to 1000 PPI	Up to 2500 PPI	Up to 30,000 PPI
Brightness	$< 2000 \text{ Cd m}^{-2}$	$< 1000 \text{ Cd m}^{-2}$	$> 10^{6} \text{ Cd m}^{-2}$
Contrast ratio	5000:1	> 10000:1	> 1,000,000:1
Lifetime	Long	Medium	Long
Environmental stability	High	Medium	High
Flexibility	Low	High	Medium
Mechanism	Backlight & color filter	Self-emissive	Self-emissive
Pixel size	Min. 32 µm	Min. 18 µm	Min. submicron
Compactness	Low	Medium	High
Operation temperature	20 ~ 80 °C	$50 \sim 70 \ ^\circ \mathrm{C}$	100 ~ 120 °C
Response time	Low (ms)	Medium (µs)	High (ns)
Cost	Low	Low	High

#### Table 1. Comparison of LCD, OLED, and micro-LED properties.



Figure 1.1 Technological development of micro-LED technology

### 1.2 Technical issues and sapphire nano-membrane for micro-LED

Many researchers have tried to develop micro-LED displays, various obstacles exist for their industrial use. Micro-LED devices are commonly fabricated by microscale etching of an LED film. As the size of each chip decreases, the ratio of the etched area to the remaining area, which is also known as kerf loss, increases. Although the kerf loss may not seem to be significant, it actually affect the production cost of the micro-LED display since a single display requires up to millions of LED chips. Moreover, the microscale etching itself degrades the quantum efficiency of micro-LEDs. Due of the high bonding energy between Ga and N and the different reactivity of GaN based on its crystallographic orientation to the wet etchant, dry etching is generally used for manufacturing. The dry etching process is usually carried out under a very high DC bias to break the strong bond between the Ga and N atoms. This procedure damages and exposes the active layer of the micro-LEDs and causes severe defects. These defects, especially on the sidewalls of multiple quantum wells (MQWs),

act as Shockley-Read-Hall (SRH) non-radiative recombination sites and leakage paths, degrading the quantum efficiency of the device.<sup>[25–32]</sup> The degradation of quantum efficiency is not critical in large-dimension LEDs because of the relatively small ratio of the sidewall compared to the undamaged radiative facet. However, as the size of the LED chip decreases, the overall performance of the micro-LED declines significantly since the ratio of the damaged sidewall to the radiative surface increases. The effect of the size of micro-LEDs on the quantum efficiency is summarized in Figure 1.2. External quantum efficiency from various studies showed a similar trend: shrinking the pixel sizes decreased the efficiency of all, red, green, and blue, LEDs. The gradient changes in the external quantum efficiency (EQE) clearly indicate the stated size effect. The size effect of green and red micro-LEDs was smaller than that of blue micro-LEDs. This phenomenon can be explained by a slower surface recombination velocity, which results from an increase in carrier localization from alloy disorder as the indium content increases.<sup>[33]</sup> Additionally, the quantum efficiencies of green and red LEDs were noticeably lower than

those of blue LEDs, indicating that further advancement is required to achieve full-color displays. Many factors contribute to lower quantum efficiencies of green and red micro-LEDs. Those include increased defect densities caused by lower growth temperature and increased strain, QCSE, and Auger recombination due to carrier localization. The problem is more crucial for red micro-LEDs where the quantum efficiencies are the lowest of the three. Moreover, the conventional transfer process including laser lift-off or chemical lift-off techniques are costly and timeconsuming for micro-LED display. According to Yole report, it would take 41 days to assemble 24.9 million individual micro-LED chips to fabricate a single 4 K display using traditional pickand-place technology. Lastly, conventional c-plane micro-LEDs suffer from wavelength and color instability caused by QCSE screening effect, which appears as a severe wavelength blue-shift with increasing optical excitation or electrical injection. Much effort has been made to develop nonpolar/semipolar III-nitride optoelectronics, but it has not been able to develop technologies with high efficiency and low prices. The covered issues in microLED technology is well organized in Figure 1.3.

To overcome the technical issues, a growth template called sapphire nano-membrane (SNM) has been introduced.<sup>[34]</sup> The 3D structured sapphire template fabricated using was photolithography, ALD, and solid phase epitaxy. As shown in Figure 1.4, discrete micro-LEDs can be grown without dry etching process with the SNM. Moreover, the grown micro-LEDs would form a self-passivated structure, owing to the different growth rates of GaN according to the growth facet. In addition, the ultra-thin structure of sapphire serves as a compliant substrate, reducing the internal strain of the GaN grown on it.<sup>[34]</sup> The effect of compliant substrate is explained in Figure 1.5. Lastly, micro-LEDs grown on the SNM can be easily transferred onto target substrate by simply breaking the legs of SNMs. The transferred micro-LEDs were fabricated into an operating device through post-process. The micro-LED device showed enhanced property compared to the dry etched reference sample. Based on these facts, SNM can be a multi-purpose growth template for micro-LEDs.

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Figure 1.2. External quantum efficiency trends depending on LED size



Figure 1.3 Technical issues in realization of micro-LED display.



Figure 1.4. Growth of discrete micro-LED array on sapphire nanomembrane



Figure 1.5. Strain in epilayers and substrate versus layer thickness ratio.

# **1.3 Crystallization of sapphire nano-membrane and growth of GaN on SNM.**

Sapphire nano-membrane is an ultra-thin 3D structure of single crystalline Al<sub>2</sub>O<sub>3</sub>. It is fabricated by patterning a photoresist by photolithography, followed by deposition of amorphous alumina using atomic layer deposition (ALD). Second photolithography and wet etching by phosphoric acid is conducted to separate the sapphire nano-membranes into discrete growth template. The photoresists are then removed by dissolving them into acetone. The amorphous alumina is then crystallize into single crystalline sapphire by thermal treatment.<sup>[34]</sup> During the thermal treatment, the amorphous alumina experience phase change to y-phase alumina and then to  $\alpha$ -phase alumina<sup>[42]</sup> as shown in Figure 1.6 The crystallization mechanism of amorphous alumina can be categorized into 2 types, which are random nucleation and growth (RNG) and solid phase epitaxy (SPE). The major crystallization mechanism of SNM is SPE, which the crystallization follows the ordered crystal information of the substrate. Through the SPE, amorphous alumina can be crystallized into single crystalline

sapphire which is the same as the substrate.

Utilizing the crystallization mechanism, homogeneous growth mask can be achieved. Since the SPE takes place near the interface between the substrate and the amorphous layer and the RNG takes place random location among the amorphous layer, partial crystallization of amorphous alumina is possible. Poly crystalline GaN grows on the poly crystalline y-phase alumina layer, not forming a GaN film. Growth rate of the poly crystalline GaN region is extremely slow, whereas the Ga adatoms diffuse to fast growth rate region which is a single crystalline sapphire. Using this principle, the partially crystallized alumina layer can be used as a homogeneous growth mask for selective area growth of GaN. This homogeneous growth mask can be advantageous since it does not induce any contamination from other materials such as Si. Moreover, using the partial crystallization principle, partially crystallized hexagonal SNM was fabricated, which can be utilized in growing high quality GaN by inducing lateral growth. The shape of the high quality GaN was determined to be hexagon for high density growth of GaN crystals. Hexagonal shaped GaN also
can be beneficial for display applications, in case of creating curved images. The partially crystallized SNM template induced lateral overgrowth of GaN using the mechanism of selective area growth. Single crystalline GaN only grew on the completely crystallized region of the SNM template, which in single crystalline α-phase alumina. Meanwhile, poly crystalline GaN grew on the  $\gamma$ -phase alumina layer. GaN crystals grown on the fully crystallized region grew laterally as the growth proceeded. The laterally grown hexagonal GaN array showed improved crystal quality. Internal strain and threading dislocation density were reduced and PL intensity was improved with improved FWHM value. The improved quality of GaN is owing to the dislocation bending as the lateral overgrowth of GaN.<sup>[42]</sup> Therefore, understanding crystallization mechanism and growth behavior of GaN can lead to a growth of high quality GaN film.



Figure 1.6. Crystallization of amorphous alumina sapphire nanomembrane.

### **1.4 Application of micro-LED: light activated gas sensor**

majority of studies on micro-LEDs have been on The implementing display technology. However, micro-LEDs are not limited to the field of display, but can be used in various applications. One of the possible application is light activated chemoresistive gas sensor. Chemoresistive gas sensor utilizes semiconducting materials such as metal oxides or 2-dimensional materials to detect the gas molecules in the air. The device measures the resistance of the sensing material deposited on electrodes and senses the change of the resistance as the sensing material react with the target gas molecules. Conventional chemoresistive gas sensors required a heating unit, to activate the sensing materials for reaction with the target gas. However, such device demanded complicated structure and high operating temperature. These factors served as barriers to gas sensors being more portable and miniaturized. To overcome the disadvantages, light-activated gas sensor mechanism was proposed. Using the light energy as an activation source of semiconducting materials, the light-activated gas sensor can be produced with low cost and

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operated with extremely low power consumption.

SnO<sub>2</sub> was chosen for semiconducting sensing material since it showed good responsibility to target gases.<sup>[43]</sup> In addition, SnO<sub>2</sub> can be fabricated into various structures which makes the surface control easy. Moreover, through doping the bandgap of the SnO<sub>2</sub> can be engineered. SnO<sub>2</sub> was synthesized into nanoparticles since it has the high surface area. The light emitted from the micro-LED activated the  $SnO_2$  nanoparticle to react with the target gas. By generating electron-hole pairs in the SnO<sub>2</sub> nanoparticle, the light illumination reduces the resistance of the device. Exposure to the target gas, the photo-generated electron-hole pairs react with the gas, inducing a change of resistance. The gas sensor is driven by detecting the change in resistance. Using the micro-LED platform, gas sensor with small configuration and extremely low power consumption can be fabricated.

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# Chapter 2. Fabrication of high efficiency, selfpassivated micro-light-emitting diodes

### **2.1 Introduction**

Micro-LED displays are emerging displays with a lot of potential advantages over conventional display technologies. They are new displays with high pixel density, high brightness, superior stability, low energy consumption and most importantly, no limitation in size, capable of covering from micro-displays for AR/VR/MR to large area displays for consumer TV. Recent demonstrations by companies and institutes shows that development of micro-LED technology is in progress. However, further research is needed before they are commercialized. The current micro-LED fabrication process contains singluation of LED film into micro-scale using plasma etching. During the etching process, the active layers are inherently damaged, resulting in degradation in quantum efficiency. Another obstacle is the unacceptable loss of LED film known as kerf loss. The mentioned

problems become more crucial as the chip size shrinks, affecting the cost of the micro-LED displays. It is highly desired to establish a scheme to fabricate high-efficiency micro-LEDs without a singulation process.

To fabricate micro-LEDs with self-passivated structures, we proposed a unique growth template called sapphire nanomembrane (SNM).<sup>[1]</sup> The SNMs are 3D bridge structures consisted of 100 nm thick single crystalline  $Al_2O_3$ . The fabrication process of the SNM array started with photolithography to make photoresist (PR) pattern on a sapphire substrate. Then, an amorphous Al<sub>2</sub>O<sub>3</sub> layer with a thickness of 120 nm was deposited by atomic layer deposition. Second photolithography and wet etching by H<sub>3</sub>PO<sub>4</sub> solution was conducted to make a discrete SNM array. After removal of PR using acetone, the template was annealed at 1100 °C for 2 hours in air to crystallize the amorphous Al<sub>2</sub>O<sub>3</sub> into single crystalline Al<sub>2</sub>O<sub>3</sub> through solid phase epitaxy.

An array of discrete micro-LEDs surrounded by a major (0001) plane, and  $\{11\overline{2}0\}$  and  $\{1\overline{1}01\}$  planes at sidewalls was grown on SNM template using MOCVD. Self-passivated structure of the

fabricated micro-LEDs, with MQWs sandwiched between n-GaN at the core and p-GaN at the outer shell, were confirmed with TEM and STEM. The size of micro-LEDs was controlled by adjusting the width and space of the SNM array. By placing several SNMs closely, larger micro-LEDs were obtained via lateral overgrowth and merge of the GaN. Structural and optical properties of the fabricated micro-LEDs were analyzed to confirm the compliant substrate effect of the SNM. Micro-Raman spectroscopy result showed reduced strain on the GaN and consequent reduction of threading dislocations were confirmed with panchromatic CL analysis. Micro-PL result showed improved internal quantum efficiency and spatially resolved CL analysis showed different spectrums emitted from various facets.

