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Fabrication of less strained and more efficient GaN LED

스트레스가 감소된 고효율 GaN LED에 관한 연구

2014년 2월

서울대학교 대학원
재료공학부
김중학
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지도교수 윤의준

이 논문을 공학박사 학위논문으로 제출함

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Abstract

Fabrication of less strained and more efficient GaN LED

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The wide-bandgap GaN and related materials have extensively been studied and utilized in important optoelectronic device applications such as light emitting diodes (LEDs) and laser diodes. However, in order to realize high-performance and reliable optoelectronic devices, high quality GaN epitaxial layers are definitely required. GaN-based epitaxial layers are often grown on foreign substrates such as ZnO, Si, LiGaO₂ and Al₂O₃. Among these substrates, sapphire (Al₂O₃) substrates are extensively used because of high quality, transparency, high temperature stability, and availability in large-area wafers. However, large mismatches in lattice constant and thermal expansion coefficient between GaN and sapphire substrates cause several severe problems in the fabrication of high efficiency optoelectronic devices.

The three major problems in the GaN-based LED structures grown on sapphire substrates are the high dislocation density in GaN due to lattice
mismatch, poor light extraction and significant wafer bowing. High density dislocations, regarded as major non-radiative recombination centers in GaN-based LEDs, typically lower the LED external efficiency and shorten the device lifetime. Moreover, the large difference in refractive index between GaN (2.4) and sapphire (1.7) results in poor light extraction due to total internal reflection. Severe wafer bowing also hinders the mass production of LEDs in large-area wafers. The thermal expansion coefficient of sapphire is much larger than that of GaN so that severe biaxial compressive stress is generated within GaN during cooling process after high temperature deposition. As a result, severe wafer bowing is occurred. Wafer bowing often causes cracks in the GaN epitaxial layers during laser radiation for lift-off process used for the fabrication of vertical LEDs. Moreover, it has been reported that the convex wafer bowing increases the X-ray rocking curve full width at half maximum (XRC FWHM) value of GaN (002) plane up to 7%, indicating the reduction of GaN crystal quality.

To overcome these problems, two methods were proposed in this study. Firstly, GaN thin film was grown on silica hollow nanosphere(S-HNS) coated sapphire substrate. Secondly, GaN thin film was grown using sapphire substrate with SiO2 thin film on its backside.

To grow GaN thin film using S-HNS coated substrate, S-HNS coated sapphire substrate was made by using nanoscale polystyrene(PS)/SiO2 coreshell sphere monolayer fabricated by modified dip coating method. After dip coating of PS/SiO2 coreshell structure, thermal annealing was followed to remove PS and fixation of S-HNS. And un-doped GaN thin film and LED structure was grown by metalorganic chemical vapor deposition(MOCVD). LED device was fabricated by conventional photolithography, dry etching,
and metal electrode deposition using LED structure with and without containing S-HNS monolayers. By insertion of S-HNS into LED structure, XRC FWHM value of (102) plane was reduced from 480 to 345 arcsec, dislocation density was reduced from $4 \times 10^8$ cm$^{-2}$ to $1 \times 10^8$ cm$^{-2}$, compressive stress of GaN thin film was reduced almost 20% and output power of LED device was increased almost 2 times. S-HNS induces nanoscale lateral epitaxial overgrowth so internal quantum efficiency is enhanced. And low refractive index of S-HNS causes photon scattering as a result light extraction efficiency is increased.

To reduce the wafer bowing, LED structure was grown on sapphire substrate with SiO$_2$ thin film on its backside. By using this method, wafer bowing is reduced almost 60% and compressive stress is also greatly reduced.

**Key Words:**

Metalorganic chemical vapor deposition (MOCVD), silica hollow nanosphere(S-HNS), modified dip coating, light emitting diode(LED), wafer bowing, dislocation density

**Student Number:** 2009-30149
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Chapter 1. Introduction

1.1. Problems of conventional GaN based LED

The group III-nitrides, including gallium nitride (GaN), indium nitride (InN), aluminum nitride (AlN), and their alloys such as InGaN and AlGaN have attracted much attention over the past few decades due to the recent realization of high brightness blue and green light emitting diodes (LEDs) and laser diodes (LDs). When group III-nitride is grown on typical wurzite structures, they can form continuous and direct bandgap alloy from 6.2 eV (AlN) to 0.7 eV (InN). So III-nitride alloy make possible to fabricate high performance LED device whose wavelength ranges from infrared (IR) to ultraviolet (UV) region, also covering full visible light region. Besides their superior optical properties, group III-nitrides shows good superior thermal stability at high temperature, large thermal conductivity, good chemical inertness, high electron velocity and good mechanical strength. General properties of nitrides are in summarized in table 1.1 and fig 1.1. Like this group III-nitride materials has much superior characteristics so they are used in many field not only LED and LED but also photodetector, high electron mobility transistor (HEMT) and field effect transistor (FET), etc.[1]

Brilliant success of LED and LD device can be attributed to the realization of epitaxial growth of GaN thin film and the excellent optical properties of InGaN layer.[2-3] Among the nitride materials, Especially GaN is much attracted by researchers because GaN is the main material used for making LED. But high quality thin film growth using GaN is very difficult. In growth of GaN, homo-epitaxy is almost impossible because of difficulties
of making nitride substrate. Generally, the equilibrium vapor pressure of nitride material is very high and the melting point of nitride material is very high and growth speed of nitride material is very slow.[4] So making nitride substrate using Czochralski method is almost impossible. For that reason, nitride materials are commonly grown by heteroepitaxy.[5-8] Especially sapphire substrate is commonly used to growing nitride thin film. But the crystallographic properties and mechanical properties between nitride thin film and sapphire substrate are very different. Large difference of thermal expansion coefficient (over 30%), lattice constant (over 17%) and refractive index (over 30%) makes problems to make high efficiency LED device. Large difference of lattice constant causes high density crystal defect such as dislocation which reduces internal quantum efficiency by enhancing non-radiative recombination and broaden XRC FWHM value of GaN thin film.[9] Large difference of refractive index between GaN, sapphire and air causes total internal reflection so photons, generated in multi-quantum well, can’t escape from the device and are disappeared.[10] Total internal reflection reduces the extraction efficiency of LED device. Therefore, the external quantum efficiency, which is proportional to multiple of extraction efficiency and internal quantum efficiency, is lowered by these two effects. Another serious problem of conventional is wafer bowing. The growth temperature of nitride thin film is very high. Especially, growth temperature of GaN thin film is almost 1100 °C and thermal expansion coefficient difference between GaN and sapphire is over 30%. Therefore severe wafer bowing occurred after cooling the substrate from growth temperature to room temperature.
<table>
<thead>
<tr>
<th>Properties</th>
<th>GaN</th>
<th>AlN</th>
<th>InN</th>
</tr>
</thead>
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<td>Bandgap energy (eV at RT)</td>
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<td>6.2</td>
<td>0.7</td>
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<td>Lattice constant (Å)</td>
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<td></td>
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<td>2.4</td>
<td>2.15</td>
<td>2.9</td>
</tr>
<tr>
<td>Dielectric constant((\varepsilon_0))</td>
<td>9.5</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>Electron effective mass(m_0)</td>
<td>0.20</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>Melting point(℃)</td>
<td>&gt;2300</td>
<td>&gt;2800</td>
<td>&gt;1200</td>
</tr>
</tbody>
</table>

Table 1.1 General properties of nitride materials
Fig 1.1 General properties of nitride materials
1.2. Researches to grow high quality GaN thin film

To solve the problems of conventional LED device, many researches are conducted and impressive results are reported. The most well known researches to solve the problems of LED device are patterned sapphire substrate (PSS), lateral epitaxial overgrowth (LEO) and fabrication of porous semiconductor structure.[11-17]

LEO is one of the most well known methods used to reduce the density of dislocation. The ELO technology can be described as follows: first, a few μm thick GaN layer is grown on sapphire or 6H-SiC, next a dielectric (SiO₂ or SiN) mask is deposited using well established technologies like CVD or PECVD. Using standard photolithographic techniques, a set of parallel stripes separated by window areas is opened in the mask. During the initial regrowth, either in MOVPE or HVPE or even sublimation growth, selective area epitaxy is achieved, which means that the regrowth is initiated in the windows without any nucleation on the dielectric mask. Under proper conditions, once the GaN growing film reaches the top of the stripes, epitaxial lateral growth over the mask starts and finally leads to a full coalescence and to a smooth surface suitable for device fabrication. The basic idea (Fig. 1.2) is that this technique may lead to a filtering of the defects: above the windows, the microstructure of the under-lying GaN template is reproduced whereas the laterally grown material (over the mask) is defect-free. The masked areas stop the propagation of threading dislocations, which arise from the template since lateral growth proceeds from TD-free vertical facets.
PSS method is also well known method to fabricate high efficiency LED device. In PSS method, embossing patterns are fabricated on sapphire substrate by reactive ion etching(RIE). After formation of patterns, GaN is grown so one step growth is possible unlike LEO method. The advantage of PSS method is controllability, LEO effect and photon scattering. Because GaN is growing only areas between patterns, LEO can be possible and high quality GaN thin film can be grown.(Fig. 1.5) The embossing patterns of PSS can effectively change the light path towards the upside of LED so light extraction efficiency also increased.

Porous semiconductor method has attracted much attention in these days. Low refractive index air in porous semiconductor enhances photoluminescence and reduces residual stress in heteroepitaxial layers. Pores in porous semiconductor are known to reduce the dislocation density and elastic strain in heterostructures. To prepare nanoporous GaN templates, many methods such as electroless etching of GaN or the growth of GaN on nanoporous aluminum nitride layers fabricated from anodic aluminum oxidation templates coupled with subsequent ICP etching have been explored.[15-17]

But to use these method, complex photolithography, etching and regrowth step is necessary. Especially, there are no reports about stress reduction in the case of LEO and PSS.

Recently, low cost, photolithography-free method was reported to grow high quality GaN epitaxial layers by using a monolayer of silica sphere. The growth of GaN on a silica sphere-coated substrate is easier and simpler than the LEO and PSS process. Using a monolayer of silica sphere method, high
efficiency LED device was made but there are no reports about stress reduction using monolayer silica sphere method.
Fig 1.2 Schematics of LEO. a) Patterned mask materials are deposited on GaN template by photolithography and ICP etching. b) GaN thin film is re-grown using GaN template containing mask patterns on it. c) Re-growth of GaN until coalescence is completed.
Fig 1.3 TEM images of LEO GaN. Filtering of dislocation by mask is clearly observed in TEM image. But in window regions, dislocations are still exist.[18]

Fig 1.4 TEM images of LEO GaN. a) Cross section along the [10-10] zone axis of a 2S-ELO film at the end of the first step. Dashed white lines join the dislocation bending points. b) Schematic representation of 2S-ELO. Dotted lines represent the shape of the ELO material at different stages of the first part of the 2SELO process. Dashed black lines join the successive edges of the top facet. Continuous black lines represent dislocations[18]
Fig 1.5 SEM images and schematics of PSS a) Plane view SEM image of PSS, b) Cross sectional SEM image of PSS, c) Schematics of light extraction (left: reference, right: PSS). In the case of planar sapphire substrate, total internal reflections are occurred. But in the case of PSS, photon scattering is occurred as a result light extraction efficiency is increased.
1.3. Synthesis of coreshell structure

In recent years, considerable effort has been devoted to the design and controlled fabrication of nanostructured materials with functional properties. The interest in nanoscale materials stems from the fact that their properties (optical, electrical, mechanical, chemical, etc.) are a function of their size, composition, and structural order. Therefore, effective strategies to build tailored nanomaterials reliably and predictably are required in order to meet the ever-increasing demands (e.g., structural and compositional complexity) placed on materials synthesis and performance by nanotechnology. Colloidal particles represent attractive building blocks from which to create ordered and complex materials. They are also of widespread interest in chemical engineering, pharmaceutical and biological applications. Over the last decade there have been immense efforts to fabricate core±shell colloidal materials with tailored structural, optical, and surface properties.[19-22] Investigations have largely been spurred by the applicability of such colloids in modern materials science, and by their technological importance: Composite colloids are utilized in the areas of coatings, electronics, catalysis, separations, and diagnostics.[19-22] The creation of core-shell colloidal particles is also of interest from a fundamental and academic viewpoint, especially in the areas of colloid and interface science. They can be utilized as model systems to investigate factors governing colloidal interactions and stabilization[23-24] and to gain valuable information on the properties of concentrated dispersions.[25] The term used to describe the synthesis of core-shell particles with defined morphologies and properties can be referred to as particle engineering.[20] This typically involves tailoring the surface properties of particles, often accomplished by coating or encapsulating them.
within a shell of a preferred material. Particle coating is carried out for a myriad of reasons.[19-22] For example, the shell can alter the charge, functionality, and reactivity of the surface, and can enhance the stability and dispersibility of the colloidal core. Magnetic, optical, or catalytic functions may be readily imparted to the dispersed colloidal matter depending on the properties of the coating. Encasing colloids in a shell of different composition may also protect the core from extraneous chemical and physical changes.[26-28] Core-shell particles often exhibit improved physical and chemical properties over their single-component counterparts, and hence are potentially useful in a broader range of applications. Therefore, methods to engineer such materials with controlled precision have long been sought.[19-20] Although a variety of procedures have been employed for their manufacture, difficulties associated with their production have limited the application of the final colloidal materials.[20,29] Furthermore, despite the fact that the advantages of uniformly coated and stable colloidal particles have been recognized for years,[1-2,30] the controlled coating of colloids with organized layers has for many years remained a technical challenge. A major requirement pertaining to the procedures used to coat particles is that they do not cause aggregation, thus rendering the particles unusable for many purposes. Optimization of the surface characteristics of particles through coating processes is also of primary importance for the successful application of composite particles.
Fig. 1.6 Schematics of synthesizing PS/SiO$_2$ core-shell sphere [31]
1.4. Stress evolution of GaN thin film

The ability to make functional GaN devices on sapphire substrates is remarkable considering the 16% lattice mismatch between GaN and sapphire. Stress in GaN is further compounded by the thermal expansion mismatch between GaN and sapphire. Since stress affects device reliability and bandgap characteristics, and may lead to dislocation generation or even cracking of the film during deposition, the stress evolution of the nitride film is important to understand. Macroscopic stresses can arise in thin films that are laterally constrained by a substrate. These stresses are typically classified as being *extrinsic*, e.g., thermal mismatch stress caused by a difference in the thermal expansion coefficient between the film and substrate, or *intrinsic*, also referred to as the growth stress.[32] Growth stress results from changes in film density due to microstructure evolution during deposition. Typical causes of growth stresses include heteroepitaxy, island coalescence, grain growth, and surface stress. A few *ex situ*, post-growth studies of GaN stress have been performed using x-ray diffraction (XRD), wafer curvature, Raman, photoluminescence, and high resolution transmission electron microscope.[33-38] All of these studies concluded that the final stress measured at room temperature was less than the predicted compressive thermal stress. A few groups speculated that GaN is under tension at the growth temperature.[34, 36-37] Alternatively, it has been suggested that during cool down from the growth temperature GaN partially relaxes its compressive thermal stress.[33, 35, 38] Hearne. et al unambiguously show that GaN grows in tension, independent of the buffer material they also find that annealing and thermal cycling result in no measurable evolution of the growth stress (and implicitly the microstructure).[39] Hearne. et al performed
real-time wafer curvature measurements with a multibeam optical stress sensor (MOSS) modified for use on reactor (Fig. 1.7). To determine the wafer curvature, the divergence of an array of initially parallel laser beams was measured on a charge coupled device (CCD) camera after reflection of the array from the film/substrate surface. Changes in wafer curvature induced a proportional change in the array spacing on the camera. Figure 1.8 shows the stress thickness versus thickness for HT GaN grown on a GaN LT buffer. The slope of the curve defines the incremental stress, with positive slope being tensile. We find that GaN grows under a constant tensile stress throughout the entire deposition. The magnitude of the tensile stress ranged from 0.14 to 0.29 GPa from run to run, but was constant during a single deposition.

Hearne. et al explains the origin of steady state tensile stress at growth stage like this. The simplest explanation is that the HT GaN is pseudomorphic to the thermally strained LT buffer. That is, if the as-grown LT buffer is mostly relaxed and is then heated from 550 to 1050 °C, the buffer is placed in a state of tension with a magnitude <0.6 GPa for GaN on sapphire, onto which the HT GaN film grows coherently. To test this hypothesis, Hearne. et al deposited HT GaN onto a LT AlN buffer. In this case, where compressive stress (which may be partly or fully relaxed) is expected for GaN on AlN, a key result is that a tensile stress of the same magnitude as that for HT GaN on a LT GaN buffer was observed (see inset in Fig. 1.7 b). Thus, the steady-state tensile stress for GaN on an AlN buffer is inconsistent with the simple explanation of a thermally stressed buffer, since net compression is expected in this case. In studies of metal films on glass substrates,[40] a tensile stress has been attributed to the onset of island coalescence. However, Hearne. et al find that the tensile stress was generated
at the earliest stages of HT GaN growth, and remains constant as the film became fully continuous. Therefore, the tensile stress observed here cannot be solely attributed to island coalescence. Tensile stresses in some polycrystalline metals have been associated with grain growth.[32] As such, a change in stress occurs during annealing. However, annealing of GaN films produced no measurable change in stress, suggesting that grain growth was not the main source of the tensile stress.

Another theory of tensile stress of GaN thin film is the temperature difference between front side and backside of substrate. Because the temperature of backside is higher than that of front side as a result in-situ wafer bowing occurred as a result tensile stress is observed. The schematic of in-situ wafer bowing is in fig. 1.9.

However, after cooling the substrate from growth temperature to room temperature, the stress state of GaN thin film is totally changed. Because the thermal expansion coefficient of GaN is much lower than that of sapphire substrate, severe wafer bowing is occurred by huge compressive stress in GaN thin film. The stress state changed from tensile stress(during growth) to compressive stress(after cooling).
Fig.1.7 a) Schematic of MOSS system installed on RDR, b) Stress thickness and reflected intensity vs thickness for HT GaN on a LT GaN buffer. Shown inset are the stress thickness and reflected intensity vs thickness for HT GaN on LT AlN buffer.[39]
Fig. 1.8 Stress thickness and reflected intensity vs thickness for HT GaN on a LT GaN buffer. Shown inset are the stress thickness and reflected intensity vs thickness for HT GaN on LT AlN buffer.[39]
Fig. 1.9 Schematics of wafer bowing in growing GaN thin film a) in-situ wafer bowing at growth step b) wafer bowing occurred after cooling from growth temperature to room temperature.
1.5. Organization of this thesis

As we discussed above, the major purpose of this proposal is to grow less strained and high quality GaN thin film. In this proposal, we report new growth strategy to make less strained and high efficiency LED device. By growing LED structure on S-HNS coated sapphire substrate, less strained and high efficiency LED was fabricated. Especially, voids in S-HNS adsorb the compressive stress in GaN thin film so wafer bowing is reduced and enhance reflectivity as a result high efficiency LED was fabricated.

