Aluminum Gallium Nitride Nanostructures for High

Efficiency Ultraviolet Light Sources

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List of Acronyms

AFM	Atomic Force Microscopy
BEP	Beam Equivalent Pressure
DBR	Distributed Bragg Reflector
EDXS	Energy-Dispersive X-ray Spectrometry
EELS	Electron Energy-Loss Spectroscopy
EL	Electroluminescence
EQE	External Quantum Efficiency
FDTD	Finite Difference Time Domain
FE-SEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
HAADF	High Angle Annular Dark Field
IQE	Internal Quantum Efficiency
LED	Light Emitting Diode
LEE	Light Extraction Efficiency
LD	Laser Diode
MBE	Molecular Beam Epitaxy
MOCVD	Metal Organic Chemical Vapor Deposition

PL	Photoluminescence
PML	Perfect Matched Layer
RF	Radio Frequency
RHEED	Reflection High-Energy Electron Diffraction
SAE	Selective Area Epitaxy
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
STEM	Scanning Transmission Electron Microscope
TM	Transverse Magnetic
UV	Ultraviolet
XRD	X-Ray Diffraction

Abstract

To date, it has remained difficult to realize efficient deep ultraviolet (UV) light emitting devices. The underlying challenges include presence of dislocations and defects, inefficient doping for Alrich AlGaN, and poor light extraction efficiency (LEE) due to in-plane transverse magnetic polarized emission. In this thesis, we have investigated molecular beam epitaxial growth and characterization of AlGaN nanostructures, as well as applications in UV LEDs and lasers, in order to address the performance bottleneck of conventional AlGaN-based planar deep ultraviolet (UV) light emitting devices. We firstly performed a systematic study on the molecular beam epitaxial growth and charge carrier transport properties of Mg-doped AlGaN with ~60% Al composition. High hole concentration of 8.7×10^{17} cm⁻³ and mobility values between 10 and 17 cm²/(V·s) were achieved at room temperature. Under optimal condition, a resistivity of 0.7 Ω cm was obtained. The conduction mechanism is identified to be hole conduction in the Mg impurity band. We also studied the improvement of LEE for transverse-magnetic (TM) polarized emission by using nanowire photonic crystals. By coupling in-plane TM-polarized emission to vertical emission at Γ point, LEE can be in principle enhanced to over 90% from below 10% in the conventional planar structure. Further considering the absorption in p-AlGaN contact layer and p-metal contact grid, LEE over 30% was predicted. To demonstrate the feasibility of nanowire photonic crystal, we developed the process of selective area epitaxy (SAE) of AlGaN nanowire and further demonstrate an LED at 279 nm. Regular and uniform AlGaN nanowire arrays with precisely controlled diameter and spacing were realized in the full compositional range. An IQE of 45% at room temperature was estimated with the presence of Al-rich shell suppressing surface nonradiative recombination. Excellent electrical and optical performance were achieved, including a small turnon voltage of 4.4 V and an output power of ~ 0.93 W/cm² at a current density of 252 A/cm². We

further studied AlN nanowall LEDs, which can exhibit IQE of ~ 60% at room-temperature, a low turn-on voltage of 7 V and higher current densities > 170 A/cm² at 12 V. We have also demonstrated electrically pumped AlGaN nanowire lasers operating at 334 nm. Due to defect-free material quality, Anderson localization of light, and Al-rich shell structure, the optical loss and absorption were minimized and the differential gain was maximized, which resulted in ultralow threshold lasing of only a few tens of A/cm². The studies in this thesis have revealed the advantages of molecular beam epitaxy (MBE) grown AlGaN nanostructures in addressing the current challenges with deep UV optoelectronic devices. Future research on the AlGaN nanostructures is finally proposed.

Résumé

Jusqu'à présent, il reste difficile de réaliser des dispositifs efficaces émettant de la lumière dans le spectre ultraviolets profonds (UV). Les défis incluent la présence de dislocations et de défauts, un dopage inefficace pour l'AlGaN riche en Al, et une faible efficacité d'extraction de la lumière (LEE) due à l'émission polarisée magnétique transversale. Dans cette thèse, une étude de la croissance épitaxiale par faisceau moléculaire (MBE) et la caractérisation des nanostructures AlGaN a été accomplie, pour des fins d'applications incluant les diodes électroluminescentes (LEDs) et les lasers UV, afin de remédier les limites de performance des émetteurs de lumière ultraviolets planaires à base d'AlGaN. Nous avons d'abord réalisé une étude systématique de la croissance par MBE et des propriétés de transport de porteurs de charge d'AlGaN dopé au Mg avec une composition de ~ 60% d'Al. Une concentration élevée en trous de 8,7 x 10^{17} cm⁻³ et des valeurs de mobilité comprises entre 10 et 17 cm²/(V·s) ont été atteintes à température ambiante. Dans des conditions optimales, une résistivité de 0,7 Ω ·cm a été obtenue. Le mécanisme de conduction est identifié comme étant la conduction du trou dans la bande d'impureté de Mg. Une étude de l'amélioration de la LEE pour l'émission polarisée transverse-magnétique (TM) a aussi été complétée en utilisant des cristaux photoniques à base de nanofils. En couplant l'émission polarisée TM dans le plan à une émission verticale au point Γ , la LEE peut en principe être augmentée de moins de 10% à plus de 90% à comparer à la structure planaire conventionnelle. Considérant en outre l'absorption dans la couche de contact en p-AlGaN et la grille de contact de métal, une LEE de plus de 30% a été prédite. Pour démontrer la faisabilité des cristaux photoniques à base de nanofils, le développement d'un processus d'épitaxie de zone sélective (SAE) de nanofils en AlGaN a été réalisé, ainsi que la démonstration d'une LED émettant à 279 nm. Des réseaux de nanofils en AlGaN avec une distribution régulière et uniforme avec un diamètre et une séparation

spatiale espacement précisément contrôlés ont été réalisés pour toute la gamme de composition. Une efficacité quantique interne (IQE) de 45% à température ambiante a été estimée avec la présence de recombinaison non radiante à la surface de la couche enveloppante riche en Al. D'excellentes performances électroniques et optiques ont été obtenues, y compris une faible tension de mise de 4,4 V et une puissance de sortie de ~ 0.93 W/cm² avec une densité de courant de 252 A/cm². De plus, une étude des LED à base de nano-murs en AlN a été accomplie, démontrant une IQE de ~60% à température ambiante, une faible tension de 7 V, et des densités de courant supérieures à 170 A/cm² à 12 V. De plus, la réalisation de lasers à pompage électrique à base de nanofils en AlGaN fonctionnant à 334 nm a été accomplie. En raison de la qualité du matériau sans défaut, de la localisation de la lumière et de la structure comportant une coquille riche en Al, la perte optique et l'absorption de lumière ont été minimisées, et le gain différentiel a été maximisé avec seulement quelques dizaines de A/cm². Les études reportées dans cette thèse révèlent les avantages des nanostructures en AlGaN par MBE afin de répondre aux défis présents avec les dispositifs optoélectroniques du spectre UV profonds. Des recherches futures sur les nanostructures en AlGaN sont finalement proposées.

Contribution of Authors

This thesis includes published manuscripts or manuscripts under review which involves contributions from the candidate and many other individuals. The contributions from vary from chapter to chapter. The contributions for each chapter are described below.

For Chapter 3, the candidate performed sample growth with contributions from Ayush Pandey and suggestions from Prof. Zetian Mi. David Laleyan did initial growth calibration and collected atomic force microscopy data. Kishwar Mashooq, Eric T. Reid, Walter Jin Shin performed characterizations including X-ray diffraction crystallography, photoluminescence measurement, and scanning electron microscopy. Prof. Zetian Mi conceived the projects, supervised the analysis, and led the project. The manuscript was written by the candidate and Prof. Zetian Mi.

For Chapter 4, the candidate built the simulation model, designed the simulation experiments, and performed data analysis. Kishwar Mashooq automatized and performed the simulation. Prof. Zetian Mi conceived the project, supervised the analysis, and led the project. The manuscript was written by the candidate and Prof. Zetian Mi with suggestions from Prof. Thomas Szkopek.

For Chapter 5, the candidate prepared patterned substrates and performed growth with suggestions from Dr. Songrui Zhao and Prof. Zetian Mi. Dr. Huy Binh Le fabricated the devices and performed device characterizations. Prof. Gianluigi A. Botton, Dr. Steffi Y. Woo, and Alexandre Pofelski did scanning transmission electron microscopy analysis on the sample. Prof. Zetian Mi conceived the experiments, supervised the analysis, and led the project. The manuscript was written by the candidate, Dr. Huy Binh Le, and Prof. Zetian Mi.

For Chapter 6, the candidate prepared patterned substrates, performed growth with suggestions from Dr. Songrui Zhao and Prof. Zetian Mi, fabricated the devices with suggestions from Dr. Huy

Binh Le, and performed device characterizations. Prof. Zetian Mi conceived the experiments, supervised the analysis, and led the project. The manuscript was written by the candidate and Prof. Zetian Mi.

For Chapter 7, Dr. Kwai Hei Li fabricated the devices and carried out the experimental measurements. The candidate performed the device design and contributed to the theoretical calculations, device fabrication, and measurements. Dr. Kwai Hei Li and the candidate made equal contributions. Dr. Songrui Zhao conducted the MBE growth of nanowires and contributed to the TEM analysis. Dr. Qi Wang contributed to preliminary works on device characteristics. Prof. Zetian Mi conceived the experiments, supervised the analysis, and led the project. The paper was written by Dr. Kwai Hei Li and Prof. Zetian Mi with contributions from other coauthors.

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Chapter 1 Introduction

1.1 Current status of ultraviolet light emitting devices

Ultraviolet (UV) light sources are a pivotal technology for a variety of applications, such as water disinfection, pollutant degradation, chemical detection, microfabrication, and high-density optical data storage [1, 2]. To date, the commonly used deep UV sources are mercury lamps, deuterium lamps, gas laser, and diode-pumped solid state lasers. They are bulky, toxic, inefficient, environmentally unfriendly, and suffer from poor beam quality, which limited their applications [3-5]. To overcome these drawbacks, the development of compact high efficiency UV light sources based on AlGaN, the ternary alloy of GaN and AlN, has attracted intense attention in the past few decades [6-15], due to the potential advantages including small device footprint, high optical output power, tunable wavelength, and relatively low cost [10, 16-28].

UV light emitting diodes (LEDs) in the UV-A and UV-B bands have been commercially available with reasonable performance. However, as shown in Figure 1-1, the external quantum efficiency (EQE) of AlGaN quantum well LEDs has reached a few percent at around 280 nm and above ~330 nm. The EQE remains lower than 1% in a large part of the UV-C band, i.e., shorter than ~250-260 nm [6, 9, 10, 29-40]. The degraded electrical and optical performance includes high turn-on voltage, lower optical output power, severe heating under high current operation, and short lifetime. For example, the turn-on voltage of an AlN LED with 210 nm emission wavelength is around 20 V, much larger than the limit imposed by the energy bandgap of AlN (~6.1 eV). Moreover, the huge cost of bulk AlN substrate makes it unrealistic for mass production [41, 42].



Figure 1-1 Variations of the EQE of AlGaN LEDs vs. emission wavelength.

Compared to UV LEDs, it is even more challenging to achieve electrically injected AlGaN planar quantum well UV laser diodes (LDs) [6, 26, 28, 43-54]. As shown in Figure 1-2, the lasing wavelengths are still limited to the UV-A band with threshold current densities in the range of 10 kA/cm² or higher [7, 8, 48, 50]. The shortest operation wavelength so far is 336 nm with very high threshold current density of a few tens of kA/cm² and peak output power up to 15 mW under pulsed injection [8, 14, 25, 55, 56]. By using bulk AlN substrate, no drastic improvement in performance has been demonstrated. The threshold current density of an LD on AlN substrate demonstrated at 368 nm is 13 kA/cm², which is similar to those grown on foreign substrates [7]. Besides electrically pumped LDs, optically pumped lasers in the deep UV spectrum have also been demonstrated [11, 13, 19, 57-60]. Lasing at 237 nm with threshold below 200 kW/cm² and at 266

nm with threshold of 41 kW/cm² was demonstrated using AlN substrate [60]. For lasers on foreign substrate, lasing at 256 nm with threshold of 61 kW/cm² and 214 nm with a threshold of 9 MW/cm² was demonstrated [11, 58].



Figure 1-2 Threshold current density as a function of wavelength for AlGaN planar UV lasers.

1.2 Fundamental challenges with AlGaN-based light emitting devices

The issues with AlGaN-based light emitting devices mainly lie in the material quality, carrier injection, and light extraction, which have limited the efficiency of UV LEDs and prevented the achievement of deep UV LDs. First, because of the lack of lattice-matched foreign substrate, the material quality of the epilayers grown on typical sapphire or SiC substrates suffers from large density of dislocations which act as non-radiative recombination centers. Second, efficient p-type doping is difficult when the Al composition is high, particularly for AlGaN epilayers grown by metal organic chemical vapor deposition (MOCVD), which degrades the carrier injection

efficiency and causes self-compensation at high doping level. Third, due to the unique valence band structure, light emission in the deep UV spectrum from high Al-composition AlGaN is transverse magnetic (TM) polarized, dominantly in the in-plane direction. The light extraction is therefore extremely inefficient.

1.2.1 Dislocation and defects in AlGaN epilayers

The most commonly used substrates for the growth of GaN, AlN, and AlGaN epilayers are sapphire, SiC, Si, which exhibit large lattice mismatch as shown in Table 1-1, leading to high density of threading dislocations on the order of 10^9 cm⁻², or larger [61, 62]. The dislocation density can be reduced to the order of 10^8 cm⁻² by using the epitaxial lateral overgrowth technique [9, 10, 19, 32, 33]. With the presence of such high dislocation density, the non-radiative recombination plays an important role in reducing the quantum efficiency of AlGaN LEDs and increasing the threshold of LDs. The lowest dislocation density, which is on the order of 10^4 cm⁻², was achieved by using bulk AlN substrate. This approach, however, suffers from the extremely high cost of the substrate and the lack of large substrate area [63, 64].

Table 1-1 A summary of the lattice constants of GaN, AlN, and common substrates.

Material	Lattice constant (Å)
GaN	a=3.189, c=5.185
AlN	a=3.112, c=4.982
Silicon	a=5.431
Sapphire	a=4.758, c=12.991
6H-SiC/4H-SiC	a=3.073, c=10.053

1.2.2 Inefficient p-type doping and hole injection

It is extremely challenging to grow p-type Al-rich AlGaN epilayers, particularly by MOCVD. Mg, typically used as the p-type dopant, exhibits prohibitively large activation energy of 400-500 meV for Al-rich AlGaN and ~600 meV for AlN [65, 66], which leads to extremely low activation efficiency and low hole concentration of $\sim 10^{12}$ cm⁻³ at room temperature [65]. As the Mg concentration increases, the formation energy of donor-like nitrogen vacancies reduces [32]. The enhanced formation of donor like defects therefore compensates p-type doping. Furthermore, the presence of hydrogen and carbon atoms in the MOCVD technique inevitably leads to the formation of Mg-H complexes and donors, suppressing the activation of Mg dopant. As a result, the Mg-doped layers typically have low hole concentration and large resistivity, which leads to poor hole injection, high turn-on voltage, electron overflow, and severe heating effect [67-69]. The quantum efficiency of deep UV LEDs is therefore limited and the population inversion for deep UV LDs is also difficult to achieve.

1.2.3 Poor light extraction

As the Al composition in AlGaN increases from 0% to 100%, the split-off hole band becomes closer to the conduction band than the heavy hole band is. As shown in Figure 1-3, because TM-polarized emission (electric field in parallel with c-axis) is generated from the transition from the conduction band to the split-off hole band and transverse electric (TE)-polarized emission (electric field in perpendicular with c-axis) is generated from the transition from the conduction band to the heavy hole band for c-plane AlGaN, the luminescence polarization gradually varies from TE-polarization to TM-polarization as the Al composition increases [70, 71], indicating that deep UV light from AlGaN is mostly emitted in the in-plane direction. The switching from TE-polarization to TM-polarization has been observed from 25% to 83% [70-73]. This kind of TM-polarized

emission severely limits light extraction efficiency to be below 10% due to total internal reflection and absorption in AlGaN contact layers with lower bandgap, giving rise to low EQE of typical cplane deep UV LEDs [74-77].



Figure 1-3 The bandstructure of AlN. Band A is the split-off hole band to which the transition from the conduction band gives TM-polarized emission [74].

1.3 Nanostructures grown by MBE: a route to overcome the challenges

The challenges in deep UV AlGaN-based light emitting devices discussed in Sec. 1.2 can be potentially addressed by using nanostructures grown by molecular beam epitaxy (MBE) due to their unique properties. First, it has been demonstrated that nearly defect-free AlGaN nanowires can be grown on foreign substrates, such as Si, SiO_x and sapphire due to the efficient surface strain relaxation [78-85]. For example, no dislocation in AlN nanowires grown on Si substrate was observed in detailed transmission electron microscopy (TEM) studies [82]. The photoluminescence (PL) spectrum exhibit nearly ten times stronger free exciton emission peaks

than conventional AIN epilayers at 6.03 eV with two phonon replica, suggesting superior material quality and optical properties [38, 84]. From temperature-dependent and power-dependent PL studies, the room-temperature internal quantum efficiency (IQE) is derived to be in the range of 80% under a broad range of excitation powers. Second, enhanced Mg dopant incorporation is demonstrated in nanowire structures. The formation energy of Mg-dopant is significantly lower in AlN nanowires than in planar AlN epilayers due to the efficient strain relaxation [82, 86-89]. The incorporation of Mg is enhanced in nanowire structures, leading to very high concentration of Mg and the formation of a Mg impurity band. The temperature-dependent electrical characterization of Mg-doped AlN nanowires also showed a small activation energy of ~ 12 meV indicating hole hopping conduction in the Mg impurity band. A hole centration of $\sim 6 \times 10^{17}$ cm⁻³ was measured at room temperature, which is nearly seven orders higher than that in AlN epilayers [90, 91]. The enhanced Mg incorporation is further confirmed by the PL associated with the Mg-acceptor related transition in Mg-doped AlN nanowires at room temperature and the AlN nanowire LED with a turn-on voltage of ~6 V which is only limited by the AlN bandgap [84, 90, 92]. Third, the light extraction efficiency for TM-polarized emission has shown dramatic improvement due to extraction from the single nanowire sidewall and scattering among nanowires [89, 93]. A light extraction efficiency of 40-50% can be expected from the single nanowire sidewall and a light extraction efficiency of 85% can be expected from nanowire arrays with precisely tailored size and position.

