The Pennsylvania State University

The Graduate School

College of Earth and Mineral Sciences

MOCVD GROWTH OF GALLIUM NITRIDE WITH INDIUM SURFACTANT

A Dissertation in

Materials Science and Engineering

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

May 2011

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ABSTRACT

Indium can act as a surfactant on the growing GaN surface without being incorporated due to its high vapor pressure at growth temperatures of 900 – 1000 °C. Thus, indium surfactant can modify the growth mode of GaN films by changing surface energy and surface kinetics of adsorbed Ga and N adatoms. In this thesis research, the effect of indium surfactant on Ga-polar and N-polar GaN films grown at 950 °C by MOCVD on various substrates such as Si-face SiC, bulk GaN, Si(111), and C-face SiC was studied to investigate the stress relaxation mechanism, structural, and optical properties of GaN films which were modified by the indium surfactant.

The effect of indium surfactant on GaN films grown on SiC was studied first. In the 1.8 μ m thick Ga-polar GaN films grown on lattice-mismatched Si-face SiC substrates utilizing indium surfactant at 950 °C, inverted hexagonal pyramid surface defects, socalled V-defects which consist of six (1011)planes, formed at threading dislocations on the GaN surface, which gave rise to the relaxation of compressive misfit stress in an elastic way. Simultaneously, enhanced surface mobility of Ga and N adatoms with indium surfactant lead to improved 2D growth, which may be contradictory to the formation of surface defects like V-defects. In order to find the driving force for V-defect formation in the presence of indium, a nucleation and growth model was developed, taking into consideration the strain, surface, and dislocation energies modified by indium surfactant. This model found that the V-defect formation can be energetically preferred since indium reduces the surface energy of the (1011) plane, which gives rise to the Vdefect formation and growth that can overcome the energy barrier at the critical radius of the V-defect. These Ga-polar GaN films were found to be unintentionally doped with Si. Thus, an investigation into the effect of intentional Si doping at a constant TMIn flow rate on GaN films was also performed. Si turned out to be another important factor in the generation of V-defects because Si may be captured at the threading dislocation cores by forming Si – N bonds, acting as a mask to locally prevent GaN growth. This behavior appeared to assist the initiation of the V-defect which enables V-defects to easily grow beyond the critical radius. Thus, introduction of indium surfactant and Si doping was found to be the most favorable conditions for V-defect formation in Ga-polar GaN films grown on Si-face SiC substrates.

The nucleation and growth model predicted that V-defects may not form in homoepitaxy because the energy barrier for V-defect formation approaches infinity due to zero misfit stress. When indium surfactant and Si dopant were introduced simultaneously during the homoepitaxial growth, V-defects did not form in 1.8 µm thick Ga-polar GaN films grown at 950 °C on bulk GaN that had very low threading dislocation density, as predicted by the nucleation and growth model. Ga-polar GaN films grown on Si(111) substrates using indium surfactant showed that additional tensile stress was induced by indium with respect to the reference GaN. Since cracking is known to be a stress relaxation mechanism for tension, the In-induced additional tensile stress is thus detrimental to the GaN films which experience the tensile thermal stress associated with the difference in coefficient of thermal expansion between GaN and the substrate during cooling after growth. The generation of tensile stress by indium seemed correlated with a reduction of V-defects since a high density of V-defects formed under the initial compressive stress at the GaN nucleation stage and then V-defect density decreased as the film grew. Even though the initial misfit stress of the GaN film grown on Si(111) was lower than that of GaN grown on SiC, a high density of V-defects were created under the initial compressive stress. Therefore, the high density of threading dislocations was believed to strongly drive the V-defect formation under In-rich conditions.

Consequently, without using high quality bulk GaN substrates, V-defects could not be avoided in Ga-polar GaN films grown on foreign substrates such as Si-face SiC and Si(111) in the presence of indium surfactant and Si dopants during growth. Thus, Npolar GaN films were investigated using vicinal C-face SiC substrates because a theoretical study utilizing first-principles calculations predicted that V-defects are not energetically favored on the N-face GaN. When indium surfactant and Si doping were used during N-polar GaN growth, V-defects did not form, as predicted by theory. This observation suggests that V-defect free N-polar InGaN alloys also can be achieved, which may enable stable green laser diodes with long lifetime to be fabricated using the high indium composition N-polar InGaN films. Fundamental studies of N-polar GaN growth with varying growth parameters such as growth temperature, two-step process, and AIN buffer layer thickness, were conducted to optimize the surface morphology and structural properties of N-polar GaN epilayers for future N-polar InGaN growth.