To reduce the compressive stress in GaN thin film, GaN is grown on sapphire substrate with SiO$_2$ thin film on its backside. Thermal expansion coefficient of sapphire is much higher than that of GaN so huge compressive stress is generated in GaN thin film. But if there are thin film which generate compressive stress into backside of sapphire substrate, the compressive stress of GaN thin film would be reduced. By this synthesis, we coated SiO$_2$ with very low thermal expansion coefficient (table 3) onto backside of sapphire substrate.

In chapter 2, MOCVD equipment used to grow GaN thin film and synthesis equipment used to synthesize the coreshell spheres were introduced. Additionally, analysis tools and measurement equipments are also introduced.

In chapter 3, 4 we discussed about the synthesis and modified dip coating of PS/SiO$_2$ coreshell spheres. To make S-HNS, PS template for SiO$_2$ shell was first synthesized and silica shell was synthesized on PS surface. After synthesizing the PS/SiO$_2$ coreshell spheres, they are coated onto sapphire substrate using modified dip coating method. The details of experiment will be shown at chapter 3 and 4.
In chapter 5, we showed characteristics of the GaN thin film grown on with and without S-HNS. The optical and crystallographic characteristics of GaN thin film will be discussed. And the details of growth and fabrication of LED are also discussed and characteristics of LED device were also discussed.

In chapter 6, we showed the method to reduce the wafer bowing of GaN thin film by deposition of the SiO$_2$ thin film on the backside of sapphire substrate. The details of experiment and compressive stress reduction results will be shown in chapter 5.

Finally summaries of this proposal will be presented in chapter 7.
1.5. Reference

1. S. Nakamura and G. Fasol, The blue diodes (Springer Berlin, 1997)
Chapter 2. Synthesis, growth and analysis tools

2.1. Synthesis and modified dip coating of PS/SiO₂ coreshell spheres

2.1.1 Synthesis of polystyrene sphere

The polystyrene was fabricated by emulsifier-free emulsion polymerization using the initiator AIBA or AIBN. PVP was used as stabilizer and styrene was used as monomer. Deionized water or deionized water/ethanol or deionized water/isopropanol were used as solvent. PVP and AIBA or AIBN were dissolved in solvent in a 250 ml twoneck flask, and the styrene was added to the solution. The reaction temperature was gradually increased to 70 and kept at this temperature for 16 h.

2.1.2 Synthesis of PS/SiO₂ coreshell spheres

The synthesis of polystyrene/silica nanospheres is as follows, 5ml of 200nm sized polystyrene nanospheres solution with 3.85 wt% is added to 95ml of ethanol. Then 5ml of ammonia solution is added to polystyrene nanospheres solution. After stirring with 750 rpm for 3 minutes, 2ml of TEOS (tetraethyl orthosilicate) is added to the mixed solution using a syringe pump. Its injection rate is 2ml/hour, TEOS (tetraethyl orthosilicate) is injected for 1 hour. And for another 1 hour, stirring of the mixed solution is kept at the same condition.
2.1.3 Modified dip coating of PS/SiO$_2$ coreshell spheres

To coat PS/SiO$_2$ coreshell spheres on sapphire substrate, sapphire substrate was immersed in Piranha solution (Sulfuric acid:peroxide=3:1, 15 min) to make hydrophilic surface. After that, wafer was rinsed in flowing de-ionized water for 20 min. The wafer was dried using spin coater. After the surface treatment of substrates, polyallylamine hydrochloride (PAH), a positively-charged polyelectrolyte, and polysodium 4-styrene sulfonate (PSS), a negatively-charged polyelectrolyte, were alternately coated on the sapphire substrates by the spin-assisted LbL deposition method. The positively charged sapphire substrates with PAH/PSS/PAH multilayer thin films were dipped into negatively charged PS/SiO$_2$ dispersion with different dipping conditions, followed by washing with distilled water. The sapphire substrates containing monolayers of PS/SiO$_2$ nanospheres were calcinated under air atmosphere at 800 °C to remove the PS cores within PS/SiO$_2$ nanospheres as well as the polyelectrolyte films coated on the sapphire substrates, leaving behind SiO$_2$ hollow shells. The S-HNSs obtained were further fixed to the substrates by post thermal treatment at 1150 °C.
2.2. Growth process and LED fabrication

2.2.1. MOCVD system

In this study, Thomas Swan 3 x 2” (incorporated 3 substrates of 2 inch size) close coupled showerhead (CCS) MOCVD system was used to grow c-plane nitride epitaxial layer. Trimethylgallium(TMGa, (CH₃)₃Ga)) and Trimethylindium(TMIn, (CH₃)₃In) were used for group III sources. Solkatronics Blue-Ammonia(NH₃) of 99.9999% purity was used for group V sources. Bis(cyclopentadienyl)magnesium (Cp₂Mg, (C₂H₅)₂Mg) and 10 ppm diluted silane(SiH₄) was installed for p-type and n-type doping, respectively. Schematic of gas delivery system of MOCVD is in fig. 2.1.

2.2.2. Sample preparation

C-plane sapphire is used as the substrate for the growth of c-plane GaN. At first, it was ex-situ cleaned at air. For ex-situ cleaning, sapphire wafer was immersed in Piranha solution(Sulfuric acid:peroxide=3:1, 15 min). After that, wafer was rinsed in flowing de-ionized water for 20 min. And wafer was dried with nitrogen. After ex-situ cleaning, wafer was loaded into the reactor and then in-situ cleaned in hydrogen ambient at ~1100 °C. Sapphire substrate with SiO₂ thin film on its backside was prepared using PECVD operated at 250 °C.

2.2.3. Device fabrication
c-plane GaN LED structures consist of n-type GaN (\(\mu m\)), three pairs of InGaN/GaN quantum well layers (nm/nm) and p-type GaN. Ti/Al/Au (50 nm/150 nm/30 nm) was deposited for n-contact, and Ni/Au (5 nm/5 nm) contact layer was deposited for p-contact, respectively.
2.3. Analysis tools

2.3.1. Field emission scanning electron microscopy (FE-SEM)

The size and shape of nanospheres in this study are measured by FESEM. The clear images of nanospheres including polystyrene/silica nanospheres, and polystyrene/silica/alumina nanospheres, are obtained with a Hitachi S-4300SE.

2.3.2. Transmission electron microscopy (TEM)

The TEM specimens were prepared using conventional mechanical polishing followed by ion milling using an specimen stage cooled by liquid nitrogen. Bright-field and high-resolution TEM images are obtained using FEI TF20 operated at 200 kV.

2.3.3 Photoluminescence (PL)

PL spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Specifically, light is directly onto a sample, where it is absorbed and imparts excess energy into the material in a process called “photo-excitation”. One way this excess energy can be dissipated by the sample is through the emission of light or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence (PL). The intensity and spectral content of this PL is a direct measure of various important material properties. PL measurement were made at room temperature using 325 nm line of He-Cd laser was used. The PL signal was dispersed by a SPEX monochromator and detected by liquid-nitrogen-cooled
charge coupled device (CCD) detector.

2.3.4 X-ray diffraction (XRD)

Panalytical X’pert instrument was used for high resolution XRD measurement and ω-scan. The angle divergence of 12 arcsec or less can be obtained by 4 bounce Ge 022 channel cut monochromator.

2.3.5 Cathodoluminescence (CL)

Gatan Mono CL3 and 4 systems were used to investigate luminescence properties of c-plane GaN samples. The CL measurements were carried out in monochromatic mode at room temperature. The acceleration voltage was varied to investigate the dependence of the CL spectra.

2.3.6 Atomic force microscopy

The AFM measurements were performed in an atmospheric ambient to investigate surface morphology of c-plane GaN sample. The Au-coated Si probes were used in noncontact mode using Seiko SPA-400. For statistical analyses, Nanotec WSxM v4.0 was used.

2.3.7 Spectrophotometer

To evaluate the optical characteristics of GaN thin film, diffuse reflectance was measured using an integrating sphere by collecting photons scattered from all the angles. The measured wavelength of GaN was range from 300 nm to 900 nm.

2.3.8 Stress measurement tools
To evaluate the compressive stress of GaN thin film, wafer bowing was measured using laser scanning technique (FSM stress measurement). The FSM scanner system uses a Non-Destructive Optilever Laser Scanning technique to measure the change of curvature induced in a wafer due to the deposited film. A schematic of the configuration is shown in Figure 2.2 Diagram of the FSM Stress measurement tool.

The laser scans the surface of the wafer and the beam is deflected by the wafer surface, reflected off a mirror, and detected by a precision position detector. Thousands of data points are obtained at high speed. A clean blank wafer is measured prior to film deposition. Its data is compared to measurements taken on the same sample after film deposition. The radius of curvature of the sample is determined from the slope of a straight line fitted to point by point subtraction data calculated from the before and after deposition scan data.
Figure. 2.1 Schematic diagram of the gas delivery system of Tomas swan MOCVD system.
Figure 2.2 Diagram of the FSM Stress measurement tool
Chapter 3. Synthesis of PS/SiO$_2$ coreshell spheres

3.1. Introduction

3.1.1 Synthesis of polystyrene sphere

Polymerization of styrene is addition polymerization. Sometimes it is called chain reaction polymerization. In this case, double bond of styrene reacts. On the other hand, another type of polymerization is condensation polymerization or step reaction polymerization.

In addition polymerization, initiator is necessary. The initiator molecules decompose and produce two initiator radicals. Radical is a species in which one or more valence electrons are unpaired. The initiator radicals react with the monomer and produce monomeric radicals. The monomeric radicals propagate by the chain reaction of the monomer and grow into oligomeric radicals. The polystyrene molecules whose degree of polymerization attained critical degree of polymerization precipitate and form nuclei. These nuclei aggregate with each other.

Meanwhile the stabilizer molecules produce the stabilizer grafted polystyrene molecules. These molecules adsorb on the particle surface. When all the particle surface is covered with these molecules, the nuclei aggregation does not occur anymore. Hereafter, particles grow by absorption of the oligomeric radicals from the solvent and their polymerization within particles. Fig. 3.1 and Fig. 3.2 are molecular structure of polystyrene and schematic representation of polystyrene synthesis, respectively.

In this study, various sized polystyrene spheres were synthesized by...
controlling the synthesis condition. But using the AIBA initiator, the size of polystyrene spheres was restricted only 500 nm. To increase the size of polystyrene spheres, we changed initiator from AIBA to AIBN. And by controlling the polarity of solution, we could synthesize micrometer size polystyrene spheres.
Figure. 3.1 Molecular structure of styrene and polystyrene.
Figure 3.2 Schematic representation of polystyrene synthesis.[1]
3.1.2 Synthesis of PS/SiO$_2$ coreshell spheres

Core–shell organic/inorganic composite particles exhibit both properties of core and shell parts and/or combined properties from both components.[2] Inorganic hollow particles derived from the core–shell particles possess uniform porosity, tailored structure, and surface properties. Therefore, core–shell composite particles and their derivatives, hollow spheres, have been widely reported because of their potential applications such as photonic crystals, drug delivery and catalysis.[2–6] Recently, charged polymer-silica composite particles have been used as an imaging materials, so-called liquid powder, for toner-type paper-like display.[7–9] The imaging particles have generally been prepared by physical mixing of colorant, charge control agent, and silica with polymer beads.[8] Unlike the physically combined composite particles, inorganic coatings may provide polymeric particles with high stability and mobility to improve display performance. Thus monodisperse polymer-silica core–shell particles can be potential imaging materials for toner-type paper-like display devices. Preparation of core–shell composite particles using polymeric templates can be categorized as 1-step (onepot) and 2-step reactions. In the first method, one-pot synthesis is attractive in terms of simplicity due to no separation process of polymeric particles between a polymerization process and an inorganic coating. Armes and coworkers reported preparation of PS-silica composite particles from a negatively charged silica sol in the presence of a neutral initiator (2,2'-azobisisobutyronitrile, AIBN), an cationic initiator (AIBA). An anionic initiator (4,4'-azobis(4-cyanovaleric acid), ACVA) leads to no or little particle formation.[10] Shim et al. have prepared PS/silica nanocomposite
particles using a positively charged silica sol and an anionic initiator (potassium persulfate, KPS).[11] Attempts for compatibility between the surface of PS particles and a silica shell have been made by using silane coupling agents.[12–13] However, one-step reaction generally leads to poor monodispersity of the resulting core-shell particles owing to interruption of silica sol suspensions in reaction media.[10–13] Two-step approach includes a separation process of polymeric template particles prior to addition of a silica precursor. This method has advantages such as monodispersity of the resulting core-shell particles and facile control of the shell structure. (Fig 3.3)

The layer-by-layer (LbL) technique was adopted to prepare PS-silica core-shell particles with controllable shell thickness.[3] Unlike multiple LbL adsorption steps, Xia et al.[14] reported PS/silica core-shell particles from −NH2 terminated PS beads and TEOS via the Stober method.[15] The simple Stober method leads to PS-silica core-shell structures with uniform, conformal shells having controllable thickness.[14] However, synthesis of the −NH2 terminated PS beads used in the research requires multiple-step processes and high cost. Wu et al.[16] described PS-SiO2 core-shell hybrid colloids prepared from AIBA-initiated PS beads and TEOS under relatively low pH (∼2.5) at high temperature (60–70 °C) for long reaction time (5 h). Hollow silica particles were also prepared using PS bead template synthesized from AIBA as an initiator and poly(viylpyrrolidone) (PVP) as a stabilizer.[17] In this work, we synthesized monodisperse PS-silica core-shell composite particles prepared from a PS bead template and TEOS as a silica precursor via the Stober method.[15] The PS bead particles with various diameter were synthesized by a surfactant-free emulsion polymerization
using a cationic azo initiator, AIBA. Silica coatings were performed under basic condition (pH 10–12.5) at ambient temperature. The resulting silica shell also exhibit smooth surface and uniform thickness. Moreover, the shell thickness is simply controlled by altering reaction time, concentration of Ammonia and TEOS concentration in the reaction mixture. The synthesis condition used to synthesize the nanoscale sized PS/SiO$_2$ core-shell spheres couldn’t applied to synthesis micrometer size PS/SiO$_2$ core-shell spheres. So to synthesize the micrometer size core-shell spheres, we modified surface of polystyrene by adsorbing PVP with heavier molecules. Because the silica shell synthesized by hydrogen bonding with PVP, heavy weight PVP enable large volume fraction of PVP chain in solvent and many reaction site because of the long chain of PVP.\cite{18} Because of these effect by modifying the surface of PS, micrometer size PS could be synthesized.

**Effect of PVP on synthesizing PS/SiO$_2$ core-shell spheres**

In synthesis of silica shell using PS spheres, the silica shell was formed by two mechanisms. First, the oligomer or silica monomer adsorbed onto PS surface or sub-nanometer sized silica nucleuses adsorbed onto + charged PS surface by electric attraction grows and forms silica shell. The schematics of silica shell growth mechanism are in fig 3.5. In synthesis of silica shell, PVP, surrounding the PS as a stabilizer, is the site for synthesizing silica shell. PVP (see Figure 3.4) is an amphiphilic polymer and it is soluble in water and many nonaqueous solvents.\cite{19-20} The characteristics of PVP arises from the presence of a highly polar amide group within the pyrrolidone ring and a polar methylene and methine groups in the ring and along its backbone.\cite{21} Due to its amphiphilic character it can be adsorbed onto many different
surfaces. The PVP makes the affinity of the PS surface to silica sufficiently high, so that no coupling agent is necessary. Like this, PVP greatly affects the formation of silica shell and aggregation of coreshell structures. Christina Graf et al reported about the importance of molecular weight of PVP when the silica shell was synthesized.[22] To achieve both a stabilization of the gold colloids during the shell growth and a higher affinity of the gold surface to silica, poly(vinylpyrrolidone) of different molar masses (3.5, 10, and 40 kg/mol) was adsorbed onto the particles. In the case of the particles stabilized with the longer polymer, mostly single gold colloids covered with a silica shell were found (see Figure 3.7 a for PVP-40 and Figure 3.7 b for PVP-10). However, the particles stabilized with PVP-3.5 form silica-covered aggregates of several gold particles (see Figure 3.7 c). Apparently, the shorter polymer cannot sufficiently stabilize the particles during the growth of the silica shell, possibly because it does not sufficiently shield the large van der Waals forces between these particles. The comparison of Figure 3.7 a and Figure 3.7 b shows a second important influence of the length of the polymer used: while the particles coated with PVP-10 have a relatively smooth and homogeneous coating thickness of the silica layer (see Figure 3.7 b), the particles coated with PVP-40 have a much more inhomogeneous coating thickness and some particles with multiple gold cores are observed (see Figure 3.7 a). The sizes of the larger two adsorbed polymers are comparable to the size of the gold colloids ($r$) 7 nm) and the thickness of the silica shell (about 10 nm); e.g., in water the hydrodynamic radius of PVP-10 is 4 nm and that of PVP 40 is 8 nm (from ref 21). The silica coating of the PVP-3.5 coated gold colloids is also smooth and everywhere is of the same size. The results obtained for the different PVP lengths show that the silica is growing
directly onto the adsorbed polymer. If a polymer is used that is very large compared to the colloid radius (such as PVP-40), sometimes particles appear to be only partially coated with silica (see Figure 3.7 c), so in this case the particles are not sufficiently stabilized by an outer silica layer during the conditions of the Stöber growth and grow together with other particles. This explains why some aggregation is observed despite the fact that a large polymer was used. The use of PVP with an average molar mass of 10 kg/mol appears to be an optimum for this size of particles, because it provides sufficient steric stabilization of the colloids to avoid aggregation during the silica shell growth, but it is on the other hand small enough to form a relatively homogeneous layer onto colloids of this size to obtain a smooth silica coating.
Figure. 3.3 Schematic of synthesizing PS/SiO2 coreshell structure.[21]
Figure. 3.4 Schematic of chemical bonding between silica shell and PVP chain[18]
Figure 3.5 Schematics of mechanism of silica shell formation. a) silica shell only grow from PS surface, b) silica shell grows at PS surface and by electric attraction between cationic PS surface and negatively charged silica nucleus.
Fig 3.6 Schematics of silica shell synthesis reaction from TEOS
Fig 3.7 TEM pictures of gold particles (7 nm radius) coated with silica after functionalization with PVP-40 (a), PVP-10 (b), or PVP-3.5 (c).[22]
3.2 Experiment procedure

3.2.1 Synthesis of polystyrene sphere

Materials
Styrene, 2,2’-Azobis(2-methylpropionamidine)dihydrochloride(AIBA) and polyvinylpyrrolidone with average molar masses of 40kg/mol(PVP-40) were purchased from Sigma-Aldrich Co.(United States of America). 2,2’-Azobis(2-methylpropionitrile) (AIBN) was bought from Junsei Co.(Japan). Ethanol was provided from J. T. baker co.(United states of America). Isopropanol was ordered from Samchun Chemicals Co.(Republic of Korea). All materials were used without further purification.

