Master's Thesis of Physics

Flexible micro light-emitting diode using single-crystalline GaN microdisk arrays grown on graphene

그래핀에서 성장한 단결정 GaN 마이크로 디스크 어레이를 사용한 유연한 마이크로 발광 다이오드

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Graduate School of Natural Sciences
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– Single–crystalline GaN microdisk growth on graphene/c–Al_2O_3 and fabrication of flexible micro–LEDs –

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Abstract

Flexible micro light-emitting diode using single-crystalline GaN microdisk arrays grown on graphene

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The Fabrication of flexible micro light-emitting diodes was studied using single-crystalline GaN microdisk arrays grown by optimized growth conditions. The epitaxial growth of single-crystalline GaN microdisk arrays on graphene layers that were directly grown on c-Al_2O_3 by chemical vapor deposition was studied using the metal-organic chemical vapor deposition (MOCVD) method. Prior to this growth nucleation sites were formed on graphene surfaces using the oxygen plasma treatment method. The growth parameters used for study were growth temperature between 1050°C and 1100°C, and growth time ranging from 20mins to 30mins. For the achievement of single-crystalline GaN micro disk structure, the growth method was studied in two ways: the use

of ZnO intermediate layer, and without the ZnO intermediate layer.

Morphology and selectivity of the GaN microdisk was observed using the field-emission scanning electron microscopy, and growth orientation of micro disk was characterized using the electron back-scatter diffraction technique (EBSD). The crystallinity was observed using x-ray diffraction (XRD), and optical characterization was done by photoluminescence (PL). The GaN micro disk showed single-crystalline properties with no in-plane orientation, which can be attributed to the influence of larger grain size or grain boundaries reduction because of the nature of underlaying graphene layer.

GaN micro-Light-emitting diodes was fabricated by growing the n-GaN, multiple quantum wells (3 layers), quantum barriers (as an interlayer between wells), and p-GaN. To achieve the light emission, the p-GaN layer was activated at 750°C, ohmic contact was formed directly on the p-GaN layer, polyimide layer was used to fill the gaps between individual disks, and the metal p-contact was formed. For the formation of n-contact the GaN micro-LED was detached from the c-Al_2O_3 substrate by chemical etching

(Using the buffered oxide etchant to etch off the SiO_2 layer), and Ti/Au was used to form the metal n−contact. The fabricated light−emitting diode was characterized using the Current− Voltage characteristics, Electroluminescence, flexibility, and bending test. The turn−on voltage was 4V, and the I−V characteristics showed the p−n junction without breakdown voltage. The EL spectrum and I−V characteristics showed the dominant peak at 460 nm. The EL spectrum remained undeformed after bending from $R= \infty$ to $R= 8$ mm.

Keyword: GaN, microdisk, single−crystal, graphene/*c*−Al_2O_3, MOCVD

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Chapter 1. Introduction

1.1. Study Background

In the bid to invent high−quality, single−crystal, flexible semiconductor−based materials and devices, numerous techniques have been utilized in material growth and fabrication[2−41,2,3]. The need for flexible devices cannot be overemphasized as it is important both in industrial usage and for flexibility in application. Therefore, research based on flexible materials such as graphene and hBN have made leading breakthroughs in the invention and development of flexible materials and their applications[4]. However, there still lingers a problem in the system of developing single−crystal material−based devices. Although the use of single−crystalline substrate for the fabrication of high−efficiency devices has been explored[5,2] there remains a gap in the successful fabrication of flexible devices using single−crystal microstructure materials. Therefore, to combat this problem a series of methods including the use of laterally large micro−sized structures grown by epitaxial lateral overgrowth (ELOG) with the aid of other nano−

sized materials, the use of as−grown graphene/c−Al_2O_3 substrate for material growths, the inclusion of novel chemical lift−off methods and transfer processes, use of the advantageous lithography methods, and most important use of microstructures that were already established by the previous work[6].

1.2. Purpose of Research

One of the various solutions that were explored in this work was the growth of crystals on 2D materials such as graphene, which have been established to share a very weak bond with the underlying substrate due to its weakly bonded layers[2]. The weak bonding makes it convenient to transfer material onto foreign/other substrates while it retains its mechanical properties such as flexibility irrespective of the level of strain or stress applied. In addition, the application of graphene and supplemental layers like the polyimide enables the fabrication of freestanding materials: which presents ample options for various methods of device fabrication. Graphene grown on the single−crystalline substrate has been advantageous due to lesser density of grain boundaries

(GBs)/larger grain size and lesser dislocations, which by extension produces more reliable thermal, electrical, and mechanical properties of graphene as-grown materials[7]. The use of single-crystal micro-disks with little or no in-plane orientation grown on as-grown graphene/c-Al_2O_3 films was the jackpot. This technique paves the way to fabricate flexible, single-crystal materials, high-efficiency micro-LEDs, solar cells, and transistors, amongst others[3].

There are various inorganic semiconductor materials explored, among which we have GaN, AlN, InGaN, etc. These compounds are outstanding in their performance during the fabrication of devices. For example, in the fabrication of micro-LEDs, homogeneous and full blue color, red color amongst other color spectrums lasting long enough for display and excellent efficiency can be realized because these materials are found most useful based on their attractive optical, electrical, and structural qualities. However single-crystal substrate-based devices make the achievements of high-efficiency devices more possible. Although, the growth of nitride semiconductors on the single-crystal substrate is not the peak expectation but the ability to eventually produce a flexible material from this semiconductor/hybrid heterostructure is the main motivation. Therefore, there is a problem in using single-crystal substrates like sapphire for material growth. This problem is unraveled using 2D materials such as graphene, as an interlayer and growth layer between the nitride semiconductor and the substrate.

This research focused on the growth of GaN 1D microstructures on graphene films for flexible and transferable micro-LEDs. This research focused more on discreet structures because during bending and flexibility characteristics examinations of continuous films, materials may be deformed due to stress and strain induced in the structure. Therefore, to maintain the mechanical properties of materials discrete structures such as micro disk[8], micro rods[9], and so on, have been used compared to the use of thin films for the fabrication of flexible devices. These structures have exceptional flexible characteristics and outstanding performance due to their ability to minimize the resulting stress and strain from mechanical effects. The metal-organic chemical vapor deposition (MOCVD) technique was used for the growth of ZnO and GaN materials. In both material growths, vertical types of MOCVD were employed to make large-scale materials and the uniform flow of gas and semiconductor material sources: used in the growth of undoped and doped materials. Furthermore, the graphene used was synthesized using the chemical vapor deposition (CVD) method on Cu foil and c-Al_2O_3 substrates.

The growth of GaN microstructures and nanostructures on graphene substrates has provided a headway for the fabrication of flexible light-emitting devices. The previous report showed that nearly single-crystalline GaN microdisk and microrods were grown on graphene and transferred onto SiO_2 and GaN micro-light emitting diodes (LEDs) were fabricated using the GaN microstructures. GaN microdisk was grown using various methods such as the use of high-density ZnO nanowalls selectively grown on graphene dots and hole-patterned graphene/SiO_2 or c-Al_2O_3 substrate, and the use of GaN nucleation sites on graphene. GaN micro-disks showed large sizes because of ELOG, furthermore, GaN micro-disks grown on this CVD-graphene transferred onto the desired substrate were observed to be nearly single crystalline[1,10,11]with varying light emissions. The growth orientation of the GaN microdisk grown on this substrate is often irregular in the in-plane orientation, creating more difficulty in achieving a single−crystalline array of the microdisk. The single−crystal microdisk was achieved with the use of GaN directly grown on *c*−Al_2O_3 using the single−crystalline substrate. There are many ways to demonstrate the applications of these materials but in this research, the application focused on the fabrication of flexible and transferable micro−LEDs.

For the growth of selective, single−crystal, and flexible GaN microstructures various growth methods were investigated using parameter control and substrate dependency. The epitaxial growth of GaN LED structure was systematically studied by varying growth parameters based on previously established work[2,9,8]. This research achieved blue light emission, and various mechanical, optical, and electrical characterizations were carried out.

Chapter 2. Background And Literature Review

A review of graphene preparation, its physical properties, and the property variation due to the preparation methods, graphene-based semiconductor materials, and the review of work done on semiconductor materials based on graphene is presented in this chapter.