TABLE OF CONTENTS

LIST OF FIGURESix	
LIST OF TABLES	ii
ACKNOWLEDGEMENTSxx	
Chapter 1 Introduction	
1.1 Motivation1	
1.2 Objective	
1.3 Thesis Outline11	
Chapter 2 Literature Review	
2.1 Overview of Group III-Nitrides for Light Emitting Devices	
2.2 Physical Properties of Group III-Nitrides and Substrates	
2.2.1 Structural, Electrical, and Optical Properties of GaN, AlN, and InN 17	
2.2.2 Substrates	
2.2.3 Buffer Layers	
2.2.4 Hexagonal Lattice	
2.3 Stress Relaxation Mechanisms in Heteroepitaxial Growth of Nitrides	
2.3.1 Misfit Dislocations	
2.3.2 Slip Systems in Hexagonal Lattice	
2.3.3 Other Stress Relaxation Mechanisms	
2.4 Indium Surfactant	
2.4.1 Surface Diffusion of Ga and N Modified by Indium Surfactant	
2.4.2 Surface Energies of GaN Modified by Indium Surfactant	
2.5 V-defect	
2.5.1 Driving Force for V-defect Formation	
2.5.1.1 Northrup's Model	
2.5.1.2 Song's Model	
2.6 Green Gap in the Solid State Laser Diodes	
2.7 N-polar GaN	
2.7.1 Hexagonal Hillock	
2.7.2 Effect of the Substrate Misorientation on the N-polar GaN51	
Chapter 3 Experimental Methods	
3.1 MOCVD System	
3.1.1 Reactor	
3.1.2 Gas Manifold Cabinet	
3.1.3 Vacuum Pump and Scrubber	
3.2 Multi-beam Optical Stress Sensor (MOSS)	

3.3 Substrate Preparation and Growth Process	63
3.3.1 Orientations of SiC, Si(111), and Bulk GaN Substrates	64
3.3.2 Substrate Cleaning Process	66
3.3.3 Growth Process	68
3.4 Characterization	69
3.4.1 X-ray diffraction (XRD)	69
3.4.2 Raman Scattering Spectroscopy	73
3.4.3 Atomic Force Microscopy (AFM)	75
3.4.4 Photoluminescence (PL)	76
3.4.5 Mercury Probe Capacitance-Voltage (C-V) Measurements	77
3.4.6 Transmission Electron Microscopy (TEM)	78
3.4.7 Secondary Ion Mass Spectroscopy (SIMS)	79
Chapter 4 GaN Growth on SiC Substrates	80
4.1 Introduction	80
4.2 Unintentionally Si-doped GaN Grown with Indium Surfactant	81
4.2.1 Experimental Details	82
4.2.2 In-situ Stress Measurements	83
4.2.3 X-ray Diffraction Analysis	87
4.2.4 Crystallinity of GaN Films	90
4.2.5 Surface Morphology and Microstructure	94
4.2.6 Discussion	97
4.3 Nucleation and Growth Model for V-defect Formation	98
4.3.1 Development of Nucleation and Growth Model	99
4.3.2 System Energy Change by V-defect Formation	103
4.3.3 Initial Nucleation of V-defect	105
4.3.4 Discussion	108
4.4 Intentionally Si-doped GaN Grown with Indium Surfactant	109
4.4.1 Experimental Details	111
4.4.2 In-situ Stress Measurements	112
4.4.3 Raman Scattering Spectroscopy Analysis	114
4.4.4 Optical Properties of GaN Films	119
4.4.5 Surface Morphology	122
4.4.6 Discussion	125
4.5 Conclusions	126
Chapter 5 GaN Growth on Bulk GaN and Si(111) Substrates	129
5.1 Introduction	129
5.2 GaN Growth on bulk GaN Substrates with Indium Surfactant	132
5.2.1 Experimental Details	132
5.2.2 Preliminary Results on the Homoepitaxy	134
5.2.3 V-defect Formation Energy in Homoepitaxy	136
5.2.4 Homoepitaxy with Indium Surfactant and Intentional Si Doping	137