Polystyrene sphere synthesis
The polystyrene was fabricated by emulsifier-free emulsion polymerization using the initiator AIBA or AIBN. PVP was used as stabilizer and styrene was used as monomer. Deionized water or deionized water/ethanol or deionized water/isopropanol were used as solvent, PVP and AIBA or AIBN were dissolved in deionized water or deionized water/ethanol or deionized water/isopropanol in a 250 mL two-neck flask and the styrene was added to the solution. The reaction temperature was gradually increased to 70 °C and kept at this temperature for 16 hour before the mixture was finally allowed to cool to room temperature. A fact that softening point of polystyrene is 90 °C is considered to determine reaction temperature. Also other papers were used to determine reaction temperature. Reaction time was determined from
previous experiment that observes mixture every one hour. When the reaction
time reached 16 hour from starting point, diameter of polystyrene was
saturated. As-synthesized polystyrene particles were repeatedly filtered and
washed to remove the residual styrene and PVP with deionized water or
deonized water/ethanol or deionized water/isopropanol. The polystyrene
spheres with various sizes were prepared by changing synthetic conditions
such as monomer concentration, initiator concentration, stabilizer
concentration and polarity of solvent. And to synthesize micrometer size
polystyrene sphere, initiator is changed from AIBA to AIBN to increase the
size of polystyrene.
Fig 3.8 Photo of synthesizing equipment of polystyrene sphere
3.2.2 Synthesis of PS/SiO$_2$ core-shell sphere

Materials
Polystyrene refined by ethanol several times was used as a template for PS/SiO$_2$ core-shell spheres. Ethanol were provided from J. T. baker co.(United States of America). TEOS were purchased from Sigma-Aldrich Co.(United States of America). All materials were used without further purification.

PS/SiO$_2$ sphere synthesis
Polystyrene spheres were used as a core templates for the synthesis of PS/SiO$_2$ core-shell spheres. The synthesis of polystyrene/silica core-shell spheres is as follows, 5ml of 200, 300, 400, 1300 and 2000 nm sized polystyrene nanospheres solution with 3.85 wt% is added to 95ml of ethanol. Then 5 ml(for 200, 300, 400 nm) and 6 ml(for 1300, 2000 nm) of ammonia solution is added to polystyrene nanospheres solution. After stirring with 750 rpm for 3 minutes, 2 ml of TEOS (tetraethyl orthosilicate) is added to the mixed solution using a syringe pump. TEOS (tetraethyl orthosilicate) was injected for 1 hour. And for another 1 hour, stirring of the mixed solution was kept at the same condition. After reaction, polystyrene/silica nanospheres are washed with ethanol and water three times using a sonicator and centrifuge equipment. Finally, polystyrene/silica nanospheres are obtained using a wet process. But in the case of micrometer size PS/SiO$_2$ core-shell spheres, the silica shell was not synthesized when the refinement condition used for nanoscale PS spheres. To synthesize the micrometer scale PS/SiO$_2$ core-shell spheres, refinement condition of PS was modified. To coat PS surface with
heavy weight PVP chain, PVP (molecular weight 75,000) was used in refinement of polystyrene sphere. The polystyrene particles were already in an ethanol solution. These particles were sedimented and a solution of PVP in ethanol was added at first refinement step and redistributed. The synthesis temperature was also changed when it compared with synthesis temperature used to synthesis nanoscale PS/SiO$_2$ core-shell structure. To increase the silica shell synthesis reaction, the synthesis temperature increased from 10 °C to 25 °C.
Figure. 3.9 Photo of synthesizing equipment of PS/SiO2 coreshell spheres
3.3. Results and discussion

3.3.1 Synthesis of polystyrene spheres

Cationic PS spheres were prepared by varying the composition of styrene, AIBA and PVP in the synthesis formulation. Monodisperse cationic PS spheres were synthesized by emulsifier-free emulsion polymerization. The size of PS spheres ranging from about 120 nm to 2000 nm in diameter synthesized.

Effect of initiator on size of polystyrene sphere

To observe the effect of initiator concentration on size of polystyrene sphere, amount of AIBA was changed from 0.1 g to 0.5 g with 0.1 g interval. Correlation between particle size and initiator concentration is classified into two cases. First case, the particle size reduces when the concentration of initiator increases. As the concentration of initiator increases, many nuclei are formed and final particle size is reduced.[23] Second case, many free radicals are made by initiator and free radicals cause growth of nuclei. So particle size increases as the concentration of initiator increase. In the case of polystyrene, AIBA initiator makes many styrene free radicals and these radicals facilitate growth of existing nuclei.[24] As a results, high concentration of initiator leads to increase of polystyrene size. The result of experiment is summarized in table 3.1 and fig 3.2. The size of PS increased from 154 nm to 243 nm as the amount of AIBA increase from 0.1 g to 0.5 g with 0.1 g intervals.

Effect of stabilizer on size of polystyrene sphere
To observe the effect of initiator concentration on size of polystyrene sphere, amount of AIBA was changed from 0.45 g to 2.45 g with 0.5 g interval. The size of polystyrene is decreased from 279 nm to 198 nm as the amount of PVP increased. The result of experiment is summarized in table 3.1 and fig 3.2. This experiment shows the relationship between concentration of stabilizer and the size of polystyrene sphere. The PVP grafted polystyrene is adsorbed onto the growing particles until there is sufficient graft to stabilize them against coalescence. So increasing amounts of PVP causes increasing concentration of PVP in solvent and so causes fast adsorption of PVP with polystyrene.

**Effect of solvent polarity on size of polystyrene sphere**

To observe the effect of solvent polarity on size of polystyrene sphere, the concentration of ethanol in solvent was increased from 0 vol.% to 20 vol. % in deionized water/ethanol system. Diameters of polystyrene spheres increased from 218 nm to 285 nm as the concentration of ethanol in solvent was increased. The result of experiment is summarized in table 3.1 and fig 3.10. Increase of ethanol concentration in solvent decreases polarity of solvent. Meanwhile polystyrene oligomers are non-polar materials. So increasing amounts of ethanol causes increasing concentration of ethanol in solvent and so solubility of polystyrene oligomer is increasing. Then the precipitation of polystyrene oligomers are difficult in a more non-polar solvent. This difficult precipitation of polystyrene oligomers causes increase in critical degree of polymerization. Namely, the size of nuclei increases so the number of nuclei decreases. In conclusion the size of polystyrene sphere increases.
Effect of monomer concentration on size of polystyrene sphere

To observe the effect of monomer concentration on size of polystyrene sphere, amount of styrene was changed from 2 ml to 14 ml with 3 ml interval. Diameters of polystyrene spheres increased from 110 nm to 235 nm when the amounts of styrene in solvent were increased from 2 mL to 14 mL in water. The result of experiment is summarized in table 3.1 and fig 3.10. Increase rate of size of PS was high when the concentration of monomer is low, but Increase rate of size of PS was slower as the concentration of monomer is increase. This experiment shows the relationship between concentration of monomer and the size of polystyrene sphere. Generally increase of concentration of monomer causes decrease of size of polymer due to increase of seed. This needs premise that monomer dissolves well in solvent. Dissolved monomer conducts a role as seed. However, in this experiment styrene is not dissolved well in water. Solubility of styrene in water is very low. So although concentration of styrene that put in synthetic pot is high enough, only very small amounts of styrene is dissolved in water. Meanwhile styrene is non-polar material and liquid at reaction temperature. Thus styrene plays a role as non-polar solvent. However, polystyrene oligomers are non-polar materials. So increasing amounts of styrene causes increasing concentration of styrene in solvent and so solubility of polystyrene oligomer is increasing. Then the precipitation of polystyrene oligomers are difficult in a more non-polar solvent. This difficult precipitation of polystyrene oligomers causes increase in critical degree of polymerization. Namely, the size of nuclei increases so the number of nuclei decreases. In conclusion the size of polystyrene sphere increases.
Synthesis of micrometer size polystyrene sphere

Using the AIBA initiator, synthesizing PS whose size larger than 500 nm is very difficult. But as the size of S-HNS increase, the void fraction is increase and volume of photon scattering center also increase. To synthesize the micrometer size PS, we changed solvent and initiator. In the case of isopropanol solvent, the polarity is much higher than ethanol so it has advantage to increase the size of PS. And initiator changed from AIBA into AIBN. As like synthesis of nanoscale PS, the variables are changed to control the size of PS. And tendency of each variables are similar to the synthesis of nanoscale PS. The synthesis condition and result is in table 3.2 and fig 3.11.
<table>
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<th>Styrene (mL)</th>
<th>AIBA (g)</th>
<th>PVP (g)</th>
<th>Size (nm)</th>
<th>Standard deviation of size (nm)</th>
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Table 3.1 Synthesis condition of nanometer sized polystyrene sphere
Figure 3.10 Size change of nanometer sized polystyrene sphere according to the reaction condition
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<th>PVP (g)</th>
<th>Size (nm)</th>
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Table 3.2 Synthesis condition of micrometer sized polystyrene sphere
Figure 3.11 Size change of micrometer sized polystyrene sphere according to the reaction condition
3.3.2 Theoretical prediction of polystyrene sphere size

**Unstabilized Solution Polymerization and Precipitation**

In the absence of steric stabilizer, polymerization of styrene in alcohols gives coagulum with molecular weight very close to that expected for solution polymerization. The absence of any gel effect on the molecular weight under these conditions suggests that the oligomeric radicals terminated in solution prior to capture by the coagulum. Whether these dead polymer chains were captured as nucleated globules or as random or collapsing coils is not important. What is important is that most of the polymer was dead when captured. In the early part of the reaction, the volume fraction of polymer is low, and the distribution coefficients of monomer and initiator are not strongly biased toward either the continuous or particle phase. As a result, the vast majority of early polymerization occurs in solution. To the extent it is possible to ignore oligomeric radical capture by growing particles in the very early part of the reaction, growth by aggregation and coalescence can be decoupled from polymerization, for separate study, as discussed below.

**Multibin Particle Aggregation Model.**

In the limit of low conversion, where solution polymerization is dominant, dead polymer chains of chain length CL are generated by a pseudo-zero-order rate, $k_1$, and then coalesce irreversibly at a diffusion-controlled rate. One of the difficulties inherent in modeling particle aggregation is the need to keep track of various populations for particles from newly formed nuclei up to particles of 10 km or more (i.e., aggregation of species from 1 to 1010 chains). Even with modern computing capacity, there are too many species to
track individually, so a method is required to group them. The best grouping method is a geometrical progression of population bins such that, for example, the particles in bin $j + 1$ are double the mass of those in bin $j$. In this case, bin 1 is assigned to the single-chain nuclei and 20-30 bins cover the whole size range. With this concept, it is a simple matter to generate the rules governing particle coalescence: two particles of the same size (i.e., both in bin $j$) coalesce to form one particle in the next higher bin $j + 1$; particle coalescence of one large and one small particle (i.e., one from bin $j$ and one from bin $i$, where $i < j$) do not significantly alter the size of the particle in bin $j$ but do bring more mass into the bin and decrease the mass and number count in bin $i$. The overall number-average particle mass, $N$, and weight-average mass, $M$, can be related to the size, $d$, given chain length, monomer molecular weight, and geometrical factors by below equations.

$$N = \sum_i m_i / n \quad (1)$$

$$M = \sum_i < m_i^2 > / m_i \quad (2)$$

$$d = \left( \frac{6N(CL)MW_s}{\pi \rho N_s} \right) \quad (3)$$

The mean particle mass of the growing particles increases with the second power of time, so the diameter of the particles grows with the $2/3$ power of time, and the number of growing particles decreases with the first power of time, as shown in eqs 4-8 (where the meaning of the symbols is explained in the appendix). For comparison, the theory of Ostwald ripening shows radius growing as $t^{1/3}$ and $N_p$ decaying as $t^{-1}$. This is in good agreement with these results when the steady generation of new material is factored out. The value of the simulation is simply to provide the constant of proportionality 0.386, in
eq 4.

\[ d_{s_0} = 0.386 \frac{6MW_s(CL)}{\pi \rho N_s} k_1k_2 t^2 \]  

(4)

We may convert from time base, \( t \), to conversion base, \( x \), with eq 7; use the eq 5 and the relation for chain length, CL(eq 6) (assuming negligible chain transfer), to transform eq 6 into eq 8.

\[ k_1 = f k_d t[I] \]  

(5)

\[ CL = k_p[M](k_1 f k_d[I])^{-1/2} \]  

(6)

\[ x = k_pt \left( \frac{f k_d[I]}{k_1} \right)^{1/2} \]  

(7)

\[ d_{s_0} = 0.386 \frac{6MW_s[M]k_2}{\pi \rho k_p N_s} \left( \frac{k_1}{f k_d[I]} \right)^{1/2} x^2 \]  

(8)

A Model for Stabilized Reactions Giving Monodisperse Particles

Multibin Kinetic Model.

The foregoing discussion provided the background against which we can begin to evaluate the effect of stabilizer on dispersion polymerization. The simplest extension of the preceding model is one where same size particle coalescence (homocoagulation) is numerically terminated at some arbitrary critical size, \( d_{crit} \). At this point, the formerly unstabilized reaction becomes stabilized, and only small-particle capture (heterocoagulation) can continue. In this case, simulation show that a monodisperse size distribution evolves after the critical point, because the diffusion-controlled scavenging of dead polymer allows smaller particles to grow faster, catching up to the larger
particles. Once the particles become monodisperse, particle diameter grows with time to the 1/3 power, as expected. It takes about 20 times as long for the particles to become monodisperse (GSD < 1.1) as it does to reach $d_{\text{crit}}$.

**What Determines $d_{\text{crit}}$?**

$d_{\text{crit}}$ is determined by the grafting mechanism of stabilization. The critical point occurs when the graft available equals the minimum graft required to stabilize the particles. The amount of graft available increases linearly with conversion for as long as solution polymerization is dominant. On the other hand, the minimum amount of graft required to stabilize the particles depends on the total surface area of the particles times some minimum coverage by graft required to stabilize a unit of particle surface, $Q_{\text{min}}$. In the beginning of the reaction, when most polymerization takes place in solution, the polymerization is unstabilized, particle diameter increases as the 2/3 power of conversion, particle count decreases, and the GSD is large, but constant. The total surface area of the particle ensemble grows with $N_p X d^2$, so the dashed line representing the minimum graft required (labeled $Q_{\text{min}}$) increases with a slope of 1/3, while the amount of graft available increases with a slope of 1. $Q_{\text{max}}$ describes the situation above which the particle surface is saturated and cannot accept more graft. When the amount of graft available equals the minimum graft required, then, by definition, the particles become stabilized. Once stabilized, the particles may grow by polymerization both inside and outside the particle. Polymer that terminates in solution is unstable with respect to coalescence and is scooped up by the larger, stabilized particles before it can become stabilized as secondary particles. Because the grafting probability is low, secondary particles would have to be large before
becoming stabilized and are usually captured by larger particles before they can become large enough. In the growth regime to the right of point A in Figure 2, the number of particles is fixed and the diameter now increases with the 1/3 power of conversion, so \( Q_{\text{min}} \) and \( Q_{\text{max}} \) coverage requirements increase with the 2/3 power of conversion. The aggregative mechanism of growth (capture of oligomeric free radicals or dead polymer from solution) results in a narrowing of the size distribution, and the GSD quickly declines. As the reaction progresses well beyond the critical point, relative importance of solution polymerization may decrease as solid-phase polymerization becomes significant. When this occurs, the amount of graft being generated will also decrease, because it is only formed in solution (the stabilizer polymer is not soluble inside the particles). However, as long as the total graft available remains between the lower and upper coverage bands, \( Q_{\text{min}} \) and \( Q_{\text{max}} \), the particle distribution can remain monodisperse.