After the growth of LED structures, p-contact metal was formed using e-beam evaporation followed by flip-chip bonding to a target substrate with an electrode array. Utilizing ultra-thin profile of the SNM, micro-LED array was massively transferred to the target substrate via mechanical lift-off process. The micro-LEDs showed improved electrical properties with lower leakage current level compared to dry-etched micro-LEDs. Moreover, our devices showed reduced quantum confined stark effect with negligible wavelength shift depending on the current density change. We assume that it is due to relaxed strain which resulted in reduced band bending. The improved properties were observed regardless of the chip size, implying that the size effect problem in micro-LED display could be controlled using the SNM technique. We believe that results presented in this work would provide a significant step towards the commercialization of micro-LED displays.

### 2.2 Experimental procedure

# 2.2.1 Fabrication of sapphire nano-membrane template and growth of micro-LEDs on it

Fabrication of sapphire nano-membrane template starts with forming a stripe pattern on the sapphire substrate using photolithography. Then, amorphous alumina with a thickness of

120 nm was deposited on it at low temperature of 110 °C to protect the photoresist using ALD. Next, second photolithography and wet etching using phosphoric acid was conducted for separation of each nano-membranes. The photoresist was removed by dipping the sample into acetone. Finally, thermal treatment at 1100 °C was conducted in air to crystallize the amorphous alumina into single crystalline sapphire using solid phase epitaxy. Consequent growth of GaN and full LED structures were conducted on the SNM template using MOCVD. The growth of GaN was conducted under condition of 1040 °C and 300 torr for 40 minute. The growth conditions and time were optimized to prevent GaN grown at the bottom from merging to the GaN grown on top of the membranes. Consequent LED structures were grown under following conditions; n-GaN was grown at 1030 °C and 400 torr for 10 minute; Superlattice layer consist of 15 periods of InGaN and GaN layer and multiple quantum well layer consist of 3 periods of InGaN and GaN layer was grown at 850 °C and 250 torr; Last p-GaN layer was grown at 900 °C and 300 torr. The overall fabrication process of SNM and consequent growth of micro-LED

array is shown in Figure 2.1.

In addition, micro-LEDs with various sizes and shapes can be obtained by controlling the space between the nano-membranes. With closely placed, GaN crystals discretely grown on the SNM merges with each other, forming a one single crystal GaN. After the merge process, a single structure of micro-LED was obtained. It is named multi-membrane and the overall process is shown in **Figure 2.2**. As shown in Figure 2, micro-LEDs with size of 20 x 20, 40 x 40, 100 x 100, and 35 x 50  $\mu$ m<sup>2</sup> was grown using various types of multi-membrane template.



Figure 2.1. (a) Schematic of fabrication process of SNM template. (b) SEM images of fabricated SNM template. SEM images of (c) GaN array and (d) LED array grown on the SNM template.



Figure 2.2. (a) Schematic of fabrication process of multimembrane template. (b) SEM images of fabricated multimembrane templates and micro-LEDs grown on it.

### **2.2.2 Characterization**

The fabrication of SNM array and the growth of micro-LED array were observed by field emission scanning electron microscope, Hitachi S-4800. Raman spectra were taken from a LabRAM HV Evolution system using a 633 nm laser to analyze the stress states of un-doped GaN layers. Temperature-dependent and room temperature PL were measured by Dongwoo Optron micro-PL system with a 325 nm He-Cd laser to analyze the optical properties. Cross-section TEM images of the micro-LEDs on SNM were observed by Titan G2 80-200. Cross-section STEM measurements were also conducted to observe the self-passivated micro-LEDs at all facets. TDD, monochromatic CL images, and spatiallyresolved CL spectra from each facet of micro-LEDs were analyzed by Gatan Mono-CL4 with an acceleration voltage of 5 kV at room temperature.

#### 2.3 Results and discussion

### 2.3.1 Structural and optical properties of single micro-LED

The un-doped GaN and micro-LEDs grown on the SNM were analyzed using various measurements. To investigate the stress level of the un-doped GaN grown on the SNM, micro-Raman spectroscopy was conducted. Figure 2.3 shows Raman spectra from a free-standing GaN, un-doped GaN on a SNM, and an undoped GaN film on a thick planar sapphire substrate. Micro-Raman spectroscopy were carried out at two positions for in-depth investigation on the stress variation in the un-doped GaN on SNM. Each positions are GaN grown on the SNM (indicated by green dot) and laterally grown GaN (indicated by blue dot), respectively, as shown in inset of Figure 2.3. The peaks of  $E_2$ -high mode were observed at 568.4 cm<sup>-1</sup> from GaN at both positions, and at 570.6 cm<sup>-1</sup> for GaN grown on planar sapphire substrate. The residual compressive stresses in the un-doped GaN grown on SNM and planar sapphire substrate were calculated to be 139 MPa and 651 MPa, respectively, considering the stress coefficient of GaN (4.3

cm<sup>-1</sup>/GPa)<sup>[3]</sup>. Although the stress relaxation of 78.6% was relatively lower than the result from our previous results (95.7%) for ultra-thin (26nm) SNM,<sup>[4]</sup> considerable stress relaxation was observed.

Figure 2.4 shows panchromatic CL images from the micro-LEDs grown on SNM and the reference sample, respectively. The green boxes in Figure 2.4(a) indicate the locations of the SNMs under the micro-LEDs. Using the panchromatic CL measurement, threading dislocations, which were shown as black dots, could be observed. The threading dislocations are generated due to lattice misfit between sapphire and GaN. They are generated when the epitaxial layer thickness increases beyond the critical thickness. As the thickness of substrate decreases, the lattice mismatch strain in epitaxial layer dramatically decreases due to strain partitioning. Such substrate is called compliant substrate. The ultra-thin nanomembrane served as a compliant substrate and shared the part of strain in the epitaxial layer and effectively reduced the generation of misft dislocations at the GaN/nano-membrane interfaces,<sup>[4]</sup> leading to less defective GaN and resultant reduction of TDD in

the epitaxial layer.<sup>[5,6]</sup> TDDs from micro-LEDs in the green boxes were measured to be  $2.87 \times 10^8$  cm<sup>-2</sup> on average, which was reduced by 37.3%, compared to that from the reference sample of  $4.58 \times 10^8$  cm<sup>-2</sup>, as shown in **Figure 2.4(b)**. Meanwhile, nearly TDD-free regions were observed from the pendeo-epitaxy GaN regions owing to lateral propagation of threading dislocations.<sup>[7]</sup> Average TDD was measured to be  $1.85 \times 10^8$  cm<sup>-2</sup>, which was reduced by 59.6%, compared to the reference sample. Further reduction of TDD can be achieved by inducing more lateral growth of micro-LEDs on SNM.

**Figure 2.5** shows Arrhenius plots of the integrated PL intensity from both the micro-LED on SNM and the reference sample over the temperature ranges from 10K to 300K. The IQE was estimated from the PL intensity ratio measured at the range between 10K and 300K by assuming that the IQE is 100% at 10K.<sup>[8]</sup> The IQE of the micro-LED on SNM was calculated to be enhanced by a factor of 1.44, compared to the reference sample. The inset of the **Figure 2.5** shows room temperature PL spectra of the samples. About 3.3 times higher integrated PL intensity was observed from the microLED on SNM than that of the reference sample. The improvement in both IQE and room-temperature PL intensity was attributed to the stress relaxation and reduced TDD in the micro-LEDs grown on SNMs. The PL peak position from the micro-LED on SNM was red-shifted by 0.12 eV, compared to that from the reference sample. The red-shift could be caused by the higher indium incorporation of the InGaN wells,<sup>[9,10]</sup> whose growth temperature was slightly lower than intention due to existence of the cavity under the SNM. Relaxed strain of GaN also can be responsible for higher indium incorporation of the InGaN wells. Using the SNM array, both blueshift induced by reduction of quantum-confined Stark effect (QCSE) and the red-shift due to higher indium incorporation were superimposed. The apparent PL red-shift indicates that the higher indium incorporation was dominant in this work. The PL full width at half maximum (FWHM) from the micro-LEDs on SNMs and the reference sample were measured to be 0.17 eV and 0.10 eV, respectively. The origin of the larger FWHM of micro-LED on SNM will be explained later.

To observe the internal structure of micro-LED on SNM,

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transmission electron microscopy (TEM) analysis was conducted. Figure 2.6(a) shows a cross-section TEM image of a single micro-LED viewed along  $[1\overline{1}00]_{GaN}$  direction. We found that a discrete micro-LED was grown on a SNM without merging with the GaN grown on the bottom substrate. The magnified scanning TEM (STEM) images in Figure 2.6(b,c) confirmed that p-type GaN layer and the InGaN/GaN MQWs were formed on all polar and semi-polar facets, implying the formation of a self-passivated structure. The red lines in insets of Figure 2.6(b,c) indicate the positions where cross-section images were taken. It was worth noting that thicknesses of MQWs on (0001) plane near the edge gradually decreased toward sidewalls of  $\{11\overline{2}2\}$  and  $\{1\overline{1}01\}$ , as shown in Figure 2.6(b,c). The broader PL spectrum from the micro-LEDs on SNMs discussed before can be explained in terms of inhomogeneous indium composition and variation in thickness on (0001) facets. Professor Funato's study also support these explanation with their research which inhomogeneous indium distributions were found in MQWs grown on (0001) facets in the micro-structures with semi-polar and non-polar facets.<sup>[11]</sup> Cross-

section STEM images of (0001),  $\{11\overline{2}2\}$ , and  $\{1\overline{1}01\}$  facets clearly show the growth rate differences depending on growth facets as shown in Figure 2.6(d-f). The thicknesses of InGaN wells were measured to be 3.01±0.13nm, 1.36±0.11nm, and  $1.35\pm0.15$  nm on (0001),  $\{11\overline{2}2\}$ , and  $\{1\overline{1}01\}$ facets, respectively. Figure 2.7(a-d) show plan-view SEM image, monochromatic CL images at 375 nm, 387 nm, and 435 nm, respectively, from single micro-LED on a SNM. The monochromatic CL measurements confirmed each emissions from all facets as shown in Figure 2.7(b-d). Emissions with shorter wavelengths were measured from the facets in order of  $\{11\overline{2}2\}$ ,  $\{1\overline{1}01\}$ , and (0001), in good agreement with the results in the literature.<sup>[11-14]</sup> The emissions at various wavelengths were attributed to the differences in growth rates and indium incorporation on each facet. In addition, the thinner InGaN quantum well in semi-polar facets reduces the QCSE and leads to an increased emission energy, which is consistent with the CL results. Points on each facet of the micro-LED in Figure 2.7(a) indicate positions where spatially-resolved CL measurement were

conducted, and the corresponding CL spectra were shown in Figure 2.7(e). Peak wavelengths of the spatially-resolved CL spectra from each facets were corresponded to the monochromatic CL measurement results shown in Figure 2.7(b-d). Two orders of magnitude stronger emission was observed from (0001) plane at 435 nm than that from semi-polar  $\{11\overline{2}2\}$  and  $\{1\overline{1}01\}$  planes. This result is different from emission properties of similar microsized light emitters with  $\{11\overline{2}2\}$ ,  $\{1\overline{1}01\}$ , and (0001) facets<sup>[14]</sup>. Hwang et al. reported superior optical properties from  $\{11\overline{2}2\}$ facets compared to those from (0001) facet, which was explained by reduced QCSE at the semi-polar facets. In our structures, however, the weaker CL signals from the semi-polar facets were observed due to extremely thin InGaN wells as confirmed in the STEM measurements. Carriers in the very thin MQWs can easily escape and do not participate in recombination. Moreover, the ultra-thin SNM significantly reduced the compressive stress in micro-LED, leading to reduction of QCSE in (0001) facet and resultant increase in overlap of electron and hole wave functions. The strong CL emission from the c-plane of the micro-LED on

SNM can be an important property for micro-LED displays. The results suggest that with proper n- and p-metal design in micro-LEDs on SNMs would suppress the emission from sidewalls with shorter wavelengths and generate the sharp emission only from (0001) plane.



Figure 2.3. Micro-Raman spectra from freestanding GaN, microsized un-doped GaN on single SNM, and un-doped GaN on planar sapphire substrate.



Figure 2.4. Panchromatic CL images of (a) a micro-LED grown on SNM and (b) reference sample.



Figure 2.5. Ahrrenius plots of temperature dependent PL from micro-LEDs on SNM and reference sample. The inset figure shows PL spectra measured at 300K from micro-LEDs on SNM and reference sample.



Figure 2.6. Cross-section TEM and STEM images of a core-shelllike micro-LED. (a) Cross-section TEM image of single micro-LED on sapphire nano-membrane with zone axis of  $[1\overline{1}00]$ direction of GaN. Cross-section STEM images with zone axis of (b)  $[1\overline{1}00]$ direction and (c)  $[2\overline{1}\overline{1}0]$  direction of GaN. STEM images of InGaN/ GaN MQWs on facets of (d) (0001), (e) ), $\{11\overline{2}2\}$ , and (f)  $\{1\overline{1}01\}$ .