5.3 GaN Growth on Si(111) Substrates with Indium Surfactant	140
5.3.1 Experimental Details	141
5.3.2 Thickness Interruption Study	142
5.3.3 Tensile Stress Generation by Reduction of V-defects	148
5.4 Conclusions	151
Chapter 6 N-polar GaN Growth on C-face Vicinal SiC Substrates	154
6.1 Introduction	154
6.2 N-polar GaN Growth with Indium Surfactant and Si Doping	158
6.2.1 Experimental Details	159
6.2.2 In-situ Stress Measurements	161
6.2.3 Surface Morphology	164
6.2.4 Crystallinity of N-polar GaN Films	168
6.2.5 SIMS Analysis	170
6.2.6 Optical Properties of N-polar GaN Films	174
6.2.7 TEM Analysis	177
6.2.8 Discussion	179
6.3 Study of N-polar GaN Growth	180
6.3.1 Experimental Details	180
6.3.2 Effect of Growth Temperatures	182
6.3.3 Two-step Process	188
6.3.4 Effect of N-polar AlN Buffer Layer Thickness	192
6.4 Conclusions	195
Chapter 7 Thesis Summary and Future Work	199
7.1 Thesis Summary	199
7.2 Future Work	203
Appendix Estimation of Threading Dislocation Density by X-ray Rocking Curve	s208
References	218

viii

LIST OF FIGURES

Figure 2.1. Bandgap energies and lattice constants of AlN, GaN, InN, and related alloys at room temperature. [Ref. Y. A. Xi and E. F. Shubert, Retrieved from http://www.ecse.rpi.edu/~schubert/Course-Teaching-modules/A39-Measurement-of-Al-content-in-AlGaN-by-X-ray-diffraction-&-transmittance.pdf, (2006).]	14
Figure 2.2. The stacking sequence of group III and N layers along the polar axes follows (a) <i>ABAB</i> in the wurtzite structure, and (b) <i>ABC</i> in the zincblende structure. [Ref. B. Gil, <i>Group III Nitride Semiconductor Compounds: Physics and Applications</i> (Oxford University Press Inc., New York, NY, 1998)]	17
 Figure 2.3. Equilibrium N₂ pressure over the MN (s) + M (l). M indicates group III metals such as Ga, Al, and In. [Ref. O. Ambacher, J. Appl. D: Appl. Phys. 31, 2653 (1998).] 	20
Figure 2.4. The crystallographic orientations of the basal plane in the hexagonal lattice. The directions are represented by four indices. The c-axis is normal to this page. [Ref. J. D. Acord, Thesis, The Pennsylvania State University, 2007.]	27
Figure 2.5. Slip systems in a hexagonal lattice. [Ref. Srinivasan <i>et al.</i> , Appl. Phys. Lett. 83, 5187 (2003).]	32
Figure 2.6. (a) – (e) are the SEM micrographs of undoped and In-doped GaN films for different TMIn flow rates of 0, 0.22, 0.44, 1.1, and 2.12 μmol/min, reported by Shu <i>et al.</i> The doping level of indium into GaN was less than 0.2 % at the 2.12 μmol/min, thus indium was used as a surfactant. Dramatic reduction of nanopits and improved surface morphology are evident when In was introduced during growth. [Ref. Shu <i>et al.</i> , Appl. Phys. Lett. 73 , 641 (1998).]	35
Figure 2.7. Schematic representation of GaN surfaces. Solid circle indicates Ga atom and hollow circle indicates N. S3, B2, and T1 have 3, 2, and 1 bonds to N, and each site can be occupied by Ga or In. [Ref. Northrup <i>et al.</i> , Phys. Rev. B 60 , R8473 (1999).]	38
Figure 2.8. Schematic representation of V-defect, also known as inverted hexagonal pyramid defect, in the nitrides	39

ix

Figure 2.9. (a) Schematic representation of V-pit with a lateral size of a and depth of h, formed on the terminated threading dislocation. (b) V-pit formation energy as a function of the diameter of V-pit. When In atom is absent, S is larger than 3.0, and S factor decreases as the indium amount increases on the GaN surface. [Ref. Northrup <i>et al.</i> , Phys. Rev. B 60, R8473 (1999).]	-1
Figure 2.10. (a) Schematic representation of V-pit that is assumed to be an inverted cone. $Z=rd$, where the ideal <i>d</i> value is 1.63. (b) The change of total system energy as a function of thickness with increasing V-pit density. The <i>f</i> is the initial misfit strain between the InGaN and GaN. [Ref. T. L. Song, J. Appl. Phys. 98 , 084906 (2005).]	.3
Figure 2.11. Quantum efficiency of InGaN and AlGaInP LEDs as a function of emission wavelength. As the peak wavelength approaches green from either red or blue, the efficiency decreases, resulting in 'green gap'. [Ref. A. Khan, Nature Photonics 3 , 432 (2009).]	.5
Figure 2.12. AFM images of InGaN:Mg films grown on (a) bulk GaN and (b) sapphire substrates. The bulk GaN substrate has lower threading dislocation density, resulting in the lower V-defect density in the green LED. [Ref. Liu <i>et al.</i> , J. Cryst. Growth 310 , 5166 (2008).]	.7
Figure 2.13. $30 \times 30 \mu\text{m}^2$ AFM amplitude images of N-polar GaN (a – e) and Gapolar GaN (f – j) with increasing Mg doping level. The height scale is $0.0 - 0.5$ V for a – e and j, and $0.0 - 0.1$ V for f – i. [Ref. Brown <i>et al.</i> , Appl. Phys. Lett. 94, 153506 (2009).]	.8
 Figure 2.14. (a) Differential interference contrast optical micrograph of MOCVD-grown homoepitaxial GaN on an N-polar GaN substrate and (b) optical micrograph of a 1 μm thick GaN film grown on an on-axis [0001] SiC substrate. High density of hexagonal hillocks (~ 50 μm size) is observed in both homoepitaxy and heteroepitaxy. [Ref. Weyher <i>et al.</i>, J. Cryst. Growth 204, 419 (1999), and D. F. Brown <i>et al.</i>, Appl. Phys. Lett. 93, 042104 (2008).]	0
Figure 2.15. TEM cross-sectional images of the columnar defect delineating the core of the hexagonal hillock. (a) Defect imaged with g in the growth direction close to the $<1\overline{100}>$ zone, and (b) weak beam image of the same defect revealing a thin planar nucleating site at the base of the column. [Ref. Weyher <i>et al.</i> , J. Cryst. Growth 204 , 419 (1999).]	2
Figure 2.16. Optical microscope images of 0.8 μ m thick GaN films grown on (0001) sapphire substrates with misorientation angles of (a) 0.5°, (c) 1°, and	