**Prediction of Particle Size.**

Given the multibin particle aggregation model for the unstabilized reaction and the relationships sketched in Figure 2, we can see that if we could predict \( Q_{\text{min}} \) and the amount of graft available, we could predict the particle size. The graft available equals the product of the number of chains formed thus far (kit) times the probability of grafting. If grafting occurs by chain transfer to stabilizer, then the probability of grafting is given by \( C_s[S](CL)/[M] \), as shown in eq 9.

\[
graft \text{ available} = C_s[S]N_dX \tag{9}
\]

\[
graft \text{ required} = (N_p \pi d_{s0}^2)Q_{\text{min}} = \frac{6[M]MW_sQ_{\text{min}}x}{\rho d_{s0}} \tag{10}
\]
The critical point occurs when the graft available equals the minimum graft required

\[
d_{\text{crit}} = \frac{6[M]MW_sQ_{\text{min}}}{\rho C_s[S]N_A} \quad (11)
\]

The critical conversion, \( x_{\text{crit}} \), can be obtained from eqs 13 and 8:

\[
x_{\text{crit}} = d_{\text{crit}}^{3/2} \left( \frac{0.386\pi k_p N_A}{6MW_s[M]k_2} \right)^{1/2} \frac{f k_d[I]}{k_i} \quad (12)
\]

Providing the number of particles becomes fixed at the stabilization point, the final particle size, \( d_f \), at the end of the reaction (irrespective of the mechanism of growth subsequent to stabilization) is given by eq 13, and by substitution, eq 14

\[
d_f^3 = \frac{d_{\text{crit}}^3}{x_{\text{crit}}} \quad (13)
\]

\[
d_f = \left( \frac{6MW_s[M]}{\rho N_A} \right)^{2/5} \left( \frac{Q_{\text{min}}}{C_s[S]} \right)^{2/5} \left( \frac{k_2}{0.386\pi k_p} \right)^{1/6} \left( \frac{k_i}{f k_d[I]} \right)^{1/12} \quad (14)
\]

**Methods of Estimation of \( Q_{\text{min}} \)**

To develop a priori predictions of particle size from dispersion polymerization where the grafting mechanism of steric stabilization is operative, we require an estimate for \( Q_{\text{min}} \), the minimum coverage by graft required to prevent coalescence. This quantity is likely related to the area of the shadow cast by the hemisphere defined by the radius of gyration of the stabilizer chains in solution, \( R_g \). The radius of gyration of the grafted stabilizer chains will be smaller than that for an ungrafted stabilizer in solution because the point of attachment to the particle may occur anywhere
along the chain. Thus, the longer end will dominate \( R_g \), so the average chain length of the long stabilizing end will be 75% of the molecular weight of the ungrafted stabilizer. Therefore, the usual expression \( R_s = A M_w^b \) for an ungrafted stabilizer becomes \( R_s = A (0.75 M_w)^b \), leading to the second half of eq 15.

\[
Q_{\text{min}} = \frac{1}{\pi R_g^2} = \frac{1}{\pi A^2 (0.75 M_w)^{2b}} \tag{15}
\]

Substituting eq 15 into eq 14 gives a model expression accounting for many of the factors influencing particle size.

\[
d_f = \left( \frac{1}{0.75^b A M_w^b} \right) \left( \frac{6 M_W S [M]}{\rho \pi N_A} \right)^{\frac{7}{2}} \left( \frac{1}{C_s [S]} \right)^{\frac{1}{2}} \left( \frac{k_2}{0.386 \pi k_p} \right)^{\frac{1}{6}} \left( \frac{k_i}{f k_d I} \right)^{\frac{1}{12}}
\tag{16}
\]

**Fraction of Graft Adsorbed.**

For simplification, the preceding discussion had assumed that all graft formed was immediately adsorbed onto the particle surface. This may be the case in polar solvents such as methanol or ethanol (as in the foregoing numerical example) but is likely not the case in solvents generating larger particles (butanol, ethanol/toluene mixture, ethanol/methoxyethanol mixtures, etc.). Lower molecular weight polystyrene and grafted polystyrene are likely to have a finite solubility in these better solvents, especially in the presence of a significant volume fraction of monomer in the starting reaction mixture. To incorporate the role of solvent in dispersion polymerization in terms of changes in the solubility of graft, it is necessary to introduce the concept of Fa: the fraction of graft that is actually adsorbed onto the particles under
conditions near the stabilization point. The main contributors to $F_a$ are likely to be the molecular weight ratio of polymer to stabilizer ($MW_p/M_w$) and the effect of solvency, represented here by an ill-defined $\exp(\Delta \delta)$ term, where $\Delta \delta$ refers to the (presumably multidimensional) solubility parameter difference between the solvent and the graft. Other contributors include the influence of molecular weight dispersity of both the polystyrene and steric stabilizer. For example, the hydrodynamic thickness of adsorbed polymers may depend on the high molecular weight tails of the distribution. As a first-order, intuitive approximation, intended to illustrate how $F_a$ can greatly influence the scaling of the final size, we imagine the adsorption isotherm to be such that, where $F_a<1$, $F_a$ increases linearly with both the molecular weight ratio and the solvent term, as suggested by eq 17. Thus, the thermodynamic probability of adsorption increases as the polystyrene molecular weight increases and as the difference in solubility parameters increases. Substituting for $MW_p$ in terms of chain length (eq 8), we obtain the full expression in eq 17.

$$F_a = K \frac{MW_p}{M_w} e^{\Delta \delta^2} = \frac{K k_p [M] MW_s}{M_w (k_f k_d [I]^{1/2})} e^{\Delta \delta^2} \quad (17)$$

This $F_a$ is introduced into the theory as a multiplicative factor in eq 6 and emerges with an exponent of -1/2 in eq 16. More significantly, $F_a$ brings with it additional dependency on monomer and initiator concentrations as well as on the molecular weight of stabilizer, generating eq 18.

$$d_f = \left( \frac{1}{0.75 A} \left( \frac{6}{\rho \pi k_f N_A} \right) \left( \frac{M_w^{1-2b}}{C_s [S] Ke^{\Delta \delta^2}} \right)^{1/2} \left( \frac{k_f^2 k_d [I] [M] MW_s}{0.386} \right)^{1/6} \right)^{2/5}$$

$$(18)$$
3.3.3 Synthesis of PS/SiO$_2$ coreshell spheres

Using the cationic PS spheres as a template for silica shell, dozens nm thickness silica shell was synthesized by Stober method. PS/SiO$_2$ coreshell spheres with monodisperse and smooth surface were successfully synthesized using various sized PS sphere.

Effect of ammonia on thickness of silica shell

Ammonia is the catalyst of the reaction and facilitates the deprotonation of OH bond formed by hydrolysis of ethanol functional groups. And condensations with another TEOS molecule are occurred as a result silica shell is synthesized. So ammonia makes more deprotonated TEOS molecules as a result the thickness of silica shell is increased. To confirm the effect of ammonia on the shell thickness, concentration of ammonia is changed from 30 ml/L to 50 ml/L with 10 ml/L interval. The thickness of silica shell is increased from 13 nm to 21 nm according to the concentration of ammonia. But the final thickness is almost same regardless of concentration of ammonia. The silica shell thickness is rapidly increased but as the synthesis time increase, silica shell thickness is saturated. And final thickness of silica shell is almost same regardless concentration of ammonia.

Effect of concentration of TEOS on thickness of silica shell

TEOS is the reactant of silica so as the amount of TEOS increase, thickness of silica shell increased. To confirm this, concentration of TEOS is varied from 20 ml/L to 40 ml/L with 10 ml/L intervals. As the concentration of TEOS increased, silica shell thickness is also increased from 20 nm to 30 nm. Reaction time was fixed 2 hours(1 hour injection of TEOS and 1 hour
reaction). Concentration of ammonia was also fixed at 50ml/L.

**Effect of reaction time on thickness of silica shell**

The reaction time of coreshell sphere synthesis is varied to check the change of shell thickness as the reaction time increase. The reaction time was varied from 2 hour to 50 hour. Concentration of ammonia is changed to confirm the final silica shell thickness. At the early stage of reaction, the thickness of silica shell is rapidly increase but after 20 h, the thickness of silica shell is saturated and further increase is not observed. As the concentration of ammonia increased, silica shell thickness is rapidly increased but thickness of silica shell is rapidly saturated when it compared with low concentration of ammonia. Ammonia the catalyst of deprotonation makes fast reaction so the increase rate of silica shell is much higher than that of low concentration of ammonia.

**Synthesis of micrometer sized PS/SiO₂ coreshell spheres**

As the size of polystyrene sphere increase, the total particle surface per volume of PS is reduced as a result parasitic reaction is occurred and unwanted small silica particles are produced and silica shell is not well synthesized.[25] The TEOS consumed to increase the existing silica nanoparticle instead of synthesizing silica shell. Because critical surface area of nucleation, the size of nucleus to prevent formation of parasitic reaction, is increase as the initial size of ps increased. To increase the reaction site for silica shell synthesis, heavy weight PVP treatment was done. By doing this, the longer functional PVP group provide the site for silica reaction as a result we can make monodisperse PS/SiO₂ coreshell spheres. And by increasing the
synthesis temperature and concentration of ammonia, thicker silica shell could be synthesized. The TEM image of micrometer size S-HNS was in Fig 3.13. As the concentration of ammonia increased, the thickness of silica shell was dramatically increased. In the case of 40 ml/L concentration ammonia, too thin silica shell was synthesized and the silica shell was collapsed during the calcination process. But in the case of 70 ml/L concentration ammonia, too thick shell was synthesized so the thickness of silica shell was not observed by TEM.
Figure 3.12 The thickness of silica shell synthesized using various synthesis condition a) concentration of TEOS, b) concentration of ammonia, c) reaction time.
Figure 3.13 Silica shell thickness change according to concentration of ammonia (a) 40 ml/L, (b) 50 ml/L (20 nm shell thickness), (c) 60 ml/L (40 nm shell thickness), (d) 70 ml/L (70 nm shell thickness).
3.4 Conclusion

In conclusion, various sized monodisperse PS/SiO$_2$ coreshell spheres were successfully synthesized by using PS sphere as a silica shell template. The polystyrene was fabricated by emulsion polymerization using the initiator AIBA or AIBN. PVP was used as stabilizer and styrene was used as monomer. By using AIBA initiator, the size of synthesized polystyrene restricted nanometer scale. So to increase the size of polystyrene sphere, AIBN initiator was used and monodisperse micrometer size polystyrene spheres were successfully synthesized. To investigate the effect of synthesis condition on size of polystyrene sphere, polystyrene spheres were synthesized at various synthesis conditions. Using the cationic PS spheres as a template for silica shell, dozens nm thickness silica shell was synthesized by Stober method. PS/SiO$_2$ coreshell spheres with monodisperse and smooth surface were successfully synthesized using various sized PS sphere.
3.5. Reference


Chapter 4. Modified dip coating of PS/SiO$_2$ coreshell spheres

4.1. Introduction

Investigation of the self-assembling of particles has become one of the most popular research topics because of the many possible application fields. There are several objects that exhibit possible self-assembling characteristics such as surfactant, block copolymer and colloidal particles in an increasing order of the object sizes. Each self-assembling object has received significant research interest for a wide variety of applications ranging from detergent to microelectronics.[1] Among these, colloidal particles, defined as small materials with at least one characteristic dimension in the range of 1 nm–1 mm, have long been used as major components of various industrial products such as inks, paints, catalysts, coatings, papers, cosmetics and photographic films.[2,3] In particular, spherical monodisperse colloidal particles may represent the simplest form of building blocks that can readily be self assembled into 2D and 3D ordered lattices on a planar substrate such as colloidal crystals or synthetic opals.[4–8] The ability to crystallize spherical colloids into spatially periodic structures has allowed us to obtain interesting and often useful functionality not only from the colloidal materials, but also from the long-range order exhibited by these crystalline lattices. The colloidal crystals can find themselves useful in a wide variety of applications such as optical filter syswitches [9], catalyst [10], photonic crystal [11], chemically biological sensor [12] and lithographic mask [13]. The fabrication routes for creating colloidal crystals can be roughly divided into two techniques: gravity
sedimentation[14] and solvent evaporation [15]. In the gravity sedimentation method, crystal formation can only occur at specific colloid volume fractions. As a result, the crystal thickness is not easily controlled. For the solvent evaporation method, a 2D colloid crystal can be obtained, and the thickness can be controlled by either varying colloid concentrations or repeated layer by-layer crystallization.

To make well-ordered and highly packed monolayer of the particles on substrates by evaporation method, many methods are reported. The most well-known methods to make monolayer of particles are spin coating method, dip coating method and Langmuir-Blodgett (LB) technique.[16-18] Among those methods, dip coating method is widely used because uniformity of the final monolayer.[17] The schematics of dip coating of particles is in fig 4.1. By pulling the substrate from colloidal solution with very slow withdrawal speed, meniscus is formed between substrate and colloidal solution. And evaporation of solvent causes capillary force between particles as a result monolayer with high surface coverage particles is fabricated. For a monolayer technique to be used in industry, it must be fast, low cost and must permit a large area of uniform monolayer to be assembled with high surface coverage. But conventional dip coating is composed of dipping the surface into the core/shell solution and pulling out the substrate with the hundred micrometer per min withdrawal velocity. Therefore if the size of substrate is larger, it needs too much time to make monolayer and controlling surface coverage in whole substrate is almost impossible. For these reasons, it can’t be applied for large sized substrate. To overcome these problems, modified dip coating is suggested in this study. By combining the layer by layer(LBL) deposition[19] and dip coating method, PS/SiO₂ core/shell spheres are
uniformly coated on 2 and 4 inch substrate. In this study, by changing the surface charge of sapphire substrate by depositing polyelectrolyte solutions of poly allylamine hydrochloride (PAH) and poly sodium styrenesulfonate (PSS) alternatively on the substrate, monolayer of core shell spheres is coated. Despite the increased demand on the usefulness and productivity in mass production of substrates with uniform and tunable surface coverage of nanomaterials, this deposition strategy has not thoroughly been explored.
Fig. 4.1. (a) Colloidal crystallization mechanism during dip coating; (b) a case of large convective flux; (c) a case of small convective flux. [20]
4.2. Experiment procedure

Materials

PAH (poly allylamine hydrochloride, $M_w = 70,000, 1\text{mg/ml}$) and PSS (poly sodium 4-styrenesulfonate, $M_w = 70,000, 1\text{mg/ml}$) were purchased from Sigma-Aldrich Co.(United States of America). Sulfuric acid and hydrogen peroxide were provided from J. T. baker co.(United states of America). All materials were used without further purification.

Modified dip coating of PS/SiO$_2$ coreshell spheres

Sapphire substrate has hydrophobic surface. To coat the coreshell spheres on substrate, the surface should be hydrophilic surface because colloidal solution with water solvent does not spread on hydrophobic surface. To change sapphire substrate into hydrophilic, piranha solution treatment (Sulphuric acid:hydro peroxide=2:1, 15 min) was conducted.[21] Piranha solution treatment breaks Al-O bonding and make hydroxyl group on sapphire substrate. This makes sapphire substrate into hydrophilic surface. After the surface treatment of substrates, polyallylamine hydrochloride (PAH), a positively-charged polyelectrolyte, and polysodium 4-styrene sulfonate (PSS), a negatively-charged polyelectrolyte, were alternately coated on the sapphire substrates by the spin-assisted LbL deposition method followed with spin assisted washing steps. The positively charged sapphire substrates with PAH/PSS/PAH multilayer thin films were dipped into negatively charged PS/SiO$_2$ dispersion with different dipping conditions, followed by washing with distilled water to remove the coreshell spheres.
coated multilayer structure. Schematics of modified dip coating experiment are in fig 4.2.
Fig. 4.2. Schematics of modified dip coating experiment
4.3. Results and discussion

To realize the uniform coverage of monolayered PS/SiO$_2$ nanosphere arrays on sapphire substrates, a novel deposition strategy combining a conventional dipping method and the layer-by-layer (LbL) deposition method was developed. The surface charge of the sapphire substrates was first varied by the deposition of polyelectrolyte multilayered films on the sapphire substrates based on the spin-assisted LbL deposition method, and the PS/SiO$_2$ nanospheres were then adsorbed on the surface-modified sapphire substrates by the dipping method. Uniformly coated PS/SiO$_2$ nanosphere monolayer arrays could be obtained only with the positively-charged substrates, which attract negatively-charged PS/SiO$_2$ nanospheres based on the long-range electrostatic interactions. (Fig 4.3) The uniform PS/SiO$_2$ monolayers with different particle size (250, 350, and 450 nm) were obtained and the surface coverage of nanospheres adsorbed on the sapphire substrates was easily increased above 50 % by simply varying the dipping time and number. Furthermore, with this novel deposition strategy, we easily secured reproducibility on the highly uniform nanosphere monolayer arrays on large-area, 2 inch, sapphire substrates with simple all solution processes. To check the uniformity of the modified dip coating, surface coverage was measured at 5 different locations. (Fig 4.4) The difference of surface coverage among the 5 points in 2 inch substrate was less than 2 %. For the suitability confirmation of coating method onto large size substrate, modified dip coating was done using 4 inch sapphire substrate. The result is in fig 4.5. To check the surface coverage uniformity, surface coverage was measured at 9 different points on 4 inch sapphire substrate. The difference of surface coverage among the 9 points was less than 5%. From 4 inch substrate dipping experiment, we can
confirm the possibility of application into industry. To calculate the surface coverage of the PS/SiO$_2$ nanospheres coated on sapphire substrates, Image J program was used. By adjusting the contrast of FE-SEM images, the PS/SiO$_2$ nanospheres coated surface and uncovered surface are converted white and black regions, respectively. (Fig 4.6) And the surface coverage was calculated by dividing the area of white region with the total area.
Fig. 4.3. Morphology of S-HNS and PS/SiO₂ arrays. a, FE-SEM image of S-HNS with 240 nm outer diameter and 20 nm shell thickness. (scale bar: 400 nm) Inset shows the TEM image of a S-HNS. b-d, FE-SEM images of PS/SiO₂ arrays coated on bare, non-charged, (b), positively-charged (c), negatively-charged (d) sapphire substrates (scale bars: 6 µm). In the case of the positively-charged substrate, the PS/SiO₂ nanospheres were uniformly coated. However, in the case of the non-charged and the negatively-charged substrates, the PS/SiO₂ nanospheres were massively aggregated and formed in isolated clusters.
Fig. 4.4. Uniformity of PS/SiO$_2$ monolayer coated on 2 inch sapphire substrate. To confirm the uniformity of surface coverage in 2 inch substrate, the surface coverages at five different locations in 2 inch substrate were compared. a, A schematic of 2 inch sapphire substrate marked with numbers from 1 to 5 indicating the points where the surface coverage was measured. b-f, The SEM images taken from point 1 (b), 2 (c), 3 (d), 4 (e), and 5 (f) (scale bars: 3 µm). The surfaces coverages of point 1, 2, 3, 4, and 5 were 42.5 %, 41.5 %, 42.6 %, 43.0 %, and 42.0 %, respectively. The difference of surface coverage among the 5 points was less than 2 %.
Fig. 4.5. Uniformity of PS/SiO$_2$ monolayer coated on 2 inch sapphire substrate. To check uniformity of modified dip coating, SEM images are taken after coreshell spheres are coated on 4 inch sapphire substrate. Surface coverage is measured at 9 points. Measurement point of surface coverage is indicated by the number and surface coverage at each point is indicated in SEM image. (scale bar: 10 µm)
Fig. 4.6 Calculation of surface coverage a) is the original FE-SEM image and Fig. 4.6 b) is the converted image by Image J program. (scale bar 4 µm)
**Controlling the surface coverage**