1.4 Overview of the thesis

In this thesis, we investigate the molecular beam epitaxy and characterization of Al(Ga)N nanostructures and further demonstrate high performance LEDs and LDs.

In Chapter 2, the growth methods for nanowires and epilayers by MBE are discussed.

In Chapter 3, we discuss high Al-composition p-type AlGaN epilayers grown by MBE technique. Detailed growth conditions and characterizations are discussed and the charge carrier transport properties are explained. The result is also compared with previous studies.

In Chapter 4, we focus on the light extraction efficiency of TM-polarized emission. A novel approach using nanowire photonic crystal to significantly enhance the light extraction of TM-polarized emission is studied by finite difference time domain (FDTD) simulation. The important parameters of a photonic crystal structure for the purpose of coupling TM-polarized emission to vertical direction surface emission is identified. Furthermore, the Purcell effect associated with photonic crystal structure is discussed and the design guideline to maximize EQE is concluded for cases of different material qualities.

In Chapter 5, the growth of regular AlGaN nanowire arrays, which are the building blocks of deep UV photonic crystal mentioned in Chapter 4, is discussed, and the demonstration of a deep UV LEDs based on such nanowire arrays is presented. Arbitrary control over the nanowire geometry and AlGaN alloy composition by the selective area epitaxy (SAE) technique is firstly discussed. Based on the SAE technique, a core-shell deep UV AlGaN nanowire LED operating at 279 nm is demonstrated and the electrical and optical characterizations are explained.

In Chapter 6, another type of nanostructure, nanowall, is investigated. The focus is on evaluating the material quality and studying the p-type doping of nanowalls. An AlN nanowall LED with detailed electrical and optical characterizations is discussed, which also exhibits similar advantages in material quality and Mg acceptor incorporation as the nanowire structure.

In Chapter 7, random lasers based on AlGaN nanowires are discussed. With all the advantages with nanowires including defect-free material quality and reduced surface recombination, it is readily feasible to achieve UV lasers using AlGaN nanowire by further exploiting the light

confinement among nanowires. The theoretical background and design of AlGaN nanowire lasers are explained. Detailed structural, electrical, and optical characterizations are discussed.

In Chapter 8, conclusion are drawn from the discussions in the previous chapters and future studies are suggested.

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Chapter 2 MBE Growth of AlGaN Nanowires and Epilayers

2.1 Growth of nanowires by spontaneous formation on silicon

AlGaN nanowire arrays can be spontaneously grown on silicon substrates under nitrogen-rich condition [1, 2]. The preparation of the silicon substrate prior to epitaxy includes removal of surface oxide by buffer hydrofluoric acid, standard solvent cleaning, and in-situ oxide desorption in the growth chamber at ~ 770 °C. The growth usually starts with the growth of GaN nanowire template for one hour at ~750 °C. To reach a nitrogen-rich condition, the Ga flux is $2-3 \times 10^{-8}$ Torr and the N₂ flow rate is 1 sccm with a radio frequency (RF) power of 350 W. Subsequently, the growth of AlGaN nanowire is initiated at a higher growth temperature of ~800 °C with the introduction of Al beam equivalent pressure (BEP) between 5×10^{-9} Torr and 6×10^{-8} Torr for various Al compositions [2, 3]. Representative nanowire morphology is shown in Figure 2-1.



Figure 2-1 A scanning electron microscopy (SEM) image of typical AlGaN nanowires spontaneously formed on silicon substrates.

Because of the nitrogen-rich growth condition, the migration length of Al adatoms is very short and significantly different from that of Ga adatoms. High Al BEP usually leads to two compositions, one Al-rich composition and one Ga-rich composition, instead of a single Al-rich composition [4]. The compositional nonuniformity is also nontrivial for moderately Al-rich composition. PL characterization, which is directly dependent on the band gap, is typically used to estimate what compositions are present in a structure. The large PL spectral linewidth of 36 nm shown in Figure 2-2 (a) indicates large compositional nonuniformity [5].



Figure 2-2 (a) PL spectra of AlGaN nanowire samples grown with a N_2 flow rate of 0.4 sccm (red) and 1.3 sccm (blue), respectively. (b) PL spectra of AlGaN nanowire samples grown with a N_2 flow rate of 0.4 sccm at different temperatures [5].

For better compositional uniformity, lower N_2 flow rate of ~0.4 sccm can be used, which reduces the chance for N to bond with Al and allows for longer migration of Al adatoms. A corresponding significantly narrower linewidth is observed in the PL spectrum of AlGaN nanowires as shown in Figure 2-2 (a). As the desorption of Ga adatoms is also enhanced under this low N_2 flow rate condition, it is viable to tune the AlGaN alloy composition by changing the growth temperature to control the presence of Ga. An increase in growth temperature enhances the desorption of Ga adatoms, thereby reducing the incorporation of Ga and increasing the Al composition as shown in Figure 2-2 (b) [5].

2.2 Growth of nanowires by selective area epitaxy

In contrast to the randomness in the nanowire arrays formed on silicon substrates, high uniformity in composition and dimension and regularity in geometric shape of nanowire arrays can be achieved by selective area epitaxy (SAE). Schematically shown in Figure 2-3, the SAE of AlGaN nanowire arrays is realized by employing a thin Ti layer as the growth mask on a GaN-on-sapphire substrate. First, a 10 nm thick Ti layer is deposited on the GaN-on-sapphire substrate. The substrate is then spin-coated with PMMA and exposed using an electron beam lithography system. After developing the sample in methyl isobutyl ketone, reactive ion etching of Ti is performed using PMMA as the etching mask. Lastly, the PMMA is removed by oxygen based reactive ion etching and the patterned substrate is thoroughly cleaned for MBE growth. Before the growth, nitridation of the Ti layer is performed at 400 °C by using nitrogen plasma to prevent the formation of cracks and degradation at subsequent high growth temperature. The nitrogen flow rate is 1 sccm and the RF power is 350 W during the nitridation. During the growth, the substrate temperature is set sufficiently high, usually above 930 °C, in order to enhance the desorption of Ga on the Ti mask. In the meantime, the N₂ flow rate is set relatively low (~0.6 sccm) to reduce the chance for Ga to get bonded with N on the Ti mask. In this way, the growth or nucleation of GaN is suppressed on the Ti mask. However, growth of GaN can still occur inside the hole arrays because the underlying substrate is also GaN. Under the optimal growth temperature and N₂ flow rate, the Ga flux should be at least 3.5-3.7×10⁻⁷ Torr to achieve a growth rate of 100-120 nm per hour. Although the

selectivity in growth is generally enhanced at higher growth temperature and lower N_2 flow rate, it is undesirable to use unnecessarily high growth temperature or low N_2 flow rate which would cause waste of elemental Ga in the cell, decrease the nanowire growth rate, or suppress growth in the hole arrays.



Figure 2-3 (a) Pre-patterned substrate with arrays of nanoscale opening apertures in the Ti mask on a GaN-on-sapphire substrate and regular nanowire array formed by selective area epitaxy of GaN. (b) SEM image showing GaN nanowire arrays selectively grown in the opening apertures. Inset: High-magnification SEM image of nanowire arrays.

AlGaN nanowire arrays are subsequently grown on such GaN nanowire template by introducing an Al BEP on the order of 10⁻⁸ Torr. Similar to the growth of epilayers, the Al composition does not depend on the Ga flux but rather on the Al BEP. Due to the difference in migration length of Ga adatoms and Al adatoms, an Al-rich shell can spontaneously form around the nanowires as the Al BEP is sufficiently high. As shown in Figure 2-4, each nanowire has a shell structure on the sidewall.



Figure 2-4 An SEM image showing AlGaN nanowire arrays with core-shell structure spontaneously formed in the selective area epitaxy process.

2.3 Growth of AlGaN epilayers

The epilayers grown in this thesis are grown under metal-rich condition wherein a monolayer of liquid Ga metal is present on the surface throughout the growth. Because the migration length of Al adatoms is short on the III-nitrides surface and Al can easily bond with N adatoms due to the large bonding strength, the lowest energy configuration of Al adatoms cannot be reached and the surface is rough without the presence of liquid Ga metal layer. A typical SEM image is shown in Figure 2-5 (a). With the presence of liquid Ga metal layer, Al adatoms firstly dissolves in the liquid Ga metal layer, which significantly extends the migration length of Al adatoms. The Al adatoms

will therefore be able to get incorporated with the lowest energy configuration and very smooth surface morphology can be obtained as shown in Figure 2-5 (b). In order to keep growth in the metal-rich condition, reflection high-energy electron diffraction (RHEED) pattern, which is a direct in-situ indicator of the surface roughness, is monitored during the growth. When the RHEED pattern is segmented as shown in Figure 2-5 (c), the surface is rough without the presence of liquid Ga metal. When the RHEED pattern is streaky as shown in Figure 2-5 (d), the surface is smooth with the presence of liquid Ga metal. Besides, the brightness of a RHEED pattern like Figure 2-5 (d) indicates how much liquid Ga metal there is on the surface. Dimmer RHEED pattern suggests more liquid Ga metal. The Ga cell temperature should be adjusted to keep RHEED pattern streaky and reasonably dim. In order to keep a reasonably dim RHEED pattern and avoid excessive Ga metal accumulation on the surface, a ten-second growth interruption, during which only the N plasma cell shutter is open, is performed periodically. A reasonably dim RHEED pattern would become slightly brighter during the interruption. If the RHEED pattern becomes very bright in spite of staying streaky, the surface would be still slightly deficient of liquid Ga metal. If the RHEED pattern has almost the same brightness, the surface has excessive liquid Ga metal.



Figure 2-5 SEM images of (a) an AlGaN epilayer grown under nitrogen-rich condition and (b) an AlGaN epilayer grown under metal-rich condition. RHEED patterns of (c) an AlGaN epilayer grown under N-rich condition (d) an AlGaN epilayer grown under metal-rich condition.

The AlGaN alloy composition under the desirable metal-rich condition is mainly determined by the Al BEP and the supply of nitrogen plasma as shown in Figure 2-6. The variation of Ga flux does not affect the alloy composition, as long as the growth is maintained under metal-rich condition. Ga acts as a surfactant for growth to achieve a smooth surface morphology, though it also gets incorporated and contributes to the growth of AlGaN epilayer. Because the bonding between Al and N is stronger than the bonding between Ga and N, N adatoms are preferentially bonded with Al adatoms first and then the remaining N adatoms get bonded with Ga. The increase

in Al BEP or the decrease in N₂ flow rate would leave less remaining N available for Ga incorporation, thereby increasing the Al composition in AlGaN epilayer.



Figure 2-6 The variation of Al composition with (a) N₂ flow rate and (b) Al BEP.

For the growth of AlGaN epilayers, it is preferable to use high growth temperature to suppress the incorporation of unwanted impurities. Oxygen is a commonly observed impurity accompanying Al source. By conducting growth at high temperature, the incorporation of oxygen is observed to be suppressed. Shown in Figure 2-7 are the oxygen concentrations in two AlGaN epilayers grown at 650 °C and 690 °C measured by secondary ion mass spectrometry (SIMS).



Figure 2-7 Oxygen impurity concentrations measured by SIMS in two samples grown at 650 °C and 690 °C. The very high peak in each curve corresponds to the surface of the substrate before growth.

2.4 Summary

We have discussed three different growth regimes, including spontaneous formation of AlGaN nanowires, selective area epitaxy of AlGaN nanowires, and epitaxy of planar AlGaN epilayers. The regime for spontaneous formation of nanowire is characteristic of high growth temperature and low Ga and Al flux under nitrogen-rich condition. Even if the nitrogen flow rate is reduced, the high desorption of Ga and Al adatoms at high growth temperature and low flux still makes the growth condition nitrogen rich. The regime for selective epitaxy of nanowires is characteristic of high growth temperature, high Ga flux, low Al flux and low nitrogen flow rate. The purpose is to achieve selectivity of growth on GaN over on the growth mask. The regime for the growth of planar epilayers is characteristic of intermediate to high growth temperature, intermediate Ga flux, low Al flux, and low nitrogen flow rate. The slightly metal-rich condition. The slightly metal-

rich condition is crucial for realizing smooth morphology of epilayers, which can be maintained based on the in-situ feedback from RHEED pattern.

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Chapter 3 Charge Carrier Transport Properties of Mg-Doped Al_{0.6}Ga_{0.4}N Grown by Molecular Beam Epitaxy

MOCVD has gained huge success in high efficiency InGaN-based visible LEDs. However, due to the presence of carbon and hydrogen atoms and the high pressure in the MOCVD growth, the incorporation of such impurities and the formation of Mg-H complexes are detrimental for efficient p-type doping of AlGaN with high Al composition. Such bottleneck has prevented the success of MOCVD in the demonstration of high efficiency AlGaN-based UV LEDs. This chapter^{*} will therefore discuss the application of molecular beam epitaxy to the growth of Mg-doped AlGaN with around 60% Al composition and the characterization of the charge carrier transport properties of Mg-doped AlGaN epilayers by standard Hall effect measurement.

Abstract

We have studied the charge carrier transport properties of Mg-doped AlGaN epilayers with Al composition ~60% grown by plasma-assisted molecular beam epitaxy. At room temperature, free hole concentration up to 8.7×10^{17} cm⁻³ was measured, and hole mobility values in the range of 10 to 17 cm²/(V·s) can be reliably achieved. Significantly, a minimum resistivity of 0.7 Ω ·cm was measured, and its dependence on the Mg dopant incorporation was identified. Detailed temperature-dependent charge carrier transport studies further revealed that the hole concentration exhibited a negligible dependence on temperature near room temperature, but increases drastically

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for temperatures above 300 °C, suggesting the importance of impurity band conduction at room temperature.

3.1 Introduction

One of the major challenges for realizing efficient mid and deep ultraviolet (UV) photonic devices, including light emitting diodes (LEDs) and semiconductor laser diodes, are directly related to the poor p-type current conduction of AlN and AlGaN. Mg is a commonly used p-type dopant in IIInitrides, but has prohibitively large activation energy (up to 500-600 meV) in Al-rich AlGaN [1-3]. The solubility of Mg acceptor dopant in AlGaN also decreases significantly with increasing Al concentration [4, 5]. Moreover, the formation energies for donor-like defects, including nitrogen vacancies (V_N and V_N^{3+}) are significantly reduced with increased Mg dopant incorporation, which leads to a strong self-compensation effect [2, 3]. For AlGaN with Al compositions ~50-60%, the achievement of efficient p-type conduction is further compromised by the formation of large densities of defects and dislocations, due to the relatively large lattice mismatch between AIN and GaN and with the commonly available substrates. Previously, the epitaxy of Mg-doped AlGaN has been intensively studied by using metal-organic chemical vapor deposition (MOCVD) [4, 6-18]. The reported free hole concentrations for Al-rich AlGaN epilayers varied from 10^{15} to 10^{17} cm⁻³ at room temperature [7, 8, 17, 18]. Improved hole concentrations have been reported by using delta-doping [11, 19], short period superlattice [9, 12-14, 20-27], polarization-induced doping [28-31], metal-modulated epitaxy [32], and indium surfactant [6, 12] but with low mobility values on the order of 1-3 cm²/(V·s) for Al-rich AlGaN at room temperature [10, 14, 27]. As a consequence, resistivity values in the range of a few to tens of Ω cm have been commonly measured for AlGaN epilayers with Al compositions in the ranges of 60-70%, compared to <1 Ω ·cm for p-type GaN [8, 11, 14, 33].

Recently, progress has also been made in the epitaxy of Al-rich AlGaN materials and their device applications by using plasma-assisted molecular beam epitaxy (MBE) [34-38]. Compared to MOCVD, the H-free growth environment minimizes the formation of magnesium-hydrogen complex and is therefore highly favorable for the activation of Mg dopant. In addition, MBE does not suffer from the significant parasitic reaction between NH₃ and trimethylaluminum precursors commonly observed in MOCVD. Previous studies further suggested that the formation of a thin liquid Ga metal layer on the growth front could promote the subsurface incorporation of Mg dopant by using MBE [39]. To date, however, a detailed investigation of the charge carrier transport properties of Mg-doped Al-rich AlGaN grown by MBE has remained lacking to our knowledge. The effect of Mg concentration on hole mobility and resistivity has also remained elusive.

In this context, we have studied the epitaxy and charge carrier transport properties of Mg-doped AlGaN with Al compositions ~60% using plasma-assisted MBE. Free hole concentrations up to ~8.7×10¹⁷ cm⁻³ were measured at room temperature. Moreover, hole mobility values in the range of 10 to 17 cm²/(V·s) can be reliably achieved. Significantly, a minimum resistivity of 0.7 Ω ·cm was measured, and its dependence on the Mg dopant incorporation was identified. Detailed temperature-dependent charge carrier transport studies further revealed that the hole concentration exhibited a negligible dependence on temperature near room temperature, but increases drastically for temperatures above 300 °C, suggesting the importance of impurity band conduction at room temperature.

3.2 Experiment details

In this study, Mg-doped AlGaN epilayers with Al content ~60% were grown using a Veeco Gen 930 MBE system equipped with a radio-frequency (RF) plasma-assisted nitrogen source. Commercial undoped AlN-on-sapphire templates from DOWA Electronics Materials Co. Ltd.

were used as the substrate. The growth conditions included a substrate temperature ~750 °C, Al beam equivalent pressure (BEP) ~ 2.0×10^{-8} Torr, and nitrogen flow of 0.3 standard cubic centimeter per minute and RF power of 350 W. These growth conditions were chosen based on extensive studies to achieve a smooth surface morphology for AlGaN epilayers with Al compositions ~60%. The growth was conducted under slightly metal rich conditions to enhance the subsurface incorporation of Mg dopant. The thickness of Mg-doped AlGaN epilayers is ~425 nm. A thin (~2 nm) p-GaN layer was grown on top of the p-AlGaN to serve as the contact layer. AlGaN epilayers with different Mg-doping concentrations were investigated and studied, which are listed in Table 3-1. The Mg-doping concentrations were derived based on secondary-ion mass spectroscopy (SIMS) measurements which was performed by EAG Laboratories. In these studies, the growth conditions were carefully controlled to obtain a similar Al composition, i.e. ~60%.