х

(e) 2° toward the a plane $(11\overline{2}0)$, and (b) 0.5° , (d) 1° , and (f) 2° toward the m plane $(10\overline{1}0)$. The inserts in (a) and (b) are enlarged threefold. [Ref. Keller <i>et al.</i> , J. Appl. Phys. 102 , 083546 (2007).]	53
Figure 3.1. Photograph of MOCVD system in 220 EE West bldg. Scrubber and rotary vane vacuum pump are behind the MOCVD system	55
Figure 3.2. (a) Photograph and (b) schematic diagram of vertically configured quartz reactor.	56
Figure 3.3. Schematic diagram of MOSS system equipped in the MOCVD system. The real-time change of beam spacing, corresponding to the film curvature, allows for the <i>in-situ</i> stress measurements.	61
Figure 3.4. Diameter, primary and secondary flat orientations, and wafer ID number of (a) carbon face up for silicon face polished wafer and (b) silicon face up for carbon face polished wafer. Primary flat is one of $\{10\overline{1}1\}$ planes and parallel to $<11\overline{2}0>$. Wafer ID is scribed on the face which is not used for epitaxy.	64
Figure 3.6. $10 \times 10 \ \mu\text{m}^2$ AFM images of (a) SiC substrate cleaned by dip in Opticlear, sonication in acetone and isopropanol, and rinse in DI water, and (b) SiC substrate further cleaned by wiping with cotton swab in acetone and additional sonication in acetone and isopropanol.	67
Figure 3.7. Photograph of a Philips X'Pert PRO MRD four-circle diffractometer located in 164 MRI building at Penn State University. High resolution mode was configured, using hybrid monochromator PreFIX module in the incident beam optics, and the triple axis & rocking curve attachments module in the diffracted beam optics.	70
Figure 3.8. The change of $\sin\theta$ with θ . The error in $\sin\theta$ caused by the same error of $\Delta\theta$ becomes smaller when θ approaches 90°. The experimental error of $\Delta\theta$ is exaggerated.	73
Figure 4.1. Stress-thickness vs. thickness as a function of TMIn molar flow rate during GaN growths at 950 °C, obtained from MOSS. The oscillation feature arises from an artifact caused by non-uniformity of the GaN film thickness across the sample.	84
Figure 4.2. Reflectivity variations on the GaN films at TMIn of 0 and 4.5 µmol/min during GaN growths at 950 °C, obtained from MOSS.	86