To controlling the surface coverage of PS/SiO$_2$ coreshell spheres, dipping time, concentration of coreshell solution and dipping number was varied. As the dipping time increase, surface coverage is also increase. The surface coverage increase rate of coreshell sphere with smaller size is much higher than that of larger size coreshell sphere.(Fig 4.7) The modified dip coating is proceed by electric attraction between positively charged substrate and negatively charged coreshell spheres. The coating procedure can be explained by electrophoresis. Without equipment for generation electric field, electrophoresis is enabled using only spin coating of polymer layer. The density of polystyrene sphere is almost equal to water and thickness of silica shell is very thin so coreshell spheres are well dispersed in water solvent. Charged substrate generates electric field so coreshell spheres are migrate into substrate. Therefore coreshell spheres are attached on substrate only by electrical attraction force between – charged core shell sphere and + charged substrate. Fig. 2e is the surface coverage versus coating time curve of coreshell spheres. The concentration of coreshell solution is 10 mg/ml regardless size of coreshell sphere. As the size of coreshell sphere decrease, the coating time for surface coverage saturation is decrease because volume charge density (total charge at unit volume) of water solvent is increase due to large surface area of coreshell spheres. And at same concentration of solution, final saturated surface coverage is almost same regardless size of core shell spheres. This phenomenon can be explained by the same total surface area of coreshell spheres absorbed onto substrate regardless size of coreshell sphere in the case of same surface coverage. The total charge density of coreshell spheres adsorbed onto substrate can be calculated by multiple of zeta
potential and surface area. So if the surface area of coreshell structure is same, the total charge adsorbed on substrate is same regardless size of coreshell spheres. Same total surface area of coreshell sphere at same surface coverage regardless size of coreshell spheres can be easily confirmed by simple calculation. When we think about dipping the 1cm x 1cm sized substrate into various concentration coreshell solutions containing 250 nm, 350 nm, 450 nm sized coreshell spheres. At this condition, number of coreshell spheres and surface area of sphere are in table 4.1.1 and 4.1.2 respectively. Number of sphere and total surface area of coreshell spheres adsorbed at substrate are in table 4.1.3 and 4.1.4 respectively. From table 4.1.4, the total surface area of coreshell spheres is same regardless size of coreshell spheres in the case of same surface coverage. To check the surface coverage change according to the dipping time using various concentrations of coreshell spheres, dipping time was varied from 20 sec to 300 sec using 350 nm size coreshell spheres. As similar to the dipping the substrate into various sized coreshell spheres, the final saturated surface coverage is almost same regardless of concentration of solution. In the case of high concentration of solution, negatively charged coreshell spheres are rapidly adsorbed onto positively charged substrate so the surface coverage is rapidly increased but the adsorbed coreshell spheres are repelling the additional adsorption of coreshell spheres as a result surface coverage is rapidly saturated. But in the case of low concentration of solution, the number of coreshell spheres located near the substrate is small so coreshell spheres electrically adsorbed onto substrate is also very small as a result the surface coverage increase rate at early stage is very low. But As the dipping time increase, the surface coverage is gradually increase and finally saturated.
Fig. 4.7 Surface coverage change as the dipping time increase
Table 4.1 Calculation of total surface area of coreshell spheres at various surface coverage and concentration

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Table 4.1 Calculation of total surface area of coreshell spheres at various surface coverage and concentration
Fig. 4.8 Surface coverage change as the dipping time increase using various concentration of solution
4.4 Conclusion

In conclusion, a novel, simple and inexpensive efficient technique of self assembled monolayer of coreshell spheres is proposed by combining the layer by layer and dip coating method. By the electrical attraction between positively charged substrate and negatively charged coreshell spheres, self assembled monolayer of coreshell spheres is enabled. Especially, conventional dip coating needs too much time to making monolayer of particles because of the very slow withdrawal speed of substrate. But in the case of modified dip coating, substrate is putting into coreshell solution for few minutes and dried by spin coating so the time for self assembled monolayer is very short. And coating condition used for small substrate can be applied for large size substrate without changing coating condition. Therefore self assembled monolayer of particle is possible regardless size of substrate. In this study, self assembled monolayer of coreshell particles are fabricated by modified dip coating using 2 and 4 inch sapphire substrate. To confirm the uniformity of surface coverage, SEM images are taken at different 5 and 9 points in substrate for 2 inch and 4 inch substrate respectively. The difference of surface coverage among the 5 points and 9 points were less than 2 % and 5% for 2 inch and 4 inch substrate respectively.
4.5 Reference


Chapter 5. High efficiency LED device fabrication using S-HNS coated sapphire substrate

5.1. Introduction

As mentioned in chapter 1, there are three main problems in conventional LED device such as high defect density, low extraction efficiency and wafer bowing.[1] These problems are caused by physical and chemical properties difference between sapphire and nitride thin film. To solve these problems many researches are conducted and they show impressive results. But the process to make high quality GaN thin film is complex as a result cost of process is increased.[2-8] The most well known researches about growth of high quality GaN thin film is LEO method.[2, 3] But there are no report addressing the reduction of compressive stress. PSS is also well known method to make high efficiency LED device. But patterning the sapphire substrate is not easy process so the product cost also increased. And there are no reports about solving the compressive stress of GaN thin film. To solve the compressive stress of GaN thin film, we report a new GaN growth scheme for improved LED performance with silica (SiO₂) hollow nanospheres (S-HNS), coated as a monolayer, on a sapphire substrate. To realize S-HNS-coated sapphire substrates, nanoscale polystyrene (PS)/SiO₂ core-shell spheres were first synthesized and coated on sapphire substrates by the modified dip coating method. The substrates were subsequently heat-treated in air atmosphere to remove the organic PS core leaving behind the
spherical hollow silica structures. Hollow spheres have extensively been studied for many applications such as catalysis, drug and gene delivery, photonics, and rechargeable batteries to name a few. In this study, S-HNSs were employed to improve the GaN materials quality and light extraction efficiency of LEDs, and also to reduce the wafer bowing. We believe that S-HNSs could induce nanoscale LEO of GaN on S-HNS coated sapphire substrates to reduce the dislocation density. In addition, GaN with S-HNSs embedded at the interface with the maximum refractive index contrast (i.e., GaN and void) enhances light scattering, resulting in the improvement of light extraction efficiency. Additionally, S-HNSs are expected to effectively reduce the compressive stress of GaN epitaxial layers, minimizing the wafer bowing. Fig. 5.1 shows the fabrication procedure of S-HNS-coated sapphire substrates and expected advantages.
Fig 5.1 advantage and schematics of growing GaN thin film using S-HNS coated sapphire substrate
5.2. Experiment procedure

The sapphire substrates containing monolayers of PS/SiO₂ nanospheres were calcinated under air atmosphere at 800 °C to remove the PS cores within PS/SiO₂ nanospheres as well as the polyelectrolyte films coated on the sapphire substrates, leaving behind SiO₂ hollow shells. The S-HNSs obtained were further fixed to the substrates by post thermal treatment at 1150 °C. After SPM treatment for cleaning the S-HNS coated substrate, GaN epitaxial growth was made on sapphire substrates with and without S-HNS by low pressure MOCVD. Trimethylgallium, trimethylindium and NH₃ were used as precursors for Ga, In, and N, and H₂ was used as a carrier gas. At first, low temperature GaN buffer layer was grown at 550 °C and at 100 Torr. Subsequently, reactor temperature was raised to 1080 °C for the growth of 3.5 μm thick un-doped GaN layer. Additional 2 μm thick Si-doped n-type GaN layer, four pairs of InGaN/GaN multiple quantum well and Mg-doped p-type GaN layer were grown. Surface of p-type GaN layer was etched until n-type GaN was exposed. Ti/Al/Au (50 nm/150 nm/30 nm) was deposited for n-contact, and Ni/Au (5 nm/5 nm) contact layer was deposited for p-contact.
5.3 Growth and characterization of un-doped GaN using S-HNS coated sapphire substrate

5.3.1 Crystal quality evaluation of GaN grown with S-HNS

To grow high quality GaN thin film, growth of the buffer layer is essential.[9] Without buffer layer, polycrystalline GaN is grown because of the large lattice constant difference and low GaN seed density. Usually, buffer layer is grown at low temperature about 550 °C as polycrystalline GaN layer. This polycrystalline GaN buffer layer is re-crystallized by thermal annealing step. By re-crystallization step, polycrystalline buffer layer changed into crystalline GaN seed and GaN thin film is grown from the crystalline GaN seed. In the case of growing GaN buffer layer using S-HNS coated substrate, number of the GaN seed density is much lower than that of reference.(Fig 5.2)

As a result, polycrystalline GaN layer is grown when GaN grown using S-HNS coated sapphire substrate is grown by normal growth condition.(Fig 5.3)

To increase the lateral direction growth, growth pressure was reduced from 300 Torr to 150 Torr. Morphological evolution during the GaN growth was studied by FE-SEM, as shown in Fig. 5.4. The time for high temperature (HT) GaN growth is varied from 1 to 10 min. FE-SEM images of plan-view (left, scale bar 4 μm) and cross-section view (right, scale bar 400 nm) of GaN layers grown at different growth times is in fig. 5.4. The GaN buffer layer was first grown at 550 °C under 100 Torr for 220 s. After the buffer layer growth (a), high temperature GaN epitaxial layers were grown at 1080 °C under 150 Torr for 1 min (b), 5 min (c), 10 min (d). e, Plan–view (left) and cross-section (right) SEM images of a fully merged GaN epitaxial layer
We noted that GaN is grown only from the exposed sapphire substrate between S-HNSs (Fig 5.4b-d). At first, GaN was grown from small area GaN seeds located between S-HNSs and as the growth time was increased, the size of GaN seeds increased and eventually grew over the S-HNSs until GaN fragments merged together laterally (Fig 5.4b-e). The final thickness of GaN epitaxial layer was 3.5 µm. To measure the crystal quality of undoped GaN epitaxial layer, X-ray diffraction (XRD), cathodoluminescence (CL), and transmission electron microscopy (TEM) were employed. To measure the crystal quality of undoped GaN epitaxial layer, XRD, CL, and TEM were employed. The dislocation density of the GaN epitaxial layer was measured by CL measurements. Fig.5.5a and 5.5b show the CL images of the GaN epitaxial layers grown on sapphire substrates with S-HNSs (a) and without S-HNSs (b). From the number of dark spots in these images, we found that the total dislocation density was reduced from $4 \times 10^8$ cm$^{-2}$ to $1 \times 10^8$ cm$^{-2}$. Dislocations are well known as the nonradiative recombination centers in LEDs.[10] The dislocation type and behavior were further analyzed by TEM. Figs. 3c-3f show the cross-section TEM images of GaN grown on a substrate containing a S-HNS monolayer and also on a conventional sapphire substrate. In order to investigate the dislocation type in more detail, TEM images were taken both under $g = [001]$ condition (a, c) as well as $g = [110]$ condition (b, d). Three kinds dislocations are observed c dislocation (Burgers vector $b=<0001>$), a dislocation (Burgers vector $b=1/3<11-20>$) and a+c dislocation (Burgers vector $b=1/3<11-23>$). According to the invisibility criteria, the invisible dislocations should be the a-type dislocations with Burgers vector $b = 1/3 <11-20>$, and the visible dislocations should correspond to either the c-type ($b = <0001>$) or (a+c)-
type \((b = 1/3 \langle11-23\rangle)\) dislocations in the TEM image with \(g = [001]\). However, in the TEM image taken under the \(g = [110]\) condition, the c-type dislocations were invisible while the a- and (a+c)-type dislocations were visible. When we compared Figs. 3b with 3d, we noticed that the number of a-type dislocations is significantly reduced. Especially, the density of edge, observed as threading a-type dislocation in TEM image taken \(g=[110]\) condition, are greatly reduced. However, the dislocation density of c-type is almost the same regardless of the presence of S-HNSs on the substrates. The reduction in the dislocation density with the substrates containing S-HNSs can be explained by nanoscale LEO. Firstly, S-HNSs directly block the propagation of dislocations. By the blocking mechanism alone, it is estimated that the dislocation density would decrease only by 30%. Further reduction in the dislocation density could be explained by the dislocation annihilation. Threading dislocations change their propagation directions to lower the elastic energy per unit length associated with them. Particularly, the a-type dislocation has the smallest energy per unit length when it is aligned normal to the c-axis. Dislocation annihilation mechanism is clearly observed in the inset of Fig 5.6b.[11] Dislocations generated from both sides of a S-HNS change their propagation directions and then encounter with each other above the S-HNS to be annihilated. The reduction of edge and mixed dislocation density can be also confirmed with XRD rocking curve measurements. We found that the XRD full width at half maximum (FWHM) values of (002) planes are 283 and 270 arcsec for the GaN layer grown with and without the presence of S-HNSs, respectively. However, the FWHM value of (102) plane is decreased from 480 to 345 arcsec for the GaN layer grown with the S-HNS monolayer. The large reduction in the FWHM value of (102) plane can be
explained by the material properties of GaN. In the case of GaN, it is well known that the FWHM values of (102) plane and (002) plane in GaN are related to the densities of edge and screw dislocations, respectively.\cite{12} As mentioned above, the density of edge dislocations is significantly decreased when GaN layer is grown from the S-HNS monolayer, resulting in the decreased (102) FWHM value. On the other hand, the screw dislocations do not change their propagation directions because the energy associated with the screw dislocation would increase if they bend normal to c-axis.
Fig. 5.2 SEM images of annealed buffer layer

a) buffer layer grown using S-HNS coated sapphire
b) buffer layer grown using conventional sapphire substrate
Fig. 5.3 SEM images of GaN layer grown by normal growth condition a) GaN layer grown on S-HNS coated substrate, b) GaN layer grown by conventional sapphire substrate.
Figure 5.4 Morphological evolution of GaN epitaxial layers grown on sapphire substrates in the presence of S-HNS monolayers. (scale bar 400 nm).
Figure. 5.5 CL images of GaN thin film. (a) GaN grown using S-HNS coated sapphire substrate. (b) GaN grown using conventional sapphire substrate (scale bar 2 μm).
Figure. 5.6 TEM images of GaN thin film grown on S-HNS coated a), b) and conventional sapphire substrate c), d). a) and c) was taken at \( g = [001] \) condition. b) and d) was taken at \( g = [110] \) condition (scale bar 200 nm)
5.3.2 Optical properties of GaN grown with S-HNS

The optical properties of the GaN layer grown on top of the S-HNS monolayer were measured. First, diffuse reflectance spectra from both GaN layers grown with and without the presence of S-HNSs were measured using an integrating sphere by collecting photons scattered from all the angles, as shown in Fig 5.7. We noticed the interference fringes from both samples due to the GaN layer of finite thickness confined between air and the sapphire substrate interfaces. The abrupt cut-off at 370 nm can be explained by the band edge absorption. The diffuse reflectance of the GaN layer grown in the presence of the S-HNS monolayer is increased by about 28% for the wavelength ranging from 400 to 900 nm. The enhancement in reflectance is attributed to the increased probability of light extraction through diffuse reflection and scattering by the low refractive index S-HNS layer introduced at the GaN epilayer/sapphire interface, and also partly to more efficient light escape from the GaN layer. The light extraction efficiencies of LEDs with and without the S-HNS monolayers were investigated by three dimensional finite difference time domain (FDTD) simulations. To confirm the effect of the surface coverage of S-HNS on light extraction efficiency, simulations were made for three different surface coverages. (i.e., 33.5, 45.6 and 62.5 %) The simulation structures are in fig 5.8. The thickness of GaN epitaxial layer is 2.3 µm, and the length and width of a simulation structure is 6.76 and 3.9 µm, respectively. In this study, a reference and a sapphire substrate with S-HNS were used. By controlling the distance between S-HNS, surface coverage is successfully controlled. Because of the finite domain size for simulation, periodic boundary condition was used at each side of the simulation structure and absorbing boundary condition was used above the
GaN layer to measure the light extraction efficiency. We found that the simulated extraction efficiency varies slightly, depending on the location of electromagnetic dipole in the quantum well. Thus, simulations were performed with 13 electromagnetic dipoles placed at different locations until the light extraction efficiency becomes saturated, as shown in fig 5.9. The simulation structures are in Fig 5.8. The electromagnetic dipole locations are indicated by sky-blue dots. The changes in light extraction efficiency of LEDs with different surface coverages of S-HNS are also shown in fig 5.9. As the surface coverage is increased, the light extraction efficiency also increases. In the case of 62.5% coverage, the extraction efficiency increases by about four times when compared with the reference sample without containing S-HNS monolayer. The maximum index contrast due to the low refractive index of the S-HNS monolayer located at the interface between GaN and the substrate efficiently reflects and scatters the light for increased light extraction efficiency.
Figure 5.7 Diffuse reflectance of un-doped GaN thin film grown on conventional sapphire substrate and S-HNS coated sapphire substrate.
Figure. 5.8 Simulation structures used to evaluate the extraction efficiency of S-HNS LED (a)-(c) LED structure with S-HNS used in FDTD simulation. Upper and lower parts are plan-view and 3-dimensional view of the simulation structure. a, LED structure with 33.5% S-HNS surface coverage. b, LED structure with 45.6% S-HNS surface coverage. c, LED structure with 62.5% S-HNS surface coverage. Arrangement in square lattice was assumed for simplification. (d)-(g) Plan-view of electromagnetic dipole location in FDTD simulation. Location of electromagnetic dipole is indicated as a sky-blue dot in each image. Simulation structure when the number of electromagnetic dipoles is 1(d), 5(e), 9(f) and 13(g).
Figure 5.9 Extraction efficiency of LED structure calculated by FDTD simulation using S-HNS coated and conventional sapphire substrate
5.3.3 Compressive stress calculation of GaN thin film

To evaluate the stresses in the GaN epitaxial layers, the actual wafer bowing with 3 µm thick GaN layers was measured by the laser scanning technique. The diameter of S-HNS was 250 nm with two different S-HNS surface coverages of 30 and 50 %. The size and thickness of the sapphire substrates were 2 inch and 430 µm, respectively. The radius of curvature was increased from 8.83 (a reference without S-HNS monolayer) to 9.69 m for 30 % coverage and to 10.68 m for 50 % surface coverage. (table 5.1) Using the radius of curvature, the stresses within the GaN thin film were estimated by the Stoney’s and the Hsueh’s equations with the elastic constants obtained from the reference. (table 5.2) [13,14] Stoney’s equation evaluates the stress of a thin film from the curvature of the substrate with the film. Stoney equation is expressed as follows;

\[
\sigma_{sh} = \left[ \frac{E_f}{1 - \nu_f} \right] (\alpha_s - \alpha_f) (T_L - T_I) = \left[ \frac{E_s}{1 - \nu_s} \right] \frac{t_s^2}{6t_f R}
\]

where \(v\) is the Poisson ratio and \(t_s, t_f\) are the thickness of substrate and thin film. \(R\) is the radius of curvature and \(\alpha_f, \alpha_s\) are the thermal expansion coefficient of thin film and substrate. \(T_L\) is the growth temperature and \(T_I\) is the initial temperature. However, Stoney’s equation can be applied only for the case when the thickness of thin film is much thinner than that of substrate. Hsueh developed the equation which can be applied for thick film by including higher order terms in their solutions to obtain better accuracy. The modified stress equation is expressed as follows;
The compressive stress was calculated using Stoney’s equation and Hsueh’s equation. The calculation results are in table 5.1 and fig 5.10. As the surface coverage is increased, the compressive stress decreases, as shown in fig 5.10. The compressive stress decreases from 706 to 636 MPa for 30 % S-HNS surface coverage and to 583 MPa for 50 % S-HNS surface coverage. This is to say that the stress is decreased by about 10 % for the 30 % S-HNS surface coverage and by 20 % for the 50 % S-HNS coverage.