2.1 Graphene and the research progress based on Graphene

The properties of graphene have made it a very common inorganic semiconductor for substrate use. The hexagonal, repeated arrangement of carbon atoms forms a two-dimensional sheet called graphene. When the crystal structure of graphene is examined, it displays a honeycomb lattice formed because of the Wigner-Seitz cell of a triangular lattice. Within the confines of hydrocarbons in Chemistry, graphene is observed to be a polycyclic aromatic hydrocarbon (It consists of numerous aromatic rings dominated by carbon and hydrogen atoms) Graphene is a layered structure with a very weak Van der Waals force between the layers. In the history of the first discovery of graphene, Professor Andre Geim' s research group proved the existence of graphene in 2004. And progress was made on these findings after a collaboration with Professor Philip Kim in 2005, which was established on the basis that free electrons in graphite are created by a rise in temperature and not at a no-temperature state (Wallace's theory)[12]. Graphene has formed the base for the fabrication of various devices such as emitting devices, sensors, and solar cells. H. Beak et al[8] grew high-quality GaN microdisk on patterned graphene films. Graphene synthesized on Ni films by chemical vapor deposition (CVD) and transferred onto SiO_2/Si substrate was used as a nucleation layer in this research for the fabrication of whispering-gallery-mode (WGD) lasing microdisk. Also, C.K. et al[13] used nitride thin films grown on graphene layers for the fabrication of light-emitting diodes. Graphene was used in this research due to its weakly bonded layered structure, for the fabrication of light-emitting diodes based on free-standing nitride materials transferred onto foreign substrates such as metal. The use of graphene for novel research directions has spurred the need for improvement in the growth of graphene and the exploration of graphene growth by various techniques using different substrates[3,14]. In this research, graphene layers prepared by the Chemical Vapor Deposition (CVD) method using methane and hydrogen as sources for graphene formation on Cu foil was used for comparison and graphene was grown directly on the sapphire substrate by Sungkyunkwan University for the growth of GaN microdisk.

2.2 Growth and Fabrication of GaN micro-LED on graphene

Over decades of years, GaN microstructures have been reported to be grown on graphene layers using intermediate structures such as ZnO nanostructures[8,10,15]. C.K. et al, 2016 grew GaN microdisks on graphene microdots. The graphene microdots were formed using negative photolithography and oxygen plasma etching without the use of growth masks. Graphene synthesized on Cu foil by CVD and transferred onto amorphous SiO_2 /Si substrate was prepared. This process was followed by the selective growth of ZnO nanowalls and subsequently the growth of GaN microdisk by the Metal-Organic Chemical Vapor Deposition (MOCVD) method. In their work, the disks were found to be double the size of the initial microdots which was an indication that epitaxial lateral overgrowth (ELOG) occurred. However, it was observed by electron backscatter diffraction that the individual disks had in-plane orientation because of the random orientation of the graphene grains in the transverse direction. They concluded that the microdisks were more polycrystalline or nearly single-crystalline. This drawback can be solved by using more single-crystal substrates for material growth which includes the use of graphene directly grown on sapphire substrates. H.B. et al, 2013 worked on the growth of GaN microdisk on ZnO nanowall coated dot patterned graphene using SiO_2 substrate and negative resist for selective etching. They used electron-beam lithography for selective growth and smaller area of growth on a smaller scale. They obtained selective growth on graphene with prospective usage in device fabrication, however, the crystallinity of individual disks can be improved using a single-crystal substrate for the microdisk growth.

C.K. et al 2014 worked on the growth of GaN microrods on graphene to build GaN/graphene heterostructure. They grew GaN microrods on the GaN buffer layer that was grown directly on graphene at an appreciably low temperature. The results yielded vertically aligned rods as confirmed in the X-ray diffraction characterization. However, the grown rods showed some unwanted extra peaks using the $\theta - 2\theta$ scan which were attributed to peaks from the GaN randomly oriented. This peak can be gotten rid of by obtaining single-crystal growth on graphene which will ensure very precise and regular diffraction at certain phi scans.

Chapter 3. Experimental Methods

This chapter gives detailed information about the apparatus/equipment used and techniques implored for material growth and fabrication of GaN micro-LED. The growth of ZnO nanowalls (which was used in this work for preliminary study) and GaN microstructures were done using the Metal-Organic Chemical Vapor Deposition (MOCVD) system. Specific information about the MO sources, gases, heating systems, and cooling systems, are penned down in this chapter. Additionally, measurement setup for different characterization techniques, various fabrication processes and methods, and maintenance methods for equipment are contained in this chapter.

3.1 Growth equipment and techniques

3.1.1 Metal-organic chemical vapor deposition (MOCVD) system

This is a method that was named by Manasevit when he observed that metal was carried by organic compounds. MOCVD is well known for the growth of III−V materials into heterostructures in a single system of apparatus. The use of MOCVD has expanded from just material growth to doping for novel research and commercial purposes. This project used vertical MOCVDs described in (Figure 3.1−Figure 3.4) to grow ZnO, GaN, and doped GaN. ZnO MOCVD had a Zn precursor used for the growth of ZnO and the other had Ga, Si, In and Mg precursors used for the growth of GaN and doped GaN. The precursors for ZnO MOCVD and Nitride MOCVD were carried by Ar and N_2 gases respectively and the MOCVD was put in a vacuum when not in use by Ar and N_2 gases respectively. Parts of the MOCVD include the cooling system, heating system (for substrates and dopants reactor lines of high vapor pressure MO sources in the case of Nitride MOCVD), gas delivery system, mass flow controller (MFC), pressure controller in conjunction with pneumatic valves, temperature controller by induction heater, low−pressure rotary pump, exhaust line, and water control system.

3.1.2 The Gas Delivery System Of MOCVD

The schematic of ZnO MOCVD is shown in Figure 3.1. High purity (99.999%) Argon was used as the carrier gas for DEZn (Zn source) and the ambient gas for the system. O_2 (99.995%) was the reacting gas with DEZn for the formation of ZnO. While the diethylzinc (DEZn) used was an electronic grade MO source. The gas flow was controlled by a mass flow control placed on the pathway of gases to the chamber. The DEZn source was put in a bubbler to control the temperature at −10°C. The flow and pressure of DEZn to the chamber were controlled by the inlet, outlet, by-pass diaphragm valve, and metering valves respectively. The temperature of the susceptor was controlled by a thermocouple positioned in an appropriate quartz tube.

As seen in Figure 3.3, from the extreme left of the figure there are three main gas supplies in the system: NH_3, H_2, and N_2. Each of these gases has a diaphragm valve attached to it to control the flow of gases in and out of the system. The diaphragm valve consists of the in, out, and throttling segments where the magnitude of gas flow can be controlled. The throttling segment of the valve has an inbuilt compressor that can be visualized as a flexible substance that easily expands inwards when opening for gas flow and compresses outwards when denying gas flow. The diaphragm valve is set to be delicate due to the light and flexible part of the throttling valve. The figure shows that NH_3 and H_2 are directly connected to the reactor chamber with a mass flow controller. While the N_2 has a direct connection with the MO sources to enable transport into the reactor chamber and is controlled by MFC for each source. All sources are kept in individual bubblers controlled at a suitable temperature. Reactants, gases, and dopants have a direct channel to the reactor compartment of the chamber. The flow rate of gas is comfortably controlled by the presence of pneumatic valves. The figure also shows bellow-shield metering valves attached to each source line to control the line pressure of reactants and dopants during growth.