Figure 2.7. Plan-view SEM image and CL emission properties of single micro-LED (a) Plan-view SEM image of single micro-LED grown on sapphire nano-membrane. Monochromatic CL images measured at wavelengths of (b) 375nm, (c) 387nm, and (d) 435nm. (e) Spatially-resolved CL spectra measured at  $\{11\overline{2}2\}$ ,  $\{1\overline{1}01\}$ , and (0001) facets. The inset figure shows the CL spectra in log scale

### 2.3.2 Fabrication of vertical type micro-LED device

Figure 2.8 shows schematic diagrams for fabrication process of a vertical-type single micro-LED. Ag-based reflective p-ohmic metal [ITO (20 nm)/Ni (0.5 nm)/Ag (250 nm)/Ni (100 nm)/Ti (20 nm)/Ni (20 nm)/Au (90 nm)] was formed on c-plane of micro-LED array by photolithography, sputtering, and subsequent lift-off process. The micro-LED array with patterned p-metal on it was flipped and transferred to metal deposited target substrate [Ti (50 nm) / Ni (100 nm) / Au (100 nm) / Sn (300 nm) / Au (50 nm) on SiO<sub>2</sub>/Si wafer] using wafer bonder. During the transfer process, the sample was maintained at 300 °C under 10 kgf for 20 minute to induce Au/Sn eutectic bonding. During the mechanical lift-off (MLO), the legs of the SNM structures were broken by the applied force, resulting in the monolithic transfer of the micro-LED array onto the target substrate as shown in Figure 2.9. After the transfer, 150 nm thick alumina was deposited by ALD for electrical isolation between the devices. Photolithography and dry etching was followed to expose the n-type GaN. SiO2 layer was formed

by sputtering for flattening the surface the sample surface. Semitransparent n-type electrode [In (20 nm)/ITO (200 nm)] was deposited by photolithography, sputtering and lift-off process on n-type GaN. For enhanced light extraction and electrical properties, the sample was annealed at 300 °C for 10 minute. Ag-based reflective p-ohmic metal was orderly patterned only on c-plane of micro-LED array to prevent the leakage current through sidewalls. The micro-LED array was successfully transferred with their pitch and shape well maintained regardless of their sizes. The I-V characteristics are shown in Figure 2.10. For comparison, characteristics of conventional 10 x 10 µm<sup>2</sup> dry etched micro-LEDs were reflected, although shapes, dimensions, and medializations are different. Two orders of magnitude lower leakage current level were observed for the micro-LED as shown in Figure 2.10, suggesting the successful effect of self-passivated structure of micro-LEDs grown on SNMs. However, turn-on voltage was rather higher than the reference sample, indicating further optimization of metallization must be followed. Figure 2.11 shows electroluminescence (EL) spectra of the single microLED as a function of injection current density. The inset image shows the effect of current density on EL peak positions. It was worth noting that emission peak shift were not observed for micro-LEDs on SNMs while blue shift induced by QCSE screening effects were clearly observed for dry etching reference sample. Such properties have been reported only from non- or semi-polar InGaN/GaN MQWs. The observations indicates that the ultra-thin SNM can reduce the compressive stress in GaN, resulting in the reduction of QCSE as discussed in the CL results.



Patterned p-metal deposition



Transfer of micro-LED array



Amorphous alumina deposition by ALD



N-metal deposition [In (10 nm) / ITO (200 nm)]



SiO<sub>2</sub> deposition by sputter and lift-off



n-GaN mesa by ICP etching

Figure 2.8. Schematic diagrams for experimental procedures for fabrication of a vertical type single micro-LED


Figure 2.9. Transferred micro-LEDs onto target substrate via MLO



Figure 2.10. I-V curves for single micro-LED and reference sample.



Figure 2.11. EL spectra as a function of injection current density for single micro-LED. The inset shows EL peak positions as a function of current density.

# 2.3.3 Structural and optical properties of multi-membrane micro-LED

The multi-membrane samples showed similar results to the single membrane samples. To investigate the stress level of the un-doped GaN grown on the multi-membranes, micro-Raman spectroscopy was conducted. Figure 2.12 shows Raman spectra from a freestanding GaN, un-doped GaN on a multi-membranes, and an undoped GaN film on a thick planar sapphire substrate. The peaks of  $E_2$ -high mode were observed at 568 cm<sup>-1</sup> from GaN on multimembranes and at 570.5 cm<sup>-1</sup> for GaN on planar sapphire substrate. Considering the stress coefficient of GaN (4.3 cm<sup>-1</sup>/GPa),<sup>[3]</sup> the residual compressive stresses in the un-doped GaN grown on multi-membranes and planar sapphire substrate were calculated to be 139 MPa and 720 MPa, respectively. It showed 80.6 % stress relaxation effect, which is considerable value.

**Figure 2.13** shows panchromatic CL images of a micro-LED grown on a multi-membrane and a reference sample, respectively. Micro-LED on multi-membrane showed an average TDD of 3.3 x

 $10^8$  cm<sup>-2</sup>, while the reference sample showed an average TDD of 8.0 x  $10^8$  cm<sup>-2</sup>, resulting in 58.7 % reduction in TDD. Interesting fact is that threading dislocations were generated in the form of a line, as shown in **Figure 2.13(b)**. Dislocations were generated directly on the SNMs due to lattice misfit or where the separate GaN islands coalescence. Meanwhile, laterally grown GaN showed extremely reduced threading dislocation generation, owing to the dislocation bending as the film growth. The results are in good agreement with the results from the previous study with single membrane micro-LED.

**Figure 2.14** shows Arrhenius plots of the integrated PL intensity from both the micro-LED on multi-membrane and the reference sample over the temperature ranges from 10K to 300K. The IQE was estimated by the similar method mentioned above. The IQE of the micro-LED on multi-membrane was calculated to be enhanced by a 66 %, compared to the reference sample.

Figure 2.15 shows the structure of micro-LEDs grown on multimembrane analyzed by TEM and STEM with zone axis of  $[1\overline{1}00]$ . It was confirmed that each GaN islands which have grown separately on SNMs completely merged and formed a single GaN crystal. The magnified TEM and STEM images were acquired to confirm that MQWs are generated in self-passivated structure along the crystal plane. The thickness of each layer was different depending on the growth facet, due to different growth rate on the crystal plane. The top and both sides of the micro-LEDs are sloped in the manner of (0001),  $\{1\overline{1}01\}$ , and  $\{11\overline{2}2\}$  facets. This truncated inverted pyramid (TIP) configuration assists in enhancing extraction efficiency in vertical LED.



Figure 2.12. Micro-Raman spectra from freestanding GaN, microsized un-doped GaN on multi-membrane, and un-doped GaN on planar sapphire substrate.



Figure 2.13. Panchromatic CL images of (a) a micro-LED grown on multi-membrane and (b) reference sample.



Figure 2.14. Ahrrenius plots of temperature dependent PL from micro-LEDs on SNM and reference sample



Figure 2.15. Cross-section TEM and STEM images of the micro-LED on multi-membrane with zone axis of  $[1\overline{1}00]$ .

### 2.3.4 Fabrication of vertical micro-LED device using multimembrane

Figure 2.16 depicts schematic diagrams for fabrication procedure of a vertical micro-LED grown on multi-membrane. For p-type ohmic metal, [Ni (10 nm)/Ag (150 nm)/Ti (50 nm)/Au (50 nm) was formed on c-plane of micro-LEDs by e-beam evaporator. Ag was adopted as a reflective metal since the device is vertical-type LED. The micro-LED array with p-metal on it was flipped and transferred to target substrate of SiO<sub>2</sub>/Si wafer with [Ti (50 nm)/Ni (100 nm)/Au (500 nm)/Sn (700 nm)/Au (5 nm)] metal on it. Eutectic bonding of Au/Sn was conducted by maintaining 280 °C while applying 300 kgf for 20 min. During the MLO, the legs of the SNMs were broken by the applied force, transferring the micro-LEDs onto the substrate. Figure 2.17 shows plan-view images of 20 x 20  $\mu$ m<sup>2</sup>, 40 x 40  $\mu$ m<sup>2</sup>, and 100 x 100  $\mu$ m<sup>2</sup> micro-LEDs after transfer through MLO. As shown in Figure 2.17, MLO process was successfully conducted regardless of the size of micro-LEDs. After the transfer, photolithography and dry etching

was conducted to expose the n-type GaN. W-PR, which is one type of photoresist with high electrical and thermal stability, was patterned on the sample to fill the empty space between the micro-LEDs. Lastly, [Cr (10 nm)/Au (300 nm)] was patterned as an ntype ohmic metal for the device. **Figure 2.18** shows plan-view and cross-section view images of the fabricated 100 x 100  $\mu$ m<sup>2</sup> micro-LED grown on multi-membrane. Transfer to the target substrate was successful and the p-metal formed solid bonding with the Si substrate. Dry etching process successfully exposed the n-type GaN and the n-type metal was well deposited on it.

**Figure 2.19(a)** shows the I-V characteristic of the 100 x 100  $\mu$ m<sup>2</sup> micro-LED device. Owing to the vertical structure of the device, current density at the same voltage was relatively high compared to the conventional dry etching micro-LEDs. **Figure 2.19(b)** shows the result of EQE measurement of 100 x 100  $\mu$ m<sup>2</sup> micro-LED according to the injection current density. The peak EQE was measured to be 4.8 %. Compared to the conventional micro-LED, the EQE value was relatively low. However, the efficiency can be boosted with various methods, including optimizing the growth

conditions and contact metal schemes, inserting distributed Bragg reflector (DBR) layer, or changing n-contact metal to transparent metals such as ITO. Also, further optimization of the fabrication process is require since current spreading was not perfect for the sample. As shown in Figure 2.19(c-f), electroluminescence was only observed at the center of the device. The restricted spreading of the current was due to inadequate n-GaN thickness. To prevent the GaN growing at the bottom from merging to the GaN grown on multi-membranes, growth time was controlled, resulting in a thin n-GaN layer of the micro-LED. To ensure sufficient n-GaN thickness, selective area growth (SAG) technique is required which will be explained in the next chapter. Figure 2.19(d,e) show the effect of the TIP structure in enhancing the light extraction efficiency. The bright light emitted along the micro-LED edge was not generated from the MQWs at the sidewall, but light refracted by the TIP structure which emitted from the c-plane locating inside. Figure 2.20 shows EL spectra of the multi-membrane micro-LED as a function of injection current density. For multi-membrane micro-LED, emission wavelengths were consistent, similar to the

results from single membrane micro-LED. The ultra-thin SNM reduced the compressive stress in GaN, resulting in the reduction of QCSE screening effect and leading to efficient recombination of the carriers.



Figure 2.16. Schematic diagram of fabrication of vertical micro-LED device using multi-membrane.



Figure 2.17. Plan-view SEM images of (a) 20 x 20  $\mu$ m<sup>2</sup> micro-LED and (d) array of 20 x 20  $\mu$ m<sup>2</sup> micro-LED, (b) 40 x 40  $\mu$ m<sup>2</sup> micro-LED and (e) array of 40 x 40  $\mu$ m<sup>2</sup> micro-LED, and (c) 100 x 100  $\mu$ m<sup>2</sup> micro-LED and (f) array of 100 x 100  $\mu$ m<sup>2</sup> micro-LED after transfer through MLO.



Figure 2.18. (a) Plan-view and (b) cross-section view SEM images of fabricated micro-LED grown on multi-membrane.



Figure 2.19. Electrical properties of micro-LED grown on multimembrane. (a) I-V curve and (b) EQE curve for micro-LED. Optical microscope images of the sample at (c) 0 V, (d) 3.2 V, (e) 3.8 V, (f) 4.2 V.



Figure 2.20. EL spectra as a function of injection current density for multi-membrane micro-LED.

#### **2.4** Conclusion

In this study, a self-passivated micro-LED array with multi-facets was grown on a 100 nm-thick SNM array. Without dry etching process for chip singulation, micro-LED was individually formed on each SNM. In addition, micro-LEDs with various sizes were obtained by controlling the space between the nano-membranes. Significant stress relaxation in the un-doped GaN was observed for both single and multi-membrane. Considerable TDD reduction and enhancement of IQE was confirmed for both micro-LEDs grown on single SNM and multi-membranes. The structures of the micro-LEDs were in self-passivated TIP configuration, protecting the active layer and enhancing the light extraction efficiency. Grown micro-LEDs were successfully transferred onto target substrate via MLO and fabricated into a LED device. Although further optimization is required, the fabricated devices showed enhanced electrical properties with lower leakage current level compared to dry etched samples. In addition, owing to the compliant substrate effect of SNM, emission wavelength was constant, independent of the injection current. From the results, SNM technology has proven that it can accelerate the commercialization of micro-LED displays.