To confirm the stress reduction of the GaN layer in the presence of S-HNS monolayers, finite element (FE) simulations, using a commercial FE software ABAQUS, were conducted. To evaluate the stress evolution in GaN with S-HNSs accurately, detailed geometry which consists of sapphire substrate, S-HNS’s, and GaN should be considered. However, this is impossible due to extremely large number of S-HNS’s (over $10^{10}$ in the considered system). Here, we conducted a unit structure whose dimension is $0.4 \times 0.4 \times 3.5 \ \mu m^3$ (fig 5.11), and adopted a periodic boundary condition along the in-plane axes under assumption of uniform stress in the inside part of wafer. Stress and strain solutions were calculated along the temperature change from $1040^\circ C$ to $25^\circ C$. Uniform temperature was assumed since the considered system was small ($0.4 \times 0.4 \times 3.5 \ \mu m^3$).
FE simulation of a full scale wafer confirmed that the stress evolution in GaN was nearly uniform in the inside of wafer, and only small part of edge region showed inhomogeneous stress distribution due to boundary effect (fig 5.12).

In addition to the periodic boundary condition, we also considered effective Young's modulus of the substrate. Contrary to the GaN epitaxial layer, the substrate, which is relatively very thick, has significant inhomogeneity along the thickness direction due to its bowing. This inhomogeneity leads an undesirable out-of-plane periodicity as well as in-plane periodicity. However, because the in-plane axial stiffness is in linear proportion to the cross-sectional area as \( k=AE/L \), where \( k \) is axial stiffness, \( A \) is cross-sectional area, \( E \) is the Young's modulus, and \( L \) is length, identical stiffness of the substrate can be derived from reduced area \( A' \) and corresponding \( E' \) which satisfy a relationship \( AE=A'E' \). Note that what is interesting here is the stress evolution in the GaN epitaxial layer, not the stress in the substrate. Therefore, one can reduce the considered thickness of substrate to e.g. 0.5 \( \mu \)m from its original (430 \( \mu \)m) in order to avoid the undesirable out-of-plane periodicity. The corresponding effective Young's modulus would be 860 times larger.

The results of simulation are in fig 5.11. As shown in fig 5.11, the compressive stress decreases over 27 % near the interface between the sapphire substrate and the GaN epitaxial layer in the case of 30 % S-HNS surface coverage. Strong stress gradient was also predicted around S-HNSs, as shown in fig 5.11. Because the edge dislocations produced at the interface generate compressive stress field along the climbing front, their propagation directions could be interfered by the stress gradient around S-HNSs (Note
that there is a negligible stress gradient in the GaN epitaxial layer on the conventional substrate without containing S-HNSs, as shown in the left-hand side of Fig. 4d. The most probable propagation path of the edge dislocations generated at both sides of a S-HNS would be towards the S-HNS to annihilate the compressive stresses applied around the S-HNS (See the inset of fig 5.6b and the right-hand side of fig 5.11).
Table 5.1 Stress, wafer bowing and radius of curvature of GaN epitaxial layers

The stress values calculated by Stoney’s formula and by Hsueh’s formula are almost the same. The thickness of GaN is relatively thin so the calculated stress values show no big difference between the two models.
<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Possion ratio</th>
<th>Biaxial modulus (GPa)</th>
<th>Thermal expansion coefficient (a-axis, $10^{-6}$/K)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>607</td>
<td>7.5</td>
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<tr>
<td>GaN</td>
<td>297</td>
<td>0.25</td>
<td>396</td>
<td>5.59</td>
</tr>
</tbody>
</table>

Table 5.2 Elastic constants of sapphire and GaN.[15]
Figure. 5.10 Compressive stress of GaN thin film grown on S-HNS coated and conventional sapphire substrate.
Fig 5.11. **FE simulation results of GaN thin film.** The stress analysis of GaN without S-HNS (left) and with a S-HNS monolayer with 30% surface coverage (right) obtained by FE simulations. Reduction in compressive stress as well as a strong stress gradient is notable around the S-HNS.
Fig 5.12. **FE simulation of a full-scale wafer.** FE simulation of a full-scale 2 inch wafer confirmed: (a) wafer bowing due to thermal mismatch between GaN thin film and sapphire substrate, and (b) nearly uniform stress distribution along in-plane axes in the inside part.
5.4 Fabrication of LED device using LED structure grown using S-HNS coated sapphire substrate

Using the less strained and high quality GaN template, LED structure was grown by MOCVD. The schematics of LED structure grown in this study are in fig 5.13. Using a 3.5 \( \mu \)m thickness un-GaN template, additional 2 \( \mu \)m thick Si-doped n-type GaN layer, four pairs of InGaN/GaN multiple quantum well and Mg-doped p-type GaN layer were grown. To evaluate the optical characteristics of LED structure, PL intensity mapping of LED structure was done. The PL intensity maps of LED structures in the presence and absence of the S-HNS monolayers are shown in fig. 5.14a and 5.14b, respectively. We note that the average PL intensity increases by three times by employing a S-HNS monolayer with a surface coverage of 30 % at the GaN/sapphire interface. This result is in good agreement with the light extraction that was enhanced by 2.8 times from the FDTD simulation with a surface coverage of 33.5 %. The PL mapping results shows slightly higher extraction efficiency than the results of FDTD simulation. This difference attributed to the crystal quality enhancement. By reduction of dislocation density, non radiative recombination center, the internal quantum efficiency is increased as a result external quantum efficiency, multiple of light extraction and internal quantum efficiency, is increased. The FDTD simulation only considers extraction efficiency but the PL mapping results contains the extraction efficiency and internal quantum efficiency so the intensity increase of PL mapping is higher than FDTD simulation results. To evaluate the out power of LED grown on S-HNS coated sapphire substrate, LED device was fabricated by conventional lithography and metal electrode deposition. Surface of p-type GaN layer was etched until n-type GaN was exposed. Ti/Al/Au (50 nm/150
nm/30 nm) was deposited for n-contact, and Ni/Au (5 nm/5 nm) contact layer was deposited for p-contact. The output power of LED is also shown in fig 5.16. The output power of LED in the presence of a S-HNS monolayer is two times higher than that without containing S-HNS at 20 mA input current. In general, the output power of LEDs in the presence of S-HNS monolayers is much higher than that of a reference LED without S-HNS regardless of input current density. We believe that the enhanced external quantum efficiency of LEDs is attributed to the enhancement in both the internal quantum efficiency (associated with reduced dislocation density) and the extraction efficiency (associated with increased diffuse reflectance). By incorporating S-HNS monolayers into GaN epitaxy scheme, LED output power significantly increases when compared with the conventional LED without containing S-HNSs.
Fig 5.13. Schematics of LED structure grown on un-GaN template grown using S-HNS coated (a) and conventional sapphire substrate (b).
Figure 5.14 PL intensity mapping of LED structure: PL intensity mappings of LED structures grown with (a) and without (b) S-HNS monolayers (scale bar 5 mm). Quadrants of 2” sapphire substrates were used for LED fabrication.
Fig 5.15. Schematics of LED device fabricated using LED structure grown on S-HNS coated (a) and conventional sapphire substrate (b).
Fig 5.16. Output power of LEDs fabricated with and without S-HNS monolayers plotted against input current.
5.5 Fabrication of LED devices using LED structures grown using various sized S-HNS coated sapphire substrate

5.5.1. Motivation of experiment

To confirm the size effect of S-HNS on the crystal quality of GaN thin film and LED performance, LED structures were grown and devices were fabricated using various sized S-HNS coated sapphire substrate. The sizes of S-HNS used in this study were 250, 450, 1000 nm. If the size of S-HNS is increased, the volume fraction of air also increased as a result LED performance and wafer bowing is also changed. The void volume of sphere on 10 x 10 μm² area according to the size and coverage of sphere is in table 5.3. As the size of sphere increased, the void volume is linearly increased at same coverage. The void with low refractive index increases the light extraction efficiency and reduces the stress of GaN thin film so we expect that LED with high efficiency and less strain is possible by insertion of large size S-HNS into GaN thin film.
### Number of polystyrene sphere

<table>
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<tr>
<th></th>
<th>10%</th>
<th>30%</th>
<th>50%</th>
</tr>
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<tbody>
<tr>
<td>250 nm</td>
<td>204</td>
<td>611</td>
<td>1019</td>
</tr>
<tr>
<td>350 nm</td>
<td>104</td>
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<td>450 nm</td>
<td>63</td>
<td>189</td>
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<td>13</td>
<td>38</td>
<td>64</td>
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<tr>
<td>2000 nm</td>
<td>3</td>
<td>10</td>
<td>16</td>
</tr>
</tbody>
</table>

### Volume of air

<table>
<thead>
<tr>
<th></th>
<th>10%</th>
<th>30%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.67 X 10^9 nm^3</td>
<td>5 X 10^9 nm^3</td>
<td>8.33 X 10^9 nm^3</td>
</tr>
<tr>
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<td>7 X 10^9 nm^3</td>
<td>1.17 X 10^10 nm^3</td>
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<tr>
<td>450 nm</td>
<td>3 X 10^9 nm^3</td>
<td>9 X 10^9 nm^3</td>
<td>1.5 X 10^10 nm^3</td>
</tr>
<tr>
<td>1000 nm</td>
<td>6.67 X 10^9 nm^3</td>
<td>2 X 10^10 nm^3</td>
<td>3.33 X 10^10 nm^3</td>
</tr>
<tr>
<td>2000 nm</td>
<td>1.33 X 10^10 nm^3</td>
<td>4 X 10^10 nm^3</td>
<td>6.67 X 10^10 nm^3</td>
</tr>
</tbody>
</table>

Table 5.3 number of sphere and volume of void according to the coverage and size of S-HNS
5.5.2. Experiment
To confirm the effect of S-HNS on crystal quality and LED device performance, 250, 450, 1100 nm sized core shell structure was synthesized by emulsion polymerization and Stober method. After that, the coreshell structures were coated on the 4 inch sapphire substrate by modified dip coating method. For consideration of size effect of S-HNS, the surface coverage of S-HNS was fixed at 30%. After annealing at 1150°C for removal of polystyrene sphere and fixation of S-HNS, un-doped and n-doped GaN were grown by MOCVD. The crystal quality of GaN template was measured and growth of GaN-InGaN multiple quantum wall and p-doped GaN was followed. And LED device was fabricated by conventional photo lithography, ICP etching and deposition of metal electrode.
5.5.3 Measurement of crystal quality

Crystal quality of GaN template was measured by evaluation of XRC FWHM. The surface morphology of GaN thin film was measured by optical microscope. By controlling the growth pressure of GaN thin film, the pit density of GaN thin film was greatly reduced. The result was in fig 5.17. The samples were grown at same batch for comparison of size effect of S-HNS on crystal quality. The XRC FWHM of GaN thin film shows minimum value for GaN thin film containing 450 nm sized S-HNS. The XRC FWHM value of GaN thin film containing 250 and 1000 nm shows almost same value. We think that minimum XRC FWHM value exist in the range from 450 to 1000 nm. The XRC FWHM values of GaN template grown on PSS and bare substrate were 280 and 190 arcsec for the 002 plane each other. In the case of (102) plane, the XRC FWHM value of GaN template grown on PSS and bare substrate were 350 and 190 arcsec each other. The GaN template grown using PSS and bare substrate was grown by their optimized condition. The crystal quality of GaN thin film is highly enhanced in the case of (102) plane and slightly enhanced in the case of (002) plane. The crystal quality enhancement was attributed to the properties of GaN thin film. The edge dislocation related to the XRC FWHM of (102) plane is greatly reduced during the LEO step and reduction of edge dislocation is reflected into the XRC FWHM value of GaN thin film.
<table>
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<th>Hollow sphere diameter (nm)</th>
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<tr>
<td>450</td>
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<td>1000</td>
<td><img src="image5.png" alt="Image" /> x200</td>
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</tr>
</tbody>
</table>

**Fig 5.17.** Optical microscope image of GaN thin film grown on various sized S-HNS coated sapphire substrate
Fig 5.18. XRC FWHM value of GaN thin film grown on various sized S-HNS coated sapphire substrate
5.5.4 Wafer bowing measurement

To measure the strain of GaN thin film, wafer bowing was measurement by laser scanning technique. The result of wafer bowing measurement was in fig 5.20. Wafer bowing result shows opposite tendency when it compared with XRC FWHM result. GaN template containing 450 nm S-HNS shows highest wafer bowing and 250 nm S-HNS shows smallest wafer bowing. The wafer bowing of GaN thin film containing 450 and 1000 nm S-HNS shows similar result. As the size of S-HNS increased, the void volume also increased therefore the strain of GaN thin film should be decreased. To explain the opposite tendency of strain of GaN thin film, simple calculation of void and SEM images were studied. There are much voids in the surroundings of S-HNS and between S-HNS. In the case of small size S-HNS, the more number of S-HNSs are needed for same coverage when it compared with larger size S-HNS. The void volume of large sphere can be calculated by

\[ \text{Volume of air} = \frac{4\pi}{3} R^3 \]  

(4)

But in the case of small size S-HNS, they are coated as aggregated structure and there are void space between S-HNS and surroundings of S-HNS.

\[ \text{Volume of air} = 4R^3 \]  

(5)

When the voids between and surroundings of S-HNS are considered, the volume of air is calculated by equation 5. From the geometric calculation, the void volume is similar regardless size of spheres. The similar size of void volume induces similar wafer bowing. But the crystal quality term also should be considered. As the crystal quality of GaN thin film increased, the dislocation density was lowered. And reduction of dislocation density induces higher wafer bowing. The XRC FWHM value of GaN thin film containing
450 nm sized S-HNS shows highest wafer bowing. The smallest value of XRC FWHM means lowest density of dislocation. The reduction of dislocation induces highest wafer bowing.
Fig 5.19. The wafer bowing of GaN thin film according to the size of S-HNS
*Volume of air* = $4R^3$ \approx \frac{4\pi}{3}R^3

**Fig 5.20. Model for the calculation of void volume**
Fig 5.21. SEM images of surroundings of S-HNS
5.5.5 Fabrication of LED device

To compare the efficiency of LED device fabricated using S-HNS coated, PSS and bare sapphire substrate, LED device was fabricated by conventional photolithography and ICP etching. The size of S-HNS used for fabrication of LED device was 450 nm. Fig 5.23 is the optical power of the 3 kinds of LED device. The optical output power of LED fabricated using PSS is the highest among 3 kinds LED device. And optical output power of LED fabricated using hollow silica sphere coated substrate is slightly smaller than PSS LED device. The optical power of LED device fabricated using S-HNS coated substrate and PSS are increased 270% and 235% when it compared with LED device fabricated using bare sapphire substrate. After dicing and packaging of LED device, EQE was measured. The EQE of LED device fabricated using PSS is also highest among the 3 kinds of LED devices. The coverage of pattern of PSS is over 50% but the coverage of S-HNS used in this study is only 30% so if the coverage of S-HNS is further increased, the output power of LED device containing S-HNS is could be higher than that of PSS LED. To compare the electrical characteristics of LED device, I-V characteristics was measured. The I-V characteristics of 3 kinds LED devices are in fig 5.24. The LED device fabricated using bare sapphire substrate shows smallest leakage current. The electrical characteristics of LED device fabricated using S-HNS shows poorest among 3 kinds of devices. This is contributed to the optimization of growth condition. The growth condition of PSS and normal LED is optimized but the growth condition of LED grown on S-HNS coated sapphire substrate was not optimized. This fact causes bad electrical characteristics of LED device. To confirm the effect of S-HNS on the extraction efficiency related with light extraction and internal quantum
efficiency related with crystal quality, IQE and extraction efficiency (EXE) was measured individually. The results are summarized in table 5.4. The IQE of LED devices fabricated using PSS and S-HNS are almost similar. However in the case of EXE, the PSS LED is 15% higher than S-HNS LED. As mentioned above, the surface coverage of patterns of PSS is much higher than that of S-HNS LED. This high surface coverage of pattern attributed to the higher light extraction efficiency. So if the coverage of S-HNS increased, the defect density is highly reduced because of the enlarged ELO area and because of the increased void volume, light extraction efficiency is also increased. Additionally, void volume is also increased as a result the wafer bowing is also reduced.
Fig 5.22. Optical power of LED device fabricated using PSS, bare and S-HNS coated sapphire substrate
Fig 5.23. I-V characteristics of LED device
<table>
<thead>
<tr>
<th>CHID</th>
<th>No</th>
<th>EQE (%) @120mA (19.6A/cm²)</th>
<th>EQE (%) @214mA (35A/cm²)</th>
<th>IQE (%) @120mA (19.6A/cm²)</th>
<th>IQE (%) @214mA (35A/cm²)</th>
<th>Extraction @120mA (%)</th>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>21.0</td>
<td>18.8</td>
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<tr>
<td>Hollow Sphere</td>
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<td>44.1</td>
<td>83.0</td>
<td>77.6</td>
<td>56.9</td>
</tr>
</tbody>
</table>