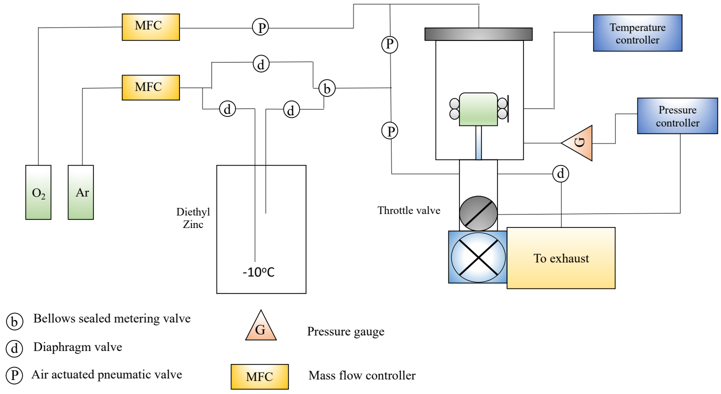


Figure 3.1: THE GAS DELIVERY SYSTEM OF VERTICAL ZNO MOCVD

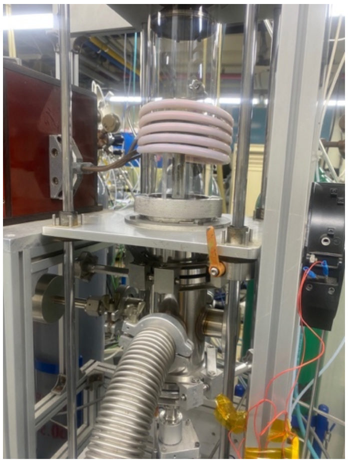


Figure 3.2: Image of Vertical ZnO MOCVD for ZnO nanowalls growth

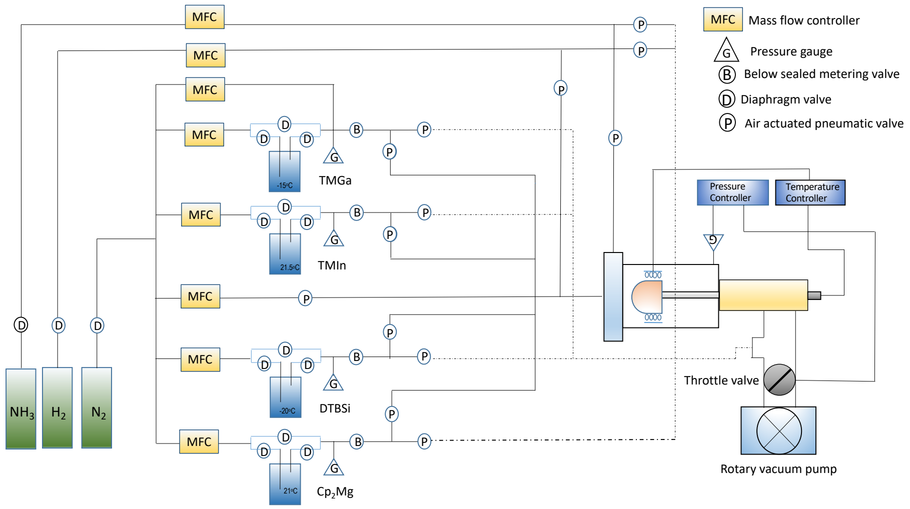


Figure 3.3: THE GAS DELIVERY SYSTEM OF VERTICAL MOCVD FOR NITRIDE SEMICONDUCTOR MATERIALS

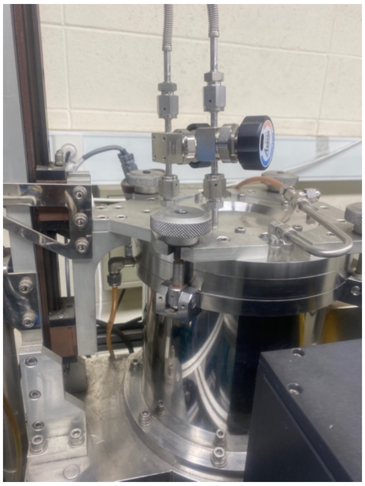


Figure 3.4: Image of vertical MOCVD for the GaN microdisk growth

3.2 Characterization Techniques of GaN Microdisk and Micro−LED

3.2.1 Field−emission scanning electron microscopy (FE−SEM)

This was used to investigate the structural characteristics of the microdisk and micro−LED. The morphology and selectivity of microdisk were observed at both 0° and 30° tilt. The acceleration voltage was around 10−30 kV. This characterization was done by Puspendu Guha at the Research Institute of Advanced Materials (RIAM) and Imhwan Kim at NICEM, Seoul National University.

3.2.2. Photoluminescence (PL) Spectroscopy

This method was used to investigate the optical properties of GaN microdisk grown on graphene layers. The PL spectrum was obtained at a temperature as low as 12K using a continuous He−Cd laser (325nm) as the source for excitation, with a set−up that consists of a monochromator (Dongwoo Optron Co. DM320i), a charge−coupled device (CCD, Andor Inc. DUO401A), cryostat, cooling system, a computer program (Andor iDus), and a rotary pump

3.2.3. Cathodoluminescence Spectroscopy

The optical property for specific GaN microdisk was observed. This method was used to compare the optical properties of GaN microdisk grown by epitaxial lateral overgrowth (ELOG). This was done at the Research Institute of Advanced Materials (RIAM) with the use of a Gatan monoCL$_4$. In this investigation, an electron beam is scanned into the GaN microdisk and each disk generates a cathodoluminescence ray that can be detected and further analyzed as an image.

3.2.4. Electron Back-scattering Diffraction (EBSD)

The growth orientation and crystallinity of GaN microdisk grown on graphene layers were observed using the EBSD. The EBSD system used comprised of a high speed and low noise CMOS image sensor, low beam current of 100pA, and low excitation voltage of 5kV. The EBSD was used for both FE-SEM and EBSD for accuracy in analysis.

3.2.5. X−ray Diffraction (XRD)

XRD was also used to investigate the crystallinity and growth orientation of GaN microdisk. The system is PAN analytic X’ pert PRO XRD system with Ni−filtered Cu K**α** radiation. In this investigation, the rocking curve, and phi−scan was observed.

3.2.6. Electroluminescence Spectrum (EL) and Current−Voltage characterization of GaN micro−LEDs on graphene layers

This technique is used to characterize the light emission from the GaN micro−LED. The set−up used for this measurement consists of an optical microscope, contact probes, Keithley 2400 for the I−V measurements, source meter, monochromator attached−CCD camera for EL emission measurements, and computer program.

3.3. Fabrication equipment and techniques

The equipment used for fabrication was a thermal evaporator for metal coating, oxygen plasma etcher for etching of PI layer and graphene layers, rapid thermal annealer for metal annealing to aid ohmic contact, and for the annealing of PI layer, and spin coater for coating of PI layer.

Chapter 4. Growth of GaN microdisk on graphene layers

4.1 Effect of growth temperature and growth time on ELOG of GaN microdisk grown on graphene layers using ZnO nanowalls as an intermediate layer

CVD−grown graphene was patterned using a SiO_2 mask by photolithography. The hole pattern was formed effectively by the reactive−ion etching (RIE) and the buffered oxide etching (BOE) method (Figure 4.1). To aid the epitaxial growth of GaN on graphene, ZnO nanowalls were selectively grown on exposed areas using DEZn and O_2 as the sources. First, the low−temperature GaN layer was coated on the ZnO nanowalls using N_2 as the DEZn carrier gas at 540°C. This step protects ZnO nanowalls from decomposing during the GaN microdisk growth[8,13] and was followed by GaN crystallinity growth on the LT−GaN layer at 1050°C (Figure 4.3) using the pulsed−mode MOCVD[10]. The growth of GaN microdisk by ELOG was studied by changing the growth time and size of ZnO nanowalls (Figure 4.5). At 2.3 μm diameter of ZnO nanowalls, GaN microdisk was 7.0 μm and 2.0 μm in diameter and height respectively at 45 mins. And as growth time increased to 75mins, diameter and height increased directly by 2.2 μm and 0.5−1.0 μm in diameter[8,10] and height respectively. In the case of 4.3 μm size ZnO nanowalls, diameter and height increment were observed to be 2.8−3.0 μm and 0.2 μm respectively. It was observed that the vertical growth of GaN microdisk is faster for a smaller diameter than for a bigger diameter while the horizontal growth can be achieved faster with a larger diameter hole size. However, it can be seen that optimum ELOG growth can be effectively obtained for a smaller diameter hole pattern.