xi

Figure 4.3. Extrapolations of measured lattice constants (a) <i>c</i> and (b) <i>a</i> of the reference GaN film against Nelson-Riley function	
Figure 4.4. (a) Lattice constants c and (b) lattice constants a measured from HRXRD at room temperature. The sign of strain is determined with respect to the lattice parameters of GaN at room temperature	
Figure 4.5. Biaxial stress change of GaN epilayers at the growth temperature of 950 °C, calculated from XRD and MOSS as a function of TMIn flow rate90	1
Figure 4.6. FWHMs of (0002), (10 $\overline{15}$), (10 $\overline{13}$), (10 $\overline{12}$), (20 $\overline{23}$), (10 $\overline{11}$), and (30 $\overline{32}$) ω -scans in the reference GaN film and the fit (solid line) based on the Srikant's model	
Figure 4.7. The estimated TD density of GaN films from XRD as a function of TMIn flow rate	
Figure 4.8. AFM images of GaN epilayers grown with increasing TMIn flow rate. (a), (b), (c), and (d) on the first column indicates AFM images over $2 \times 2 \ \mu m^2$ area, and (e), (f), (g), and (h) on the second column shows images over $50 \times 50 \ \mu m^2$ area.	
Figure 4.9. The density and area fraction of V-defects with increasing TMIn flow rate, measured from AFM images over five randomly selected $50 \times 50 \ \mu\text{m}^2$ area	
Figure 4.10. Bright field cross-sectional TEM images of (a) V-defect and (b) area next to V-defect	
Figure 4.10. V-defects are assumed to be a cone which has the radius of <i>r</i> and the height of <i>h</i> . One side length of the given system is $a (a \gg r)$	0
Figure 4.11. The change of total system energy as a function of V-defect radius (a) under Ga-rich, and (b) under In-rich conditions. In both cases, the edge dislocation energy was considered. E_b represents the barrier energy for the V-defect formation. The calculation was performed with Eq. (4.13)	4
Figure 4.12. The system energy change under Ga-rich and In-rich conditions as a function of V-defect size that forms on edge TD. To illustrate the initiation of nano-sized V-defect, this figure was replotted at different scale from Fig. 4.11	6
Figure 4.13. The system energy change as a function of V-defect radius when V-defect forms at the terminated screw TD, edge TD and bulk region without any TD	7

Figure 4.14. Stress-thickness vs. thickness of GaN films grown at 950 °C by MOCVD, obtained from the MOSS. Compressive stress relaxes in the presence of indium surfactant and further relaxation occurs when SiH ₄ was introduced for Si doping at the fixed TMIn flow rate 4.5 μmol/min113
Figure 4.15. Raman scattering spectra of GaN films with indium surfactant and Si-doping. E ₂ (high) and A ₁ (LO) are excited in the given configuration of $z(x, x)\overline{z}$
Figure 4.16. Frequency change of E ₂ (high) mode in GaN films corresponding to the film stress. Solid curves indicate the fitted data by pseudo-Voigt function116
Figure 4.17. Biaxial stress obtained from Raman and MOSS at the growth temperature of 950 °C117
Figure 4.18. Intensity ratio of A ₁ (LO) mode to E ₂ (high) mode in all GaN epilayers
Figure 4.19. Photoluminescence spectra obtained from GaN films at room temperature
Figure 4.20 . AFM images of GaN eplilayers. (a), (b), (c), and (d) show AFM images over $2 \times 2 \ \mu m^2$ and (e), (f), (g), and (h) show AFM images over $50 \times 50 \ \mu m^2$
Figure 5.1. Curvature change of 1.1 μm thick GaN grown on bulk GaN at 1100 °C
Figure 5.2. AFM image of 1.1 μ m thick GaN grown on bulk GaN substrate at 1100 °C. The scanned area in the AFM micrograph is 2 × 2 μ m ² and the RMS roughness is 0.16 nm. 136
Figure 5.3. System energy change as a function of V-defect radius. As the misfit stress is reduced from -0.9 GPa to 0 GPa (homoepitaxy), the energy barrier and critical radius for V-defect formation keep increasing
Figure 5.4. Curvature changes of 1.8 µm thick GaN films grown on bulk GaN at 950 °C with indium surfactant and Si doping. During these homoepitaxial growths, no significant curvature changes are observed
Figure 5.5 . AFM images of GaN eplilayers grown on bulk GaN substrates with indium surfactant and Si doping. (a), (b), and (c) show AFM images over $2 \times 2 \ \mu m^2$ and (d), (e), and (f) show AFM images over $50 \times 50 \ \mu m^2$ 139