Table 3-1 List of Mg-doped AlGaN epilayers with different Mg-doping concentrations. For each Mg-doping level, multiple samples were studied. The listed hole concentration and mobility values are the average values measured at room temperature for multiple samples with the same Mg-doping levels.

Sample	Mg concentration (cm ⁻³)	Hole concentration (cm ⁻³)	Hole mobility (cm²/(V·s))	Resistivity (Ω·cm)
А	5.05×10 ¹⁸	2.31×10^{17}	15.3	1.81
В	5.55×10 ¹⁸	3.12×10 ¹⁷	11.1	1.82
С	6.04×10 ¹⁸	5.98×10 ¹⁷	11.6	0.90
D	7.54×10 ¹⁸	8.53×10 ¹⁷	10.6	0.69
Е	1.14×10 ¹⁹	5.64×10 ¹⁷	7.77	1.43
F	2.71×10 ¹⁹	5.46×10 ¹⁷	5.33	2.15

3.3 Results and discussion

The X-ray diffraction (XRD) pattern of Sample F with Mg concentration of 2.71×10^{19} cm⁻³ is shown in Figure 3-1 (a). The two peaks corresponding to the AlN template and AlGaN epilayer are identified. The full-width-at-half-maximum for the AlGaN epilayer is ~375 arcsec, which is slightly larger than that (358 arcsec, not shown) of undoped AlGaN epilayers, indicating enhanced compositional inhomogeneity due to the presence of Mg. Shown in Figure 3-1 (b) is a representative atomic force microscopy (AFM) image, which exhibits smooth surface morphology (RMS roughness ~0.27 nm), comparable to previously best reported roughness of Mg-doped AlGaN epilayers [20, 40]. It was also observed that the surface morphology degraded with the emergence of pits or grains as more Mg dopant was incorporated.



Figure 3-1 (a) XRD spectrum of a Mg-doped Al_{0.58}Ga_{0.42}N epilayer sample. (b) AFM height profile of the surface of the Mg-doped Al_{0.58}Ga_{0.42}N epilayer sample. The RMS roughness is ~0.27 nm.

We studied the charge carrier transport properties of Mg-doped AlGaN epilayers by performing Hall effect measurements. Metal contacts consisting of Ni/Au/Ni/Al/Au (15 nm/15 nm/15 nm/300 nm/20 nm) were defined using photolithography and deposited by e-beam evaporator, followed by an annealing at 500 °C for 1 minute in air ambient. The thin (~2 nm) p-GaN contact layer was isolated and removed to avoid any effect to the measured electrical properties. The hole concentration, hole mobility, and resistivity were then measured using van der Pauw method in argon ambient. Variations of the hole concentration and mobility versus Mg-doping density were first investigated at room temperature. Shown in Figure 3-2 (a), the measured hole concentration increases as the Mg dopant incorporation increases until the Mg concentration reaches ~7.54×10¹⁸

cm⁻³ and the free hole concentration reaches $\sim 8.7 \times 10^{17}$ cm⁻³ which is higher than the previously reported values for AlGaN epilayers with similar Al compositions [8, 10, 39]. With further increasing Mg concentration, the hole concentration shows a decreasing trend. The decrease of hole concentration with increasing Mg incorporation has also been observed for heavily Mg-doped GaN and AlN, which is attributed to the degradation of material quality with heavy Mg-doping and the strong self-compensation effect, due to the formation of Mg complexes and donor-like defects such as nitrogen vacancies [2, 3, 5, 41]. Multiple samples were studied at each doping level to further confirm the results, shown in Figure 3-2 (a). The doping efficiency, defined as the measured hole concentration divided by the Mg dopant concentration, is derived to be in the range of ~2-11%, which is comparable to previously reported values of ~1.2-14% for Mg-doped AlGaN with similar Al composition [8, 14, 27] and that for Mg-doped GaN [32, 42].



Figure 3-2 Variations of (a) hole concentration, (b) hole mobility, and (c) resistivity with Mg concentration for AlGaN epilayers with Al compositions ~60% measured at room temperature. The red dashed lines serve as a guide. For each Mg-doping level, multiple samples were studied and shown in the figures.

The measured hole mobility versus Mg concentration is shown in Figure 3-2 (b). The maximum hole mobility values are measured to be $17.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ at room temperature, which was obtained for AlGaN epilayers with Mg-doping concentration~ $5.05 \times 10^{18} \text{ cm}^{-3}$ (hole density ~ $2.31 \times 10^{17} \text{ cm}^{-3}$). The measured mobility shows a monotonously decreasing trend from $17.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ to $5.6 \text{ cm}^2/(\text{V}\cdot\text{s})$ with increasing Mg concentration to $2.71 \times 10^{19} \text{ cm}^{-3}$. Illustrated in Fig. 2(b), mobility values in the range of $10-17 \text{ cm}^2/(\text{V}\cdot\text{s})$ can be reliably measured for Mg-doped AlGaN epilayers with hole concentrations of $2-8 \times 10^{17} \text{ cm}^{-3}$. The reduced mobility with increasing Mg-doping concentration is likely related to the scattering due to enhanced formation of compensating defects and complexes. For comparison, hole mobility values of $1-3 \text{ cm}^2/(\text{V}\cdot\text{s})$ have been commonly reported for Mg-doped AlGaN with similar Al compositions grown by MOCVD [10, 14, 27]. Variations of the overall resistivity versus Mg concentration are further shown in Figure 3-2 (c). It is seen that the resistivity reaches a minimum value ~ $0.7 \ \Omega\cdot\text{cm}$ for Mg-doping density ~ $7.54 \times 10^{18} \text{ cm}^{-3}$ (hole concentration ~ $8.7 \times 10^{17} \text{ cm}^{-3}$).



Figure 3-3 Variations of (a) hole concentration and (b) hole mobility with measurement temperature for Samples D and F.

To elucidate the p-type conduction mechanism of Mg-doped AlGaN epilayers, we have further performed temperature-dependent Hall measurements. Shown in Figure 3-3 (a) are the measured hole concentrations versus temperature for Samples D and F, which have Mg concentrations of 7.54×10^{18} cm⁻³ and 2.71×10^{19} cm⁻³, respectively. The hole concentrations of both samples showed a very weak dependence on temperature in the range of 300 to 400 K. The derived activation energy is 11 meV and 2.7 meV for Samples D and F, respectively. Such small activation energy values cannot be explained by the thermal ionization of Mg dopants, which is generally characterized by an activation energy \sim 300 meV for Al_{0.6}Ga_{0.4}N. The underlying mechanism is likely related to hole hopping conduction in the Mg impurity band [8, 43]. At relatively large Mg

concentrations, the distance between adjacent Mg impurity atoms decreases, and the probability for holes to hop from one localized state to the nearest state in space, or through variable ranging hopping increases significantly. This hopping conduction is characteristic of a small activation energy. Activation energy values in the range of 0-50 meV were previously measured for Mg-doped AlGaN epilayers and superlattices [6, 8, 9, 14]. It is also of interest to note that in the



Figure 3-4 (a) Variation of resistivity versus measurement temperature for Samples D and F. (b) Summary of the resistivity for previously reported Mg-doped AlGaN epilayers (solid square) and AlGaN superlattices (open circle) with different Al compositions [2, 6, 8-17, 20-24, 26, 27, 33, 40, 44].

temperature range (400 - 550 K), the hole concentration shows a slightly decreasing trend with increasing temperature. This unconventional variation in hole concentration can also be explained

by the two-band conduction model, i.e., conduction in the impurity band as well as in the valence band. When the temperature increases, a larger number of Mg dopants are activated, and the number of holes contributing to impurity band conduction decreases. Because the impurity band conduction is still dominant, the measured effective hole concentration therefore shows a reduction with increasing temperature. As the temperature further increases, more Mg dopants are activated and the conduction in the valence band becomes dominant over the conduction in the impurity band. Consequently, the measured hole concentration is mostly affected by the holes in the valence band and shows a drastic increase with temperature above ~550 K. In this temperature range, the activation energy is derived to be 363 meV for Sample F and 325 meV for Sample D, which are in good agreement with previously reported Mg activation energy for AlGaN with similar Al compositions [10]. Similar trend has also been measured in doped GaN and AlN, due to the formation of impurity bands [43, 45, 46].

Illustrated in Figure 3-3 (b), the mobility of both samples showed a steady reduction with temperature. By fitting the data using a power law relation with temperature, it is seen that the mobility of sample F is proportional to $T^{1.93}$, and the mobility of sample D is proportional to $T^{2.2}$. Though different from typical dependence following $T^{1.5}$ due to phonon scattering, similar power dependence, such as $T^{1.8}$ and $T^{2.2}$, has been previously measured for Mg-doped GaN [47, 48].

Variations of the resistivity versus temperature for Samples D and F are further shown in Figure 3-4 (a). The resistivity of both samples firstly shows an increasing trend with temperature due to the degraded mobility. At elevated temperatures (>600 K), the resistivity exhibits a decreasing trend, due to the significantly enhanced Mg dopant activation. Illustrated in Figure 3-4 (b) is a brief summary of some previously reported resistivity values of Mg-doped AlGaN [2, 6, 8-17, 20-24, 26, 27, 33, 40, 44]. It is seen that the measured resistivity of 0.7 Ω ·cm is significantly smaller

than previously reported values of Mg-doped AlGaN epilayers. A room temperature resistivity of 47 Ω ·cm has been reported for Mg-doped AlGaN epilayers grown by MOCVD with similar Al composition, and 10 Ω ·cm has been also reported for Al composition less than 50% [7, 8]. It is worthwhile mentioning that based on SIMS analysis, the carbon impurity concentration is ~ 5×10¹⁶ cm⁻³ in the Mg-doped AlGaN epilayers grown by MBE, which is significantly reduced compared to previously reported values for AlGaN epilayers grown by MOCVD [49, 50]. The reduced impurity incorporation, together with the H-free growth environment and enhanced Mg dopant incorporation using plasma-assisted MBE all contribute to the significantly reduced resistivity of Mg-doped AlGaN epilayers in the presented study.

3.4 Conclusion

In summary, we have shown that Mg-doped Al_{0.6}Ga_{0.4}N grown by plasma-assisted MBE can exhibit free hole concentrations up to 8.7×10^{17} cm⁻³ at room temperature. Relatively large hole mobility values in the range of 10 to $17.2 \text{ cm}^2/(\text{V} \cdot \text{s})$ can be reliably obtained. Significantly, a low resistivity of 0.70 Ω ·cm was measured at room temperature. These studies will be instrumental to address the efficiency bottleneck of mid and deep UV LEDs and to realize high performance AlGaN-based semiconductor laser diodes.

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Chapter 4 Improving the Efficiency of Transverse Magnetic Polarized Emission from AlGaN Based LEDs by Using Nanowire Photonic Crystal

The emission from Al-rich AlGaN planar structure is dominantly transverse magnetic (TM) polarized, which means that the emission direction is mostly in the in-plane direction. As a result, the extraction efficiency of transverse magnetic (TM) polarized emission is extremely low due to total internal reflection. This chapter^{*} will discuss the improvement of LEE by the scattering in nanowire photonic crystals. The Purcell effect of nanowire photonic crystal as an approach to enhance IQE will also be discussed.

Abstract

AlGaN-based deep ultraviolet (UV) light emitting diodes (LEDs) are attractive for a wide range of applications. To date, however, the best reported external quantum efficiency (EQE) for LEDs operating in the wavelength range of ~240 nm is well below 1%. In this work, we have performed detailed studies of the EQE of AlGaN nanowire photonic crystal LEDs in this wavelength range by finite difference time domain simulation. By coupling in-plane emission to vertical emission, light extraction efficiency (LEE) over 90% can, in principle, be expected from the device top surface for transverse magnetic polarized photons that was not previously possible in conventional planar quantum well devices. Taken into account practical limitations including the absorptive p-Al(Ga)N contact and the presence of metal contact grid, LEE in the range of 30-40% is also

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expected. Moreover, due to the Purcell effect, the radiative recombination rate and therefore internal quantum efficiency (IQE) can be significantly modified in nanowire photonic crystal structures. We have established the design principles and ultimate efficiency limit of AlGaN nanowire photonic crystal LEDs: For AlGaN LEDs with very high IQE, EQE >70% can, in principle, be expected by operating near the Γ point of nanowire photonic crystals, whereas for structures with relatively low IQE it is preferred to operate near the M point to enhance the IQE while maintaining reasonably high LEE.

4.1 Introduction

Semiconductor light emitters, including light emitting diodes (LEDs) and lasers that can operate efficiently in the deep ultraviolet (UV) wavelength range are essentially required for a broad range of applications, including water purification, disinfection, and chemical and biochemical sensing [1-7]. AlGaN alloys have direct energy bandgap in the wavelength range of ~200 nm to 360 nm and have emerged as the material of choice for UV optoelectronics. To date, however, it has remained extremely challenging to achieve high efficiency AlGaN deep UV light emitters particularly for high AlN content with emission wavelengths between ~200 nm and 240 nm. For example, the best reported external quantum efficiency (EQE) for LEDs operating in the wavelength range of 240 nm is well below 1% [8-10]. Among the reasons for low EQE, there is a problem of the light extraction of the dominant transverse magnetic (TM) polarized emission (E||c-axis) at high AlN content, in addition to the low injection efficiency and the low internal quantum efficiency (IQE) due to the presence of large densities of defects and dislocations and the strong quantum-confined Stark effect [11-13]. In the past decade, intensive studies have been performed to enhance the luminescence efficiency and to explore various techniques to improve the LEE,

including strain and polarization engineering, surface roughening, patterned substrates and photonic crystals, but with limited success [14-18].

Recently, significant progress has been made in the epitaxy and device application of AlGaN nanowire heterostructures [19-24]. Due to the efficient strain relaxation, nearly defect-free AlN and AlGaN nanowires can be achieved on Si, sapphire, metal template and other foreign substrates [20, 25-27]. These wide bandgap nanostructures can exhibit relatively high luminescence efficiency and efficient current injection at room-temperature [28, 29]. Recent studies on GaN-based nanowires have shown, both theoretically and experimentally, that the formation of nanowire photonic crystal structures, by precisely controlling the size, spacing and morphology of nanowires through selective area epitaxy, can significantly enhance the luminescence emission intensity and stability [30]. Studies have been performed on enhancing the LEE using AlGaN nanowires, which, however, have been limited to either single nanowires [8, 31], or emission from the lateral surfaces of nanowire ensembles [32]. For practical device application, the efficient extraction of TM polarized photons from the top surface of a relatively large area device is highly desired.

In this work, we have performed detailed studies of the ultimate efficiency limit of high AlN content AlGaN deep UV LEDs with TM polarized emission by using nanowire photonic crystal structures. It is observed that, in a well-designed AlGaN nanowire photonic crystal LED structure, the LEE can, in principle, reach over 90% for TM polarized emission from the device top surface by finite difference time domain (FDTD) simulation, which is due to the efficient diffraction of in-plane TM polarized emission to out-of-plane surface emission at the Γ point. Taken into account practical limitations including the absorptive p-Al(Ga)N contact and the presence of metal contact grid, LEE in the range of 30-40% is also expected. Moreover, due to the Purcell effect, the radiative

recombination rate and therefore IQE can be significantly modified in nanowire photonic crystal structures, which can be exploited to further enhance the device efficiency. The critical dependence of LEE on various design parameters, including nanowire height, nanowire diameter, variations in the emission wavelengths, and spectral linewidths are studied. Strategies for achieving maximum EQE for given material quality have also been identified. Our calculation shows that the proposed nanowire photonic crystal LED structures are robust and experimentally feasible. The present study reveals the extraordinary potential of AlGaN nanowire photonic crystals for achieving high efficiency deep UV light emitters, which has the potential to provide a paradigm shift for deep UV optoelectronics.

4.2 Simulation Details

Schematically shown in Figure 4-1 (a), the LED heterostructure consists of n-type Al(Ga)N nanowire template, n-type AlGaN cladding layer, undoped AlGaN active region with embedded quantum dots/wells, and p-type AlGaN top contact layer. The nanowires are hexagonal in shape and are arranged in a triangular lattice. As shown Figure 4-1 (b), the lattice constant and diameter of the nanowires are defined as *a* and *d*, and the thicknesses of the AlN and AlGaN segments are L_1 and L_2 , respectively. The nanowire array is placed above the UV-reflective substrate in a hexagonal area with a side length of 7 µm as shown in Figure 4-1 (c), and FDTD simulation is performed using the software package Lumerical FDTD Solutions. A UV-reflective substrate with nearly 100% reflectivity can be realized by using AlGaN/AlN distributed Bragg reflectors (DBRs) [33]. The boundary conditions are perfect matched layers (PMLs) set by the software package, which is a standard technique in FDTD simulation to truncate the simulation space without the reflection of outgoing waves back to the simulation space [34, 35]. Detailed mathematical description of such boundary conditions can be found in Refs. 34 and 35. A 1 µm distance was left

between the photonic structure and any PML as shown in Figure 4-1 (c). Assuming that the emission is 100% TM polarized, a TM polarized dipole source with central wavelength of ~239 nm is positioned in the active region of only the very center nanowire in the array, which is appropriate for estimating LEE for a large area LED device [36]. The LEE is calculated by integrating the power going upward within a rectangular region above the nanowire array. The area of the rectangular region is sufficiently large to collect the light extracted from the surface. The spectrum of the source is set to have a linewidth (full-width-at-half-maximum (FWHM)) of 50 nm to obtain the broadband response of the photonic structure. The refractive indices of AlGaN and AlN segments are 2.45 and 2.1, respectively [37]. The actual refractive indices, however, may vary depending on the material quality and compositional distribution. The device design, described below, can be readily optimized based on the actual refractive indices. Due to the large bandgap in AlGaN and AlN cladding layers, absorption of emitted light is approximated to be zero.