Table 5.4 Optical characteristics of LED device
5.6 Conclusion

In conclusion, less strained and high efficiency LED device was fabricated by using sapphire substrate with S-HNS coated on it. The very low refractive index S-HNS were used as a LEO mask for the growth of GaN thin film and photon scattering center. By nanoscale LEO and photon scattering, high quality GaN thin film and high extraction efficiency was enabled. S-HNS reduced dislocation density from $4 \times 10^8 \text{ cm}^{-2}$ to $1 \times 10^8 \text{ cm}^{-2}$. Dislocation which is direct nonradiative recombination center reduces internal quantum efficiency so reducing the dislocation density increase the internal quantum efficiency. Especially, reduction of edge dislocation density was confirmed by TEM measurement. In the case of edge dislocation, they can reduce their energy by bending their propagation direction normal to c axis. The increase of light extraction efficiency is confirmed by measurement of diffuse reflectance which is directly related with light extraction efficiency. The diffuse reflectance increased 30% when S-HNS used for growing LED structure. Efficiency of LED device was calculated by multiple of internal quantum efficiency and light extraction efficiency. So by increasing internal quantum efficiency and extraction efficiency, the output power of LED device is increased almost 80% when it compared with reference. Additionally, the reduction of compressive stress of GaN thin film is confirmed by FE simulation and laser scanning technique. In FE simulation, the compressive stress at the surrounding of S-HNS is reduced almost 30% when it compared with reference. The reduction of the compressive stress of GaN thin film is also confirmed by experiment. In the case of 3 µm thickness GaN thin film with 50% surface coverage of S-HNS, the compressive stress
of GaN thin film is reduced about 20%. By insertion of S-HNS into GaN thin film, high quality and less strained with high extraction efficiency LED structure was fabricated. To confirm the size effect of S-HNS onto the characteristics of LED device, LED device was fabricated using 250, 450 and 1000 nm sized S-HNS. To compare the efficiency of LED device, LED devices were fabricated using PSS and bare sapphire substrate. The EQE of PSS is highest and 17% higher than that of S-HNS LED. And EQE of PSS and S-HNS is increased 270% and 230% when it compared with LED fabricated using bare sapphire substrate. To compare IQE and EXE of three kinds of LED devices, IQE and EXE of LED devices were measured individually. The IQE of LED device fabricated using PSS and S-HNS shows almost same value. But in the case of EXE, PSS LED is 15% higher than that of S-HNS LED. The higher light extraction efficiency can be attributed to the high surface coverage of PSS. The surface coverage of S-HNS used in this study was about 30% but in the case of PSS LED, the surface coverage of pattern is almost 50%. This high surface coverage induces high extraction efficiency. If the surface coverage of S-HNS is increased, the void volume is also increased. In this case, the extraction efficiency is further increased because of the increase of low refractive index volume and stress of LED is further decreased because of the increase of void volume. So when the surface coverage of S-HNS increased, the efficiency could be almost similar to the efficiency of PSS LED.
5.7 Reference


Chapter 6. Growth of LED structure using sapphire substrate with SiO₂ thin film on its back side

6.1. Introduction

As a type of III-V wide-band-gap semiconductor,[1] single crystal GaN has received considerable attention in recent years.[2] It has potential use in areas such as laser and light emitting diodes[3,4] as well as solar-blind photodetectors. For growth of the III nitrides, the most extensively used substrate material is sapphire.[5] Large-area and good quality crystals of sapphire are easily available and their cost is low. Sapphire is stable at high temperatures and the growth technology of nitrides on sapphire is now fairly mature. The stress in the films often originates from epitaxy[6] in the growth processes and from TEC mismatch[7] in the post-growth processes by both metal-organic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy. For example, the stress typically observed is dominated by thermal stress in the post-growth processes, which is known to cause defects or damage in the films, including dislocation,[8] buckling,[9] cracking, etc. Cracks normally extend to the principal tensile stresses within the thin brittle layers and interact with the interfaces of GaN/sapphire. Due to the mismatch of TECs between the GaN film and sapphire, wafer bowing will occur after cooling because the GaN film is mechanically constrained by the sapphire. Thermal stress,[10] wafer bending[11] and cracking[12] are the main
drawbacks that hamper production of large-area GaN substrates and the application of GaN films. Wafer bowing and stress concentration significantly influences not only mechanical performance of devices but also their optical, electrical and magnetic properties.[13] Therefore, reducing wafer bowing and stress concentration in GaN films is very important.

Except the compressive stress caused by post cooling process, the tensile stress induced at the growth stage is also serious problem. Because of the tensile stress caused by coalescence of GaN seed and temperature difference between front and back side substrate, the full contact of the substrate with the susceptor is lost. For a concave bowing, the wafer edges are expected to be cooler than the center, whereas for a convex bowing the center is expected to be cooler. This is especially important for the growth of GaN-based LED structures with a homogenous emission wavelength and involves an additional difficulty when going to 4 in or larger substrates. In the case of larger substrate, the peak wavelength uniformity in same wafer would be bad because of non uniformity of In content in InGaN layer.

In this study, to reduce the wafer bowing caused at post cooling process, LED structure is grown using sapphire substrate with SiO₂ thin film on its backside. The thermal expansion coefficient of sapphire is much higher than that of GaN so deposition of thin film with very low thermal expansion coefficient will reduce the compressive stress in GaN thin film. By increasing the thickness of SiO₂ layer coated on the backside of Al₂O₃ from 0 µm to 6 µm, the compressive stress is reduced from 764 MPa to 280 MPa. Deposition of SiO₂ thin film on backside of substrate is also effective to solve peak wavelength inhomogeneity in wafer. SiO₂ thin film, with very low thermal expansion coefficient and deposited on the back side substrate, suppresses the
thermal expansion of backside as a result wafer bowing in the growth stage is suppressed. The schematics of advantages of growing GaN using sapphire substrate with SiO$_2$ thin film on its backside is in fig 6.1.
6.2. Experiment procedure

SiO$_2$ thin film was deposited on the one side of double-side polished sapphire substrate by plasma enhanced chemical vapor deposition (CVD). The thickness of deposited SiO$_2$ thin film was varied from 1 $\mu$m to 4 $\mu$m to confirm the stress reduction according to the thickness of SiO$_2$ thin film. After deposition of SiO$_2$, LED structure was grown using low pressure MOCVD. The total thickness of LED structure is about 5 $\mu$m measured by PL mapping.
Fig 6.1 schematics of experiment and advantages experiment a) growing LED using conventional sapphire substrate, b) growing LED using sapphire substrate with SiO₂ layer on its backside.
6.3. Results and discussion

6.3.1 Wafer bowing measurement and PL mapping of LED structure

After growing LED structure using conventional sapphire substrate and sapphire substrate with SiO$_2$ layer on its backside, wafer bowing was measured. The wafer bowing and radius of curvature according to the thickness of SiO$_2$ layer was in fig 6.2. To measure the wafer bowing, Ni layer with 5 nm thickness was deposited onto SiO$_2$ layer to prevent penetration of laser into wafer. The wafer bowing decreases linearly with the increase of thickness of SiO$_2$ layer. In the case of 4 µm thickness SiO$_2$ layer, the wafer bowing is reduced almost 60%. The radius of curvature is increase parabolically with the thickness of SiO$_2$ layer. From the wafer bowing, the stress reduction is clearly observed. To evaluate the crystal quality of GaN thin film, XRD measurements was done. The FWHM values of XRC are in fig 6.3. The FWHM value and thickness of SiO$_2$ shows no big relationship. From the XRC measurements, we confirm that the SiO$_2$ film does not affect the crystal quality of GaN thin film. To evaluate the homogeneity of peak wavelength of LED in wafer, PL mapping was done. The results of PL mapping are in table 6.1. The average wavelength of wafer shows no big relationship with thickness of SiO$_2$ layer deposited onto backside of sapphire substrate. To measure the homogeneity of wavelength, peak wavelength difference and standard deviation of peak wavelength in one wafer were measured. The results are in table 6.1. The peak wavelength difference in one wafer is from 5 nm to 10 nm and shows no big relationship with thickness of SiO$_2$ layer. The standard deviation of peak wavelength in one wafer is about
5 nm and shows no big relationship with thickness of SiO$_2$ layer. The PL mapping results is not agreeing well with the assumption. To explain the disagree between assumption and experiment, growth temperature of LED structure should be considered. The growth temperature of un-doped GaN layer is almost 1150 °C but growth temperature of GaN/InGaN multi quantum well layer is much lower than that of un-doped GaN layer. And the size of substrate is only 2 inch so wafer bowing at InGaN growth stage is not serious. As a result, In incorporation in-homogeneity in wafer at InGaN growth stage is not becoming a serious problem.
Fig 6.2 (a) wafer bowing and (b) curvature of GaN thin film grown on conventional and SiO₂ thin film backside coated sapphire substrate.
Fig 6.3 XRC FWHM values of GaN thin film grown on conventional and SiO$_2$ thin film backside coated sapphire substrate
<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Wavelength</th>
<th>Wave length difference in wafer</th>
<th>Wavelength STDE</th>
</tr>
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<tbody>
<tr>
<td>0 µm</td>
<td>438.1 nm</td>
<td>5 nm</td>
<td>3.6 nm</td>
</tr>
<tr>
<td>1 µm</td>
<td>437.6 nm</td>
<td>5 nm</td>
<td>5.2 nm</td>
</tr>
<tr>
<td>2 µm</td>
<td>436.6 nm</td>
<td>10 nm</td>
<td>5.0 nm</td>
</tr>
<tr>
<td>3 µm</td>
<td>434.1 nm</td>
<td>5 nm</td>
<td>4.7 nm</td>
</tr>
<tr>
<td>4 µm</td>
<td>434.1 nm</td>
<td>10 nm</td>
<td>5.9 nm</td>
</tr>
</tbody>
</table>

Table 6.1 XRC FWHM values of GaN thin film grown on conventional and SiO₂ thin film backside coated sapphire substrate
6.3.2 Stress calculation of LED structure

To calculate the stress of the thin film, Stoney’s equation is generally used. But because of the assumptions used in Stoney’s equation, there exist some limitation when calculating the stress of the thin film. The main assumptions are: i) both the film and substrate thicknesses are small compared to the lateral dimensions; ii) the film thickness is much less than the substrate thickness; iii) the substrate material is homogeneous, isotropic, and linearly elastic, and the film material is isotropic; iv) edge effects near the periphery of the substrate are inconsequential and all physical quantities are invariant under change in position parallel to the interface; v) all stress components in the thickness direction vanish throughout the material; and vi) the strains and rotations are infinitesimally small. To overcome the limitation of Stoney’s equation, Hsueh and Freund developed newly designed equation by insertion of higher order terms. In this study, the stress of GaN thin film is calculated by Stoney, Hsush and Freund’s equation for the exact calculation.

Stoney equation

Curvature-based techniques for the measurement of stress in thin films are gaining increasingly widespread use. The Stoney formula serves as a cornerstone of experimental work on stress measurement in thin films bonded to substrates. In its most basic form, the formula provides an expression for the curvature $k$ of the substrate in terms of the residual force $f$ in the film (interpreted as a force per unit distance along the interface) due to misfit or other residual elastic strain; this expression is
where \( h_s \) and \( M_s \) are the thickness and the biaxial elastic modulus of the substrate. The formula does not involve the properties of the film material, nor does it presume of any particular through-the-thickness distribution of the film stress with resultant \( f \). Stoney equation follows from an analysis of a model of the film–substrate system which is based on several assumptions, and the point of the present discussion is to examine the range of applicability of some of these assumptions in light of current practice. The main assumptions are: i) both the film and substrate thicknesses are small compared to the lateral dimensions; ii) the film thickness is much less than the substrate thickness; iii) the substrate material is homogeneous, isotropic, and linearly elastic, and the film material is isotropic; iv) edge effects near the periphery of the substrate are inconsequential and all physical quantities are invariant under change in position parallel to the interface; v) all stress components in the thickness direction vanish throughout the material; and vi) the strains and rotations are infinitesimally small. In the case of GaN growth, the compressive stress is mainly generated by the difference of thermal expansion coefficient between sapphire and GaN so the Stoney equation can be expressed below equation.

\[
\sigma_{th} = \left[ \frac{E_f}{1 - \nu_f} \right] (\alpha_s - \alpha_f) (T_L - T_f) = \left[ \frac{E_s}{1 - \nu_s} \right] \frac{t_s^2}{6t_f R} \tag{2}
\]

Hsueh’s equation
In Hsueh’s equation, the strain component decomposed into a uniform component and a bending component and these can be expressed as follow equation.[14]

\[ \varepsilon = c + \frac{z - t_b}{r} \quad \text{(for } t_s \leq z \leq h_n \text{)} \quad (3) \]

\( C \) is the uniform strain component and dictates the location of the bending axis (which is defined as the line in the cross section of the system where the bending strain component is zero), and \( r \) is the radius of curvature of the system. It should be noted that the bending axis is different from the conventional neutral axis where the normal stress is zero. And thermal strains of substrate and thin film can be expressed as follows

\[ \sigma_s = E_s (\varepsilon - \alpha_s \Delta T) \quad \text{(for } t_s \leq z \leq 0 \text{)} \quad (4) \]

\[ \sigma_f = E_f (\varepsilon - \alpha_f \Delta T) \quad \text{(for } f = 1 \text{ to } n \text{)} \quad (5) \]

\( E_f \) is Young’s modulus of layer I of the film. It should be noted that one-dimensional geometry is considered. For two dimensional geometry, stresses in the system become biaxial and the solution can be obtained by replacing Young’s modulus, \( E \), with biaxial modulus, \( E/(1-v) \), in Eq 4 where \( v \) is poisson’s ratio. The three parameters \( c, t_b, r \) in equation 3 are determined by following three boundary conditions. First, the resultant force due to the uniform strain component is zero

\[ E_s (\varepsilon - \alpha_s \Delta T)t_s + \sum_{i=1}^{n} E_i (c - \alpha_i \Delta T)t_i = 0 \quad (6) \]

Second, the resultant force due to the bending strain component is zero

\[ \int_{t_s}^{0} \frac{E_s (z - t_b)}{r} \, dz + \sum_{i=1}^{n} \int_{h_i}^{h} \frac{E_i (z - t_b)}{r} \, dz = 0 \quad (7) \]

Third, the sum of the bending moment with respect to the bending axis is in
equilibrium with the applied moment, such that
\[
\int_{z_1}^{z_2} \sigma_s (z - t_b) dz + \sum_{i=1}^{n} t_i \sigma_i (z - t_b) dz = M \tag{8}
\]
Where M is the applied moment per unit width of the multilayer. Solutions of equation 3-8 yield
\[
c = \frac{(E_s t_s \alpha_s + \sum_{i=1}^{n} E_i t_i \alpha_i) \Delta T}{E_s t_s + \sum_{i=1}^{n} E_i t_i} \tag{9}
\]
\[
t_b = \frac{-E_s t_s^2 + \sum_{i=1}^{n} E_i t_i (2h_{i-1} + t_i)}{2(E_s t_s + \sum_{i=1}^{n} E_i t_i)} \tag{10}
\]
\[
\frac{1}{r} = \frac{3[E_s(c - \alpha_s \Delta T)t_s^2 - \sum_{i=1}^{n} E_i t_i (c - \alpha_i \Delta T)(2h_{i-1} + t_i) + 6M}{E_s t_s^2 (2t_s + 3t_b) + \sum_{i=1}^{n} E_i t_i [6h_{i-1}^2 + 6h_{i-1} t_i + 2t_i^2 - 3t_b(2h_{i-1} + t_i)]} \tag{11}
\]

With the aforementioned solutions of c, t_b and r the general solutions for the strain/stress distributions in multi-layers are complete.

In the case of binary system, the stoney’s equation and thermal stress equation can be expressed as follows.

\[
\sigma_s = \frac{1 + \gamma \delta^3}{1 + \delta} \frac{E_s}{1 - \nu_s} \frac{t_f^2}{6t_f R} \tag{12}
\]
\[
\sigma_{th} = \frac{1 + \gamma \delta^3}{1 + \gamma^2 \delta^4 + 2\gamma (2\delta + 2\delta^3 + 3\delta^2)} \frac{E_f}{1 - \nu_f} (\alpha_s - \alpha_f) \Delta T \tag{13}
\]

where \( \delta = \frac{t_f}{t_s}, \gamma = \frac{t_f}{t_s}, M = E/(1 - \nu) \)
Freund’s equation

Freund derive the equation, which can be applied for thick film, by considering the stationary of potential energy at equilibrium condition.[15] In Freund’s equation, there is one assumption that the film material is also homogeneous and the stress is uniform through the thickness of the film. A polar section of the system is shown in the inset in Fig. 6.4, with the film and substrate thicknesses labeled as $h_f$ and $h_s$, respectively, and similarly for the elastic modulus $E$, Poisson ratio $\nu$, and biaxial modulus $M=E/(1-\nu)$. Cylindrical $(r, \theta, z)$ coordinates are adopted with the origin on the geometrical midplane of the substrate and the polar axis, or $z$ direction, perpendicular to the interface as shown.

Mismatch strain is a system parameter denoted by $\varepsilon_m$; in terms of lattice parameters of the film and substrate, say $a_f$ and $a_s$, respectively, it is defined for an epitaxial system by $\varepsilon_m=(a_s-a_f)/a_f$. Mismatch strain can also arise from the difference in thermal expansion characteristics or other physical sources. Due to the assumption of all stress components in the thickness direction vanish throughout the material and axial symmetry, the only nonzero stress components in polar coordinates at any material point are $\sigma_{rr}(r,z)$ and $\sigma_{\theta\theta}(r,z)$; the corresponding elastic strain energy density is expressed as

$$U(r,z) = \frac{E}{2(1-\nu^2)} [\varepsilon_{rr}(r,z)^2 + \varepsilon_{\theta\theta}(r,z)^2 + 2\nu \varepsilon_{rr}(r,z)\varepsilon_{\theta\theta}(r,z)]$$

(13)

for the appropriate choice of material constants within either the film or substrate. For small deformation, the elastic strains are conveniently
expressed in terms of $u(r)$ and $w(r)$, the radial and transverse displacements of points on the substrate midplane, respectively, as

$$
\varepsilon_{rr} = u'(r) - zw''(r) + \varepsilon_m \quad (14)
$$

$$
\varepsilon_{\theta\theta} = \frac{u'(r)}{r} - \frac{zw'(r)}{r} + \varepsilon_m \quad (15)
$$

where the prime denotes differentiation with respect to the argument. The mismatch strain is understood to be identically zero in the substrate, so the strain expressions (314, 15) are valid in either material. The strategy adopted here is to select plausible parametric forms for $u(r)$ and $w(r)$, and then to invoke the principle of stationary potential energy to determine optimal values of the parameters involved. For small deflections, the radial and transverse deformations are uncoupled and a reasonable choice for the midplane displacement is

$$
u(r) = \varepsilon_o r + \varepsilon_m r, \quad \omega(r) = \kappa r^2 / 2 \quad (16)$$

where $\varepsilon_0$ represents the extensional strain of the substrate midplane and $\kappa$ represents the curvature of this plane. The total potential energy of the system is calculated in terms of $\varepsilon_0$ and $\kappa$ according to

$$
V(\varepsilon_o, \kappa) = 2\pi R \left[ h_0 \left( H + \frac{h}{2} \right)^2 U(r, z) r dr dz \right] \quad (17)
$$

The equilibrium requirement that potential energy must be stationary is enforced with the conditions $\partial V/\partial \varepsilon = 0$ and $\partial V/\partial \kappa = 0$ from which it follows that

$$
\kappa = 2 \frac{6\varepsilon_m}{h_s} h m \left[ \frac{1 + h}{1 + hm (4 + 6h + 4h^2) + h^4 m^2} \right] \quad (18)
$$

where $h = h_f / h_s$ and $m = M_f / M_s$. This is the generalization of the Stoney formula for uniform mismatch strain in the film for arbitrary thickness ratio and arbitrary modulus ratio. The factor outside the square brackets in
equation (18) is $k_{Sf}$, and $k \rightarrow k_{Sf}$ as $h \rightarrow 0$.