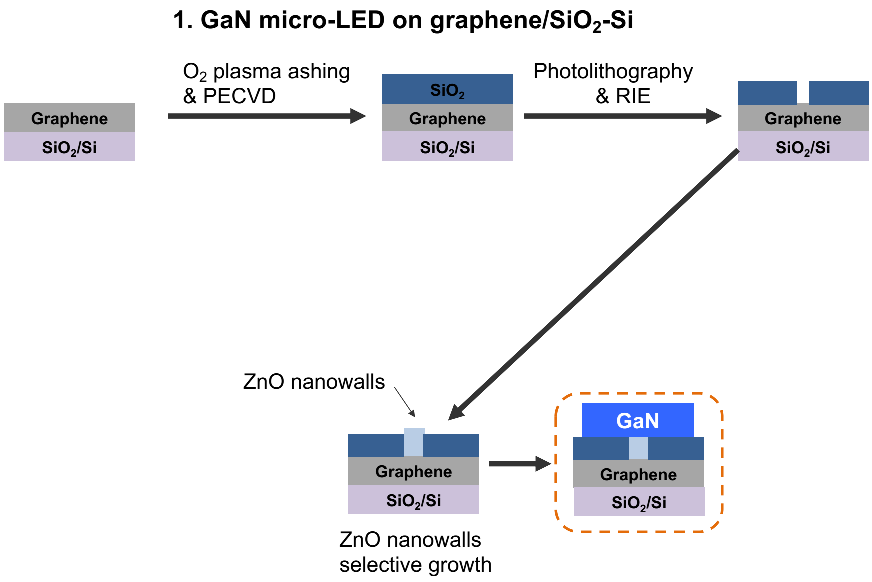


Figure 4. 1: Schematics for the growth of GaN microdisk on ZnO/graphene/SiO_2

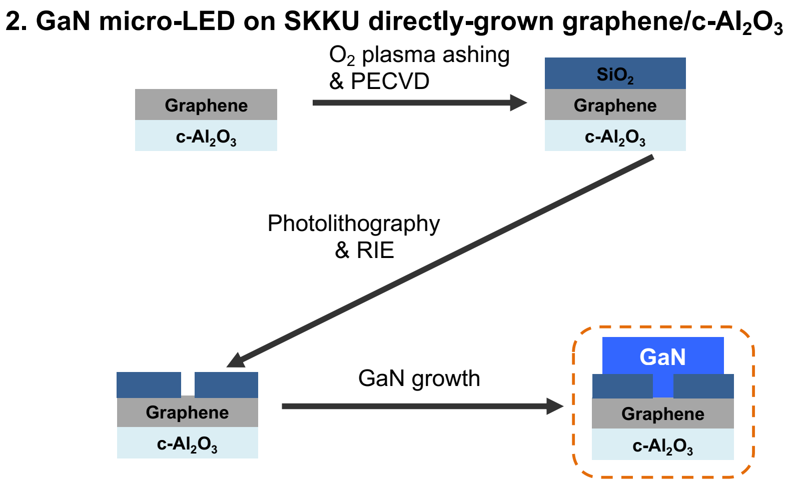


Figure 4. 2: Schematics for the growth of single−crystalline GaN microdisk on graphene/c−sapphire

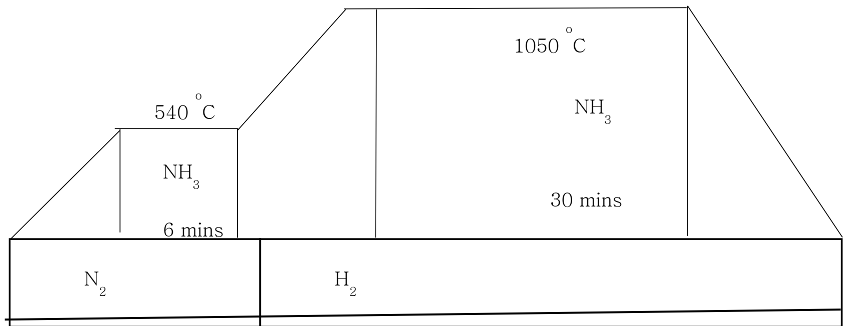


Figure 4. 3: Growth profile of GaN microdisk on ZnO nanowalls

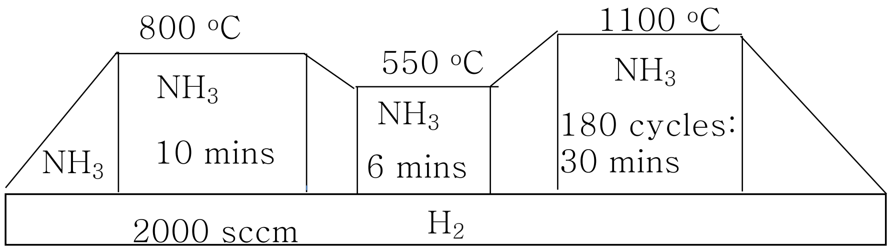


Figure 4. 4: Growth profile of GaN microdisk on graphene

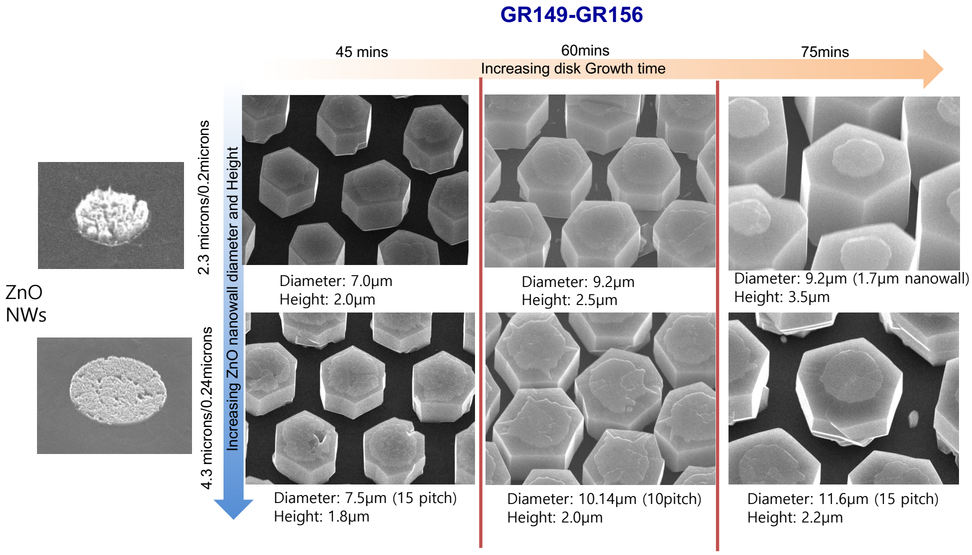


Figure 4. 5: Plot of GaN microdisk growth dependency on ZnO nanowalls diameter against Growth time

4.2 Growth and characterization of GaN microdisk grown on ZnO/graphene/c−Al_2O_3

A similar method as described in section 4.1 was used to grow GaN microdisk on ZnO/graphene/c−Al_2O_3 (Figure 4. 6). The grown microdisk on ZnO was studied using electron backscatter diffraction (EBSD) to examine the growth orientation and crystallinity of the microdisk, Photoluminescence was used to characterize the optical property of GaN microdisk grown on ZnO/graphene/c−Al_2O_3. The field−emission scanning electron microscope showed as expected GaN microdisk was grown selectively with size increment both vertically and horizontally. The result was well comparable with the disks grown on SiO_2 substrates. The microdisk further showed a uniform orientation of the disk in the normal direction using the EBSD (Figure 4. 7)However, the transverse direction IPF maps examination appeared to be like microdisk grown on polycrystalline graphene layers. Although, the substrate used was a graphene directly grown on single−crystalline c−Al_2O_3, which was a clear reason to expect a single crystal/

uniformly oriented micro disk. However, the results from EBSD analysis can be tied to the inhomogeneous in-plane orientation of the GaN micro disk grown on ZnO/graphene/c-Al_2O_3 substrate[16]. This result is like that obtained by Chung et al, 2016, who observed that polycrystalline graphene has a major effect on the crystallinity of GaN micro disk due to the density of the grain boundaries of the underlying graphene.

The Photoluminescence (PL) spectrum of the GaN microdisk array was obtained at room temperature using the helium-cadmium (He-Cd) in continuous wave mode as an excitation source. In Figure 4. 8 The PL peak showed dominance at 3.472 eV, and extra peak at 3.429 which can be attributed to the inherent defect caused by NH_3-pulsed mode. A somewhat deep-level emission was observed at 2.2 eV, which can be attributed to near-band-edge (NBE) emission related to the deep levels and excitons[17].