Figure 4-1 (a) Schematic of the proposed AlGaN nanowire LED heterostructure.(b) Top view of the nanowire photonic crystal. (c) Schematic of the simulation space for the nanowire photonic crystal LED structure.

4.3 **Results and Discussion**

Shown in Figure 4-2 (a) is a typical bandstructure for TM polarization of an AlGaN nanowire photonic crystal structure calculated using the finite-element method simulation package RF module of Comsol Multiphysics. The Γ point is defined as (0,0) and the M points are defined as $\pm K_1/2$, $\pm K_2/2$, and $\pm (K_1-K_2)/2$, where K_1 and K_2 are the primitive vectors in the reciprocal space as shown in Figure 4-2 (b) [38-40]. The photonic crystal is beneficial for maximizing LEE near the 4^{th} band Γ point because near the 4^{th} band Γ point the mode profile has even symmetry for the outof-plane electric field distribution, with the largest overlap with the nanowire center region, shown in the inset of Figure 4-2 (a), which can efficiently diffract light to the vertical direction [41]. Due to the near-zero in-plane wavevector, the wavevector is mostly pointing out-of-plane, indicating that the TM polarized emission is scattered to vertical surface emission [42]. Since a photonic crystal structure can also change the optical density of states surrounding the active region, the IQE of an LED will be affected by the modified radiative recombination rate under Purcell effect. In this regard, the M point can significantly enhance the IQE because 3 pairs of M points are each coupled by the first order Bragg scattering $(K_1, K_2 \text{ or } K_1 - K_2 \text{ in Figure 4-2 (b)})$ forming resonant standing waves in the structure [42, 43]. As both large values of LEE and IQE are critical for achieving high EQE in an LED, it is necessary to understand how LEE and IQE are affected by the photonic crystal structure and how to use photonic crystal structure to optimize the ultimate EOE.

We first discuss the design of nanowire photonic crystal LED structures on how to maximize LEE for TM polarized photons. Important design parameters include the nanowire diameter (*d*), lattice constant (*a*), and the device layer thicknesses (L_1 and L_2). The calculation flow chart in identifying the optimum values of *d*, *a*, L_1 and L_2 is shown in Appendix A. As the Γ point can be achieved at

the same wavelength with different combinations of nanowire diameters and lattice constants, we firstly varied the nanowire diameter and the lattice constant while keeping Γ point at $\lambda = 239$ nm.

Table 4-1 Calculated light extraction efficiency (LEE) for $\lambda = 239$ nm, L₁ = 400 nm and L₂ = 120 nm for three different designs of AlGaN nanowire photonic crystal structures, i.e. three different combinations of (d, a).

<i>a</i> (nm)	<i>d</i> (nm)	LEE
130	120	63%
140	110	56%
160	95	96%

Three representative combinations of (d, a) and the corresponding LEE are summarized in Table 4-1. It is observed that the highest LEE (~96%) is achieved for d = 95 nm and a = 160 nm. This is attributed to the high out-of-plane coupling constant at this d/a ratio [44]. After optimizing at a = 160 nm and d = 95 nm using limited three conditions listed in Table 4-1, the 4th band (n = 4 in Figure 4-2 (a)) Γ point is estimated to be 239 nm. Therefore, the subsequent study in this work will be mostly focused on the wavelength at 239 nm. It is important to note that the concept presented in this study can be readily extended to other operating wavelengths. Figure 4-2 (c) shows the LEE for both planar and nanowire photonic crystal LED structures. The planar film has the same layers and thicknesses as the nanowires. It is evident that LEE is significantly enhanced from ~10% in the planar structure to more than 90% in the photonic crystal structure, which is attributed to the coupling to vertical emission at the 4th Γ point. It is therefore evident that operating near the Γ point can significantly enhance the LEE. Detailed studies further show that the nanowire height, including variations in L_1 and L_2 can slightly affect LEE. For example, LEE varies between 81% and 96% as L_2 changes from 80 to 200 nm while keeping L_1 at 400 nm (see Appendix B).



Figure 4-2 (a) The bandstructure for TM polarization of an AlGaN photonic crystal structure calculated using the finite-element method simulation package RF module of Comsol Multiphysics. The lattice constant a is 160 nm and the nanowire diameter d is 95 nm. The inset shows the electric field intensity profile in a unit cell near the 4th band Γ point. (b) Schematic for the reciprocal lattice for a hexagonal nanowire array, showing that, due to the near-zero in-plane wavevector, the wavevector is mostly pointing out-of-plane. (c) The calculated LEE for an ideal nanowire photonic crystal structure on a UV-reflective substrate (red dots), and for two realistic cases including: i) on a substrate with nearly zero reflectivity (green triangle), and ii) the presence of absorptive p-GaN and metal contact grid (blue diamonds). The calculated result for a conventional planar LED structure is also shown for comparison (black square).

In addition, we have performed calculations for two non-ideal cases, including i) zero reflectivity of the underlying substrate/template, and ii) the presence of absorptive p-GaN and metal contact grid, which are more representative of real experiments. For Case i), the calculated LEE is in the range of 40-50%. In Case ii), the p-GaN contact layer has a thickness of 10 nm, and Ni/Au (20 nm thick) metal contact grid is placed on the device top surface (see Appendix C). LEE over 30% is calculated at the designed wavelength, shown in Figure 4-2 (c). The LEE can be further enhanced

by minimizing the thickness of the p-GaN contact layer, and/or by replacing it with a less absorptive p-AlGaN contact layer. In addition, it is worth mentioning that upon annealing the Ni/Au contact layer may become partially transparent, which will also enhance the LEE.



Figure 4-3 (a) Variations of LEE with respect to dipole positions. The inset shows the schematic for different dipole positions in the nanowire structure. The n-AlN segment length (L_1) and the total AlGaN segment length (L_2) are kept at 400 nm and 120 nm, respectively. The lattice constant *a* is 160 nm and the nanowire diameter *d* is 95 nm. (b) Variations of the LEE with respect to nanowire diameter for emission wavelengths at 239 nm with zero linewidth broadening (red square) and with a realistic 15 nm linewidth broadening (blue dot). The lattice constant *a* is 160 nm.

In the calculations above, the light source is positioned in the center region of the LED active region. Experimentally, multiple AlGaN quantum dot/well layers are commonly incorporated in the device active region. Moreover, depending on the lateral size of the nanowires, quantum dots/wells may form in the center, or on the lateral semipolar planes of nanowires [21, 45]. Therefore, we have studied the LEE for a dipole at different positions. Illustrated in the inset of Figure 4-3 (a), positions 1 to 5 are used to simulate spatial variations along the *z*-axis, while

positions 6 to 9 refer to variations in the *x-y* plane. Shown in Figure 4-3 (a), it is observed that the LEE stays nearly constant for spatial variations along the nanowire growth direction (from positions 1 to 5 along the *z*-axis), and exhibits a small (~5%) reduction for variations along the lateral dimension (*x-y* plane). It is therefore seen that spatial variations of the quantum dot/well emitters in the device active region has a very small, or negligible effect on the LEE.

We have further investigated the effect of nanowire diameter variations on the LEE. Shown in Figure 4-3 (b) (red squares), the maximum LEE at $\lambda = 239$ nm is obtained for an optimum nanowire diameter of 95 nm. In the range of 80 nm to 100 nm, LEE still maintains ~85% or higher. Further increasing nanowire diameters leads to significantly reduced LEE (<70%). This is because the 4th band redshifts with increasing nanowire diameter and, consequently, the operating wavelength (239 nm) becomes closer to the M point rather than Γ point. At or near the M point, the coupling to vertical emission becomes less efficient, leading to a reduction of LEE. With the use of selective area epitaxy, it has been demonstrated that variations of the diameter and spacing of AlGaN nanowires can be controlled to be within ~ 20 nm [26, 46-48]. Therefore, the proposed AlGaN nanowire photonic crystal LED structure is experimentally feasible. The analysis described above is for a single wavelength at or near Γ point. In practice, due to the homogeneous and inhomogeneous broadening, spectral linewidths of AlGaN light emitters are generally in the range of 10 to 20 nm. We have therefore calculated the LEE considering a FWHM of 15 nm, illustrated in Figure 4-3 (b) (blue dots). It is seen that the LEE exhibits a negligible change, compared to that of an LED structure with zero linewidth, which means that the LEE remains high though the emission wavelength deviates away from the exact Γ point (See Appendix D). Even considering large variations of the nanowire size, the LEE can, in principle, reach ~75%, or higher for an AlGaN LED device with TM polarized emission.



Figure 4-4 Variation of the IQE (a) and EQE (b) for AlGaN nanowire photonic crystal LED structures by changing the nanowire diameter from 80 nm, through 95 nm (Γ point), to 110 nm (M point), while keeping other design parameters identical. Calculations were performed for the intrinsic material IQE (η_{IQE0}) in the range of 10% to 90%. The peak emission wavelength is at 239 nm with a realistic spectral linewidth ~15 nm. The n-AlN segment length (L_1) and the total AlGaN segment length (L_2) are kept at 400 nm and 120 nm, respectively. The lattice constant *a* is 160 nm.

An additional benefit offered by nanowire photonic crystal LEDs is that the IQE can be enhanced, due to the Purcell effect [49]. We have calculated the Purcell factor for different nanowire photonic crystal designs (see Appendix E) [50]. Variations of the IQE for AlGaN nanowire photonic crystal LEDs are shown in Figure 4-4 (a) for η_{IQE0} in the range of 10% to 90%, where η_{IQE0} is the IQE of the LED active region without the presence of photonic crystal structure. The nanowire diameters are varied from 80 nm, through 95 nm (Γ point), to 110 nm (M point), while keeping other design parameters identical. It is seen that significantly enhanced IQE can be expected when operating at, or near the M point. For example, an IQE value of 20% can be enhanced to >30% when operating at the M point. It is important to note that these analyses are performed based on realistic FWHM \sim 15 nm. Even larger enhancement of IQE can be expected for emitters with narrower linewidths.

Finally, to achieve high efficiency deep UV light emitters, it is essential to maximize the EQE, *i.e.* the product of IQE and LEE. Our studies (see Appendix E) suggest that, if the material quality is high with very large IQE (>90%), then the design should be focused on how to enhance the LEE. In this case, the device should operate near the Γ point, with the maximum achievable EQE >70%, indicated by the black arrow in Figure 4-4 (b). In practice, due to the presence of defects, Auger recombination, and quantum-confined Stark effect, η_{IQE0} is relatively low for deep UV LEDs. For devices with a relatively low η_{IQE0} of 30%, the IQE can be enhanced to ~44% when operating near the M point, leading to a relatively high EQE of 32%, indicated by the red arrow in Figure 4-4 (b), which is significantly higher than that (~12%) when operating at the Γ point and that (~3%) of conventional planar LEDs.

4.4 Conclusion

In conclusion, we have investigated the design of AlGaN nanowire photonic crystal LEDs operating in the deep UV wavelength range. It is observed that very large LEE can, in principle, be achieved for TM polarized photons, which was previously not possible for planar quantum well devices. Detailed studies further suggest that the proposed AlGaN nanowire photonic crystal LED structures are robust and experimentally feasible, given the recent advances in the site-controlled epitaxy of nanowire heterostructures, and offer rich opportunities to significantly enhance the ultimate EQE of AlGaN deep UV light emitters with both high and low material quality. For example, for AlGaN LEDs with very high material quality, EQE >70% can be expected by operating near the Γ point of nanowire photonic crystals, whereas for structures with relatively low

material quality it is preferred to operate near the M point to enhance the IQE while maintaining reasonably high LEE. The design parameters so far are mostly focused on the Γ point and the M point in the 4th band. By extending the design parameter space, the K point and higher bands could also be utilized to enhance the LED performance, which is now under investigation.

4.5 Appendices





Figure 4-5 Calculation flow chart for determining *d*, *a*, *L*₁, and *L*₂.

Figure 4-5 shows the flow for determining d, a, L_1 , and L_2 . First, two-dimensional finite-element method simulation was performed to calculate the bandstructure for different (d, a) combinations and those with Γ point at 239 nm were identified. Then we arbitrarily assigned L_1 to be 400 nm and L_2 to be 100 nm. LEE was then calculated using three-dimensional FDTD simulation and the best (d, a) combination was identified. Using the best (d, a) combination, L_1 and L_2 are optimized again. With the new values for L_1 and L_2 , LEE was finally calculated for different (d, a) combinations for comparison.

Appendix B The Effect of Nanowire Length on the Light Extraction Efficiency (LEE)

Based on the optimum design described in the main text, we have further calculated the LEE by varying the nanowire height, including L_1 and L_2 , while keeping d as 95 nm and a as 160 nm. Shown in Figure 4-6 (a), the LEE exhibits negligible variation, in the range of 87% to 94% for different L_1 values while keeping L_2 at 80 nm and 200 nm, respectively. Similar studies were also performed by varying L_2 while keeping L_1 at 400 nm. Illustrated in Figure 4-6 (b), the LEE varies between 81% and 96% as L_2 changes from 80 to 200 nm and L_1 is kept 400 nm. Though this dependence is not significant, the effect of L_2 should be taken into account for optimizing the actual device performance.



Figure 4-6 (a) Dependence of LEE on the n-AlN segment length L_1 . (b) Dependence of LEE on the total length L_2 of AlGaN segments. The n-AlN segment length L_1 is fixed as 400 nm. The lattice constant *a* is 160 nm and the diameter *d* is 95 nm.

Appendix C Description for the Structure with a p-GaN Layer and Metal Contact Grids

Compared to the ideal case presented in the manuscript, Case ii) considers more practical experimental conditions, including the incorporation of absorptive p-GaN and metal contact grid. Based on the same nanowire structure shown in Figure 4-1 (a) in the manuscript, a 10 nm thick p-GaN layer is added on the device top surface, shown in Figure 4-7. Metal contact grids consisting of 10 nm Ni and 10 nm Au were then deposited on top of the nanowires. The width of the metal contact grid is 30 nm.



Figure 4-7 Schematic for the structure for Case ii), including a p-GaN layer and metal contact grids.

Appendix D Tolerance for Mismatch between Operation Wavelength and Γ Point

As shown in Figure 4-8, the LEE remains above 80% in a wide wavelength range around 240 nm. As the wavelength decreases from 240 nm to 225 nm, the in-plane wavevector increases to $0.36\pi/a$ in the Γ -K direction or $0.35\pi/a$ in the Γ -M direction. For longer wavelengths between 240 nm and 255 nm, the LEE is also high because of the TM polarization bandgap. As long as the emission spectrum has a reasonably narrow FWHM of around 15-20 nm and the peak wavelength is not far from the Γ point, the overall LEE will remain high. Our design to maximize LEE can tolerate large mismatch between Γ point and the peak wavelength.



Figure 4-8 Variation of LEE with wavelength. The lattice constant *a* is 160 nm and the diameter *d* is 95 nm. The n-AlN segment length L_1 is fixed as 400 nm. The total length L_2 of AlGaN segments is fixed as 120 nm.

Appendix E Purcell Factor, Internal Quantum Efficiency (IQE), and External Quantum Efficiency (EQE) of AlGaN Nanowire Photonic Crystal Structures



Figure 4-9 Purcell factor for different wavelengths when the diameter is 95 nm and 110 nm. The lattice constant is 160 nm. The n-AlN segment length L_1 is fixed as 400 nm. The total length L_2 of AlGaN segments is fixed as 120 nm.

We have calculated the Purcell factor for different nanowire photonic crystal designs by taking the ratio of the actual emitted power in the photonic crystal structure to the emitted power as if in a

homogeneous isotropic bulk AlGaN material [50]. Shown in Figure 4-9 is the Purcell factor at different wavelengths as the nanowire diameter changes. Depending on the design parameters, a relatively large Purcell factor of ~5 can be achieved, which is expected to significantly enhance the IQE.

In order to understand the how IQE and EQE are affected in a photonic crystal structure, we have taken into account the radiative recombination rate modified by the Purcell effect. The radiative recombination rate can be written as,

$$R'_{r}(\lambda) = F_{p}(\lambda)R_{r}$$
(4-1)

where λ is the wavelength, $F_p(\lambda)$ is the Purcell factor, and R_p is the radiative recombination rate in a homogeneous bulk material without Purcell effect [51]. Note that both the Purcell effect and LEE are wavelength-dependent. We therefore further express IQE as,

$$\eta_{\rm IQE} = \frac{\int R_r'(\lambda)g(\lambda)d\lambda}{\int [R_r'(\lambda) + R_{nr}]g(\lambda)d\lambda}$$
(4-2)

where $g(\lambda)$ is a Lorentz function approximating a photon distribution with a linewidth $\Delta \lambda$ at a center wavelength λ_0 ,

$$g(\lambda) = \frac{1}{2\pi} \frac{\Delta \lambda}{\left(\lambda - \lambda_0\right)^2 + \left(\Delta \lambda / 2\right)^2}$$
(4-3)

Considering that the IQE of a homogeneous material without Purcell effect being $\eta_{IQE0} = R_r / (R_r + R_{nr})$, Eqn. (4-2) can be written as,

$$\eta_{\text{IQE}} = \frac{\int F_{p}(\lambda)g(\lambda)d\lambda}{\int [F_{p}(\lambda) + 1/\eta_{\text{IQE0}} - 1]g(\lambda)d\lambda}$$
(4-4)

It can therefore be seen that the Purcell factor $F_p(\lambda)$ can modify the IQE in a photonic crystal structure significantly. In order to achieve high efficiency deep UV light emitters, it is essential to maximize the EQE. Taking into account the Purcell effect, the EQE of AlGaN nanowire photonic crystal LEDs can be expressed as,

$$\eta_{\rm EQE} = \eta_{\rm INJ} \frac{\int F_p(\lambda) \eta_{\rm LE}(\lambda) g(\lambda) d\lambda}{\int [F_p(\lambda) + 1/\eta_{\rm IQE0} - 1] g(\lambda) d\lambda}$$
(4-5)

where η_{INJ} is the injection efficiency and $\eta_{\text{LE}}(\lambda)$ is the LEE. It is seen that the optimal design for high efficiency AlGaN nanowire photonic crystal LEDs depends on η_{IQE0} , *i.e.* the material quality.