**Stress calculation by Stoney’s, Freund’s and Hsueh’s equation**

The calculated stress is in table 6.2. and fig 6.5. As the thickness of SiO2 layer increased, the compressive stress value is reduced greatly. The calculated compressive stress shows no big difference between 3 models. Because the thickness of LED is very thin when it compared with thickness of sapphire substrate(430 µm), the stress value shows no big difference. So the higher order term value isn’t enough to give difference to total stress value. Because the curvature is highly increased according to the thickness of SiO2 thin film, the compressive stress is also highly reduced as the thickness of SiO2 layer increased. In the case of 4 µm thickness of SiO2, the total stress is reduced almost 60%. To confirm the stress reduction after removing the substrate, laser lift off is done using LED structure grown on using sapphire substrate with 2 µm SiO2 thin film on its backside. Optical microscope image of LED structure after removal of substrate is in fig 6.6. The reduction of wafer bowing is observed after removal of substrate. The wafer bowing is reduced 50% after the removal of substrate in the case of 2 µm SiO2 thin film. The thermal expansion coefficient of sapphire is much higher than that of GaN as a result severe wafer bowing is occurred after cooling from growth temperature to room temperature. SiO2 with very low thermal expansion coefficient deposited at the backside of sapphire substrate prevent the shrinkage of sapphire substrate during cooling process. Therefore, the total stress of GaN thin film is greatly reduced.
FIG. 6.4. The solid (dashed) curve is the locus of points in the parameter plane for which the Stoney formula overestimates (underestimates) the curvature by 10%. A schematic of the film–substrate system showing relevant dimensions appears as an inset.[15]
<table>
<thead>
<tr>
<th></th>
<th>Stress (MPa)</th>
<th>Curvature (m)</th>
<th>Bowing (µm)</th>
<th>GaN thickness (µm)</th>
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<tr>
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<td>Freund</td>
<td>Stoney</td>
<td>Hsueh</td>
<td>Freund</td>
</tr>
<tr>
<td>Ref</td>
<td>736</td>
<td>773</td>
<td>765</td>
<td>4.07</td>
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<tr>
<td>4 µm</td>
<td>285</td>
<td>299</td>
<td>295</td>
<td>10.92</td>
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Table 6.2 Compressive stress value calculated by Stone’s, Freund’s and Hsueh’s equation
FIG. 6.5. Compressive stress value calculated by Stone’s, Freund’s and Hsueh’s equation
FIG. 6.6. Optical microscope image of LED film taken after laser lift off
6.3.3 Fabrication and characteristics of LED device

To confirm the effect of stress reduction onto the device performance, LED device was fabricated using LED structure grown on sapphire substrate with SiO$_2$ thin film on its backside. The schematic of chip design is in fig 6.7. The size and interval of LED device is 1 mm X 1 mm and 300 µm. The schematic of LED device structure was in fig 6.8. For transparent electrode, ITO layer was used and Ti/Al/Ti/Au(30/100/30/200 nm) metal layer was used as a n and p pad metal. The optical microscope image and photo of 2 inch LED substrate are in fig 6.7b and 6.7c each other. To characterize the LED device, average value of device characteristics of thousands LED was measured by prober at 100 mA injection. The results are summarized in table 6.3. The forward voltage of LED device is similar regardless of thickness of SiO$_2$ layer. The threshold voltage of reference LED device is highest among the LEDs but the difference is not high. Dominant peak wavelength of LED device was also measured by prober. The wavelength of reference, 1, 2, and 3 µm thickness SiO$_2$ layer deposited sample is similar. The output power was measured by probe machine. Output power of reference LED device is higher than that of LED devices with SiO$_2$ layer on its backside. We think that generated photon at the MQW are locked between SiO$_2$ and GaN layer. All LED samples were fabricated using 2 side polished sapphire substrate. And the sample susceptor was made of metal and vacuum system operated during the measurement so the backside of sample and susceptor are attached. In the case of reference sample, there is no SiO$_2$ layer so the total generated photons are reflected at the sapphire and metal susceptor interface but in the case of sample with SiO$_2$ layer on its backside, the some of the generated photons are locked in the SiO$_2$ layer at the backside of sapphire substrate. As a result,
total output power of LED device is lowered. To confirm the stress reduction effect on the external quantum efficiency, external quantum efficiency was measured as the increasing the current. The results are in fig 6.9. Fig 6.9a is EQE of LED device fabricated using sapphire substrate with SiO2 layer on its backside. And fig 6.9b is the EQE of LED device fabricated using normal sapphire substrate and sapphire substrate with SiO2 layer on its backside. From 6.9a, the EQE is increased as the thickness of SiO2 layer is increased. As the stress is reduced, the EQE of LED device is increased. But when EQE of the LED fabricated using bare sapphire substrate is compared with the EQE of LED fabricated using sapphire substrate with SiO2 layer on its backside, the EQE of LED device made using bare sapphire substrate is higher than that of LED device made using sapphire substrate with SiO2 layer on its backside in the case of LED device with 1 and 2 µm thickness SiO2 on its backside. The higher EQE of LED device fabricated using bare sapphire substrate can be attributed to the growth condition optimization and relatively low stress reduction rate. In the case of LED device fabricated using sapphire substrate with SiO2 layer on its backside, heat transfer from the susceptor into front surface of sapphire substrate is different from the bare sapphire substrate. Therefore optimization of growth temperature is necessary. Especially, in the case of 1 and 2 µm thickness SiO2 layer case, the stress reduction rates are 18 and 30%, respectively. The stress reduction rate of compressive stress is relatively low. However, the EQE of LED device fabricated using sapphire substrate with 3 µm thickness SiO2 layer on its backside is higher than that of LED device fabricated using bare sapphire substrate. In the case of 3 µm thickness SiO2 sample, the reduction of compressive stress is over 40%. The great reduction of compressive stress
causes the enhancement of EQE. As a result, although the growth condition is not optimized, the EQE of LED device with SiO₂ layer on its backside is higher than that of reference LED device. The voltage-current characteristics of LED device are in fig 6.10. As the thickness of SiO2 layer increased, the electrical properties of LED device is enhanced.
FIG. 6.7. Schematics of LED chip
FIG. 6.8. Schematics and image of LED device (a) schematics of LED device, (b) optical microscope image of LED device, (c) photo of 2 inch substrate containing LED device
<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>1 μm</th>
<th>2 μm</th>
<th>3 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_f$ (V)</td>
<td>3.33</td>
<td>3.28</td>
<td>3.26</td>
<td>3.22</td>
</tr>
<tr>
<td>$W_D$ (nm)</td>
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<td>447.8</td>
<td>448.2</td>
<td>449.2</td>
</tr>
<tr>
<td>$LI$ (mW)</td>
<td>26.9</td>
<td>24</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 6.3 Summarization of LED device performance
FIG. 6.9. EQE of LED device (a) EQE of LED device fabricated using sapphire substrate with SiO$_2$ layer on its backside, (b) EQE of LED device fabricated using bare sapphire substrate and sapphire substrate with SiO$_2$ layer on its backside.
FIG. 6.10. Voltage-current characteristics of LED device (a) I-V characteristics of LED device fabricated using sapphire substrate with SiO$_2$ layer on its backside, (b) I-V characteristics of LED device fabricated using bare sapphire substrate and sapphire substrate with SiO$_2$ layer on its backside.
6.4 Conclusion

In this study, compressive stress of GaN thin film is greatly reduced by deposition of SiO$_2$ thin film on the backside of sapphire substrate without crystal quality lowering. Wafer bowing of LED structure is occurred because of the high thermal expansion coefficient of sapphire substrate so deposition of material with very small thermal expansion coefficient at the backside of substrate can prevent shrinkage of sapphire substrate as a result wafer bowing of LED structure can be suppressed. The thermal expansion coefficient of SiO$_2$ layer is about 3 times smaller than that of GaN so deposition of SiO$_2$ at the backside of substrate can successfully forbid the wafer bowing. To observe the stress reduction according to the thickness of SiO$_2$, thickness of SiO$_2$ layer is varied from 1 $\mu$m to 4 $\mu$m with 1 $\mu$m interval. As the thickness of SiO$_2$ increased, the stress reduction is greatly increased. In the case of 4 mm thickness SiO$_2$, the reduction of compressive stress is almost 60% compared with reference. We expect that deposition of SiO$_2$ layer on the backside of sapphire substrate can be used for growing stress free LED structure. Using the less strained LED structures, LED devices were fabricated by conventional photolithography and ICP etching. By reducing the compressive stress of GaN thin film, the EQE of LED device is increased and voltage-current electrical characteristics of LED device is enhanced. But in the case of output power, the photons generated in InGaN MQW are locked in interface between sapphire and SiO$_2$ layer. As a result, the output power of LED device fabricated using sapphire substrate with SiO$_2$ layer on its backside.
6.5 Reference

Chapter 7. Conclusions

In this study, we investigated the less strained and high efficiency LED device. For these purpose, LED structure is grown on hollow silica sphere coated sapphire substrate and sapphire substrate with SiO₂ thin film on its backside.

To make hollow silica sphere coated sapphire substrate, PS/SiO₂ coreshell spheres were first synthesized. PS/SiO₂ coreshell spheres were synthesized by synthesis of silica shell using PS template. For the synthesis of uniformly sized PS spheres, synthesis condition of PS is well controlled. By controlling the concentration of AIBA initiator, PVP stabilizer, polarity of solvent and reactants, monodisperse PS sphere was well synthesized. AIBA initiator makes free radicals of styrene so as the concentration of AIBA increase, the size of PS sphere is also increased. As the concentration of PVP increased, the PVP adsorb the polystyrene sphere and prevent further adsorption of styrene on the existing PS sphere. Therefore size of PS is decreased as the concentration of PVP increased. By controlling these characteristics, various sized monodisperse PS spheres were synthesized from 150 nm to 430 nm. To increase the size of PS, initiator was changed from AIBA to AIBN. By using the AIBN initiator, monodisperse PS sphere whose size is over 1000 nm successfully synthesized.

Using the monodisperse PS sphere, silica shell was synthesized. To controlling the thickness of silica shell, concentration of ammonia, TEOS and reaction time was controlled. As the concentration of ammonia catalyst
increased, the thickness of silica shell is also increased. Because catalyst facilitates the reaction of synthesis of silica as a result increase of ammonia induces the fast increase of silica shell. Increase of reaction time also increase the thickness of silica shell. By controlling these characteristics, the thickness of silica shell is controlled from 10 nm to 60 nm.

For uniform self assembled monolayer of coreshell spheres, modified dip coating is newly designed in this study. By combining LBL and conventional dip coating method, uniform arrangement of coreshell spheres is enabled. Electrical attraction force between negatively charged coreshell sphere and positively charged substrate attach the coreshell sphere onto substrate and multilayered coreshell spheres were removed by washing step. By this method, monolayer of coreshell spheres was fabricated for very short time.

After modified dip coating of coreshell spheres, thermal treatment was done to remove PS core and fixation of S-HNS. After thermal treatment, GaN thin film was grown using S-HNS coated substrate. By nanoscale LEO and photon scattering, high quality GaN thin film and high extraction efficiency was enabled. S-HNS reduced dislocation density from $4 \times 10^8$ cm$^{-2}$ to $1 \times 10^8$ cm$^{-2}$. Especially, reduction of edge dislocation density was confirmed by TEM measurement. In the case of edge dislocation, they can reduce their energy by bending their propagation direction normal to c axis. The increase of light extraction efficiency is confirmed by measurement of diffuse reflectance which is directly related with light extraction efficiency. The diffuse reflectance increased 30% when S-HNS used. So by increasing internal quantum efficiency and extraction efficiency, the output power of
LED device is increased almost 80% when it compared with reference. Additionally, the reduction of compressive stress of GaN thin film is confirmed by FE simulation and laser scanning technique. In FE simulation, the compressive stress at the surrounding of S-HNS is reduced almost 30% when it compared with reference. The reduction of the compressive stress of GaN thin film is also confirmed by experiment. In the case of 3 µm thickness GaN thin film with 50% surface coverage of S-HNS, the compressive stress of GaN thin film is reduced about 20%. By insertion of S-HNS into GaN thin film, high quality and less strained with high extraction efficiency LED structure was fabricated.

To reduce the compressive stress of GaN thin film, GaN thin film is grown by deposition of SiO₂ thin film on the backside of sapphire substrate. The wafer bowing of LED structure is occurred because of the high thermal expansion coefficient of sapphire substrate so deposition of material with very small thermal expansion coefficient at the backside of substrate can prevent shrinkage of sapphire substrate as a result wafer bowing of LED structure can be suppressed. The thermal expansion coefficient of SiO₂ layer is about 3 times smaller than that of GaN so deposition of SiO₂ at the backside of substrate can successfully forbid the wafer bowing. To observe the stress reduction according to the thickness of SiO₂, thickness of SiO₂ layer is varied from 1 µm to 4 µm with 1 µm interval. As the thickness of SiO₂ increased, the stress reduction is greatly increased. In the case of 4 mm thickness SiO₂, the reduction of compressive stress is almost 60% compared with reference.
국문 초록

기존의 LED 광 소자의 경우 동종 기판을 사용한 예외가 불가능하기 때문에 이종 기판에 주로 성장이 이루어진다. 이종 기판으로 가장 많이 사용되는 기판은 사파이어 기판이지만 격자상수 차이 균열을 차이 열팽창 계수 차이로 인하여 여러 가지 문제가 생기게 된다. 기존 LED의 가장 큰 문제점은 격자 상수 차이로 인한 많은 결정 결함 밀도 그리고 균열을 차이로 인하여 생성된 빛이 소자 밖으로 빠져나가지 못하고 소멸함으로 광 추출 효율이 낮아지는 점 또 다른 문제점으로는 사파이어와 결화물 박막간의 열팽창 계수 차이로 인하여 성장 후 난각시 wafer 의 bowing이 생성된다는 점이다. 이런 문제를 해결하고자 많은 연구가 이루어졌다. 대표적인 예로 기판을 선택적으로 막고 측면 성장을 유도함으로써 결정 결함 밀도를 줄이는 LEO 방법 그리고 사파이어 기판을 패팅닝 함으로써 결정 결함을 줄이고 광 추출 효율을 높이는 연구 등이 있다. 하지만 이런 연구들인 경우 photolithography, etching 등 공정 비용이 매우 비싸며 복잡하다는 단점이 있다. 이러한 문제를 해결하고자 본 연구에서는 두 가지 방법의 연구를 진행하였다.

첫 번째로 본 연구에서는 hollow silica sphere가 코팅된 사파이어 기판을 사용하여 LED를 제작 함으로써 wafer bowing을 줄이고 격
균열물의 hollow silica sphere(S-HNS)를 GaN 박막 내에 인입함으로써 광 추출 효율을 높였다. S-HNS를 사용한 GaN 성장의 경우 측면 성장이 유도 됨으로써 결정결합 밀도 또한 줄일 수 있는 장점이 존재한다. S-
HNS가 코팅된 기판을 제조하기 위하여 본 연구에서는 먼저 polystyrene sphere를 합성하는 방법을 개발 하였다. 수백 나노에서 수 마이크론
싸이즈의 polystyrene sphere를 제작하는 연구를 진행하였으며 이 polystyrene sphere 위에 stober 방법으로 silica shell을 합성하는
연구를 또한 진행 하였다. 제작된 PS/SiO2 coreshell sphere를 기판에 균일하게 코팅 하기 위하여 본 연구에서는 modified dip coating 방식을 새롭게 개발 하였다. Modified dip coating 방식은 기존의 dip coating 방식과 LBL method 방식을 결합하여 기존의 coating 방법의 단점을 극복하기 위해 개발된 코팅 방법이다. 기존의 dip coating 방식의 경우 코팅 시간이 매우 길기 때문에 대면적 기판에 적용이 어려우며 이로 인하여 실제 산업에 적용이 어려운 점이 있다. 본 연구에서 개발된 modified dip coating 방식은 2, 4 inch 기판에서 균일성을 확인 하였으며 코팅 시간 또한 매우 짧은 시간 내에 가능 한 것을 확인 하였다. PS/SiO2 coreshell sphere가 코팅된 기판을 열처리를 통하여 hollow silica sphere가 코팅된 사파이어 기판을 제작 하였다. 열처리는 2 단계로 진행을 하였으며 먼저 template인 PS sphere를 제거하는 단계 그리고 hollow silica sphere를 기판에 고정시키는 두 번째 열처리 단계를 진행 하였다.

열처리 후에 hollow silica sphere가 코팅된 사파이어 기판을 사용하여 LED 구조를 성장하고 LED 소자를 제작 하였다. LED 소자 제작시 결정 결합 밀도가 크게 줄어드는 것을 확인하였으며 diffuse reflectance 측정을 통하여 광 추출 효율 역시 크게 증가한 것을 알 수 있었다. 또한 GaN 박막 내의 stress가 줄어드는 것을 확인 할 수 있었으며 그 원인을 분석하기 위하여 FE simulation을 실시 하였다. Simulation 결과 S-HNS 주변으로 stress가 집중이 되면서 주변 GaN 박막 내의 stress가 줄어드는 것을 확인 할 수 있었다. 이점은 S-HNS의 SEM image를 통해 확인 할 수 있었다. 또한 LED 제작시 output power가 기존의 LED에 비하여 80% 이상 증가한 우수한 LED를 제작 할 수 있었다. 이런 LED 효율의 증가는 광 추출 효율 증가로 인한 점 그리고 결정 결합 밀도의
감소로 인한 내부 양자 효율의 증가로 인한 것으로 판단 된다.
본 연구에서 또 다르게 진행한 연구로는 사파이어 기판에 SiO2 후막을 증착하고 LED를 제작한 내용이다. 후막의 두께를 1~4 마이크로 미터까지 증가시켜 가면서 실험을 진행하였을 때 stress가 60% 이상 줄어드는 것을 확인 할 수 있었으며 소자 제작시 동작 전압이 기존 LED에 비하여 줄어드는 것을 확인 할 수 있었다.