#### 2.5 Bibliography

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# Chapter 3. Study on crystallization of amorphous alumina and growth mechanism of GaN

#### **3.1 Introduction**

Fabricating a highly efficient display have been an objective of the researchers. Micro-LED is one of the most promising technology with its superior properties over other displays.<sup>[1-4]</sup> However, there are technical issues to overcome for realization of micro-LED displays. Those are high kerf loss, low quantum efficiency, and time-consuming transfer process. To solve the problem, sapphire nano-membrane template, which is a 3D structured growth template for micro-LED was introduced.<sup>[5]</sup> With the SNM, various sizes and shapes of micro-LEDs can be obtained without dry etching process. In addition, the ultra-thin structure of SNM serves as a compliant substrate, reducing the internal strain of micro-LEDs grown on it. In order to fully utilize the SNM template, fabrication process and mechanism of the SNM must be understood. During the crystallization process of amorphous

alumina, 2 different growth mechanism is involved. One is random nucleation and growth (RNG) and the other is solid phase epitaxy (SPE). The most important principle in the fabrication of SNM is SPE. Only with the SPE, the 3D structure amorphous alumina can be crystallized into single crystalline sapphire and acts a growth template for micro-LEDs. Although crystallization of SNM mainly depends on the SPE, RNG also takes place during the crystallization. In this chapter, studies on crystallization process of SNM will be introduced and various applications using the difference of SPE and RNG will be proposed. By controlling the crystallization which depends on the amorphous layer thickness, a homogeneous growth mask for GaN and subsequent micro-LEDs was achieved.<sup>[6]</sup> This homogeneous growth mask can be advantageous since it does not induce any contamination during the growth. Using the homogeneous growth mask, selective area growth (SAG) of GaN on SNM was obtained

In addition, by controlling the thermal treatment time, partial crystallization of SNM was accomplished. Single crystalline GaN only grows on the fully crystallized region while poly crystalline GaN islands grow on the partially crystallized region, suppressing the growth of GaN. Using this phenomenon, selective area growth of GaN can be achieved without additional growth mask. Utilizing the principle, an array of high quality hexagonal GaN was grown on the partially crystallized hexagonal sapphire nano-membrane (HSNM)

#### **3.2 Experimental procedure**

#### 3.2.1 Selective area growth of GaN using amorphous alumina

The first step for fabrication of SNM template is forming a desired pattern on a sapphire substrate using photolithography. On the pattern, amorphous alumina was deposited at relatively low temperature of 110 °C using ALD. Second photolithography and wet etching using phosphoric acid was conducted to separate each nano-membranes. After wet etching, the sample was dipped into acetone to remove the photoresist. Finally, thermal treatment at 1100 °C was conducted to crystallize the amorphous alumina into single crystalline sapphire using SPE. For selective growth of GaN

using the homogeneous growth mask, second deposition of amorphous alumina with a thickness of 240 nm was conducted. PR was patterned on the sample so that the top surface of the SNM was exposed. Exposed amorphous alumina was etched away using 85.0 % phosphoric acid at 50 °C and residual PR was removed by acetone. An un-doped GaN array was grown at 1050 °C and 100 torr by MOCVD. The overall experimental process is shown in **Figure 3.1**.

# 3.2.2 Hexagonal GaN array on fully- and partially crysatllized HSNM

Growth of GaN on partially crystallized hexagonal GaN was conducted through the following steps. Hexagonal PR pattern was formed on a sapphire substrate followed by amorphous alumina deposition at 110 °C using ALD. Hole patterned second photolithography and wet etching using phosphoric acid was conducted to expose the PR inside the HSNM. The PR was dissolved into acetone. By controlling the thermal treatment time, either fully crystallized HSNM or partially crystallized HSNM could be selectively achieved. Growth of GaN on the HSNM was conducted by MOCVD at 1050 °C and 100 torr. **Figure 3.2** shows the overall experimental process.

#### 3.2.3 Characterization

The overall experimental process was observed by field emission scanning electron microscope, Hitachi S-4800. Raman spectra were taken from a LabRAM HV Evolution system using a 633 nm laser to analyze the stress states of un-doped GaN layers. PL were measured by Dongwoo Optron micro-PL system with a 325 nm He-Cd laser to estimate the crystal quality of the sample. Crosssection TEM images of the selectively grown GaN and hexagonal GaN on partially crystallized SNM were observed by JEM-2100F. Cross-section STEM measurements were also conducted to observe the crystal structures. TDD, monochromatic CL images, from hexagonal GaN was analyzed by Gatan Mono-CL4 with an acceleration voltage of 5 kV at room temperature.



Figure 3.1. Schematic diagram of fabricating sapphire nanomembrane with homogeneous amorphous alumina growth mask and consequent growth of GaN.



Figure 3.2. Fabrication process of fully- or partially- crystallized HSNM and consequent growth of GaN

#### **3.3 Results and discussion**

#### 3.3.1 Crystallization of sapphire nano-membrane

A SNM template is fabricated by crystallizing 3D structured amorphous alumina membrane into single crystalline sapphire. During the crystallization process, amorphous alumina experience 2 steps of phase change; from amorphous to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The sapphire substrate is made of alpha-phase Al<sub>2</sub>O<sub>3</sub>, which has a hexagonal lattice symmetry. The unit cell of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> consist of ABAB stacking of O planes along the c-direction with Al in 2/3 of the octahedral interstitial positions, as shown in Figure 3.3(a). Meanwhile,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is in cubic spinel structure with vacancies on part of the cation positions. The unit cell of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> consist of ABCABC stacking of O with Al occupied in both octahedral and tetrahedral position, as shown in Figure 3.3(b). Crystallization of amorphous alumina to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> proceeds through 2 types of mechanism. One is RNG in which the

crystallization occurs at random location in the amorphous

alumina layer. Crystallization process through RNG starts with formation of crystalline nuclei in the amorphous layer. As the crystallization proceeds, the crystallites grow larger while more nuclei forms. As a result, the amorphous film crystallize into poly crystalline alumina layer with poly grains. On the other hand, SPE only takes place at the interface between a single crystal layer and amorphous layer. During the SPE, the crystalline layer provides a template for ordered crystallization, inducing a layer by layer conversion of atoms at the interface. The transition interface moves toward surface of the amorphous layer, forming a single crystalline epitaxial layer. Since rearranging the amorphous atoms into crystal requires lower activation energy than random nucleation, SPE normally occurs at lower temperature compared to RNG.

**Figure 3.4** shows the phase transition of amorphous alumina nanomembrane to sapphire nano-membrane. The first phase transition of amorphous alumina to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> starts at around 780 °C. At the temperature, SPE of amorphous alumina to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> starts at the interface of the sapphire substrate and RNG starts at the random

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sites of the amorphous nano-membrane. As shown in Figure **3.4(a)**, SPE interface moves upward as the crystallization proceeds. However, the SPE interface could not progress through the RNG area. As the temperature increases, second phase transition from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurs, at temperature over 920 °C. During the second phase transition, only SPE crystallization was observed and randomly generated nuclei were not observed. It is because the activation energy for RNG of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is much higher than the activation energy for SPE, which requires much higher temperature than 1100 °C. Thus, only SPE was carried out during the crystallization, forming single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sapphire nano-membrane. Details for crystallization of SNM are described in other literature.<sup>[7,8]</sup>



Unit cell of  $\alpha$ -alumina

Unit cell of γ-alumina

Figure 3.3. Unit cell of (a)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3.</sub>



Figure 3.4. Phase transition of (a) amorphous alumina to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> during crystallization of sapphire nanomembrane.
# **3.3.2** Selective growth of GaN on SNM with amorphous alumina homogeneous growth mask

To utilize the crystallization principles in various applications, further cycles, and 1500 cycles, respectively. The samples' thickness was measured to be 40, 80, and 120 nm each. During the growth of GaN using MOCVD, the temperature of the growth chamber increases up to 1050 °C, inducing crystallization of amorphous alumina. The samples consisted of single-crystalline GaN, single crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and sapphire substrate without polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, meaning that amorphous alumina was crystallized only by SPE. The thickness of amorphous alumina layer was thin enough to be crystallized only by SPE before the RNG started. The crystallized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer was confirmed by selected area diffraction patterns (SADPs), as shown in Figure **3.5(d-f)**. The SADPs exhibited diffraction patterns of GaN, labeled as  $(002)_{GaN}$ ,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> labeled as  $(111)_{\gamma$ -alumina, and sapphire substrate, labeled as  $(006)_{\alpha-alumina}$  which were aligned in the same crystallographic orientation. Crystalline α-Al<sub>2</sub>O<sub>3</sub> was not observed

since crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> required much higher energy. Such crystallization occurs over temperature of 1100 °C, which exceeds growth temperature of GaN.

To induce RNG during the thermal crystallization, samples with thicker amorphous alumina layer was needed. The sample was prepared by depositing 3000 cycles of Al<sub>2</sub>O<sub>3</sub> using ALD, which were measured to be 240 nm in thickness, as shown in Figure 3.6. The high temperature of the growth chamber during the GaN growth induced crystallization of amorphous alumina. For the thick amorphous alumina sample, poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was observed, indicating that RNG also occurred during the GaN growth. Since the difference between activation energy for SPE and RNG is relatively small for crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the temperature increase rate of the MOCVD chamber is very fast, RNG of the amorphous alumina started before the SPE process completely crystallized the thick amorphous alumina layer. The RNG of amorphous alumina started by forming crystal seeds at random locations of the amorphous alumina layer. As the temperature increases, the seeds grew by crystallizing nearby

amorphous alumina into the same crystal structure to them. At the same time, more crystal seeds were generated at other random locations. Repeating the process, the crystal seeds grew into poly grains of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. The polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, which crystallized via RNG, located at the surface of the ALD deposited Al<sub>2</sub>O<sub>3</sub> layer, while single crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, which crystallized via SPE, placed at the interface between the sapphire substrate. The polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer blocked the progress of SPE. Since the polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is in the same crystal phase to the single crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, additional energy is required to change the crystal structure of the polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The different growth process created a double layer with two different types of crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, consisted of singlecrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the bottom and polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the top. The polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the surface suppressed the growth of single crystalline GaN film on it. As shown in the planview FE-SEM images in Figure 3.6(a, b), GaN grains were grown on the sample with thick amorphous alumina. Instead of forming a film, poly GaN grains did not merged completely, but remained

in separate crystals. It is because the GaN crystals were terminated with slow growth rate facets, extremely suppressing additional growth of GaN crystals. The result was different from those of previous samples with relatively thin amorphous alumina layer, which showed single crystal GaN film on single crystallized y-Al<sub>2</sub>O<sub>3</sub>. Such phenomenon can be utilized to selective area growth of GaN by depositing thick amorphous alumina on the unwanted region of sapphire substrate. The thick amorphous alumina mask will suppress the growth of GaN on it while single crystalline GaN grows on the exposed sapphire substrate. The mechanism of the suppressed growth of GaN on the polycrystalline substrate will be explained afterward.

To fully utilize the homogeneous growth mask of amorphous alumina, our team applied the technique to SNM for selective area growth of GaN and consequent micro-LEDs. By converging the two methods, suppression of unwanted growth at the bottom region of the SNM, which was one of the issues of the SNM technique, could be expected. The experimental process is explained in **Figure 3.1**.

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Figure 3.7 shows FE-SEM images of selectively grown GaN on the SNM with homogeneous growth mask. Figure 3.7(a-c) show plan-view FE-SEM images of SNM with homogeneous growth mask after growth of 0, 10, and 40 minutes, respectively. Figure 3.7(d-f) show bird's eye-view FE-SEM images of SNM with homogenous growth mask after growth of 0, 10, and 40 minutes, respectively. As shown in Figure 3.7(a,d), homogeneous growth mask was only formed on the bottom region of the SNM template and the legs of the SNMs. The top surface of the SNM was exposed to serve as a growth template for GaN. The fabricate sample was put into growth chamber of MOCVD and GaN was deposited on it. As shown in Figure 3.7(b,e), GaN crystallites were formed on the SNM after growth of 10 minutes. As the growth proceeds, GaN grown on the exposed SNM, where amorphous alumina was etched, merged to form a single GaN crystal via Stranski-Krastanov growth mode. Meanwhile, poly crystalline GaN crystallites were formed on the bottom region where growth mask was not etched. Those GaN crystallites did not merged to form a single crystalline GaN film, but remained in poly crystalline state. **Figure 3.7(c,f)** show SNM with homogeneous growth mask after growth time of 40 minutes. GaN film was only grown on the SNM but not on the bottom region. The existence of homogeneous growth mask suppressed the growth of GaN on it, resulting in GaN crystallites with extremely slow growth rate. These results are in agreement with those of our previous experiments of thick amorphous alumina layer on sapphire substrate. The structure of the GaN grown on the SNM was similar to those observed in our previous result, with the truncated inverted pyramidal profile.