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Chapter 5 Selective Area Epitaxy of AlGaN Nanowire Arrays across Nearly the Entire Compositional Range for Deep Ultraviolet Photonics

Following the efficient p-type doping of AlGaN by molecular beam epitaxy and the theoretical discussion on the functionality of AlGaN nanowire photonic crystals, this chapter^{*} will present the experimental realization of such regular nanowire array across the entire compositional range by molecular beam epitaxy. An LED at 279 nm based on well-controlled regular nanowire arrays and its structural, electrical, and optical characterizations will be discussed.

Abstract

Semiconductor light sources operating in the ultraviolet (UV)-C band (100-280 nm) are in demand for a broad range of applications but suffer from extremely low efficiency. AlGaN nanowire photonic crystals promise to break the efficiency bottleneck of deep UV photonics. We report, for the first time, site-controlled epitaxy of AlGaN nanowire arrays with Al incorporation controllably varied across nearly the entire compositional range. It is also observed that an Al-rich AlGaN shell structure is spontaneously formed, significantly suppressing nonradiative surface recombination. An internal quantum efficiency up to 45% was measured at room-temperature. We have further demonstrated large area AlGaN nanowire LEDs operating in the UV-C band on sapphire substrate, which exhibit excellent optical and electrical performance, including a small turn-on voltage of \sim 4.4 V and an output power of \sim 0.93 W/cm² at a current density of 252 A/cm². The controlled

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synthesis of AlGaN subwavelength nanostructures with well-defined size, spacing, and spatial arrangement and tunable emission opens up new opportunities for developing high efficiency LEDs and lasers and promises to break the efficiency bottleneck of deep UV photonics.

5.1 Introduction

Light sources that emit in the ultraviolet (UV)-C band (< 280 nm) are in demand for a broad range of applications, including water purification, disinfection, surface treatment, and medical diagnostics [1-7]. AlGaN, with tunable energy bandgap from 6.2 eV to 3.4 eV, has emerged as the material of choice for realizing all semiconductor based deep UV (DUV) light sources, which can potentially replace conventional mercury and xenon lamps. While high performance GaN-based devices have been demonstrated in the blue and near-UV wavelength range, the performance of AlGaN light-emitting diodes (LEDs) degrades considerably with increasing Al composition [8-13]. For instance, the external quantum efficiency (EQE) of AlGaN quantum well LEDs is well below 10% in a large part of the UV-C spectrum [10, 12, 14]. One of the primary challenges for the extremely low efficiency is associated with the dominance of transverse magnetic (TM) polarized optical emission, with the electric field direction parallel to the *c*-axis, due to the negative crystal field splitting energy of Al-rich AlGaN [15]. The TM polarized emission prevents the extraction of photons from the top *c*-plane surface. The resulting light reabsorption not only leads to extremely low efficiency but further causes severe heating effect and device instability.

Recent studies suggested that the efficiency bottleneck of DUV light sources could be addressed by using nanowire photonic crystals: Light extraction efficiency exceeding 70% has been predicted by exploiting the light transmission regime of AlGaN nanowire photonic crystal structures [16]. Moreover, AlGaN nanowires offer several additional advantages compared to conventional quantum well structures, including significantly reduced defect formation and much more efficient *p*-type current conduction, due to the reduced Al-substitutional Mg-dopant formation energy [17-21]. The achievement of such unprecedentedly high efficiency photonic crystal light emitters, however, requires a precise control of the nanowire size, spacing, and spatial arrangement. The currently reported AlGaN nanowires have been largely formed spontaneously [22-25], with random variations in size, spacing, and geometry, which leads to strong light trapping effect and extremely low light extraction efficiency [25-27]. Such issues can be potentially addressed by using the technique of selective area epitaxy [28-36]. In this process, the nanowire formation and nucleation only takes place in the nanoscale apertures created on a substrate using a top-down approach, due to the growth selectivity in the opening apertures vs. on the mask [32, 35, 36]. To date, however, selective area epitaxy has not been successfully applied to Al-rich AlGaN nanowires [30, 37-41], and there has been no demonstration of AlGaN nanowires emitting in the UV-C band by selective area epitaxy [40], which is partly limited by the high temperature (often >1,000 °C) required for AlN epitaxy and the lack of a suitable growth mask.

In this context, we report on the site-controlled epitaxy and structural and optical characteristics of AlGaN nanowire arrays with Al incorporation controllably varied across nearly the entire compositional range. Selective area epitaxy of AlGaN nanowires with controlled size and spacing is achieved by growing AlGaN on a GaN nanowire template using plasma-assisted molecular beam epitaxy (MBE). It is also observed that an Al-rich AlGaN shell structure is spontaneously formed, which can significantly suppress nonradiative surface recombination based on previous studies [19, 22, 24, 25, 42]. An internal quantum efficiency up to 45% was measured at room-temperature. We have further demonstrated large area AlGaN nanowire LEDs operating in the UV-C band on sapphire substrate, which exhibit excellent optical and electrical performance, including a small turn-on voltage of ~4.4 V and an output power of ~0.93 W/cm² at a current density of 252 A/cm².

5.2 Selective area epitaxy of AlGaN nanowire arrays over the entire compositional range

Illustrated in Figure 5-1 (a) is the selective area epitaxy of Al_xGa_{1-x}N nanowire arrays on a GaN nanowire template formed on c-plane GaN-on-sapphire substrate. A thin Ti layer (~ 10 nm) was first employed as the growth mask for the selective area epitaxy of GaN nanowires [30, 43]. Nanoscale hexagonal apertures, with a lateral size d arranged in a triangle lattice of a lattice constant *a* were fabricated using e-beam lithography and reactive ion etching. Prior to the growth of nanowires, nitridation of the Ti mask was performed at 400°C to prevent crack and degradation during the growth process [30, 32, 35, 37, 38, 44]. GaN nanowire templates were then grown with a substrate temperature of 955°C, nitrogen flow rate of 0.55 sccm, and Ga flux of $\sim 3.7 \times 10^{-7}$ Torr using a Veeco GENxlor MBE system [36]. Subsequently, Al_xGa_{1-x}N nanowires were grown with substrate temperatures and nitrogen flow rates in the range of 935°C to 1025°C and 0.3 sccm to 0.55 sccm, respectively. Ga and Al beam fluxes were varied in the range of $\sim 10^{-7}$ to $\sim 4.2 \times 10^{-7}$ Torr and $\sim 10^{-8}$ to $\sim 7.1 \times 10^{-8}$ Torr, respectively to tune the alloy composition and emission wavelength. The substrate temperature mentioned here refers to the thermocouple reading on the backside of the substrate. The real substrate surface temperature is estimated to be ~100-150°C lower, depending on the substrate and sample size. Because of the shadowing effect of GaN nanowires, direct epitaxy of AlGaN on the substrate is largely eliminated. Shown in Figure 5-1 (b) is a scanning electron microscope (SEM) image of GaN/Al_xGa_{1-x}N nanowire arrays, which exhibit controlled size and spacing and well-defined hexagonal morphology, with a very high degree of uniformity. Detailed scanning transmission electron microscopy studies (see Appendix) further confirm that an Al-rich AlGaN shell structure is spontaneously formed surrounding the nanowires, which can suppress nonradiative surface recombination [19, 25, 42].



GaN on sapphire substrate

Figure 5-1 (a) Left: Nanoscale aperture arrays defined by e-beam lithography on a 10 nm thick Ti mask on a *c*-plane GaN-on-sapphire substrate. Right: Schematic of the selective area epitaxy of GaN/Al_xGa_{1-x}N nanowires on the patterned substrate.
(b) An SEM image of GaN/Al_xGa_{1-x}N nanowire arrays grown by selective area epitaxy.

Photoluminescence (PL) spectra of these $Al_xGa_{1-x}N$ nanowire arrays were measured at roomtemperature. The nanowire sample was excited using a 193 nm ArF excimer laser, and the PL emission was collected and spectrally resolved by a high-resolution spectrometer and detected by a liquid nitrogen cooled charge coupled device detector. Illustrated in Figure 5-2 (a), strong PL emission from 210 nm to 327 nm was measured from $Al_xGa_{1-x}N$ nanowires grown with different Al compositions. The correlation between the energy bandgap of $Al_xGa_{1-x}N$ and Al composition *x* can be approximately derived from the equation below [40].

$$E_{\sigma} = 6.015x + 3.39(1 - x) - 0.98x(1 - x)$$
(5-1)

Illustrated in Fig. 2(b) are variations of the PL emission wavelength vs. Al composition. It is seen that $Al_xGa_{1-x}N$ nanowires with Al composition varying across nearly the entire compositional range, *i.e.* from x = 0 to 1 can be readily achieved by selective area epitaxy. For comparison,

previous studies on the selective area epitaxy of Al_xGa_{1-x}N nanowires were largely limited to Al composition below 40% [40].



Figure 5-2 (a) Normalized room-temperature PL spectra of $Al_xGa_{1-x}N$ nanowire arrays with Al compositions tuned from ~20% to 100%. (b) Plot of emission wavelength vs. Al composition for AlGaN nanowires demonstrated in this work (blue diamond) and reported previously (red circle) by selective area epitaxy.

5.3 Selective area epitaxy and characterization of AlGaN nanowire LEDs

The realization of high quality Al-rich $Al_xGa_{1-x}N$ nanowire arrays by selective area epitaxy provides a distinct opportunity to demonstrate high efficiency nanowire light emitters operating in UV-C band [16, 43]. In this work, we first investigated the epitaxy and electrical and optical performance of AlGaN nanowire LEDs operating at ~280 nm. Illustrated in Figure 5-3 (a) is the schematic diagram of $Al_xGa_{1-x}N$ nanowire LEDs grown on *c*-plane sapphire substrate, which consists of a 300-nm Si-doped GaN, 80-nm Si-doped $Al_{0.64}Ga_{0.36}N$, 30-nm undoped $Al_{0.48}Ga_{0.52}N$ active region, and 60-nm Mg-doped $Al_{0.64}Ga_{0.36}N$ segment. The growth for $Al_xGa_{1-x}N$ nanowire LED structures included the following steps. The *n*- and *p*-type $Al_xGa_{1-x}N$ cladding layers were



epitaxy. (b) PL spectra of AlGaN nanowire LEDs grown by selective area epitaxy. (b) PL spectra of AlGaN nanowire LED heterostructures measured at 300 K under different excitation powers. Each spectrum was normalized by its individual peak intensity and shifted vertically for display purpose. (c) Variations of the PL spectral linewidth and peak energy as a function of excitation power. (d) Arrhenius plots of the integrated PL intensity measured from 14 K to 300 K for the active region (E₁) emission and the whole spectra. The inset shows PL spectra measured between 300 K and 20 K under an excitation power of 50 mW. E₁, E₂ and E₃ correspond to peak emissions from Al_{0.48}Ga_{0.52}N active region, Al_{0.64}Ga_{0.36}N cladding layers, and GaN, respectively.

grown with the substrate temperature of 1025°C, nitrogen flow rate of 0.55 sccm, and Ga and Al beam fluxes of $\sim 3.7 \times 10^{-7}$ Torr and $\sim 3.7 \times 10^{-8}$ Torr, respectively. The AlGaN active layer

sandwiched between the *n*- and *p*-type cladding layers was grown with Ga and Al beam fluxes of $\sim 3.7 \times 10^{-7}$ Torr and $\sim 3.0 \times 10^{-8}$ Torr, respectively. Mg beam flux was $\sim 3.2 \times 10^{-9}$ Torr for the Mg-doped AlGaN layer. During the growth of AlGaN nanowire segments, the lateral growth is enhanced, due to the small diffusion length of Al atoms, which leads to increased nanowire diameter and reduced air gap between adjacent nanowires. The approximate axial and lateral growth rates are ~ 150 nm/hr and ~ 20 nm/hr, respectively.

Optical properties of Al_xGa_{1-x}N nanowire LED heterostructures were studied using temperaturedependent PL spectroscopy. Illustrated in Figure 5-3 (b) are the normalized PL spectra measured at room temperature under different excitation powers. At a relatively low excitation power of 4 mW, PL emission (~283 nm) from the Al_{0.48}Ga_{0.52}N active region dominates, confirming the excellent carrier confinement provided by the core-shell structure. The spectral linewidth is ~11 nm, which is narrower compared to that of previously reported spontaneous AlGaN nanowires [19, 22, 24, 42], due to the improved size uniformity. With increasing excitation power, a shorter wavelength emission peak $E_2 \sim 255$ nm emerges, which corresponds to the emission from Al_{0.64}Ga_{0.36}N cladding layers. It is also seen that, with increasing excitation power, the emission peak E₁ (~283 nm) remains highly stable, shown in Figure 5-3 (c). The spectral linewidth exhibits a small broadening with increasing power. Illustrated in the inset of Figure 5-3 (d) are the PL spectra measured between 20 K and room-temperature under an excitation power of 50 mW. The emission peaks E₁ and E₂ (~255 nm) correspond to the transitions in the Al_{0.48}Ga_{0.52}N active region and Al_{0.64}Ga_{0.36}N cladding layers, respectively. The GaN-related emission (E₃) at ~355 nm is also identified at low temperature. S-shaped behavior was not observed for the peak position of E₁. Fig. 3(d) shows the integrated PL intensities for emissions from both the whole spectra and active region as a function of temperature under excitation of 50 mW. The internal quantum efficiency can be approximately estimated by $I_{PL}(RT)/I_{PL}(LT)$, wherein $I_{PL}(RT)$ and $I_{PL}(LT)$ are the integrated PL intensity measured at room temperature and low temperature, respectively. By assuming a nearunity quantum efficiency at 14 K, the internal quantum efficiency of the active region emission (E₁) is derived to be ~45% at room temperature, which is comparable with previously reported high quality Al_xGa_{1-x}N quantum well structures [10, 45, 46]. However, it is worthwhile mentioning that the measurement of internal quantum efficiency may depend on the excitation power [46, 47]. In our studies, the internal quantum efficiency was measured to be ~49% under excitation power ~100 mW. For nanowire devices, the internal quantum efficiency may also be affected by the presence of surface states/defects. In this regard, the incorporation of a large bandgap AlGaN shell structure can significantly reduce the effect of surface recombination on the quantum efficiency. The internal quantum efficiency of the presented AlGaN nanowires can be further improved by optimizing the growth conditions and the large bandgap AlGaN shell coverage.



Figure 5-4 (a) Current-voltage characteristics of AlGaN nanowire LEDs with an area of $50 \times 50 \ \mu\text{m}^2$. Inset: *I-V* characteristics of device under forward and reverse bias displayed in semi-log scale; (b) Electroluminescence spectra of AlGaN nanowire LEDs measured under different injection currents. (c) Power density and peak position as a function of current density measured at room-temperature under pulsed biasing condition.

AlGaN nanowire LEDs were subsequently fabricated and characterized. First, polyimide (PI2610 from HD MicroSystems) was spin-coated to serve as a surface planarization and passivation layer, followed by dry etching to reveal the nanowire top surface. Prior to contact metallization, the surface was treated with hydrochloric acid to remove any oxides. Ni (20 nm)/Au (10 nm) and Ti (20 nm)/Au (100 nm) contact layers were subsequently deposited on the device top surface and n-GaN template to serve as p- and n-metal contacts, respectively. An annealing at 550 °C was performed in N₂ gas ambient for 1 min. Subsequently, metal grid patterns were deposited on the device surface to facilitate current injection. Although the device fabrication process is more involved compared to the previously reported controlled coalescence of AlGaN nanowire LEDs [48], the controlled synthesis of AlGaN subwavelength nanostructures with well-defined size and spacing opens up new opportunities for developing high efficiency LEDs and lasers. The devices exhibit excellent current-voltage (I-V) characteristics. Shown in Figure 5-4 (a) is the I-V curve for a device with a size of $50 \times 50 \ \mu\text{m}^2$, which exhibits a turn-on voltage of ~4.4 V. A current density of 100 A/cm² was measured for a bias voltage of \sim 5.0 V, which is better than previously reported Al_xGa_{1-x}N quantum well LED devices operating at similar wavelengths [49-51]. The roomtemperature electroluminescence (EL) spectra are shown in Figure 5-4 (b). The devices exhibit strong emission at 279 nm. With increasing injection current, the peak emission (E₁) exhibits a small blue-shift as shown in Figure 5-4 (c), *i.e.* from 279.6 nm at 50 A/cm² to 278.9 nm at 252 A/cm². The weaker emission peak at 260 nm is due to electron overflow and the resulting emission from the *p*-Al_{0.64}Ga_{0.36}N layer. The output power density as a function of injection current density is also shown in Figure 5-4 (c). The measurements were performed for current density up to 252 A/cm² under pulsed mode (1% duty cycle) to reduce any heating effect. The output power density increases near-linearly with increasing injection current. The output power at current density of 252 A/cm² is estimated to be ~0.93 W/cm². The output power can be significantly increased by optimizing the nanowire size and spacing to achieve enhanced light extraction for TM polarized emission [16]. Moreover, the device performance can be further improved by utilizing the scheme of tunnel junction to significantly enhance the hole injection and transport [52, 53].

5.4 Summary

In summary, with the use of a GaN nanowire template, we have successfully demonstrated the selective area epitaxy of Al_xGa_{1-x}N nanowire arrays with Al composition varying across nearly the entire compositional range. The nanowires exhibit spontaneously formed core-shell structure and relatively high internal quantum efficiency at room temperature. With the use of selective area epitaxy, we have further demonstrated functional AlGaN nanowire LEDs operating in the UV-C band, which exhibit excellent electrical and optical performance. The controlled synthesis of AlGaN subwavelength nanostructures with well-defined size, spacing, and spatial arrangement and tunable emission opens up new opportunities for developing high efficiency LEDs and lasers and promises to break the efficiency bottleneck of deep UV photonics.

5.5 Appendix

Detailed structural characterization of Al_xGa_{1-x}N nanowire arrays was performed by an aberrationcorrected FEI Titan Cubed 80-300 scanning transmission electron microscope (STEM) operated at 200 kV on a cross-sectional TEM specimen of the nanowire arrays prepared by focused ion beam milling using a Zeiss NVision 40 dual-beam system with deposited Pt and C as protection layers. Atomic-number sensitive (Z-contrast) high-angle annular dark-field (HAADF) image of an array of Al_xGa_{1-x}N nanowire LED heterostructure observed in cross-section along the a-plane orientation is shown in Figure 5-5 (a). A higher magnification image is shown in Figure 5-5 (b).