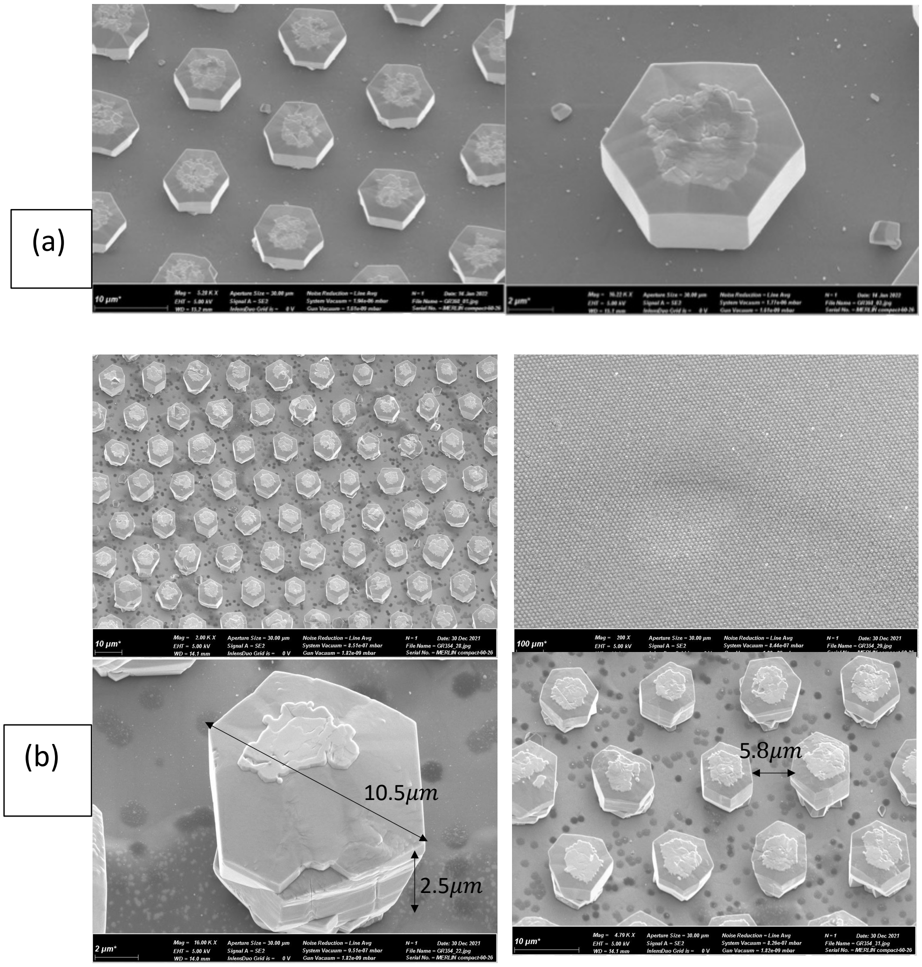


Figure 4. 6: FE-SEM 30℃ tilt image of GaN microdisk grown on ZnO coated 5μm patterned graphene/c−Al_2O_3 (a) few arrays of microdisk immediately showing the alignment and selectivity of disk arrays (b) combined image of microdisk showing magnification from 2 μm to 100 μm, diameter of disk after ELOG growth, disk to disk distance (pitch) of disk arrays

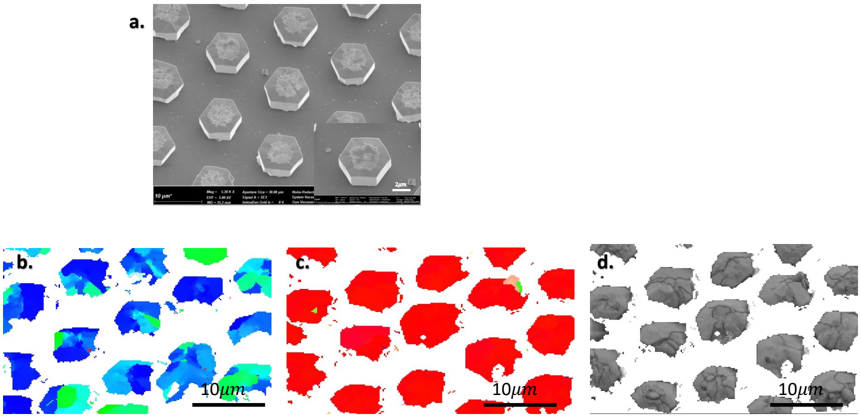


Figure 4. 7: EBSD analysis of GaN microdisk grown on ZnO graphene/c−sapphire (a) 30°C tilt view of FESEM image of GaN microdisk, (b) Transverse direction IFP maps of GaN microdisk array, (c) Normal direction IFP maps of GaN microdisk, (d) large scale grain boundary IFP maps

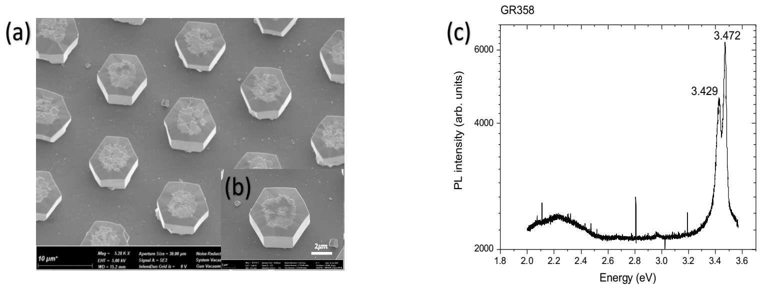


Figure 4. 8: Optical Characterization of GaN microdisk array grown on ZnO/graphene/c−Al_2O_3 (a) Structural Image of GaN/ZnO/graphene/c−Al_2O_3 structure (b) larger magnification of (a). (c) photoluminescence of (a) at room temperature(a).

4.3 Growth and characterization of GaN microdisk on graphene/c-Al_2O_3

In this experiment, graphene was grown directly on the c-Al_2O_3 substrate using the Chemical vapor deposition (CVD) technique and GaN microdisk was grown on the prepared graphene/c-Al_2O_3 substrate. Nucleation sites were formed on the graphene surface by rapid oxygen plasma treatment that produces atomic cliffs[17] for 2s and a SiO_2 mask patterning method as seen in Figure 4. 2 above. For good alignment of microstructures and controlled growth direction, a buffer layer was formed on graphene[9] before the two-step growth of the GaN microdisk was done. The sufficient nitridation treatment and buffer layer were adequate to create in-plane orientation of individual microdisks grown on graphene. The growth of GaN microdisk on graphene/c-Al_2O_3 was done using the vertical metal-organic chemical vapor deposition (MOCVD) technique with Trimethylgallium (TM) and NH_3 as the sources, and Hydrogen as the ambient gas. The nitridation was done at $800^{o}C$ for 10mins, and the GaN buffer growth was done at $550^{o}C$ for the formation of the seeding layer. The temperature was again raised to $(1050-1150)°C$ to grow GaN microdisk selectively by the NH_3-pulsed mode for 20-30 mins. This step was proven to support the lateral growth of GaN on graphene layers[16]. The effect of growth temperature on GaN microdisk on graphene was further studied. The temperature of GaN microdisk growth reduced the pulsed lateral overgrowth (PLOG) ratio but increased the top surface of the microdisk changed in morphology due to low temperature for crystallinity. Also, the effect of growth time of GaN microdisk growth was observed to be significant in lateral and vertical growth of GaN microdisk on graphene (Figure 4. 9).

The as-grown GaN microdisk on hole-patterned graphene/c-Al_2O_3 was first structurally characterized using the Field-Emission scanning electron microscopy (FE-SEM), and electron backscatter diffraction (EBSD) technique. The EBSD analysis was used to inspect the out-of-plane and in-plane crystal orientation of hexagonal GaN microdisk arrays grown on graphene layers. Figure 4. 10 shows the orientation of orthogonal crystallographic axes in the wurtzite crystal structure, mapped out in the normal and transverse directions respectively, using the inverse pole figure (IPF). Such that red, green, and blue corresponds to the three crystallographic orientations respectively. The projection along <001> axis showed a red color on the whole area of disk arrays, demonstrating that all GaN microdisk were found to be orientated only in the c-axis direction irrespective of possible presence of an in-plane orientation (Figure 4. 10d). Furthermore, the IPF map in the projection along <010> axis corresponding to map orientation in transverse direction displayed blue color. The epitaxial growth of GaN microdisk was done on CVD-graphene films grown on *c*-Al_2O_3 substrate. Where the orientation of graphene grains is said to be directionally defined and not random, indicating the absence of in-plane orientation among the individual microdisk (Figure 4. 10e). The hypothesis that single-crystalline GaN microdisk can be epitaxially and selectively grown on graphene is backed up by these EBSD results. The aligned orientation, homogeneity, and crystallinity of GaN microdisk was improved by using graphene films directly grown on single-crystal substrate and speculated to have larger grains.

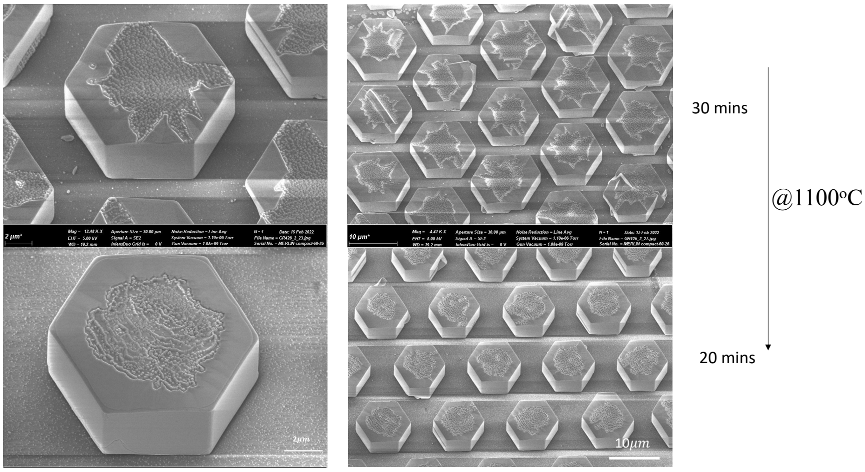


Figure 4. 9: FE-SEM image GaN microdisk grown on the graphene/c-sapphire substrate at 1100℃ for 30 mins and 20 mins respectively