Compared to our previous result of GaN grown on the SNM, selectively grown single crystalline GaN on the SNM with the homogeneous growth mask showed a thicker profile under the same growth conditions. As shown in **Figure 3.8**, a considerable increase in the thickness of GaN was observed. GaN grown on the SNM with homogeneous growth masked showed over 2 times thicker structure compared to the GaN grown on the pristine SNM. Without the growth mask, growth rate of the GaN on the SNM was similar to that of the GaN grown on the bottom. The thickness ratio between GaN grown on top of the SNM and on the bottom of the SNM was 1.15. On the other hand, the ratio between the GaN grown on the top of the SNM and the GaN grown on the bottom of the SNM was 18.8, which was much higher than that of the bare SNM. The growth mask suppressed GaN growth on the bottom region while accumulating growth of GaN on the SNM.

The difference in growth rates of GaN according to the growth facets is the major reason of the suppressed growth of GaN on the polycrystalline alumina. On the single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, epitaxially grown GaN seeds formed on it possessed same crystallographic orientation and domains since they were originated from the same crystal. As the growth proceeds, GaN seeds grow and merge to form a single crystalline GaN film. On the other hand, GaN crystallites with different crystallographic orientation and domains were generated on the poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> since the substrate itself contains grains with different orientations. The GaN crystallites with different orientations do not merge to form a single crystal but grows by itself. However, as the growth proceeds, the facets of GaN crystallites were

terminated into slow growth rate facets according to the convex growth mechanism of GaN.<sup>[9]</sup> As the GaN crystallites were terminated with slow growth rate facets, the relative density of Ga adatoms at the masked region increases due to decreased interaction of adatoms with the GaN islands.<sup>[10]</sup> The excess Ga adatoms diffuse to the low density region where the Ga adatoms actively participate in the GaN growth, which is the top of the SNM. Owing to the increase of Ga adatom density, the growth of GaN is accumulated on the SNM while the growth of GaN at the bottom is suppressed. These extreme imbalance of growth rate results in the selective area growth of GaN.



Figure 3.5. Cross-section TEM bright-field images of (a) GaN grown on 500 cycles of amorphous alumina, (b) 1000 cycles of amorphous alumina and (c) 1500 cycles of amorphous alumina. SADPs were observed at (d) GaN on 500 cycles of amorphous alumina, (e) 1000 cycles of amorphous alumina and (f) 1500 cycles of amorphous alumina.



Figure 3.6. Plan-view SEM images of (a), (b) GaN grown on thick amorphous alumina. Cross-section TEM bright-field images of (c) GaN on thick amorphous alumina. SADPs observed at (d) GaN on thick amorphous alumina (marked by a green dotted circle in (c)) and (e) GaN and ploly  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the sapphire substrate (marked by orange dotted circle in (c))



Figure 3.7. Plan-view SEM images of (a) SNM array with amorphous alumina and GN selectively grown on the SNM array with amorphous alumina after growth time of (b) 10 min. and (c) 40 min. Bird's eye-view SEM images of (d) SNM array with amorphous alumina and GaN selectively grown on the SNM array with amorphous alumina after growth time of (e) 10 min. and (f) 40 min.



Figure 3.8. Plan-view and cross section-view SEM images of (a), (b) GaN grown on SNM without SAG and (c),(d) GaN grown on SNM with SAG. (e) Top to bottom thickness ratio of GaN grown on SNM with and without SAG.

### 3.3.3 Structural properties of GaN grown on SNM with amorphous alumina homogeneous growth mask

To confirm the existence of each crystal structures of the samples, various analysis was conducted. The existence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was confirmed by X-ray diffraction (XRD) theta/2theta scans ranging from 25 to 45° of 2theta. As shown in Figure 3.9, the (002) peak of single crystalline GaN was observed at 34.5624° with the (006) peak of single crystalline sapphire at 41.6738°. Only the GaN grown on the SNM with a thick amorphous alumina homogeneous growth mask sample exhibited X-ray diffraction patterns of y-Al<sub>2</sub>O<sub>3</sub> at 34.5616° and 41.6738°. From the result, it was confirmed that amorphous alumina transformed into poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the GaN growth and the thickness of amorphous alumina determines the existence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The diffraction patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited broader profile compared to the other single crystalline peaks since the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> signals were collected from the poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer at the bottom region.

To further investigate the crystal structure of the GaN on the SNM with an amorphous alumina homogeneous growth mask sample, TEM analysis was conducted. Figure 3.10(a) shows a crosssection TEM image of GaN grown on the SNM with a homogeneous growth mask. From previous results of fabrication of SNM, the SNM marked with a blue dashed line was confirmed to be single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> which is the same crystal structure to that of the sapphire substrate. The poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, which was crystallized from additionally deposited amorphous alumina layer, is also shown in Figure 3.10(a, c). Crystallization of thick amorphous alumina into polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is explained in Figure 3.6, was confirmed by SADPs as shown in Figure 3.10(c), which contains different patterns of polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> labeled as (440)<sub> $\gamma$ -alumina</sub>. It is confirmed that polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, covered the bottom region, part of the outer sidewall of the SNM, and the inner part of the SNM. GaN Growth of GaN was extremely suppressed on the polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer with only thin layer of polycrystalline GaN on it. From the results polycrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer successfully served as a growth mask of GaN. Single crystalline GaN was epitaxially grown on the top of the SNM, where the single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was exposed, confirmed by SADPs as show in **Figure 3.10(b)**. The SADPs shown in **Figure 3.10(b)** consist of diffraction patterns of single-crystalline GaN, labeled as (002)<sub>GaN</sub>, and SNM, labeled as (006)<sub> $\alpha$ -alumina</sub>, which are aligned in the same crystal orientation, confirming the epitaxial growth of single crystalline GaN on the SNM. Moreover, epitaxial lateral overgrowth (ELO) of single crystalline GaN is observed in **Figure 3.10(a)**. It is confirmed that GaN crystal grew both vertically and laterally on the SNM. The horizontal progress of the dislocation line confirmed ELO of GaN, which is shown as dark line in a single crystalline GaN.

In addition to serving as a growth template for GaN and micro-LEDs with self-passivated structures, the SNM also reduces defect generation, of GaN grown on it by working as a compliant substrate.<sup>[5]</sup> Owing to its extremely thin profile, even compared to GaN grown on it, the SNM takes majority of the strain. By taking the strain induced by misfit of lattice constants and difference in thermal expansion coefficients between GaN and sapphire, the

generation of the defects in GaN is restrained. However, to selectively grow GaN on the SNM, the sidewall of the SNM in this study has been thickened by the additionally deposited thick amorphous alumina, which worked as a growth mask for GaN. To investigate the effect of the thickened sidewall of the SNM, micro-Raman spectroscopy was conducted. Figure 3.11 shows Raman spectra from the freestanding GaN, GaN grown on the SNM with an amorphous alumina homogeneous growth mask, and GaN grown on a planar sapphire substrate, which was measured to evaluate the compliant substrate effect of the SNM with a thick amorphous alumina homogenous growth mask. The peaks of E<sub>2</sub>high mode were observed at 567.7 cm<sup>-1</sup> for GaN on the SNM with a thick amorphous alumina homogeneous growth mask and at 570.2 cm<sup>-1</sup> for GaN on the planar sapphire substrate. The residual compressive stress in the GaN grown on the SNM with a thick amorphous alumina homogenous growth mask and planar sapphire substrate were calculated to be 69.8 and 651 MPa, respectively, considering the stress coefficient of GaN (4.3 cm<sup>-</sup> <sup>1</sup>/GPa).<sup>[11]</sup> The stress relaxation effect of the SNM with a thick

amorphous alumina homogeneous growth mask was calculated to be 89.3%, which was bigger than our previous result of 78.6%. Although the thickness of the SNM sidewall had been increased, the stress relaxation effect of the GaN grown on the SNM was enhanced. The enhanced stress relaxation effect of the GaN grown on the SNM with a thick amorphous alumina homogeneous growth mask is assumed to be owing to the increased thickness of GaN compared to that of GaN grown on the bare SNM. For the SNM with thick amorphous alumina homogeneous growth mask sample, the growth of GaN on the SNM was accumulated as explained before. As the ratio of GaN to SNM thickness increased, the compliant substrate effect of the SNM became more effective and more dislocation bended laterally. This resulted in reducing even more stress applied to the GaN grown on it. From our study, it can be concluded that thick amorphous alumina successfully worked as a homogeneous growth mask and improved the growth rate and crystal quality of GaN.



Figure 3.9. X-ray diffraction theta/2theta scan spectra for GaN grown on SNM with different thickness of amorphous alumina SAG.



Figure 3.10. Cross-section TEM bright-field images of (a) GaN selectively grown on SNM with amorphous alumina. SADPs observed at (b) GaN on SNM (marked by a blue dotted circle in (a)) and (c) poly  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the bottom (marked by red dotted circle in (a)).



Figure 3.11. Raman spectra from free-standing GaN, GaN on SNM with thick amorphous alumina SAG, and GaN on the planar sapphire substrate.

# 3.3.4 Growth of GaN on fully- and partially crystallized HSNM

Hexagonal-shaped GaN array was grown on the hexagonal-shaped SNM to minimize the kerf loss with highest chip density, enhance light extraction, and realize greater angular resolution. Crystallization of the amorphous alumina hexagonal sapphire nano-membrane (HSNM) was controlled by anneal time for application to various techniques. In this chapter, growth of high quality hexagonal shaped GaN on the partially crystallized HSNM is explained. By adopting partially crystallization of amorphous HSNM technique, lateral growth of GaN was induced which resulted in high quality GaN film with low defect density and reduced internal strain. Overall experimental process of the study is illustrated in Figure 3.2, which covers the fabrication of HSNM and growth of GaN on it. Corresponding plan-view scanning electron microscopy (SEM) images of HSNM array and growth of GaN on it is shown in Figure 3.12. The hexagonal-shaped PR array was well defined and the amorphous alumina was deposited

on the first PR-patterned sapphire substrate, maintaining the hexagonal PR as shown in Figure 3.12(a, b), respectively. Figure **3.12(c)** shows second PR-patterned sample in which holes were formed at the center of the hexagonal array. After the exposed alumina was etched by phosphoric acid, PR was also removed by acetone, resulting in the hexagonal amorphous alumina nanomembrane array as shown in Figure 3.12(e). Fully and partially crystallized HSNMs were fabricated by controlling the subsequent thermal treatment time as shiwn in Figure 3.12(f, g). Figure **3.12(h, i)** show SEM images of GaN after growth of 10 minute on the fully and partially crystallized HSNM, respectively. Different growth behaviors of GaN on the fully and partially crystallized HSNM were clearly shown as expected. The unique GaN growth behavior on partially crystallized HSNM was observed irrespective of the location in the 2-inch sapphire substrate as well as the size of hexagon. After the GaN growth for 90 min as shown in Figure 3.12(j), a hexagonal GaN array with six  $\{1\overline{1}01\}$  and (0001) facets was successfully formed on HSNMs.

Figure 3.13 shows SEM images of GaN growth and schematic

diagrams for explanation of growth behavior as a function of growth time on the partially crystallized HSNM. Figure 3.13(a) shows plan-view SEM image of partially crystallized HSNM, which does not show much difference from that of fully crystallized HSNM. After GaN growth for 10 minute, large GaN islands were selectively grown on the upper outer parts of membrane while only small GaN crystallites were grown at the center of the membrane as shown in Figure 3.13(b). GaN was also grown on bottom part between hexagons, because the bottom parts were fully crystallized to single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which is the same crystal structure to sapphire, by SPE. The crystallized sapphire acted as a growth template for GaN with similar lattice constant and crystal symmetry. Figure 3.13(c) shows appearance of six  $\{1\overline{1}01\}$  and  $\{11\overline{2}2\}$  facets at inner and outer sides of HSNM, respectively. The convex growth mode where a growth facet with relatively slow growth rate, such as  $\{1\overline{1}01\}$ , remain was dominant at the outer side of hexagon.<sup>[12,13]</sup> The six  $\{1\overline{1}01\}$  facets prevailed throughout the subsequent GaN growth. On the other hand, GaN at the inner side was laterally over grown under the

concave growth mode in which the facet with higher growth rate such as  $\{11\overline{2}2\}$  survives. After the appearance of six  $\{11\overline{2}2\}$ facets, lateral growth of GaN was accelerated. A hexagonal GaN array with only  $\{1\overline{1}01\}$  and (0001) facets was finally formed on HSNMs after the coalescence of GaN islands as shown in **Figure 3.13(f)**. The unique shape of the GaN can be advantageous when developed into micro-LED. The six  $\{1\overline{1}01\}$  facets can form a truncated inverted pyramid structure to improve light extraction of the device.