Figure 5-5 STEM studies of AlGaN nanowire heterostructures. (a) Low magnification STEM- HAADF image of multiple AlGaN nanowire devices in cross-section and oriented along the $[11\overline{2}0]$ axis. (b) High magnification STEM-HAADF image of one nanowire (c) PCA-treated EELS elemental maps representing respectively, the distribution of Ga and Al in pseudo-color overlay (green for Al and red for Ga). (d) and (e) the distribution of Ga using its L_{2,3}-edge and the distribution of Al using its K-edge in greyscale.

The brighter intensity regions correspond to the n-GaN nanowire template and the darker intensity regions correspond to AlGaN LED heterostructure. Electron energy-loss spectroscopy (EELS) was also carried out for elemental mapping of the AlGaN heterostructure and shown in Figure 5-5 (c)-(e). An Al-rich core-shell configuration was observed. The underlying growth mechanism is directly related to the incorporation of Al and Ga adatoms and growth conditions. At elevated temperatures, such as the growth temperatures used in this study, the Ga adatom diffusion length is significantly larger than that of Al adatom, forming Ga-rich core of the nanowire. Simultaneously, a large number of Al adatoms get incorporated directly on the sidewalls, resulting in the formation of an Al-rich shell on the nanowire sidewalls. It is worthwhile mentioning that in

these studies, due to the instability of the Al effusion cell, the top AlGaN segment has higher Al composition that the lower AlGaN cladding layer.

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Chapter 6 Molecular Beam Epitaxial Growth and Characterization of AlN Nanowall Deep UV Light Emitting Diodes

In contrast to spontaneously formed random nanowires, nanowall structure can be defined by electron beam lithography with well-controlled dimension, which makes it suited for large area device fabrication process and light extraction from the sidewall. This chapter^{*} will investigate into the growth and properties of AlN nanowall structure and correlate the advantages of nanowalls with nanowires.

Abstract

We have demonstrated large area AlN nanowall light emitting diodes grown on sapphire substrate, which operates at 214 nm. Through detailed temperature and power dependent photoluminescence measurements and rate equation analysis, a relatively high internal quantum efficiency (~60%) was derived for AlN nanowall structures at room-temperature. A consistent blueshift in the emission wavelengths was measured with decreasing nanowall widths, due to the reduced tensile strain distribution. The devices exhibit excellent current-voltage characteristics, including a turn-on voltage of 7 V and current densities > 170 A/cm² at 12 V.

Manuscript

Due to the unique large direct bandgap (~6.1 eV), AlN has attracted significant attention for application in deep ultraviolet (UV) photonics, including light emitting diodes (LEDs), lasers,

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photodetectors and waveguides, which are important for a broad range of applications, such as sterilization, water purification, medical treatment, and Raman spectroscopy [1-9]. To date, however, the efficiency of AlN or Al-rich AlGaN deep UV LEDs is significantly lower than that of GaN-based blue LEDs. For example, for LEDs operating in the wavelength range of <240 nm, the external quantum efficiency is well below 1% [10, 11]. The underlying challenges include the formation of large densities of defects and dislocations in the device active region during AlN heteroepitaxy [12-15], the extremely inefficient p-type conduction, and the poor light extraction efficiency. Mg has been utilized as p-type dopants in III-nitrides, but its activation energy is prohibitively large (up to 600 meV) in AlN^{1,13}, leading to extremely low doping efficiency at roomtemperature. Moreover, attempts to enhance Mg concentrations in AlGaN epilayers often leads to undesired strain effects and the formation of extensive defects including N vacancies, which provide strong compensation effects [16-19]. Consequently, previously reported c-plane AlN planar LEDs have a very high turn-on voltage of over 20 V [1]. Furthermore, because the light emission from AlN is TM polarized ($\mathbf{E} \parallel \mathbf{c}$), the majority of photon emission is beyond the cone for light extraction, leading to very low light extraction efficiency for conventional AlN and Alrich AlGaN LEDs [2, 3, 20].

Recent studies suggested that these critical challenges can be potentially addressed by exploiting Al(Ga)N nanostructures [21-23]. Significantly reduced strain distribution and a minimal level of defect formation have been demonstrated in AlGaN nanostructures, due to the efficient surface strain relaxation. More recently, it has been discovered that the Al-substitutional Mg-dopant formation energy is drastically reduced in AlN nanowires, compared to epilayers, leading to significantly enhanced Mg-dopant incorporation. At room-temperature, free hole concentration up to 6×10^{17} cm⁻³ have been measured in AlN nanowires [24], compared to the reported values of ~

 10^{11} cm⁻³ in Mg-doped AlN epilayers [1, 25]. More recently, AlGaN nanowire LEDs and laser diodes operating in the UV-C band (< 280 nm) have been demonstrated [21, 26-29]. However, due to the lack of deep UV transparent electrode, relatively thick metal contact layers are deposited on the nanowire surface to enhance current spreading, which severely limits the light extraction efficiency [30].

In this chapter, we have investigated the molecular beam epitaxy (MBE) and performance characteristics of AlN nanowall LEDs operating at 214 nm. Compared to conventional nanowires, nanowall structures exhibit well controlled geometry and are ideally suited for the fabrication of large area devices. Moreover, TM polarized light emission can be efficiently extracted from the lateral surface of nanowall structures, schematically shown in Figure 6-1 (a). Detailed temperaturedependent photoluminescence (PL) measurements and rate equation analysis suggest the internal quantum efficiency (IQE) of AlN nanowalls can reach up to 60% at room-temperature. It is observed that the electrical and optical performance of AlN nanowall LEDs depends critically on the width of the wall structures. The emission wavelengths of AlN nanowall LEDs showed a consistent blueshift with decreasing nanowall widths, which is explained by the reduced tensile strain distribution. Highly efficient current injection is achieved in AlN nanowall LED structures with smaller widths, due to the significantly enhanced Mg dopant incorporation. For AlN nanowall LEDs with wall widths of 410 nm, the turn on voltage is < 7 V, and current densities > 170 A/cm² is obtained at 12 V, which are significantly better than conventional c-plane AlN epilayer LEDs.¹ Our studies have shown the extraordinary potential of nanowall structures as a building block for achieving high performance deep UV optoelectronic devices.

In this study, GaN nanowall structures were first created on n-type GaN template on sapphire substrate using e-beam lithography and dry etching techniques. The wall widths were varied in the



Figure 6-1 (a) Schematic for the efficient extraction of TM polarized light from the nanowall structures (top), compared to the poor light extraction in the planar structure (bottom). The black arrows indicate the light polarization. (b) Schematic of an AlN nanowall LED grown on GaN template on sapphire substrate. The device heterostructure is shown in the inset. (c) and (d) SEM images of AlN nanowall structures.

range of 100 nm to 1 μ m. The surface of GaN nanowalls was smoothened by wet etching in KOH solution [31]. Schematically shown in Figure 6-1 (b), AlN was then grown on the GaN nanowall structures using a Veeco Gen II MBE system equipped with a radio frequency plasma-assisted nitrogen source. The growth conditions included an Al flux of 3.2×10^{-8} Torr, nitrogen flow rate of 0.22 sccm and plasma power of 350 W, and growth temperature of 800 °C. Scanning electron microscopy (SEM) images of AlN nanowalls are shown in Figure 6-1 (c) and (d). It is seen that AlN nanowalls exhibit smooth surface morphology on both the top and lateral surfaces, due to the efficient surface stress relaxation, whereas materials deposited in the regions between the

nanowalls showed rough surface with the presence of dips and voids. The vertical and lateral growth rates for AlN nanowall structures were ~1 nm/min and 0.2 nm/min, respectively. The thickness of the grown AlN layer was ~120 nm. Mg-doped AlN nanowalls with Mg flux of 3.70×10^{-8} Torr were also grown and characterized.

Optical properties of AlN nanowall structures were studied using temperature and powerdependent photoluminescence measurements. A pulsed 193 nm ArF excimer laser was used as the excitation source. Shown in the inset Figure 6-2 (a) is the PL spectrum of AlN nanowalls with wall widths ~410 nm. A distinct emission peak at ~210 nm from free exciton emission was measured



Figure 6-2 (a) Plot of the internal quantum efficiency (IQE) (left axis) and relative external quantum efficiency (right axis) of an AlN nanowall structure vs. carrier generation rate measured at different temperatures. PL spectrum of the AlN nanowall structure measured at room-temperature is shown in the inset. The arrows indicate phonon sideband emissions. (b) PL spectra of Mg-doped AlN nanowall structures measured under excitation powers varying from 50 mW to 300 mW at room-temperature.

at room-temperature. In addition, two phonon replicas, with energy separation ~100 and 200 meV from the free exciton emission, respectively, were also clearly measured, which are indicated by the arrows shown in the inset of Figure 6-2 (a). The direct measurements of phonon sideband emission at room-temperature suggests superior material quality of the presented AlN nanowalls [32, 33]. Based on the energy separation between the phonon replicas and the excitonic emission, the phonon replicas are likely due to the interaction between surface optical (SO)-phonons and electrons [22].

The IQE was calculated by studying the PL spectra of the non-doped AlN nanowall samples at different temperatures and under different excitation powers using the following rate equations [34, 35].

$$G = AN + BN^2 + CN^3 \tag{6-1}$$

$$I = \theta B N^2 \tag{6-2}$$

$$\eta_i = I / (\theta G) \tag{6-3}$$

where G is the carrier generation rate, A is the Shockley–Read–Hall recombination coefficient, B is the radiative recombination coefficient, C is the Auger recombination coefficient, N is the carrier concentration, I is the measured PL intensity, and η_i is the IQE. θ is a constant and is determined by the optical setup. The generation rate G is derived from,

$$G = P\alpha(1-R) / (A_{\text{spot}}E_{\text{ph}})$$
(6-4)

where *P* is pump laser power, α is the absorption coefficient, *R* is the reflectivity, A_{spot} is the laser beam size on the sample, and E_{ph} is the photon energy. The reflectivity *R* is ~0.12, the spot size A_{spot} is ~0.09 mm², and the absorption coefficient α is ~3.87×10⁵ cm⁻¹ [36]. In this analysis, the Auger recombination coefficient *C* is assumed to negligible, due to the large bandgap of AlN [37]. By fitting the calculated generation rate as a function of the measured PL intensity *I*, we can obtain θ and $A/\sqrt{\theta B}$. IQE can be further calculated from Eqn. (6-3). It is important to note that, in this rate equation analysis, the derived IQE is independent of the values *A* and *B* and has been considered as a relatively accurate reflection of the true quantum efficiency of the studied materials.[35] Shown in Figure 6-2 (a) is the calculated IQE vs. carrier generation rate and the measured relative external quantum efficiency (EQE $\propto I/G$). The simulation agrees well with the experimental results in the wide temperature range of 15 K to 300 K and for various carrier generation rates. It is seen that the IQE exhibited an increasing trend with increasing excitation and decreasing temperature. At room temperature, it can reach up to 60%, suggesting superior material quality [22]. A list of the derived *A* and *B* parameters is shown in Table I.

Table 6-1 The derived A and B parameters of AlN nanowall structures at different temperatures.

Temperature (K)	$A (10^8 \text{ s}^{-1})$	$B (10^{-17} \text{ m}^3 \text{s}^{-1})$
15	8.06	7.60
100	9.36	4.37
200	10.52	2.66
300	12.78	1.90

Strong photoluminescence emission at room-temperature was also measured for Mg-doped AlN nanowall structures. Shown in Figure 6-2 (b) are the PL spectra for nanowall arrays with 410 nm widths under varying excitation powers. Besides the free exciton emission peak at ~210 nm, there is another peak at 234 nm due to Mg-acceptor related transition [1, 25, 38]. The shoulder at ~250

nm of the emission spectra is attributed to transitions of electrons bound to nitrogen vacancy with triple positive charges (V_N^{3+}) and Mg acceptors [16].

We have subsequently investigated the fabrication and characteristics of AlN nanowall LEDs. Schematically shown in the inset of Figure 6-1 (b), the AlN nanowall LED structure consists of Si-doped AlN, non-doped AlN, and Mg-doped AlN segments, with each layer approximately 40 nm thick. A 3 nm p-GaN layer was deposited on the top surface to serve as p-contact. The growth conditions were similar to those described above. The fabrication of AlN nanowall LED is briefly described. A 300 nm thick SiO_x layer was first deposited on the nanowall structures for surface passivation and electrical isolation. Subsequently, part of the SiO_x layer was selectively etched using standard photolithography and wet etching techniques. p-Metal contact consisting of Ni/Au (15nm/15nm) was then deposited on the top surface of nanowall structures by using e-beam lithography and metallization. Ti/Au n-metal contact layers were deposited on n-GaN buffer layer using photolithography and dry etching process.

Current-voltage characteristics of AlN nanowall LEDs were measured under continuous wave biasing conditions at room-temperature. Shown in Figure 6-3 (a) are the current-voltage characteristics of AlN nanowall LEDs with wall widths of 410 nm, 640 nm, and 860 nm, respectively. The length of each nanowall structure in these LED devices is 120 μ m. The devices exhibit excellent current-voltage characteristics, with turn-on voltages ~ 7 V, which is significantly smaller than that of previously reported c-plane AlN epilayer LEDs [39]. It is also observed that AlN nanowall LEDs of narrower widths showed much higher injection current density. This is due to the reduced defect distribution and more efficient Mg-dopant incorporation in AlN nanowall arrays with narrower widths. Previously it has been demonstrated that the formation energy for Al-substitutional Mg-dopant formation is drastically reduced in AlN nanostructures, compared to

epilayers, due to the efficient surface stress relaxation [21, 40]. The large concentrations of Mg dopants leads to the formation of Mg impurity band in AlN nanowalls as well as significantly broadened acceptor level distributions [24], evidenced by the broad PL spectral linewidth associated with Mg acceptor transition shown in Figure 6-2 (b). Consequently, a portion of Mg acceptors have significantly reduced activation energy, schematically shown in Figure 6-3 (b), thereby enabling efficient hole conduction in AlN that was previously difficult to achieve in AlN epilayers. Shown in Figure 6-3 (a), the current density can reach over 170 A/cm² at 12 V at room-temperature.



Figure 6-3 (a) Current-voltage characteristics of AlN nanowall LEDs with different wall widths measured at room-temperature. (b) Schematic illustration of the formation of an Mg impurity band and the reduced activation energy for a portion of the Mg acceptors, due to the significantly broadened Mg acceptor level distribution.

AlN nanowall LEDs exhibit strong electroluminescence (EL) emission. Shown in Fig. 4(a) are the EL spectra of AlN nanowall devices with a wall widths of 410 nm measured at room-temperature, which is centered at 214 nm. Variations of the integrated EL intensity vs. current are shown in

Figure 6-4 (b). A maximum output power of 70 nW was measured, which was primarily limited by the light extraction and electron overflow effect. It is expected that there exists an optimum wall width for achieving maximum quantum efficiency and output power, which is currently being investigated. In contrast to EL peak position at ~210 nm for previously reported strain-free AlN nanowire LEDs [1, 20, 21], the peak position at 214 nm indicates that there is a small amount of tensile strain for AlN nanowalls grown on GaN. It has been previously reported that the presence of tensile strain in AlN epilayers grown on Si substrates can cause the free exciton transition to redshift by 0.07 to 0.1 eV, compared to the strain-free AlN epilayers [41, 42]. Based on studies of the effect of strain distribution on excitonic transition in AlN [41], the emission peak of 214 nm corresponds to a uniaxial strain of -0.0038. We have further measured the emission characteristics of AlN LEDs with various nanowall widths. Illustrated in Figure 6-4 (c), there is a consistent blueshift in the emission wavelengths with decreasing nanowall widths, which is well explained by the reduced tensile strain distribution in nanowall structures with smaller widths. The corresponding tensile strain is further analyzed and is shown on the top axis of Figure 6-4 (c).



Figure 6-4 (a) Electroluminescence (EL) spectrum of AlN LEDs with a wall width of 410 nm. (b) Variations of integrated light intensity vs. current density. (c) Variations of the EL emission peak vs. nanowall widths. The corresponding tensile strain distribution is shown on the top axis.

In summary, we have demonstrated AIN nanowall LEDs that can exhibit significantly improved optical and electrical performance, compared to conventional AIN epilayer devices. Detailed temperature and power-dependent photoluminescence measurements and rate equation analysis suggested that the AIN nanowalls exhibited relatively high internal quantum efficiency (~60%) at room-temperature. It is further observed that AIN nanowall LEDs with smaller wall widths exhibited a consistent blue shift in the emission wavelengths, due to the reduced strain distribution, and more efficient current injection, due to the significantly enhanced Mg-dopant incorporation. Such AIN nanowall devices are well suited for large area, high power applications. It is envisioned that Al(Ga)N and In(Ga)N nanowall heterostructures will emerge as a viable architecture for achieving high efficiency deep UV, visible and infrared photonic devices, including LEDs, laser diodes, photodetectors, solar cells and solar fuel devices, as well as high frequency and high power transistors.

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Chapter 7 Ultralow Threshold, Electrically Injected AlGaN Nanowire Ultraviolet Lasers on Si Operating at Low Temperature

Thanks to the advantages of nanowires that have been discussed in this thesis, nanowires are not only beneficial for LEDs but also ideal building blocks for laser devices. In this chapter^{*}, we will perform a simulation study on the Anderson localization of light as a way to provide optical feedback in random nanowires and identify the geometry parameter range that is favorable for light confinement. The growth of the random nanowire laser will be presented and the structural, electrical, and optical characterizations will be discussed.