xiii

Figure 5.6. Stress-thickness data of GaN films grown on Si(111) substrates at 950 °C using 90 nm thick AlN buffer layers. For the indium surfactant effect, TMIn flow rate of 6.8 μmol/min was used during GaN growth1	42
Figure 5.7. AFM images of 1.8 μ m GaN films grown (a) without indium surfactant and (b) with indium surfactant (TMIn = 6.8 μ mol/min). The scan area was 50 × 50 μ m ² 1	.43
Figure 5.8 . AFM images of GaN eplilayer grown on Si(111) substrates using AlN buffer layers over $50 \times 50 \ \mu\text{m}^2$. (a) and (b) show GaN films without indium at 0.5 $\ \mu\text{m}$ and 1.0 $\ \mu\text{m}$. (c), (d), and (e) show GaN films grown with indium surfactant at 0.5 $\ \mu\text{m}$, 1.0 $\ \mu\text{m}$, and 1.4 $\ \mu\text{m}$.45
Figure 5.9. Area fraction and density of V-defects in the GaN film grown on Si(111) with indium surfactant (6.8 µmol/min) as a function of film thickness.	.46
Figure 5.10. (a) Average radius and (b) maximum radius of V-defects in the GaN films grown on Si(111) substrate with indium surfactant as a function of film thickness, estimated from AFM images in Fig. 5.8(c) - (e) and Fig. 5.7(b)1	.47
 Figure 5.11. Zipping process of each GaN nuclei at the initial stage of film growth on substrate. GaN film becomes tensile due to the zipping process that reduces the volume between GaN nuclei. [Refs. Nix <i>et al.</i>, J. Mater. Res. 14, 3467 (1999) and J. D. Acord, Thesis, The Pennsylvania State University, 2007]. 	.49
Figure 5.12. Schematic representation of removal process of V-defects when the GaN film grows. Filling V-defects may lead to tensile stress generation because GaN films try to reach each other towards the center of V-defect, and fill the volume corresponding to V-defects. The film curvature due to tension on the right side is exaggerated.	.50
Figure 6.1. Wurtzite crystal structures of (a) Ga-polar GaN and (b) N-polar GaN. The arrow indicates the growth direction. [Ref. Sumiya <i>et al.</i> , MRS Internet Journal of Nitride Semiconductor Research 9 , 1 (2004).]	56
Figure 6.2. $10 \times 10 \mu\text{m}^2$ AFM images of (a) Si-face SiC (on-axis) for Ga-polar GaN growth and (b) C-face vicinal SiC substrate misoriented towards $<11\overline{20}$ > by 3.57 degree from the c-axis for N-polar GaN growth. The RMS surface roughness is 0.12 nm and 0.10 nm, respectively	.60
Figure 6.3. Stress-thickness versus film thickness in N-polar GaN epilayers grown on vicinal C-face SiC substrates at 950 °C by MOCVD. Indium	

xiv

- Figure 6.4. Reflectivity variations of Ga-polar and N-polar GaN films grown on SiC substrates at 950 °C. The reflectivity was measured by MOSS integrated onto the MOCVD system. 163

- **Figure 6.7.** SIMS results on (a) the reference N-polar GaN and (b) N-polar GaN grown with indium surfactant (TMIn = $4.5 \mu mol/min$). The indium concentration was below the sensitivity of SIMS equipment in both samples.....172

- Figure 6.10. (a) Cross-sectional bright-field TEM image of N-polar GaN film grown with indium surfactant, collected along the $[1\overline{1}00]$ zone axis under

multi-beam diffraction condition. A high density of stacking mismatch boundaries appears to be inclined by approximately 4 degree from surface normal. (b) High-resolution TEM image collected from a stacking mismatch boundary. Stacking mismatch at the boundary seems to be nearly parallel to $[000\overline{2}]$. (c) Experimental and JEMS-simulated CBED patterns confirm the N-polarity of GaN film grown on vicinal C-face SiC substrate with indium......178

Figure 6.11. AFM images of N-polar GaN epilayers grown on vicinal C-face SiC	
substrates as a function of growth temperature. (a), (b), (c), and (d) on the	
first column indicate AFM images over $2 \times 2 \ \mu m^2$ area, and (e), (f), (g), and	
(h) on the second column show images over $20 \times 20 \ \mu\text{m}^2$ area. The arrow	
indicates the misorientation direction of substrate towards $<11\overline{2}0>$ from the	
c-axis1	183
Figure 6.12. RMS surface roughness of 1.1 µm thick N-polar GaN films as a	
function of growth temperature, estimated from AFM images over $2 \times 2 \ \mu m^2$	

Figure 6.16. FWHMs of (0002) and (3032) planes in x-ray rocking curves (ω -	
scans) in 1.1 µm thick N-polar GaN films grown by two-step process as a	
function of HT GaN growth temperature.	192

Figure 6.18. AFM images of 1.1 μ m N-polar GaN film grown at 1100 °C on 30 nm thick AlN buffer layer over (a) 2 × 2 μ m² area and (b) 20 × 20 μ m² area. The white arrow indicates the misorientation direction of vicinal C-face SiC substrate.