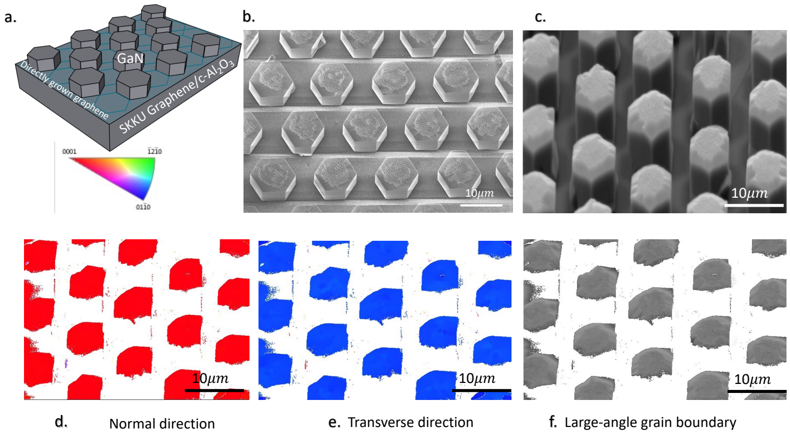


Figure 4. 10: Electron Back-scattering analysis of GaN microdisk grown on graphene/c-sapphire (a) Schematics of GaN microdisk on graphene (b) 30℃ tilt FESEM image of GaN microdisk, (c) FESEM image of EBSD analysis (d) Normal direction IFP maps of GaN microdisk, (e) Transverse direction IFP maps of GaN microdisk, (f) large scale grain boundary

The selective growth orientation of GaN microdisk and its crystallinity was further investigated using X-ray diffraction (XRD). 4.11b shows the scan results of GaN microdisk grown on graphene. The range of angles was -50^{o} – 400^{o}. The wurtzite crystal peaks were observed at 30, 90, 150, 210, 270, and 330 respectively. The ϕ scan showed 6 peaks separated each by 25^{o}, showing a 6-fold symmetric structure. There was no observed additional peak in the XRD spectra which implies the highly single crystallinity of the disk arrays. The rocking curve of the GaN microdisk grown on graphene/c-Al_2O_3 was also measured as in c. The full width at half-maximum (FWHM) of the GaN micro disk was estimated to be 0.22^{o} which defines the thin sharp peak that gives information about the single crystallinity of the material. The XRD and EBSD data provided a strong suggestion that the GaN microdisk are orientated in a singular direction i.e., homogenous in-plane orientation of disk arrays with underlying substrate and can be referred to as single-crystalline. This quality makes it a good fit for the fabrication of high-efficiency optoelectronic devices[2].

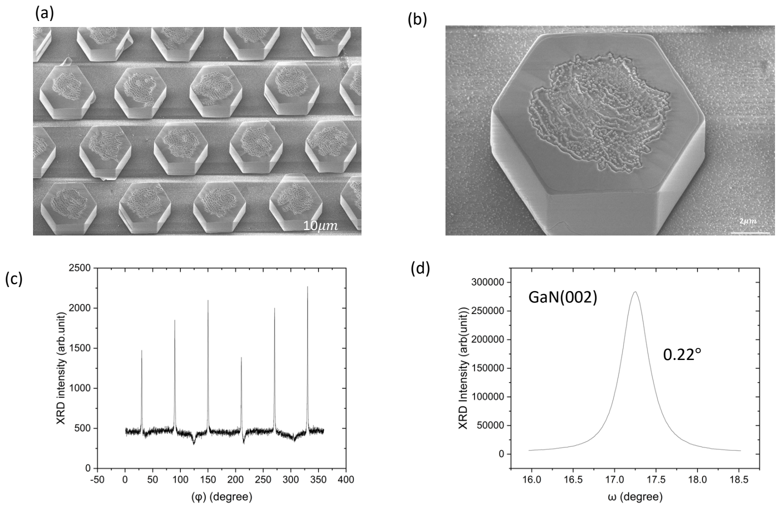


Figure 4. 11: Xray diffraction analysis of microdisk using the (c) phi scan, with 25° inter peak distance for 6-fold symmetric crystal structure and (d) rocking curve

4.4 Comparisons of GaN microdisk grown on graphene layers with GaN microdisk grown on ZnO/graphene layers.

The above results in sections 4.1– 4.3 have given a detailed explanation of different cases of GaN microdisk grown on graphene layers. However, with deep comparisons between two major cases: (1) GaN microdisk grown on graphene/c–Al_2O_3, and (2) GaN microdisk grown on ZnO/graphene/c–Al_2O_3.The comparisons of both cases were done using electron back–scattering diffraction (EBSD). Figure 4. 12 showed that GaN microdisk grown directly on graphene showed similar blue color in transverse direction, (which gives information about the in–plane orientation of microdisk) from all microdisk while that grown on ZnO showed some domains that led to unwanted green colors from other directions aside from the transverse direction[16].

The orientation of the GaN microdisk has a major effect on the crystallinity of GaN material and microdevices. The two cases of GaN microdisk growth structure were compared using the optical properties obtained by the photoluminescence spectrum at low temperatures. A clear difference was seen in the existence of an extra defect peak in the ZnO−based GaN microdisk while the absence of such a peak was observed in the GaN/graphene sample[9]. The presence of the ZnO intermediate layer makes the GaN microdisk vulnerable to more defects due to the dislocation from the center of disk surface area, where the ZnO is located, which is what influenced the presence of the visible extra peak in the spectrum.

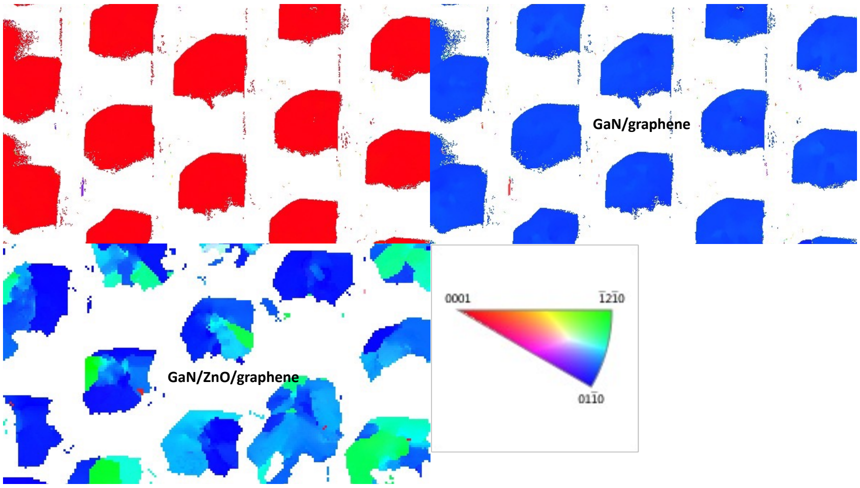
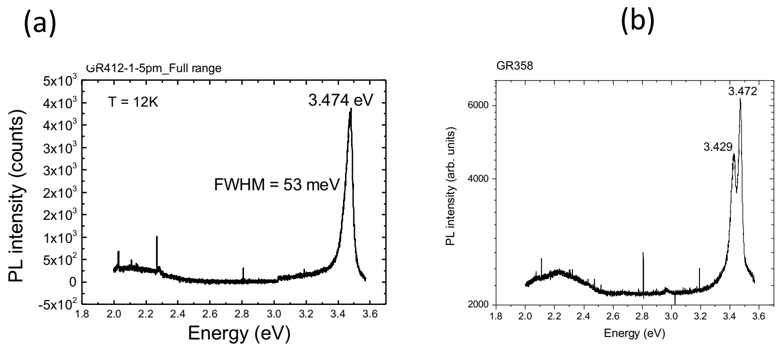


Figure 4. 12: Comparison of GaN microdisks based on growth orientation by electron back-scattering diffraction (EBSD)



GaN/graphene/c-Al_2O_3 GaN/ZnO/graphene/c-Al_2O_3

Figure 4. 13: Comparison of GaN microdisk based on optical properties using the photoluminescence spectrum at low temperature (a) PL spectrum from GaN microdisk grown directly on graphene (b) PL spectrum from GaN microdisk grown on ZnO/graphene

Chapter 5. Fabrication of flexible GaN micro-LED using single-crystalline GaN microdisk arrays on graphene/c-Al_2O_3

5.1 Growth of GaN micro-LEDs on graphene/c-Al_2O_3 using the metal-organic chemical vapor deposition (MOCVD) technique

The grown GaN microdisk was used as a template for the fabrication of p-n junction GaN micro-LEDs on graphene/*c*- Al_2O_3 with insertion of 3 periods of In_xGa_{1-x}/GaN as the multiple quantum wells (MQW). An n-doped-GaN was formed by conformally coating the un-doped GaN microdisk in form of a flat and smooth-walled pyramidal shape[2]. Thereafter, MQWs were formed on the sidewalls of the *n*-GaN by an MOCVD continuous growth mode. And then the p-GaN was finally deposited, which gave the flat top surface (Figure 5. 1). The GaN micro-LED structures were selectively grown on neat and well-shaped facets.