Abstract

Ultraviolet laser radiation has been adopted in a wide range of applications as diverse as water purification, flexible display, data storage, sterilization, diagnosis, and bioagent detection [1-3]. Success in developing semiconductor-based, compact ultraviolet laser sources, however, has been extremely limited. Here we report that defect-free, disordered AlGaN core-shell nanowire arrays, formed directly on a Si substrate, can be used to achieve highly stable, electrically pumped lasers across the entire ultraviolet AII (UV-AII) band ($\sim 320 - 340$ nm) at low temperature. The laser threshold is in the range of tens of amps per centimetre squared, which is nearly three orders of magnitude lower than those of previously reported quantum-well lasers [4-6]. This work also reports the first demonstration of electrically injected AlGaN-based ultraviolet lasers

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monolithically grown on a Si substrate, and offers a new avenue for achieving semiconductor lasers in the ultraviolet B (UV-B) (280–320 nm) and ultraviolet C (UV-C) (<280 nm) bands.

7.1 Main text

Compared with the conventional excimer ultraviolet lasers or frequency doubled/tripled solid-state lasers, AlGaN-based ultraviolet devices offer an enormous number of advantages, which include high efficiency, small size and low power consumption. Progress in this field, however, has been severely limited by the large dislocation densities and residual strain introduced during the growth of AlGaN epitaxial layers, which can induce wafer bowing and cracking and lead to unacceptably high optical cavity loss. Consequently, the operation wavelengths of electrically injected ultraviolet laser diodes have been limited to the ultraviolet AI band (\sim 340–400 nm), with the threshold current density in the range of 10,000 A cm⁻² or higher [4-10], in spite of intensive studies on improving the optical gain of AlGaN with a high Al content [11-15]. Alternatively, nearly defect-free single-nanowire laser [16, 17] or nanowire laser arrays [18-22] have been investigated extensively. Owing to the complicated fabrication and/or growth process, an electrically injected nanowire ultraviolet laser has hitherto not been realized, severely limiting their practical applications. Here, by exploiting the Anderson localization of light [23-25] in selforganized AlGaN/GaN nanowire heterostructures spontaneously formed on the Si substrate, we demonstrate ultralow-threshold lasing in the entire UV-AII band, the shortest wavelengths ever reported for any electrically injected semiconductor lasers. Such a lithography-free process for fabricating defect-free nanowire laser arrays on large-area Si substrates provides many attractive advantages, including low cost and ultralow power consumption, and enables a new generation of electrically injected semiconductor lasers with operation wavelengths far beyond those previously possible.

Anderson localization relies on the use of multiple scattering in a random cavity. The challenges in the implementation in practical devices are directly related to the fabrication of such optical cavities in a low-cost, scalable and controllable process [26-30]. In this work, we first studied the design of lithography-free disordered nanowire arrays required for a stable lasing operation in the UV-AII band, schematically shown in Figure 7-1 (a), and we further show that these requirements can be achieved readily by self-organized AlGaN nanowire arrays formed on a Si substrate using radiofrequency plasma-assisted molecular beam epitaxy (MBE). It is known that the formation of high-quality factor (Q) random lasing is strongly related to the strength of light localization in the random cavity system, which is governed by the orientation, size and filling fraction of the nanostructures [26]. For a vertically aligned, randomly distributed, subwavelength-scale nanowire array, the density of nanowires plays a crucial role in sustaining a random lasing action. The low density of nanowire structures would not support random lasing, and the scattering mean free path has to be optimized. We performed a detailed two-dimensional (2D) simulation to identify the dependence of the optical resonance (wavelength \sim 330 nm) on the nanowire diameter and filling factor, as shown in Figure 7-1 (b) (also see Supplementary Section 1). In this simulation, a 15% diameter variation is assumed, based on the typical variations of self-organized GaN nanowire structures. The probabilities of forming a high-Q cavity versus the average nanowire diameter and filling factor are shown in Figure 7-1 (b). It is clear that high-Q cavities can form with a high probability in disordered nanowire arrays with average diameters of \sim 70–75 nm and filling factors of ~30%. Such randomly distributed nanowires mimic the configuration obtained by selforganized nanowire arrays directly on the Si substrate, described below. The simulated profile of the mode in one random cavity with Q as high as 20,000 is shown in Figure 7-1 (c).



Figure 7-1 Simulation of AlGaN nanowire random cavity and optical and structural characterization. (a) Schematic diagram illustrating the formation of a closed-loop path inside AlGaN nanowire arrays; red arrows denote the photon path. (b) Probability of forming high-Q cavity versus filling factors and diameters of nanowires. (c) Simulation result showing the profile of the electric field E_z for a high-Q cavity; black hexagons represent spontaneously formed nanowires. (d) Schematic of AlGaN nanowire double-heterostructures. (e) PL spectrum measured at room temperature. (f) A 45° tilted SEM image of nanowire arrays grown on a Si substrate.

To achieve optical confinement along the vertical direction, AlGaN nanowire doubleheterostructures were designed. Schematically shown in Figure 7-1 (d), the undoped AlGaN active region is sandwiched between n-AlGaN and p-AlGaN cladding layers. The thicknesses of the AlGaN active region and the n-AlGaN and p-AlGaN layers are ~50, 150 and 150 nm, respectively. The average Al compositions in the active region and cladding layers are estimated to be in the range ~30% and 56%, respectively (see Supplementary Section 2). Such AlGaN nanowire doubleheterostructures were grown on Si-doped GaN nanowire templates on an n-type Si(111) substrate by MBE without using any external metal catalyst (see Methods). A thin (~25 nm) GaN:Mg layer was grown as the top contact layer. The nanowire heterostructures exhibit strong photoluminescence (PL) emission at room temperature, shown in Figure 7-1 (e). Extensive growth optimization was performed to achieve AlGaN nanowire arrays that can meet the aforementioned design requirements, in terms of both the nanowire diameter and filling factor. Structural properties of such nanowire arrays are first characterized by scanning electron microscopy (SEM). Shown in Figure 7-1 (f) is an SEM image taken at a 45° angle. It is seen that the nanowires are aligned vertically on the Si substrate and exhibit a high degree of size and height uniformity. The average filling factor is expected to be smaller than it appears in the SEM image because of the tapered nanowire morphology (described below). More detailed studies further confirm that the average spacing between nanowires is much less than the emission wavelength, and thus enables recurrent multiple scattering inside nanowires (see Supplementary Section 4).



Figure 7-2 Characterization of a single AlGaN nanowire. (a) High-resolution TEM image taken from the interface between a *p*-AlGaN cladding layer and a *p*-GaN contact layer. The arrow indicates the nanowire growth direction. The dark region corresponds to *p*-GaN and the bright region corresponds to *p*-AlGaN. (b) HAADF image of a single AlGaN nanowire. The arrow indicates the growth direction. (c) Al and Ga element mapping for the selected region in (b). It is clear that in the active region Ga content is increased, whereas the Al content is decreased. (d) The EDXS line scan across the active region along the axial direction, showing the Al and Ga compositional changes in the active region. (e) The EDXS line scan along the radial direction of the active region indicates the presence of Al-rich AlGaN shells (Al, green curve; Ga, blue curve). The red lines in the insets of (d) and (e) denote where the EDXS line scans were performed.

We further performed structural studies of AlGaN nanowire double-heterostructures by transmission electron microscopy (TEM). A high-resolution TEM image taken from the interface between the p-AlGaN cladding layer and the p-GaN contact layer is shown in Figure 7-2 (a). It is clear that both the p-AlGaN and p-GaN regions are free of stacking faults and misfit dislocations. More importantly, a sharp heterointerface can be clearly observed. Detailed high-resolution TEM studies further confirm that the whole AlGaN nanowire is free of extended defects and dislocations. Elemental mapping was carried out in the scanning transmission electron microscopy (STEM) mode. Illustrated in Figure 7-2 (b) is a high angle annular dark field (HAADF) image, which clearly shows that the nanowire is inversely tapered, that is, the diameter increases along the growth direction and becomes nearly constant in the top region. Consequently, this leads to a strong photon confinement in the active region of the nanowire laser structures and any optical loss through the Si substrate is greatly minimized (see Supplementary Section 3). Al and Ga element mapping is shown in Figure 7-2 (c) in pseudo colours, with the mapping region marked in Figure 7-2 (b). It is clear that in the active region the Ga content is increased whereas the Al content is decreased. This Al/Ga composition change is further confirmed by the energy-dispersive X-ray spectrometry (EDXS) line scan across the active region along the axial direction, illustrated in Figure 7-2 (d). In addition, the EDXS line scan across the active region but along the radial direction indicates the presence of Al-rich AlGaN shells (Figure 7-2 (e)). Such a spontaneous formation of Al-rich AlGaN shells can be ascribed to the much slower Al adatom migration compared to that of Ga adatoms. The enhanced Al composition in the near-surface region can lead to a strong carrier confinement, and thereby significantly reduce nonradiative surface recombination and enhance the carrier-injection efficiency in the active region of the nanowire laser [31].

Subsequently, nanowire light-emitting devices were fabricated using standard photolithography, surface passivation and planarization, and contact-metallization techniques (see Methods). The current-voltage characteristics are shown in Figure 7-3 (a), and a very low leakage current under a reverse bias is indicated in the inset. The lasing characteristics of AlGaN nanowires were investigated by electrical injection under a continuous-wave operation at various temperatures. Figure 7-3 (b) shows the electroluminescence (EL) spectra of AlGaN nanowire devices measured at 6 K. Under varying current densities, it was observed that sharp peaks were superimposed on the broad spontaneous emission background of the AlGaN active region. Two discrete peaks centred at 332.7 nm and 334.1 nm were measured. As the latter peak is clearly dominant, its threshold and linewidth properties were analysed (analysis of the lasing peak at 332.7 nm is shown in Supplementary Section 6). Figure 7-3 (c) and (d) show the plots of the integrated intensity and linewidth of the dominant peak as a function of the current density, respectively. A nonlinear increase of the emission intensity and spectral narrowing near the threshold provides unambiguous evidence for the achievement of lasing. At the lasing threshold, the spectral linewidth is as narrow as 0.2 nm, which is limited by the spectral resolution of the set-up. The lasing threshold is estimated to be ~12 A cm⁻², which was derived by taking into account the nanowire structure, filling factor and active lasing area ($\sim 10 \ \mu m \times 10 \ \mu m$). It is nearly three orders of magnitude lower than those of previously reported GaN-based ultraviolet lasers [4-6]. The output power is estimated to be $\sim 2 \mu W$ at an injection current of 30 A cm⁻². Figure 7-3 (e) shows the plot of peak positions as a function of current densities. It was observed that the lasing wavelengths remain virtually unchanged when the injection current increases from threshold to ~ 6 times above threshold, which suggests that the lasing emission is dominated by the extremely stable excitonic transition rather than by the emission related to electron-hole plasma. The ultralow threshold is attributed to the

high-Q optical resonance, the nearly defect-free AlGaN nanowires, the drastically reduced nonradiative surface recombination offered by the AlGaN core–shell structures and possibly the strong quantum-confinement effect related to the nanometric compositional fluctuations of the active region [32, 33].



Figure 7-3 Device performance and characterization. (a) I-V characteristics of the AlGaN nanowire laser; the inset shows the I-V curve on a semi-log scale. (b) Emission spectra measured at 6 K under different current densities. The black arrow denotes that the current density increases from 7.7 A cm⁻² to 22 A cm⁻² and the inset shows an enlarged view of the lasing spectra. (c) and (d) Integrated intensity (c) and linewidth (d) of the lasing peak at 334.1 nm as a function of injection-current density. (e) Plot of peak position versus current density. (f) EL spectra measured at different operation temperatures.

Temperature-dependent measurements were also carried out for a fixed current density of ~27 A cm⁻². When the temperature rises from 6 to 100 K, both discrete sharp peaks exhibit redshifts of ~0.7 nm, shown in Figure 7-3 (f). The redshift can be attributed to two main factors. With the increase in temperature, the bandgap shrinkage of the AlGaN active region gives rise to a peak-gain shift. The other contributing factor is related to the refractive index change inside the random cavities because of the thermal effect. Analysis of the lasing performance at various temperatures is described in Supplementary Section 7.

As shown in the detailed modelling, the resonance cavity formed by disordered nanowire arrays can be tuned by rational design of the nanowire structures. In this regard, we performed extensive measurements and observed ultralow-threshold lasing in various device structures (see Supplementary Section 9). The emission wavelength can be tuned across the entire ultraviolet-AII band (~320 nm to 340 nm), the shortest wavelength ever reported for an electrically injected semiconductor laser. Also, we performed analyses that further confirmed the measured ultralow-threshold lasing was not caused by lasing from single nanowires (see Supplementary Section 8).

In summary, we have demonstrated that AlGaN core–shell nanowires can function as highly scattered random media to support a closed-loop mode by recurrent multiple scattering, which leads to ultralow-threshold electrically injected lasers in the wavelength range of ~320 to 340 nm on a Si substrate. This study effectively connects the concept of the Anderson localization of light and the self-organized formation of nanowires and provides a viable approach for the practical implementation of the elegant concept of random lasers in a low-cost, scalable and controllable process. It is expected that by further tuning the nanowire parameters, ultralow-threshold nanowire lasers across the entire UV-A, -B and -C spectral ranges could be achieved on a Si substrate for biochemical, sensing, communication and lighting applications.

7.2 Methods

Nanowire Laser Design and Simulation

Given that the nanowire diameter and operation wavelength are much smaller than the nanowire length, a 2D simulation was performed to find out the probability of forming a high-Q random cavity for AlGaN nanowire arrays. In this study, the nanowires were considered to be hexagonal. The crucial parameters for a random nanowire array are the average diameter d and the filling factor. The diameters were distributed randomly with a lower limit of 0.85d and an upper limit of 1.15d. The positions of the nanowires were also assumed to be distributed randomly. For any given combination of average nanowire diameter and filling factor, about 200 random nanowire arrays were generated and the possible modes around 330 nm were computed by the RF module of Comsol Multiphysics 4.3b. The optimal combination of filling factor and average diameter to achieve high-Q cavity modes was finally obtained, and provided guidance for the subsequent growth and characterization of nanowire laser structures.

Molecular Beam Epitaxial Growth

In this study, catalyst-free, vertically aligned AlGaN nanowire double-heterostructures were grown on two inch (5 cm) n-Si(111) substrates by a Veeco Gen II MBE system equipped with a radiofrequency plasma-assisted nitrogen source under nitrogen-rich conditions. Prior to the growth, the oxide on the Si surface was removed by hydrofluoric acid (10%) and further thermally cleaned *in situ* at ~770 °C. The RHEED (reflection high-energy electron diffraction) pattern of the Si substrate prior to nanowire growth is shown in Supplementary Section 2(Supplementary Fig. 2a). During the growth process, the nitrogen flow rate was kept at 1.0 standard cubic centimetre per minute, with a forward plasma power of ~350 W. GaN nanowires were grown at ~750 °C, and the AlGaN cladding segments and active region were grown at
relatively high temperatures of 800 °C. The active region and p- and n-cladding layers were grown with Al beam equivalent pressures (BEPs) of $\sim 1.30 \times 10^{-8}$ Torr and $\sim 3.93 \times 10^{-8}$ Torr, respectively, with a constant Ga BEP of $\sim 2.75 \times 10^{-8}$ Torr. The Si-doping level in the n-cladding layer was estimated to be $\sim 5 \times 10^{17}$ cm⁻³.

Structural Characterization

The SEM images were taken using a Hitachi S-4700 system. The experiments were performed with a 45° angle. An accelerating voltage of 10 kV and a current of 10 μ A were used for imaging. The detector was cooled with liquid nitrogen. HAADF and EDXS were performed in the STEM mode of a Tecnai G² F20 S/TEM system, which was equipped with a Gatan 4 k × 4 k CCD (charge-coupled device) camera. The operation voltage was 200 kV. The cold finger was cooled with liquid nitrogen to avoid contamination. Curve smoothing was performed for the EDXS data.

Device Fabrication

The electrically injected devices were fabricated using standard microfabrication procedures. Prior to the deposition of metal contacts, the air voids between adjacent nanowires were filled with polyimide to isolate the p- and n-type faces electrically. The top p-type surfaces of the nanowires were exposed by the etch-back process using oxygen plasma. The mesa region was then defined by the photolithography process, and p- and n-contacts were deposited using an e-beam evaporator followed by rapid thermal annealing at 550 °C for one minute. A detailed fabrication process flow is shown in Supplementary Section 5.

Device Characterization

PL measurements were carried out at room temperature using a 266 nm diode-pumped solid-state laser. For the EL measurement, the wire-bonded device was mounted inside the cryostat with the

quartz top cover and the cooling system was fixed on a motorized x-y stage (Aerotech's ANT130-XY-ULTRA), which provided precise mapping over about a $10 \times 10 \ \mu\text{m}^2$ lasing region. The emitted signals were collected by an ultraviolet objective and detected by a liquid-nitrogen cooled CCD attached to a 550 mm spectrograph with 1,200 grooves per millimetre, which offered a spectral resolution of ~0.14 nm. The temperature-dependent measurements were performed in a temperature-controlled liquid helium cryostat.

7.3 Supplementary Information

S1. Modeling of the optical cavity resonance modes

Light is scattered among nanowires after being emitted. Under proper configuration, a close loop can form and result in random cavity with high quality factor. In order to reveal the possibility of forming high quality factor cavity in the wavelength range of around 330 nm, the position, diameter, and orientation for each nanowire are randomly generated with certain deviations. The filling factor plays a role in generating the random positions, and the filling factor is correlated with our grown nanowire structures. Some possible modes are calculated and one example cavity is shown in Figure 7-4 (a) with a quality factor of 20,000 at 334 nm. The light grey regions are nanowires and the dark grey region is air. The electric field $E_{\parallel \text{c-axis}}$, which is perpendicular to the page, is shown in Figure 7-4 (b).



Figure 7-4 (a) A microcavity formed by randomly distributed nanowires. Light grey regions denote nanowires and dark grey region denotes air. (b) Profile of the electric field $E_{\parallel c-axis}$.