To investigate the crystalline states of HSNM and GaN on them, analysis for TEM images and corresponding diffraction patterns was conducted as shown in **Figure 3.14** and **Figure 3.15**. **Figure 3.14(a)** shows cross-sectional TEM images of GaN on partially crystallized SNM after growth time of 10 minute along zone axis of  $[11\overline{2}0]$  direction of GaN. By simply controlling the thermal treatment time in the furnace, SPE to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was stopped halfway before fully crystallizing the HSNM. The SPE growth fronts of alumina at upper parts of membrane were clearly observed by contrasts, leading to different initial growth behavior of GaN on

them. High resolution TEM image at the interface between bottom part of membrane and sapphire substrate was shown in Figure 3.14(c). The inset of Figure 3.14(c), corresponding diffraction pattern, shows that the bottom part of ALD deposited alumina was fully crystallized to  $\alpha$ -phase Al<sub>2</sub>O<sub>3</sub> by SPE. Figure 3.14(d) shows high resolution TEM image at the interface between upper crystallized membrane and GaN on it. The in- and out-of-plane diffraction patterns of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and GaN were fully aligned, indicating the epitaxial relationships between the membrane and GaN. Figure 3.14(e) shows enlarged TEM images and corresponding diffraction patterns of the point where SPE stopped. Growth of single crystalline GaN on fully crystallized part of HSNM was confirmed in addition to epitaxial lateral overgrowth toward poly crystalline  $\gamma$ -phase part of HSNM. On the other hand, only tiny poly crystalline GaN islands were formed on poly crystalline as shown in Figure 3.14(f). We speculated the GaN on poly crystalline membrane was terminated by facets with slow growth rate, leading to the poly GaN crystallites.<sup>[6]</sup> After the growth time of 90 min in MOCVD, fully coalesced 2.88 µm-thick

GaN with  $\{1\overline{1}01\}$  and (0001) was grown on the partially crystallized SNM as shown in Figure 3.15(a). Figure 3.15(c) shows High resolution TEM image at the interface between bottom part of membrane and sapphire substrate. Crystallization via SPE was confirmed with the measurement. Figure 3.15(d) shows epitaxially grown GaN film on crystallized HSNM with the aligned diffraction pattern in the inset of the image. Figure 3.15(e) shows enlarged TEM images and corresponding diffraction patterns of the point where SPE stopped. During the further growth time of 80 min, GaN grown on the single crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was laterally grown over the poly crystalline GaN islands on the poly crystalline  $\gamma$ -phase alumina membrane. Growth of the poly crystalline GaN stopped finally when the single crystalline GaN islands covered and coalesced with each other. With additional growth, a single crystalline hexagonal GaN was obtained with fully filled smooth surface as shown in Figure 3.15(a).



Figure 3.12. SEM images for fabrication process of hexagonal GaN array on fully- and partially crystallized HSNM.



Figure 3.13. Growth mechanism of hexagonal GaN on partially crystallized hexagonal SNM. (a) Partially crystallized hexagonal SNM. (b)-(f) SEM images of GaN grown on partially crystallized SNM with different growth time of from 10 min. to 90 min., with interval of 20 min. (g) Schematic growth and coalescence process of GaN on partially crystallized SNM.



Figure 3.14. Cross-sectional TEM and STEM images of GaN on partially crystallized SNM after 10 min. growth. (a) Plan-view image of GaN on partially crystallized SNM. The inset line indicates where the TEM and STME analysis was performed. (b) Cross-sectional TEM image of GaN on partially crystallized SNM. (c)-(f) STEM images of GaN on partially crystallized SNM at different points.



Figure 3.15. Cross-sectional TEM and STEM images of GaN on partially crystallized SNM after 90 min. growth. (a) Planview image of GaN on partially crystallized SNM. The inset line indicates where the TEM and STME analysis was performed. (b) Cross-sectional TEM image of GaN on partially crystallized SNM. (c)-(e) STEM images of GaN on partially crystallized SNM at different points.

# 3.3.5 Structural properties of GaN grown on fully- and partially crystallized HSNM

Structural and optical properties of the GaN on fully and partially crystallized HSNMs were characterized by panchromatic CL, micro-PL, and Raman spectroscopy as shown in Figure 3.16. Figure 3.16(a, b) show panchromatic CL images of GaN grown on fully crystallized HSNM. TDDs were measured to be  $7.8 \times 10^8$ cm<sup>-2</sup>. TDDs were generated all over the HSNM region due to lattice mismatch and thermal expansion coefficient difference of GaN and sapphire. Figure 3.16(c, d) show panchromatic CL images of GaN grown on partially crystallized HSNM. The number of TDs from the sample was measured to be  $1.9 \times 10^8$  cm<sup>-2</sup>, which was significantly lower value compared to that of the fully crystallized HSNM sample. Especially, TDDs in overgrown high quality GaN, where the amorphous alumina HSNM was crystallized into poly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was 4.96x10<sup>7</sup> cm<sup>-2</sup>, indicating high quality GaN with extremely low defect density. The region is where the main active layer of hexagonal micro-LED

will be positioned, expecting the highly efficiency micro-LEDs with enhanced quantum efficiency. The nearly TDD-free region was result of lateral overgrowth of GaN which excludes vertical propagation of threading dislocations.<sup>[14]</sup>

Figure 3.16(e) shows micro-PL analysis results from GaN on fully crystallized HSNM, GaN on partially crystallized HSNM, and GaN on bare sapphire substrate. About 1.29 and 1.53 times higher integrated PL intensity achieved from GaN on partially SNM, compared to GaN on fully crystallized SNM and bare substrate, respectively. FWHM was also reduced from 6.30 nm and 6.89 nm to 6.15 nm by introducing the partially crystallized SNMs as a growth template for micro-LEDs. The outstanding optical properties were originated from the better crystallinity and superior TDDs measured in CL and resultant enhanced radiative recombination. The PL peak positions of the all samples were observed around 362 nm, and there was no significant difference. The exact stress states of GaN of each sample were also analyzed by measuring the peak shift from strain-free GaN in Raman spectroscopy, as shown in Figure 3.16(f). The peak positions of  $E_2$ -high mode were obtained at 567.8 cm<sup>-1</sup>, 567.6 cm<sup>-1</sup>, and 570.1 cm<sup>-1</sup> for GaN on fully and partially crystallized HSNMs and GaN on bare sapphire, respectively. The calculated stress considering the stress coefficient of GaN (4.3 cm<sup>-1</sup>/GPa)<sup>[11]</sup> was 93.02, 46.51, and 627.91 MPa, respectively, which means significant stress relaxation of GaN on HSMNs. The stress in GaN was effectively shared to the ultra-thin nano-membrane, i.e., compliant substrate.<sup>[7]</sup>

It is expected that the superior characteristics will help improve performance of micro-LEDs in the future. Micro-LEDs grown on the partially crystallized HSNM template will exhibit higher quantum efficiency with enhanced light extraction owing to its truncated inverted pyramid structure with hexagonal direction. Moreover, the crystal quality of the micro-LED grown on partially crystallized HSNM will be superior compared to that of the other LEDs with lower TDDs and internal strain and higher PL intensity with enhanced FWHM value.



Figure 3.16. Analysis result of GaN on hexagonal SNM. (a), (b) CL measurement result of GaN on fully crystallized SNM. (c), (d) CL measurement result of GaN on partially crystallized SNM. (e) and (f) PL and Raman spectroscopy results of each sample.

#### **3.4 Conclusion**

In conclusion, crystallization mechanism of amorphous alumina was studied to utilize the different crystallization principles in various applications. A contamination-free SAG of GaN was achieved using amorphous alumina, which is the same material composition as the sapphire substrate. The thick amorphous alumina-deposited layer crystallized into polycrystalline  $\gamma$ -phase alumina through the RNG process during the growth of GaN in the MOCVD chamber. Polycrystalline GaN grains were grown on the polycrystalline  $\gamma$ -phase alumina with an extremely slow growth rate and acted as an ELO mask. Meanwhile, the exposed SNM, consisting of  $\alpha$ -phase alumina, served as the epitaxial growth template of high-quality, low-stress, single crystalline GaN.

In addition, by controlling the crystallization of amorphous alumina, partially crystallized SNM template was fabricated. A hexagonal partially crystallized SNM array was proposed as a growth template for a high quality hexagonal micro-LED array. The unique configurations which have both single- and poly-

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crystalline ultra-thin membrane provided selective growth and subsequent lateral overgrowth of GaN. The growth behavior eventually induced the improved structural and optical properties of epilayer. We expect that hexagonal partially crystallized SNMs can be a strong platform for highly efficient micro-LEDs due to the superior intrinsic GaN properties and unique configuration of TIP structures with six  $\{1\overline{1}01\}$  facets of GaN.
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# Chapter 4. Micro-LED based light activated gas sensor

## **4.1 Introduction**

Micro-LED, an inorganic light emitting diode with scale of under 100 micrometer, has a potential for next generation lighting source with its advanced characteristics including long lift time, high brightness, high quantum efficiency, or fast response time. Owing to its superior properties over other technologies, numerous researches are in progress to utilize micro-LED in various applications. Not only in the field of large-area displays that are generally used, but also in various field such as vehicle LEDs, wearable LED, or AR/VR LEDs are being studied. In addition, due to its small configuration and high stability, various researches are being conducted to utilize micro-LEDs for medical or optical communication purposes. In this chapter, a study that integrates micro-LEDs with chemoresistive gas sensors and employs them as a light activated gas sensors will be covered.

With the development of technologies such as IoT and smart home environments, demand for gas sensor technology that can detect dangerous gases is increasing. The sensors are required to be extremely small with low power consumption. Portability of the device is another requirement for future device. To meet with the demands of the industry, our team focused on chemoresistive gas sensor which utilize semiconducting material as a sensing material. The semiconducting materials react with the target gas and induce a change in the resistance. Chemoresistive gas sensor detects the change of the resistance of the material. It has been attracting interests of the field with its superior properties such as low cost, low power consumption, high sensitivity, and high selectivity.<sup>[1-8]</sup> However, there are still issues with the technology. Most of the conventional gas sensing materials require external energy to be activated and to react with the target gas. Conventional gas sensors used a thermal energy for the purpose, inserting heater in the sensor device. However, the operating temperature was relatively high, near or over 100 °C, which limited the portability of the device. Moreover, due to the presence of a heater, the structure of

the device has been complicated and power consumption has increased. To overcome the issues, the concept of a light activated gas sensor has been proposed. The light activated gas sensor provides the energy required for the gas reaction of a material in the form of light. Such type of a gas sensor can simplify the device structure and enhance the portability with low operation temperature. In addition, by adopting micro-LED technology, a light activated gas sensor with extremely small configuration and low power consumption can be fabricated.

In this chapter, a light activated gas sensor based on micro-LED platform will be introduced. Micro-LED platform, consisted of interdigitated electrode (IDE) on micro-LED with the size of 20 x 20  $\mu$ m<sup>2</sup>, was fabricated from LED epi-wafer via semiconductor FAB process. SnO<sub>2</sub> nanoparticles (NPs), which are metal oxides synthesized by hydrothermal method, were drop-casted on the IDE as a sensing material for NO<sub>2</sub> gas. The electrical and optical property of the micro-LED was analyzed. Moreover, the reaction of the SnO<sub>2</sub> NPs to the NO<sub>2</sub> gas under light illumination was confirmed and its sensing properties such as gas reaction, stability,

or detection limit was measured. Light activated gas sensor was successfully fabricated and future concept for multi-sensing light activated gas sensor array has been proposed.