5.2 Fabrication process of GaN micro-LED using single-crystal GaN microdisk arrays

For the fabrication of GaN micro-LED, the *p*-GaN layer was activated at 750°C for 10 mins using the rapid thermal annealing method. Then a thin metal layer of Ni/Au (5nm/5nm) was coated to form ohmic contacts on the *p*-GaN layer. To achieve easy lift-off and proper demarcation between the n and p contact, the microdisk sample was coated with polyimide. And then, the metal p-contacts were formed by Ni/Au (20nm/20nm) and annealed at a temperature below 400°C due to the PI layer present in the structure. The SiO_2 mask was dissolved by buffered oxide etchant (BOE) and the GaN disk array was easily lifted by the thermal release tape. Then n-contact was formed at the back of the sample after the lift-off process, with Ti/Au (20nm/20nm). For the device set-up, GaN micro-LED was transferred onto silver paint-coated Cu foil at 190°C and annealed in air ambient using the rapid thermal annealing method for 3 mins at 300℃. A similar growth process and lift-off technique was used for GaN microdisk grown on graphene/SiO_2 substrate to serve as a reference for the sample of interest. GaN micro-LED structure was fabricated on the as-grown GaN microdisk using the SiO_2 substrate for the fabrication of blue micro-LEDs with appropriate n and p contacts as reported by Y.T. et al[18].

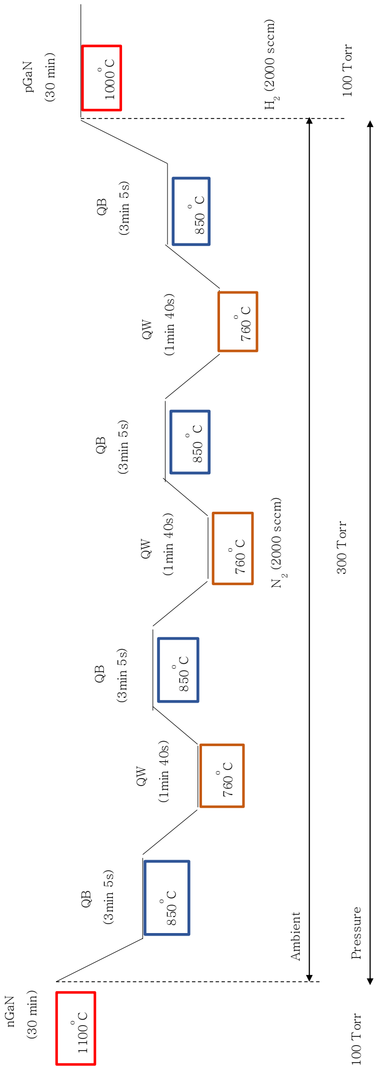


Figure 5. 1: Profile diagram for GaN micro−LED growth

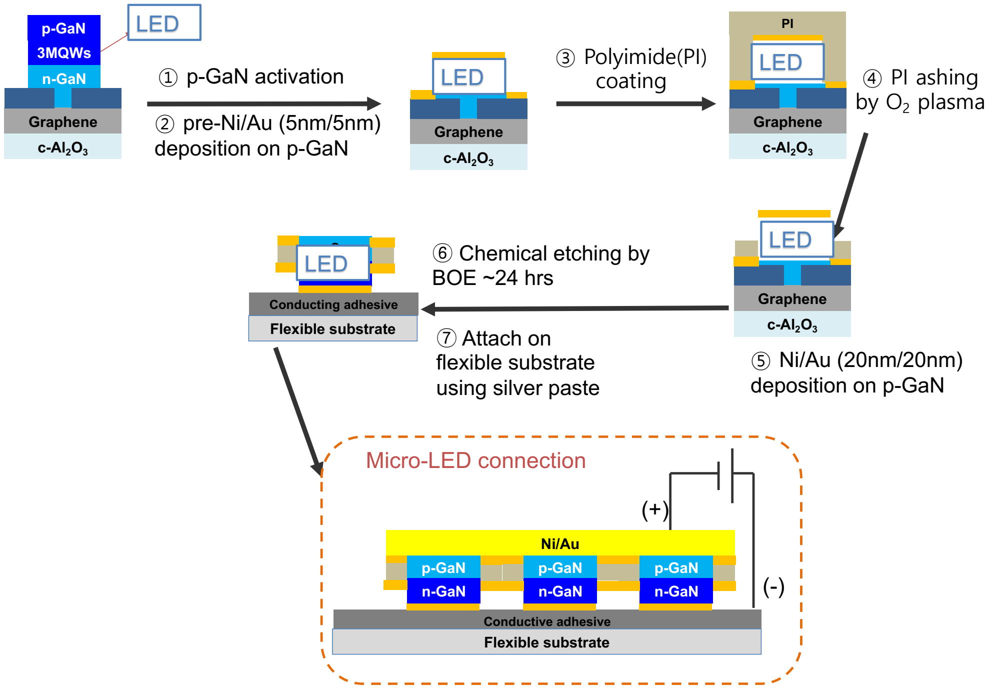


Figure 5. 2: Schematics for flexible GaN micro-LED fabrication process

5.3 Electrical characterization of GaN micro−LED grown on single−crystal GaN microdisk arrays

GaN micro−LED was characterized using the EL and I−V with bias voltage ranging from −4 to 10V. Figure 5. 3 shows a high magnification of the optical light emission image at 28.4 mA from the micro–LEDs transferred onto an Ag coated Cu foil. A full blue light emission was observed and clearly visible with the naked eyes within a specific area of contact under the typical room illumination condition. The clear distinction between each microdisk pixel makes it desirable for display purposes. Furthermore, the light emission characteristics of an individual GaN micro–LED was investigated by a magnified image of the optical view as seen in the inset of Figure 5. 3a. Light was emitted from both the center ELOG region with a dominant blue light emission from the ELOG region compared to the center. This result proposes that the performance of micro–LED based on graphene can be enhanced using ELOG method.

Figure 5. 3c shows the quantitative EL characteristics of micro–LED array at applied bias voltage ranging from 8–10 V. At zero bias voltage no emission observed, as the bias voltage was

slightly increased to 8 V a low electroluminescence intensity was observed with a current flow of 26.7 mA. The EL peak experienced a blue shift in value in the direction of 500 nm wavelength. This shift can be attributed to $In_xGa_{1-x}N/GaN$ MQWs[17,19,20] composition in the LED structure. Also, a somewhat broad shoulder at 510 nm was observed which can be associated with the deep-level emission from the *p*-GaN layer[2,21] and the nonuniformity in the thickness of quantum well layers formed on the facet of *n*-GaN microdisks[19,22].A further increase in the current to 10 mA resulted into a proportional increase in the EL intensity and a dominant peak of 463 nm. It was observed that despite the uniform light emission there still exist some dead local areas, which is suspected to be from the failure of conducting layer to uniformly make electrical contact with whole area of the micro-LED arrays[1,23,24]. Some of the assumed to be dead spot lighted up at a higher voltage bias, implying that individual LEDs lights up at its own turn-on voltage. However, this nonuniformity in turn-on voltage[25] can be attributed to irregular current injection across the whole surface of disk in contact with metal layer [26] . Additionally, electrical characterization of micro-LEDs was further investigated by the I–V characteristics of the LEDs. Figure 5. 3(d) shows the expected rectifying behavior of a *p–n* junction with turn–on voltage of 4 V and a minute value of current leakage within the range of -5×10^{-4} mA at 4 V. The increase of bias voltage showed a rapid increase in current flow and light emission intensity. This result is a clear indication that at the *p–n* junctions and the MQWs layers of micro–LEDs carrier injection and recombination that is said to be radiative produces the EL emission.