S2. Estimate of the Al composition of AlGaN nanowires

During the growth of the laser active region and cladding layers, the Al beam equivalent pressure (BEP) was ~1.30 × 10⁻⁸ Torr and ~3.93×10⁻⁸ Torr, respectively. The Ga BEP was ~ 2.75×10⁻⁸ Torr. In this growth, no surfactant or external metal catalyst was utilised. The RHEED image of the Si(111) substrate after the thermal oxide desorption at 770 °C is shown in Figure 7-5 (a). From the photoluminescence (PL) emission spectra, we can estimate Al composition for the active region, which is in the range of 12 % to 25 % for peak emission wavelengths in the range of 340 to 320 nm, i.e. the UVA-II band, if the quantum confinement effect related to the local compositional variation in the active region is not considered. However, due to the presence of Al-rich shell surrounding the active region, the average Al composition in the active region is estimated to be 30 %. Based on the Al and Ga flux ratios used in the growth of the different layers, we further estimated the compositions for the AlGaN cladding layer is ~56 %. It is worthwhile mentioning that in self-organised AlGaN nanowires, spontaneous core-shell structures are formed, which lead

to the presence of Al-rich shell region. Such core-shell structures are beneficial in suppressing nonradiative surface recombination.



(b)	GaN:Mg	
	AlGaN:Mg	
	AlGaN	
	AlGaN:Si	
	GaN:Si	
	Si(111)	

Figure 7-5 (a) RHEED image of the Si (111) substrate after thermal oxide desorption, showing the 7×7 surface reconstruction pattern. (b) Schematic diagram illustrating various layers in nanowires. The average Al compositions of active region (AlGaN) and *p*- and *n*-cladding layers (AlGaN:Mg and AlGaN:Si) are estimated to be 30 % and 56 % respectively.

S3. On the optical confinement in the vertical direction of the nanowire structures

Based on the TEM image (see Figure 7-2 (b) in the main text), AlGaN nanowires grown on Si exhibit inversely tapered geometry, i.e. the diameter increases along the growth direction. Therefore, taking into account the air gap among nanowires, the effective refractive index has a minimum at the nanowire bottom (nanowire/substrate interface). Furthermore, with lower Al composition than the barrier, the active region has a higher refractive index, thereby leading to strong light confinement in the active region of the nanowires. In the simulation, the diameter at the bottom is approximated to be half of the diameter of the top part. The calculated effective refractive index profile and the resulting strong optical confinement along the nanowire growth direction are schematically shown in Figure 7-6.



Figure 7-6 Variations of the effective refractive index as a function of distance from the substrate/nanowire interface (right axis), which contributes to the strong optical confinement along the nanowire growth direction. The simulated electric field perpendicular to the *c*-axis shows strong confinement around the active region of the nanowires. Below 0 nm is silicon substrate and above 650 nm is air.

S4. Structural characterization of the nanowire size distribution



Figure 7-7 Top-view FE-SEM images showing the size variation of nanowires.

The scale bars represent 500 nm in length.

The surface morphologies of nanowire cavity structures are captured using field-emission scanning electron microscopy (FE-SEM), shown in Figure 7-7. The top-view image indicates that the

AlGaN core-shell nanowires with lateral sizes ranging from 70 to 90 nm are randomly distributed on Si substrate. Due to the tapered structure, the average filling factor is expected to be smaller than that shown in the SEM images in Figure 7-7.





Figure 7-8 Schematic diagrams illustrating the fabrication process. (a) Selforganised AlGaN nanowire arrays formed on Si substrate using radio frequency plasma-assisted molecular beam epitaxy. (b) Nanowires planarised using polyimide resist by spin-coating. (c) Dry etching process to reveal the top surfaces of nanowires. (d) Deposition of metallic contact grids.

The air-gaps between adjacent nanowires were firstly filled with polyimide resist by spin-coating process to passivate the nanowire surface and planarise the device, as illustrated in Figure 7-8 (b). An etch-back process using reactive ion etching was performed to expose the top surfaces of nanowires, as described in Figure 7-8 (c). The patterns of *p*-type metal contact corresponding to mesa emission area were then photo-lithographically defined. Prior to the deposition of the *p*-type metal contact, the entire sample was immersed into a bath of 49 % hydrochloric acid for 1 min to remove any oxidised layer on the *p*-GaN surface. Subsequently, a Ni/Au (5 nm/5 nm) *p*-type and Ti/Au (20 nm/120 nm) *n*-type contacts were deposited on the top planarised surface and the backside of the substrate respectively by electron beam evaporation, followed by thermal

annealing at 550 °C for 1 min in N₂ ambient. The resultant device structure is depicted in Figure 7-8 (d).



S6. Lasing characteristics of the mode at 332.7 nm

Figure 7-9 (a) EL spectra measured under various injection currents; the black arrow denotes that the current density increases from 7.7 A/cm² to 22 A/cm². The emission peak indicated by the green arrow is analyzed. (b) Integrated intensity and (c) linewidth of the lasing peak at 332.7 nm as a function of injection current density. The red lines in (b) are guide to the eye.

As shown in Figure 7-9 (a), two narrow emission peaks are measured. Characterization of the dominant peak is described in the main text. Detailed analysis also confirms the mode at 332.7 nm exhibit lasing properties. Shown in Figure 7-9 (b), the intensity exhibits a nonlinear increase with injection current, and the lasing threshold is estimated to be $\sim 16 \text{ A/cm}^2$. Lasing is further confirmed by the linewidth reduction at the threshold current, shown in Figure 7-9 (c).

S7. Temperature dependent lasing characteristics of AlGaN nanowire lasers

The random laser operating at 80 K is characterised, illustrated in Figure 7-10. The threshold current density was measured to be in the range of 10 - 15 A/cm² for the dominant emission peak, and the spectral linewidth above threshold is ~ 0.3 nm. The lasing peaks were measured up to ~

120 K. The absence of lasing above 120 K is likely related to the enhanced nonradiative recombination and reduced optical confinement of the closed-loop cavity at higher operating temperature [34, 35].



(b) Integrated output intensity and (c) linewidth vs. injection current density for the peak at 334.5 nm. The red lines in (b) are guide to the eye.

S8. On the possibility of lasing from single nanowire

Fabry–Pérot cavity mode has been commonly reported as the lasing mechanism for single nanowire lasers, attributed to the optical confinement along the wire-geometry with the natural facets [17, 36]. However, in this work, the vertical resonant mode is unlikely to appear since the bottom GaN segment and Si substrate would lead to severe absorption. Moreover, subwavelength scale nanowire structures are not expected to support whispering gallery mode which would experience high scattering losses in dense nanowire arrays due to the size non-uniformity and the coupling loss between adjacent nanowires. Therefore, the occurrence of the optical confinement within the individual nanowire can be ruled out. On the other hand, piles of randomly-distributed and vertically aligned nanowires can induce light scattering when light strikes at the boundary of

nanowires. AlGaN nanowires serving as the highly scattering media allows the formation of the closed-loop path of light inside a random laser by recurrent multiple scattering.



S9. Observation of other lasing actions in nanowires structures

Figure 7-11 EL spectra showing different lasing peaks in various AlGaN nanowire structures under electrical injection.

The spontaneously formed AlGaN nanowire arrays can provide different cavity paths with coherent optical feedback and are capable of supporting different closed-loop modes. To verify such random lasing behavior, we examined various AlGaN nanowire devices, and lasing emission wavelengths ranging from 319 nm to 335 nm were observed. Some of the representative spectra are shown in Figure 7-11.

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Chapter 8 Conclusion and Future Work

8.1 Conclusion

In this thesis, we have investigated AlGaN nanostructures as the approach to address the challenges of deep ultraviolet (UV) light emitting diodes (LEDs) and laser diodes (LDs) based on planar AlGaN structure, including the presence of large densities of dislocations, poor p-type doping, and low light extraction efficiency. Below is a summary of the conclusions from this thesis.

First, we obtained high hole concentrations up to 8.7×10^{17} cm⁻³ at room temperature in Mg-doped p-type AlGaN epilayers with Al composition around 60% by using molecular beam epitaxy (MBE). Relatively high hole mobilities between 10 and 17.2 cm²/(V·s) and a very low resistivity of 0.70 Ω ·cm were also be achieved at room temperature. Such charge carrier transport properties are attributed to the suppressed incorporation of undesirable impurity atoms under ultrahigh vacuum and the hydrogen-free growth environment, which confirms the advantage of MBE over MOCVD in achieving efficient p-type doping for high Al composition AlGaN.

Second, by using finite difference time domain (FDTD) simulation, we investigated the benefits of AlGaN nanowire photonic crystal in enhancing the light extraction efficiency (LEE) and internal quantum efficiency (IQE) for deep UV light emission with transverse magnetic (TM)-polarization due to the high Al composition. In contrast to light extraction efficiency below 10% in the planar structure, light extraction efficiency more than 90% can be expected by coupling in-plane direction TM-polarized emission to vertical emission in a properly designed photonic crystal for operation at the Γ point. Considering the absorption in p-AlGaN contact and metal contact grid, light extraction higher than 30% is still possible. A final EQE higher than 70% can be expected for AlGaN nanowire photonic crystal LEDs with high IQE. The strategy for low material quality is, however, different. For relative low material quality exhibiting low IQE, the Purcell effect in a photonic crystal designed for M point operation can be used to enhance IQE without much degradation in the light extraction efficiency. The photonic crystal structure also possesses reasonable tolerance for variations in the geometry dimension, which makes it experimentally feasible.

Third, the growth of LEDs at 279 nm based on uniform AlGaN nanowire arrays arranged in a regular triangular lattice was demonstrated, which can serve as the building block for nanowire photonic crystals. Nanowire geometry was controlled with a precision of ~ 20 nm and the AlGaN nanowire alloy composition was achieved across the full range by the selective area epitaxy technique. The formation of Al-rich shell was also demonstrated, leading to an IQE of 45% at room temperature due to reduced non-radiative surface recombination. The LED had a small turn-on voltage of ~ 4.4 V. The output power was around 0.93 W/cm² at a current density of 252 A/cm². This demonstration proved an approach to realize nanowire photonic crystal with arbitrary geometry and composition in order to engineer the structural, electrical, and optical properties of LEDs and LDs.

Fourth, the advantages of the nanowall structure were studied. Derived from detailed temperature and power-dependent PL measurement, the AlN nanowalls exhibited a high IQE of around 60% at room temperature. Compared to the incorporation of Mg in planar AlN structure, enhanced Mg acceptor incorporation has been confirmed from the PL spectra with a transition between conduction band and Mg acceptor levels, lower turn-on voltage of \sim 7V, and the wall-width dependent current-voltage characteristics. Reduced strain distribution in smaller wall width was observed from a blue shift of the emission wavelength with reduced wall width. Based on these characterizations, the nanowall structure exhibits similar advantages as the nanowire structure. It

is also important to note that the nonradiative surface recombination starts to dominate as the wall width decreases. Proper choice for the wall width and suppression of surface recombination by Alrich shell is critical for optimizing the device performance.

Lastly, electrically injected UV random lasers grown on silicon substrate were demonstrated. The lasing threshold is only a few tens of A/cm², which is three orders of magnitude lower than conventional AlGaN LDs. The unprecedented low lasing threshold is attributed to nearly defect-free material quality, suppressed surface non-radiative recombination, and optical feedback due to Anderson localization of light. This demonstration provides a new route to realize electrically injected low-cost deep UV lasers.

8.2 Future work

8.2.1 Nanowire photonic crystal surface emitting lasers

-			
	Design	Lattice constant (nm)	Diameter (nm)
-	Design 1	250	220
	Design 2	330	320
	Design 3	300	270

Table 8-1 Designs for photonic crystal surface emitting lasers at ~ 365 nm.

Based on the discussions in Chapters 4 and 5, it is readily possible to develop an AlGaN nanowire photonic crystal surface emitting laser working at the Γ point or M point. To start with, the target wavelength is ~365 nm. This wavelength can be realized by AlGaN/GaN quantum well or quantum dot structure. The Al composition is ~10% for the guiding layer and ~30% for the cladding layer. The guiding layer thickness is 150-200 nm and the cladding layer thickness is ~300 nm. Possible designs of the lattice constant and diameters for Γ point operation for are listed in the Table 8-1. The mode profiles within a unit cell for the three designs in Table 8-1 are shown in Figure 8-1, which all exhibit large overlap with the center of nanowire.



Figure 8-1 Mode profiles for (a) Design 1 (b) Design 2, and (c) Design 3.

In addition, it is possible to incorporate two different photonic crystals in one device as shown in Figure 8-2, where the inner photonic crystal I designed for M point has stronger optical feedback and the outer photonic crystal II designed for Γ point couples in-plane stimulated emission to vertical surface emission. By using photonic crystal I operating at M point as the active area, the structure can potentially exhibit reduced lasing threshold.



Figure 8-2 Schematic for a device incorporating two different photonic crystals.

8.2.2 AlGaN nanowire deep UV LEDs by selective area epitaxy

Though the LED operation wavelength in Chapter 5 is 279 nm, the approach presented in Chapter 5 can be applied to an AlGaN nanowire LED at ~240 nm as proposed in Chapter 4, which has dominant TM-polarized emission. Due to lower desorption rate of Al adatoms than Ga adatoms, the selective area epitaxy of AlN nanowire will be performed at a higher temperature than the temperature of GaN nanowire described in Chapter 5. The UV-reflective substrate will be AlGaN DBRs consisting of different compositions optimized for reflection band at 240 nm [1]. The active region will incorporate multiple quantum wells or quantum dot stacks, which will be optimized for PL intensity. Temperature-dependent and power-dependent PL measurement will be further performed to estimate the IQE of the active region. Besides using metal contact grid for reducing absorption, highly UV-transparent boron nitride, which is typically p-type, could also be used to replace p-AlGaN for hole injection [2]. According to the IQE measured from the active region, the design of nanowire diameter, spacing, and length will follow the guidelines discussed in Chapter 4 to optimize either light extraction efficiency or IQE in order to maximize EQE. The EQE of the device is expected to be enhanced from currently below 0.1% to >10%. Detailed structural, electrical, and optical characterizations will be performed to understand the improvement in the device performance.

8.2.3 AlGaN nanowall LED

We have extended the concept of AlN nanowall discussed in Chapter 6 to AlGaN nanowall and the work is currently in progress. Nanowalls were firstly prepared by lithography and dry etching on AlN-on-sapphire substrates. The etching depth was about 700 nm and the wall width varied from 1.5 μ m to 3 μ m. The spacing between the nanowalls is kept 2 μ m. The n-type AlGaN layer was thick (~250 nm) for the ease in fabrication. The active region included three Al_{0.5}Ga_{0.5}N/Al_{0.65}Ga_{0.35} quantum wells. The growth of the active region has been firstly optimized using planar AlN template for strong PL intensity. The p-type AlGaN layer thickness was relatively thin (~60 nm) in order to minimize the resistance. The growth of p-type AlGaN layer adopted the condition discussed in Chapter 3. Between the active region and the p-AlGaN layer, there was an 10-15 nm thick electron blocking layer with Al composition of 80%. After the p-AlGaN layer is a 3 nm p-GaN contact layer. A representative SEM image of the nanowalls after growth is shown in Figure 8-3, which exhibits highly uniform well-controlled geometry and morphology.



Figure 8-3 An SEM image of as-grown AlGaN nanowalls.

The structure was subsequently fabricated into devices. Firstly, lithography was performed to define etching mask on top of nanowall arrays. Dry etching was then performed until n-AlGaN was revealed and the photoresist etching mask was removed by solvent. SiO_x was subsequently deposited as an electrical isolation layer to separate following p-metal contact with n-AlGaN. Before the deposition of p-metal contact, careful lithography overlay was performed to expose the

region only exactly on top of nanowalls and SiO_x on top of the nanowalls was etched by buffer hydrofluoric acid. After the p-metal contact deposition, SiO_x in the region for n-metal contact was etched and n-contact and aluminum probe pad were finally deposited. In order to have ohmic contact, annealing was performed at 400 °C for 1 minute in air.

Preliminary electrical and optical characterizations have been performed. The current-voltage characteristics exhibits a low turn-on voltage of \sim 5 V as shown in Figure 8-4 (a) with negligible leakage current under reverse bias. A single peak at 282 nm is observed in the EL spectra in Figure 8-4 (b).

It remains unclear how the thickness of active region and number of quantum wells would affect the device performance. In addition, the growth condition for the electron beam blocking layer is not optimized yet. Further investigation will be conducted to understand and optimize the performance of AlGaN nanowall LEDs.



Figure 8-4 Electrical and emission characteristics of an AlGaN nanowall LED. (a) Current-voltage characteristics. (b) EL spectra under different current densities.

8.2.4 AlGaN nanowire edge emitting laser

With the capability of selective area epitaxy to control nanowire diameter and spacing arbitrarily, very small spacing between nanowires can be realized to make an extended nanowire array functioning as a single waveguide, which is an ideal structure for edge-emitting lasers. Due to the very small spacing between nanowires, optical loss from scattering among nanowires will be minimized. The schematic for an AlGaN nanowire edge-emitting laser based on such a structure is illustrated in Figure 8-5. Highly regular and uniform GaN nanowire template is firstly grown by selective area epitaxy following the process discussed in Chapter 5. The 300 nm thick n-Al_{0.8}Ga_{0.2}N cladding layer, 100 nm thick undoped guiding layer, 300 nm thick p-Al_{0.8}Ga_{0.2}N cladding layer, and 20 nm thick p-GaN contact layer will be grown on top of the n-GaN nanowire template as shown in Figure 8-5. The undoped guiding layer consists of an Al_{0.55}Ga_{0.45}N layers embedded with five stacks of Al_{0.35}Ga_{0.65}N quantum dots which are beneficial for reducing lasing threshold due to the large gain offered by three-dimensional quantum confinement. The compositional difference between the guiding layer and the cladding layers is large enough to offer sufficient refractive index contrast for photon confinement in the guiding layer and minimization of absorption in the GaN segment or the top p-contact. Because this structure still consists of nanowires, enhanced Mg dopant incorporation is expected compared to planar structure. Therefore, efficient hole injection, which is a crucial condition not met yet in the efforts for planar deep UV LDs, can be achieved in our structure. After the growth, SiO_x is deposited near the both ends of the waveguide. The SiO_x layers will be patterned by electron beam lithography or focused ion beam to form SiO_x (46.8 nm)/air (70 nm) distributed Bragg reflectors (DBRs) to provide optical feedback at ~ 280 nm. The n-contact and p-contact will finally be deposited in a conventional way involving lithography, dry etching, and metal deposition.



Figure 8-5 Schematic for an AlGaN nanowire edge-emitting laser at ~ 280 nm.

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