Figure A.1. Microstructures of group III-nitrides are typically represented by columnar structures with a very low angle distribution. (a) Tilt and (b) twist of columnar structures are schematically illustrated with respect to growth direction of the c-axis of GaN films. [Ref. B. Gil, <i>Group III Nitride Semiconductor Compounds: Physics and Applications</i> (Oxford University Press Inc., New York, NY, 1998).].	.208
Figure A.2. Misorientations of sub-grains leads to (a) tilt (screw TD) and (b) twist (edge TD). [Ref. M. A. Moram and M. E. Vickers, Rep. Prog. Phys. 72, 036502 (2009).]	.210
Figure A.3. XRD rocking curves (square data points) and Voigt fit (red solid lines) of (a) (0002) and (b) (3032) planes in GaN film.	.214
Figure A.4. FWHMs of (0002), $(10\overline{1}5)$, $(10\overline{1}3)$, $(10\overline{1}2)$, $(20\overline{2}3)$, $(10\overline{1}1)$, and $(30\overline{3}2) \omega$ - scans as a function of inclination angle and the fit lines of three models. Twist can be obtained at the inclination angle of 90°.	.216

xvii

LIST OF TABLES

Table 2.1. Physical properties of wurtzite GaN, AlN, and InN. ⁵¹	.21
Table 3.1. Selection rules of the allowed phonon modes, depending on the Raman scattering geometries, for the hexagonal wurtzite GaN. ¹¹³	.75
Table 3.2. Typical phonon frequencies of the heteroepitaxially grown hexagonal wurtzite GaN (50 \sim 70 µm) at room temperature. The values in brackets derive from bulk GaN. ^{113,114}	.75
Table 3.3. Detection limits for selected elements of GaN films in SIMS analysis, provided by EAG.	.79
Table 6.1. The measured FWHMs of $(000\overline{2})$ and $(30\overline{32})$ planes, and TD density	
in N-polar GaN films. FWHM of $(10\overline{1}0)$ was estimated from $(30\overline{3}\overline{2})$.169
Table 6.2. FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1	
μ m thick N-polar GaN films and on (0002) and (3032) planes in 1.0 μ m thick Ga-polar GaN films as a function of growth temperature. FWHM of (1010) was estimated from FWHM of (3032) and (3032) planes. TD density	
was calculated by Eq. 4.4 and 4.5	.186
Table 6.3. FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1 µm thick N-polar GaN films grown by two-step process as a function of HT GaN growth temperature. 140 nm thick LT GaN was grown first at 950 °C prior to HT GaN growths. FWHM of $(10\overline{10})$ was estimated from FWHM of $(20\overline{22})$ plane. TD density and be for 4.4 and 4.5	101
(3032) plane. TD density was calculated by Eq. 4.4 and 4.5.	. 191
Table 6.4. FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1 μ m thick N-polar GaN films grown at 1100 °C on 30 nm and 90 nm thick AlN buffer layers. FWHM of $(10\overline{10})$ was estimated from FWHM of $(30\overline{32})$. TD density was calculated by Eq. 4.4 and 4.5	.195
Table A.1. FWHMs and Lorentzian content factors of x-ray rocking curves on	
(0002), (1015), (1012), (2023), (1011), and (3032) planes in sample A	.215

 Table A.2. Estimated twist and TD densities of sample A, B, and C obtained from x-ray rocking curves and plan-view TEM.

 217

ACKNOWLEDGEMENTS

First of all, I would like to thank my advisor, Prof. Joan M. Redwing. When I was having a hard time, she gave me the opportunity so that I could continue with research and finish my Ph. D. She always supported me with her advice and encouragement, and allowed for freedom in research. I also would like to thank all the committee members, Prof. Elizabeth Dickey, Prof. Christopher Muhlstein, and Prof. Francesco Costanzo for valuable comments and suggestions. I would like to thank the MOCVD folks, Ian Manning, Jeremy Acord, Sarah Eichfeld, and Jarod Gagnon who shared the MOCVD system, for valuable discussions and great help. I also wish to express my thanks to the other Redwing group members (Leo, Chito, Sharis, Joe, Mel, Pramod, and Rob) for all their help and support. I would like to extend my thanks to Xiaojun Weng for TEM work, William Everson in the Electro-Optic Center (EOC) for SiC wafer dicing, Dave Snyder at the EOC for indirect help, and Maria Dicola at the Materials Research Laboratory (MRL) for Si wafer dicing. I also would like to acknowledge the National Science Foundation (NSF) for funding my research project.

During my Ph. D. course, I have had a lot of support from present and past Korean students in MATSE and EE departments. I would like to thank U Hyeok Choi, who spent difficult times with me, providing lots of help. June Hyeok Lee provided me with great help whenever I had issues in XRD measurements. From time to time, I had discussions about my research with Hangbum Shin. I have had enjoyable discussions with Sungmin Bae about our hobbies. I also would like to show my gratitude to Yonsei Alumni at Penn State for their help and support.