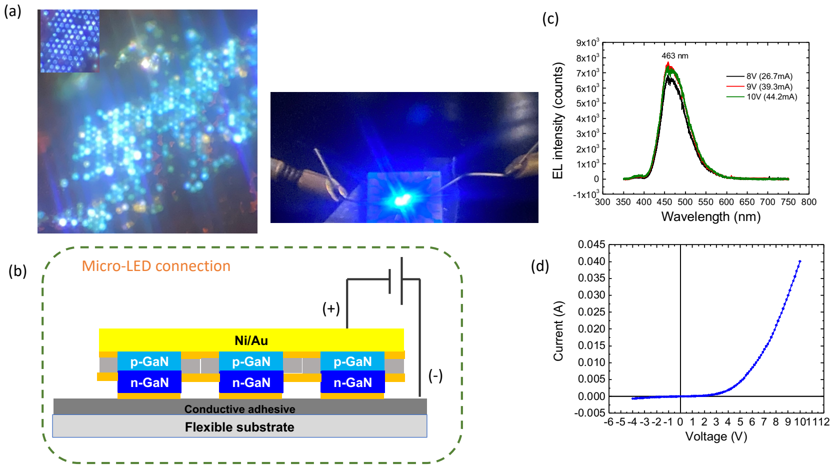


Figure 5. 3: micro−LED fabrication images and connection set−up: Optical images of micro−LEDs taken using the optical microscope (a) Optical image of light emission using an optical microscope in the illuminated room; (b) electrical connection set−up for LED; (c) EL spectra at various voltage bias at room temperature (d) I–V characteristics of micro−LED with voltage sweep from −6 V to 12 V

5.4. Mechanical characterization of GaN micro-LED using single-crystalline GaN microdisk arrays

A micro-LED substrate carrier, 10 mm long was bent to form a radius of 5 mm curve, and it was observed that the dominant EL peak retained its position and consistency in EL intensity (Figure 5. 4). The microstructure of the LEDs makes it an advantage for this accommodation of extreme bending conditions[27]. Electrical characteristics of light emission were investigated in detail using the EL characteristics. The effect of mechanical deformation was further investigated by rolling up the microdisk around a thin wire of a 1mm radius as seen in Figure 5. 4(b). Figure 5. 4c shows that at room temperature EL spectra intensity decreased as the bending radius changed from infinity to 8 mm and further decreased at a 5 mm radius. However, there was no observable change in the EL position and shape, indicating that flexible microstructures did not lose their optical characteristics during bending or mechanical deformation. Although a crack was observed on the contact pad and therefore attribute this observation to the reason for a reduction in EL intensity

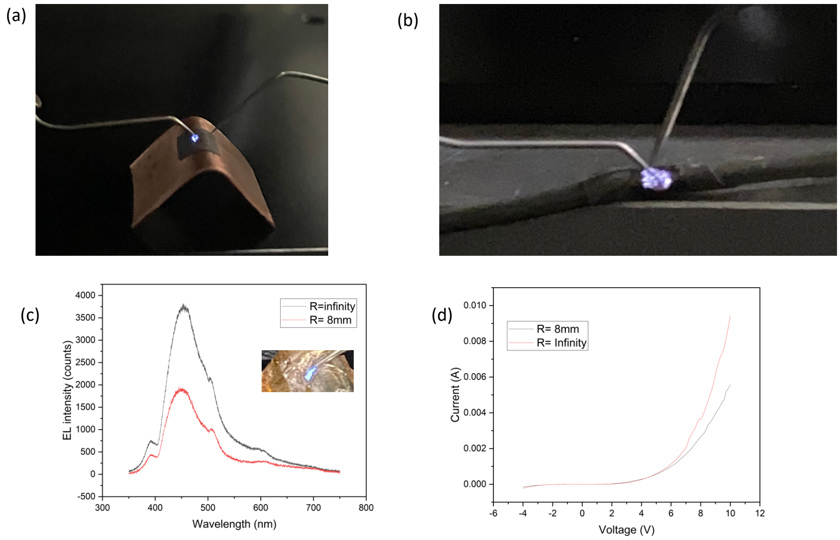


Figure 5. 4: Mechanical characterization of GaN micro−LED (a) Optical image of flexible GaN micro−LEDs transferred onto a conducting tape; (b) Optical image of flexible GaN micro−LEDs rolled on a thin wire (c) EL spectrum of. bending test for micro−LED at infinity and bending radius of 8mm; (d) current−voltage characteristics of bending test for micro−LED at infinity and bending radius of 8 mm

Chapter 6. Conclusion

In conclusion, a single-crystalline GaN microdisk was epitaxially grown on the graphene/c-Al_2O_3 substrate at 1100℃ for 20 mins with a pre-nitridation treatment before the LT-GaN growth. The grown microstructure was structurally characterized by Field-effect scanning electron microscopy (FESEM), electron backscatter diffraction (EBSD), and X-ray diffraction (XRD). The microdisk was observed to be uniformly oriented in the normal and transverse direction, single-crystal, and uniformly aligned. The microdisk was observed to possess a 6-fold symmetry in the XRD crystallinity examination. The fabricated LED was characterized by I-V and Electroluminescence (EL) characteristics. The fabricated LED structure showed light emission between 2V and 10V with emission intensity directly proportional to the bias voltage supply. The LED was seen to accommodate its electrical, structural, and optical properties while the bending test took place. The light emission displayed a reduction in current level and EL intensity but conserved the spectrum and I-V characteristics.

Abstract in Korean

그래핀에서 성장한 단결정 GaN 마이크로 디스크 어레이를 사용한 유연한 마이크로 발광 다이오드

토빌로바 그레이스 파분미

물리천문학과

서울대학

유연한 마이크로 발광 다이오드의 제작은 최적화된 성장 조건에 의해 성장한 단결정 GaN 마이크로 디스크 어레이를 사용하여 연구되었다. 화학기상증착법에 의해 c−Al_2O_3에서 직접 성장시킨 그래핀 층에서의 단결정 GaN 마이크로 디스크 어레이의 에피택셜 성장(epitaxial growth)은 MOCVD(Metal−organic chemical vapor deposition)법을 이용하여 연구하였다. 이러한 성장 이전에 산소 플라즈마 처리 방법을 사용하여 그래핀 표면에 핵 생성 부위가 형성되었다. 연구에 사용된 성장 매개변수는 1050oC와 1100oC 사이의 성장 온도와 20분에서 30분 사이의 성장 시간이었다. 단결정 GaN 마이크로 디스크 구조의 달성을 위해 ZnO 중간층을 사용하는 방법과 ZnO 중간층을 사용하지 않는 방법 두 가지 방법으로 성장 방법을 연구하였다.[2]

[2] 이 논문의 저자는 한국 정부의 후원을 받는 글로벌 코리아 장학생이다.

GaN 마이크로 디스크의 형태와 선택성은 전계방출 주사전자현미경을 이용하여 관찰하였으며, 마이크로 디스크의 성장 방향은 전자 후방 산란 회절기술(EBSD)을 이용하여 나타나 이었다. 결정성은 XRD(X-ray diffraction)를 이용하여 관찰하였으며, 광학적 특성화는 PL(Photoluminescence)에 의해 수행되었다. GaN 마이크로 디스크는 일정한 면내 배향성을 갖는 단결정 특성을 보였는데, 이는 그래핀 층의 하층 특성으로 인해 입게 감소의 영향을 받은 것으로 보인다.

GaN 마이크로 발광 다이오드는 n-GaN, 다중 양자 우물 (3-4층), 양자 장벽 (우물 사이의 층 간으로) 및 p-GaN을 성장시켜 제조되었다. 발광 달성을 위해 p-GaN 층을 750℃ 에서 p-GaN층을 활성화하고, p-GaN층 위에 직접 ohmic 콘택트를 형성하였으며, 개별 디스크 사이의 간격을 메우기 위해 폴리이미드층을 사용하였으며, 금속p-콘택트를 형성하였다. n-contact의 형성을 위해 GaN micro-LED는 화학적 에칭(Buffered oxide etchant를 사용하여 SiO2 층을 에칭)에 의해 c-Al2O3 기판으로부터 분리하 되었다. (완충 된 산화물 식각 제를 사용하여 SiO_2 층을 식각) 하고, Ti/Au를 사용하여 금속 n-contacts를 형성하였다. 제조된 발광 다이오드는 I-V 특성, Electroluminescence, 유연성, 굽힘 및 탈착상 테스트를 사용하여 특성 화하였다. 턴온 전압은 4V였으며, I-V 특성은 파괴 전압 없이 p-n 접합을 나타내었다. EL 스펙트럼 및 I-V 특성은 460nm에서 지배적인 피크를 보여주었다. EL 스펙트럼은 R=

∞에서 R= 8mm로 벤딩된 후에도 변형되지 않은 상태로 남아 있었다.

키워드: GaN, 마이크로 디스크, 단결정, 그래핀/c−Al_2O_3, MOCVD

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[24] (Andrew Carlson, 2012)
[25] (Sands, 1999)
[26] (Chung, 2010)
[27] (Harris, 2016)