# **4.2 Experiment**

## 4.2.1 Fabrication of micro-LED gas sensor platform

Overall fabrication process of the micro-LED gas sensor platform is shown in **Figure 4.1(a)**. Conventional LED on sapphire substrate, which consist of layers of [un-doped GaN / n-type GaN / 8 periods of superlattices / 4 periods of multiple quantum wells / p-type AlGaN barrier / p-type GaN], was prepared. Mesa pattern was formed using photolithography on the LED and etched using inductively coupled plasma (ICP) etcher. Then, current spreading layer composed of [Ni (5 nm)/Au (5 nm)] was patterned on the p-GaN layer using photolithography and E-gun evaporator. After lift-off process, the sample was annealed at 500 °C in atmosphere condition using rapid thermal annealing (RTA) system for ohmic

contact formation at the Ni and p-GaN interface. n-type contact metal consist of [Cr (20 nm)/Au (200 nm)] was patterned on the sample using photolithography and E-gun evaporator, followed by SiO<sub>2</sub> dielectric layer deposition by plasma enhanced chemical vapor deposition (PECVD) system. To expose the n-contact pad region, patterning through photolithography and dry etching of SiO<sub>2</sub> layer was conducted using reactive ion etching (RIE). After etching, p-contact metal of [Cr (20 nm)/Au (200 nm)] was patterned and deposited using the same method to the n-contact metal. Second passivation layer of SiO<sub>2</sub> was deposited using PECVD followed by patterning and RIE etching. Lastly, interdigitated electrode (IDE) composed of [Cr (20 nm)/Au (200 nm)] was patterned on the outer most layer for gas sensor measurement. For better understanding, the cross-sectional structure of the device is depicted in the Figure 1(b). Each layers of semiconducting material or metals were designed to be electrically separated by SiO<sub>2</sub> dielectric layer.

## 4.2.2 Hydrothermal synthesis of SnO<sub>2</sub> nanoparticle

SnO<sub>2</sub> nanoparticles (NPs) were prepared by a facile one-step hydrothermal synthesis. First, 3g of SnCl<sub>4</sub>·5H<sub>2</sub>O were dissolved in 60 ml of deionized (DI) water under vigorous stirring until the solution turned into a transparent state. The solution was transferred into a 100 ml Teflon-lined autoclave and was moved into a dry oven. The hydrothermal synthesis was conducted at 200 °C for 24 hour, followed by natural cooling to room temperature. Then, the solution containing SnO<sub>2</sub> NPs was centrifuged by ethanol and DI water to collect SnO<sub>2</sub> NPs powder and remove the residue. The collected powders were dried at 60 °C overnight and were prepared for further characterization and gas sensing measurements.

### 4.2.3 Gas sensing measurement

The  $SnO_2$  NPs were uniformly coated on the IDE of micro-LED platform by a drop-casting method and dried on a hot plate to effectively remove the solvent. After two repetitive drop-casting processes, RTA was conducted in the  $N_2$  atmosphere at 350 °C for 10 min. The sensor sample was inserted into the gas sensing chamber for measurement. The real-time electrical resistance was measured by Keithley 236 source-meter under an applied voltage of 0.5 V. The dry air and various target gases were injected into the quartz tube with the concentration controlled by mass flow controllers (MFCs).

# 4.2.4 Characterization

The structure of the devices were characterized using an optical microscope (Nikon). Current-voltage characteristics of the LED devices were measured using a probe station and a Keithley 4200. Crystal structure of the SnO<sub>2</sub> NPs were observed by TEM (JEM-2100F) including STEM, HRTEM, and EDS modes.





#### 4.3 Results and discussion

## 4.3.1 Micro-LED array for gas sensor platform

Figure 4.2 shows optical microscope images of micro-LED platforms with various sizes. To investigate the size effect on emission property and gas sensing property, micro-LEDs with different sizes, 20 x 20, 50 x 50, and 100 x 100  $\mu$ m<sup>2</sup> were prepared as shown in Figure 4.2(a-c), respectively. It was found that 2 x 2 array of micro-LEDs with n- and p- contact pads and IDEs were successfully formed. P-type contact metal and n-type contact metal was successfully formed and separately connected to the LED. IDEs were deposited on the SiO2 dielectric layer which located right on the micro-LED. To increase the effective contact area of the sensing materials, IDEs with multiple electrodes were designed. Due to the limitations of space, the number of electrodes differed according to the size of the mciro-LEDs. Figure 4.3(a-c) show I-V characteristics of micro-LED platform with various LED sizes, 20 x 20, 50 x 50, and 100 x 100  $\mu$ m<sup>2</sup>, respectively. From linear curves, it was confirmed that p-type and n-type ohmic contacts were successfully formed on the LEDs. Turn-on voltage was measured to be around 3.3 V from the I-V results. Low reverse leakage current level from logarithm curves show that the SiO<sub>2</sub> passivation layer successfully separated each layer. The inset images show electroluminescence image of each micro-LEDs. Since the intensity of emitted light depends on the size of the LEDs, micro-LED with 100 x 100  $\mu$ m<sup>2</sup> shows the brightest EL image.



Figure 4.2. Optical microscope images of micro-LED gas sensor platform with size of (a)  $20 \times 20 \ \mu\text{m}^2$ , (b)  $50 \times 50 \ \mu\text{m}^2$ , and (c)  $100 \ \times 100 \ \mu\text{m}^2$ 



Figure 4.3. Current-voltage curves of micro-LEDs with size of (a) 20 x 20  $\mu$ m<sup>2</sup>, (b) 50 x 50  $\mu$ m<sup>2</sup>, and (c) 100 x 100  $\mu$ m<sup>2</sup>. The inset images show electroluminescence of each micro-LEDs.

## 4.3.2 Synthesis of SnO<sub>2</sub> NPs

SnO<sub>2</sub> NPs were synthesized by the hydrothermal method after the preparation of precursors. The synthesized products were collected by centrifugation and dispersed in DI water followed by the dropping process on micro-LEDs. The synthesis mechanism of SnO<sub>2</sub> NPs is illustrated in Figure 4.4. In case of SnO<sub>2</sub> NPs, SnCl<sub>4</sub>·5H<sub>2</sub>O was dissolved in DI water and the synthesis was conducted at 200 °C for 24 h. The first step is nucleation and selfassembly where SnCl<sub>4</sub>·5H<sub>2</sub>O gradually forms SnO<sub>2</sub> nuclei and particles are aggregated by self-assembly. The second step is Ostwald ripening where smaller particles deposit on larger particles and big particles are formed. The final step is oriented attachment where particles collide and link together.<sup>[9]</sup> The adjacent particles are unstable and combine along a specific orientation which results in larger secondary particles formation. Figure 4.5 shows the TEM images of SnO<sub>2</sub> NPs where SnCl<sub>4</sub>·5H<sub>2</sub>O was used as Sn precursor. SnO<sub>2</sub> NPs were successfully synthesized with a uniform distribution, as shown in the low magnification TEM image in Figure 4.5(a). Figure 4.5(b,

c) show HRTEM images of  $SnO_2$  NPs. Crystal structure of  $SnO_2$  was confirmed by the HETEM measurement results with inter planar spacing and diffraction pattern, as shown in the figure. The readied sample was drop-casted on the micro-LED platform as shown in **Figure 4.6**.



Figure 4.4. Synthesis mechanism of SnO<sub>2</sub> NPs.





Figure 4.6. Drop casting of SnO<sub>2</sub> NPs onto micro-LED platform

## 4.3.3 Gas sensing properties

The gas sensing measurements were conducted in the quartz tube inside the furnace, which consisted of a gas mixing chamber and MFCs as shown in **Figure 4.7**. Samples were set in the quartz tube connected to the power supply and I-V source meter for LED operation and resistance change detection, respectively. MFCs were set to control the gas flow of the target gases. Figure 4.8 shows gas sensing properties of SnO<sub>2</sub> NPs to 5 ppm of NO<sub>2</sub> under blue light illumination with various light intensity. As shown in Figure 4.8(a), the base resistance of the device reduced as the injection current increased. The increase in injection current resulted in increased emission light intensity of the micro-LEDs as shown in Figure 4.8(c-e). The decrease of base resistance was due to the higher photon energy with higher light intensity, which induced increased generation of electron-hole pairs. The photogenerated electron-hole pairs contributed to increase in photocurrent of the SnO<sub>2</sub> NPs, resulting in decreased base resistance. Figure 4.8(b) shows the response of the device

depending on the injection current of micro-LEDs. The response, which indicates the ratio of resistance variation in air and NO<sub>2</sub> atmosphere, was obtained by the following equation; Response =  $(R_g-R_a)/R_a$ . The response of the device decreased with the increasing light intensity. This is due to over generation of electron-hole pairs. Since the particles possess limited reaction sites to the target gas, the resistance change induced by gas reaction has its lamination. However, electron-hole pair generation is accelerated as the light intensity increases with no limitations, resulting in decreased change of resistance. From the results it can concluded that an optimal light intensity exist with low base resistance and high response. Every sensing curve showed the full recovery after the reaction with NO<sub>2</sub> molecules, indicating that visible light illumination was an effective approach for room temperature NO<sub>2</sub> sensing. Moreover, the applied voltage was 0.5 V during the gas sensing measurements with injection of 1 mA for activation of micro-LED, which exhibited the extremely low electrical power consumption.

The gas sensing stability and reliability evaluation of SnO<sub>2</sub> NPs

were conducted, as shown in Figure 4.9(a). Figure 4.9(a) shows the gas sensing curves of 4 repetitive pulses of  $NO_2$  gas (5 ppm) under blue light illumination with injection current of 1 mA. A repeatable NO<sub>2</sub> sensing was operable at room temperature without any degradation of gas sensing performance. Figure 4.9(b) shows the response curves of SnO<sub>2</sub> NPs to various concentrations of NO<sub>2</sub> gas (200 ppb, 400 ppb, 600 ppb, 800 ppb, and 1000 ppb). Although the concentration was extremely low, the sensor exhibited a good response and maintained a stable room temperature sensing. The response was plotted as a function of gas concentration and linearfitted to investigate the degree of linearity and calculate the detection limit, as shown in Figure 4.9(c). The slope was 0.368 ppb<sup>-1</sup> with an R<sup>2</sup> value of 0.9961, implying a linear relationship between response and gas concentration. Based on the linear relationship, the detection limit was calculated by extrapolating response-concentration relationship.<sup>[10]</sup> The the theoretical detection limit was estimated to be 2.71 ppt under blue light illumination. These outstanding features make SnO<sub>2</sub> NPs favorable for detecting an extremely low concentration of NO<sub>2</sub> in exhaled breath with a low power consumption.



Figure 4.7. Gas sensing measurement system.



Figure 4.8. (a) Resistance curves (b) response curves of  $SnO_2$  NPs to  $NO_2$  gas under blue light illumination with different light intensity. EL images of micro-LED with injection current of (c) 1 mA, (d) 2 mA, (e) 3 mA.



Figure 4.9. (a) Gas sensing curves to 4 pulses of 5 ppm of  $NO_2$ , (b) response curves and (c) calibration of responses to 200-1000 ppb of  $NO_2$  of  $SnO_2$  NPs under blue light illumination with injection current of 1 mA.

# 4.4 Conclusion

For application of micro-LED, we introduced monolithic gas sensor platform based on the micro-LED. Micro-LED platform for 2 x 2 array of gas sensing was fabricated via FAB process. The fabricated micro-LED exhibited fine current-voltage a characteristics with bright emission of blue light. The power consumption of the device was measured to be extremely low, which agrees with the well-known advantage of micro-LED. For sensing material, SnO<sub>2</sub> NP was selected. Utilizing the SnO<sub>2</sub> NPs, we accomplished ultrasensitive room temperature NO<sub>2</sub> detection using micro-LED activation. Base resistance of SnO<sub>2</sub> NPs was measured to be decrease with the increasing light intensity, owing to the enhanced photo-generation of electron-hole pairs. However, the response of the device decreased under brighter condition, due to acceleration of electron-hole recombination. We found the optimal light intensity for highest sensing property with extremely low power consumption. The sensor exhibited sustainable gas sensing performance even after long-term relaxation. The

theoretical detection limit was extremely low (2.71 ppt) compared to previously reported works. Thanks to promising features of  $SnO_2$  NPs on micro-LED device, this study is expected to contribute to a broad expansion of room temperature operable gas sensor with extremely low power consumption.

# 4.5 Bibliography

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# **Chapter 5. Summary**

## **Summary**

This thesis has covered fabrication of high efficiency micro-LED display using a template called sapphire nano-membrane. The principles needed for the fabrication process was studied as well as unique application of the principles. In addition, novel application of micro-LED to gas sensor, instead of display, was handled.

First, a self-passivated micro-LED array with multi-facets was grown on a 100 nm-thick SNM array. Without dry etching process for chip singulation, micro-LED was individually formed on each SNM. In addition, micro-LEDs with various sizes were obtained by controlling the space between the nano-membranes. Significant stress relaxation in the un-doped GaN was observed for both single and multi-membrane. Considerable TDD reduction and enhancement of IQE was confirmed for both micro-LEDs grown on single SNM and multi-membranes. The structures of the microLEDs were in self-passivated TIP configuration, protecting the active layer and enhancing the light extraction efficiency. Grown micro-LEDs were successfully transferred onto target substrate via MLO and fabricated into a LED device. Although further optimization is required, the fabricated devices showed enhanced electrical properties with lower leakage current level compared to dry etched samples. In addition, owing to the compliant substrate effect of SNM, emission wavelength was constant, independent of the injection current. From the results, SNM technology has proven that it can accelerate the commercialization of micro-LED displays.

Second, crystallization mechanism of amorphous alumina was studied to utilize the different crystallization principles in various applications. A contamination-free SAG of GaN was achieved using amorphous alumina, which is the same material composition as the sapphire substrate. The thick amorphous alumina-deposited layer crystallized into polycrystalline  $\gamma$ -phase alumina through the RNG process during the growth of GaN in the MOCVD chamber. Polycrystalline GaN grains were grown on the polycrystalline  $\gamma$ - phase alumina with an extremely slow growth rate and acted as an ELO mask. Meanwhile, the exposed SNM, consisting of  $\alpha$ -phase alumina, served as the epitaxial growth template of high-quality, low-stress, single crystalline GaN. In addition, by controlling the crystallization of amorphous alumina, partially crystallized SNM template was fabricated. A hexagonal partially crystallized SNM array was proposed as a growth template for a high quality hexagonal micro-LED array. The unique configurations which have both single- and poly-crystalline ultra-thin membrane provided selective growth and subsequent lateral overgrowth of GaN. The growth behavior eventually induced the improved structural and optical properties of epilayer. We expect that hexagonal partially crystallized SNMs can be a strong platform for highly efficient micro-LEDs due to the superior intrinsic GaN properties and unique configuration of TIP structures with six  $\{1\overline{1}01\}$  facets of GaN.

Third, monolithic gas sensor platform based on the micro-LED has been introduced. The fabricated micro-LED exhibited a fine current-voltage characteristics with bright emission of blue light.

The power consumption of the device was measured to be extremely low, which agrees with the well-known advantage of micro-LED. For sensing material, SnO<sub>2</sub> NP was selected. Utilizing the SnO<sub>2</sub> NPs, we accomplished ultrasensitive room temperature NO<sub>2</sub> detection using micro-LED activation. Base resistance of SnO<sub>2</sub> NPs was measured to be decrease with the increasing light intensity, owing to the enhanced photo-generation of electron-hole pairs. However, the response of the device decreased under brighter condition, due to acceleration of electron-hole recombination. The sensor exhibited sustainable gas sensing performance even after long-term relaxation. The theoretical detection limit was extremely low (2.71 ppt) compared to previously reported works. Thanks to promising features of SnO<sub>2</sub> NPs on micro-LED device, this study is expected to contribute to a broad expansion of room temperature operable gas sensor with extremely low power consumption.

기술의 발전으로 디스플레이 분야에서 패러다임의 변화 가 일어났다. 디스플레이는 초고화질 디스플레이, 헤드업 디스플레이, 플렉서블 또는 웨어러블 디스플레이, 증강 현실, 가상 현실 및 혼합 현실 디스플레이를 포함하는 애 플리케이션을 위한 고해상도. 고 안정성 및 소형 크기가 요구된다. 이러한 응용에 있어서, 액정표시장치(LCD)나 유기발광다이오드(OLED)와 같은 종래의 디스플레이 기 술은 적합하지 않은데, 이는 LCD가 시야각이 좁고, 에너 지 소비가 높으며, 백라이트 유닛의 필요성에 의해 어려 움을 겪는 반면, OLED 역시 시야각이 좁고, 환경 안정성 이 낮기 때문이다. 따라서, 마이크로 발광 다이오드 (micro-LED)는 차세대 디스플레이 기술의 핵심으로서 학 계 및 업계로부터 상당한 관심을 받고 있다. 디스플레이 의 증가하는 수요를 충족시키기 위해 연구자들과 회사들 은 마이크로 LED에 초점을 맞추고 있다.

마이크로 LED 기술은 2000년대 초 Jiang 교수에 의해 처음 소개된 이후 계속 발전해 왔다. 여러 회사와 연구원 들이 마이크로 LED 기술을 사용하여 디스플레이를 구현 하려고 시도했다. 패시브 매트릭스 디스플레이가 먼저 시 도되었고, 이어서 액티브 매트릭스 디스플레이와 마이크 로 LED를 이용한 풀 컬러 디스플레이가 시도되었다. 최

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근 여러 회사가 대면적 마이크로 LED TV를 출시하고 있 다. 그러나, 마이크로 LED 디스플레이를 구현하는 데에 는 여전히 기술적인 문제가 있다. 마이크로 LED는 일반 적으로 LED 필름을 마이크로 스케일로 에칭하여 제조된 다. 각 칩의 크기가 작아질수록 식각 손실이 커져 생산 비용에 영향을 미친다. 또한, 건식 식각 공정은 LED의 활성층을 손상시켜 마이크로 LED 소자의 양자 효율을 저하시키는 것으로 나타났다. 또한, 레이저 리프트오프 또는 화학적 리프트오프 기술을 포함하는 종래의 이송 공정은 마이크로 LED 적용에 비용이 많이 들고 시간이 많이 소요된다. 마지막으로, 양자-가둠 스타크 효과 (QCSE)에 의해 유도되는 방출 파장의 이동 또한 디스플 레이 장치에 문제가 될 수 있다.

본 논문에서는 상기와 같은 문제점을 해결하기 위하여 사파이어 나노멤브레인(SNM) 기술을 소개하였다. 마이크 로 LED의 제조 과정과 그에 따른 성장을 조사했다. SNM 에서 성장한 마이크로 LED는 타겟 기판으로 이송되어 LED 소자로 제작되었다. SNM의 결정화 과정과 GaN의 성장 메커니즘이 조사되었다. 마지막으로 마이크로 LED 기반의 광활성화 가스 센서 어레이를 제작하고 그 가스 감지 특성을 조사하였다.

SNM 템플릿의 제작은 다음과 같은 과정을 통해 수행되었다. 사파이어 기판에 포토 레지스트(PR) 패턴을 만드

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는 포토리소그래피로 시작했다. 그 후, ALD에 의해 120 nm 두께의 비정질 Al<sub>2</sub>O<sub>3</sub>층이 증착되었다. SNM 어레이를 만들기 위해 H<sub>3</sub>PO<sub>4</sub> 용액에 의한 2차 포토리소그래피 및 습식 에칭을 수행하였다. 아세톤을 이용하여 PR을 제거 한 후. 템플릿을 1100°C에서 공기 중에서 2시간 동안 어 닐링하여 비정질 Al2O3를 고상 에피택시를 통해 단결정 Al<sub>2</sub>O<sub>3</sub>로 결정화하였다. 마이크로 LED는 유기 금속 화학 증착법(MOCVD)을 사용하여 SNM에서 성장되었다. 나노 멤브레인 사이의 공간을 조절함으로써 다양한 크기와 형 태의 마이크로 LED를 얻을 수 있었다. SNM 템플릿에서 성장한 마이크로 LED는 자체 패시브 구조로 내부 변형 및 스레드 전위 밀도 감소, 내부 양자 효율 및 광발광 강 도 향상 등 향상된 특성을 보였다. 마이크로 LED는 Au-Sn 합금의 공융 결합을 위해 300℃ 및 10 kgf 미만에서 기계적 리프트오프를 사용하여 Si 기판으로 이송되었다. 제작된 장치는 드라이 에칭된 기준 샘플에 비해 향상된 누설 전류 레벨을 보였다. 또한, SNM 상에서 성장한 마 이크로 LED 소자는 주입 전류를 100 A/cm<sup>2</sup>까지 증가시 켰음에도 발광 파장의 이동이 거의 없는 반면, 건식 에칭 된 기준 시료는 상당한 피크 이동을 보였다. 이는 샘플의 QCSE 스크리닝이 감소했기 때문이며, 이는 SNM의 준 수 기질 효과로 인해 성장한 마이크로 LED의 내부 변형 이 감소했기 때문으로 해석된다.
둘째, SNM 의 결정화 과정을 조사하여 GaN 의 새로운 선택적 영역 성장(SAG)에 활용하였다. 비정질 알루미나의 단결정 사파이어로의 결정화는 고상 에피택시(SPE)를 통해 수행되었다. 계면에서의 결정화의 활성화 에너지가 비정질층의 중간에 있는 핵생성 에너지보다 낮기 때문에 SPE 는 단결정층과 비정질층의 계면에서 시작된다. 이러한 차이를 이용하여 두꺼운 비정질 알루미나를 증착하여 GaN 용 균질 성장 마스크를 성공적으로 발명하였다. 두꺼운 비정질 알루미나가 단결정으로 완전히 변형되기 전에 GaN 의 성장이 시작되어 그 위에 다결정질 GaN 섬이 형성되었다. 두꺼운 비정질 알루미나를 선택적으로 증착하여 GaN 의 선택적 면적 성장을 달성하였다. 선택적으로 성장한 GaN 어레이는 Ga atoms 가 노출된 성장 부위에 확산되었기 때문에 기준 샘플에 비해 훨씬 빠른 성장률을 보였다.

또한 GaN의 SNM과 SAG의 결정화 원리를 이용하여 고 효율 육각형 GaN 어레이를 제작하였다. 먼저 육각형 GaN의 성장을 위해 육각형 모양의 SNM이 제작되었다. 열처리 시간을 제어하여 육각형 SNM의 결정화를 중간에 서 중지하였다. 결정화가 완료되지 않은 영역에서 GaN 피막을 성장시키지 않았기 때문에, 단결정 영역에서의 선 택적 성장 GaN을 달성하였다. 바깥쪽 육각형에서 성장

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한 GaN막이 안쪽으로 자라 빈 공간을 채웠다. 90분의 성 장 후, 완전히 성장된 육각형 GaN 배열이 달성되었다. 육각형 GaN은 횡방향으로 성장한 영역에서 스레드화 전 위가 생성되지 않았기 때문에 감소된 변형률과 TDD를 보였다.

마지막으로 마이크로 LED 어레이를 기반으로 광활성화 화학 저항성 가스 센서 어레이를 제작하였다. 화학 저항 성 가스 센서(chemoristive gas sensor)는 대상 가스와의 반응에 의한 저항의 변화를 감지하는 가스 센서의 한 종 류이다. 종래의 가스 센서는 대상 가스로 감지 물질의 활 성화를 위해 외부 히터가 필요하여 장치의 복잡한 구조 와 높은 생산 비용을 유도하였다. 종래의 가스 센서의 단 점을 극복하기 위해 광활성화 가스 센서가 연구되고 있 다. 마이크로 LED가 적용된 광활성화 원리를 이용해 낮 은 생산비용으로 전력 소모가 적은 장치를 제작할 수 있 다. 이를 위해 마이크로 LED 상에 IDE(Interdigated Electrode)를 이용하여 가스 센서 적용을 위한 마이크로 LED 플랫폼을 제작하였다. SnO2 나노입자는 금속 도핑이 나 장식에 의해 높은 선택성으로 양호한 신뢰성과 안정 성을 보여 물질을 감지하기 위해 선택되었다. SnO2 나노 입자 용액을 마이크로 LED 플랫폼에 드롭 캐스팅하고 가스 센싱 시스템을 사용하여 NO<sub>2</sub>에 대한 센싱 특성을 테스트하였다. 광 강도가 증가함에 따라, 광 생성 전자- 정공 쌍이 증가하여 샘플의 기저 저항이 감소했습니다. 그러나 SnO<sub>2</sub> 나노 입자의 반응은 전자-정공 쌍의 재조합 증가로 인해 감소하였다. 가스 센서의 기저 저항과 반응 을 고려하여 최적의 광 강도 값을 선택하였다. 최적의 광 강도 하에서 신뢰성, 선형성, 검출 한계 등 다양한 가스 감지 특성을 분석하였다. 청색광 조명 하에서 시료는 NO<sub>2</sub> 펄스를 4회 반복한 후 일정한 기저 저항과 신뢰성 을 보였다. 또한, 시료는 가스 농도의 증가에 따른 반응 에서 선형적인 증가를 보였다. 반응과 가스 농도의 선형 관계로부터 SnO<sub>2</sub> 나노 입자 샘플의 검출 한계는 2.71 ppt로 계산되었으며, 이는 샘플이 이러한 낮은 값으로 NO<sub>2</sub> 가스를 검출할 수 있음을 의미한다.

키워드: 에피 성장, 마이크로 발광 다이오드, 갈륨 나이트라이드, 고상 에피택시, 유기 금속 화학 증착법, 가스 센서, 금속산화물, 나노입자

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## **Publication list**

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