I have learned sincerity and honesty from my parents since my childhood. I cannot express my deepest thanks with words. Thank you for your love and trust in me. My brother, who is a catholic priest, has always prayed for me. Your advice and humor were always great support.

Finally, to my wife, Jeehye Stella Hahn, I knew that we were meant to be together. Thank you for your patience during all those times when I had to focus on my experiments and dissertation. You were always very supporting, encouraging, and entertaining. Without your love and support, I would never have made it. You always complete me. I love you.

Chapter 1

Introduction

1.1 Motivation

Growth of high quality group III-nitrides, GaN, AIN, InN, and their alloys, is crucial for the fabrication of highly efficient light emitting devices and high power electronic devices.¹ Since lattice-matched substrates are not readily available, heteroepitaxial growth of III-nitrides on lattice-mismatched substrates such as sapphire and SiC has been a common method, resulting in misfit strain. This misfit stress induces structural imperfections such as threading dislocations (TDs), misfit dislocations, stacking faults, V-defects, etc., depending upon the particular strain relief mechanism.²⁻⁴ Therefore, research has focused on understanding the correlation between film strain and microstructure, which is a key determinant of film properties. In order to control defects and improve surface morphology in epilayers, a variety of growth conditions have been exploited by tuning process variables such as temperature, pressure, and source input ratio. One of the ways to manipulate the structural properties of thin films is through the use of a surfactant such as indium, which alters surface energy and kinetic processes such as adsorption, desorption, and surface diffusion of adsorbed chemical species on the growing epilayers.⁵

Indium has been reported as an applicable surfactant to GaN films in that In can segregate and wet on the growing GaN surface without forming alloys due to its volatility at growth temperatures of 900 – 1000 °C. It was experimentally demonstrated that the presence of indium improved the surface morphology, structural, and optical properties of GaN films grown on sapphire substrates.⁶⁻¹³ The high density of pits disappeared on the GaN surface and the surface morphology became smoother as a result of improved step-flow growth.⁶ In-surfactant induced strain relaxation and reduced mosaicity in GaN, providing the possibility of strain control.⁷ The TD density in GaN was reduced and the linewidths of photoluminescence (PL) peaks were narrowed by increasing the amount of In surfactants.¹² However, a few studies observed no stress change using indium surfactant with a thin GaN layer of ~ 200 nm and the linewidth of the x-ray diffraction peak remained similar although the In surfactant lead to enhanced optical properties of GaN.^{14,15} Therefore, while improved step-flow growth has been a common observation, conflicting results were reported on the crystallinity and stress of the GaN films grown with indium surfactant.

In addition, although there have been reports that surface pits disappeared by improved surface diffusion with the aid of indium surfactant on the GaN surface, inverted hexagonal pyramidal surface defect, also known as V-defect or V-pit, is a predominant surface defect in the InGaN films grown on GaN, where indium can act as a surfactant at growth temperatures below 800 $^{\circ}$ C.¹⁶⁻²⁶ V-defect is known to be an elastic stress relaxation mechanism, and this extended surface defect is always connected to the defects such as edge or screw TDs.^{16,27} Hence, it is believed that the formation of V-defect may be energetically favorable over threading dislocations. In the InGaN films grown on GaN, the size and density of V-defects tends to increase as the indium composition is raised in the InGaN film. Since InN has greater lattice constant *a* than that of GaN, the greater

compressive misfit stress and higher indium composition in the InGaN films have been believed to be important factors in V-defect formations. Theoretical studies revealed that indium behaves as a differential surfactant, which reduces the surface energy of the ($10\overline{1}1$) plane more over the (0001) surface.⁵ This surface energy reduction may give rise to the higher probability of V-defect formation because a V-defect consists of six ($10\overline{1}1$) planes that can be stabilized under indium rich conditions on the GaN surface.

In this thesis study, the first goal was to investigate the effect of indium surfactant on the stress evolution and structural properties of GaN epilayers grown on SiC by metalorganic chemical vapor deposition (MOCVD). The stress change was characterized by in-situ wafer curvature measurements, using a multi-beam optical stress sensor (MOSS), combined with *ex-situ* high resolution x-ray diffraction (HRXRD). The structural properties of the GaN films were analyzed by x-ray rocking curves, atomic force microscopy (AFM), and transmission electron microscopy (TEM) to identify the stress relaxation mechanism modified by indium. The compressive stress, induced by the misfit strain between the GaN epilayer and SiC substrate, was found to be relaxed elastically by the formation of V-defects due to the presence of indium surfactant while improved step-flow growth was simultaneously induced by indium. A nucleation and growth model was developed, taking into consideration the surface, dislocation, and strain energies in order to explain the driving force for V-defect formation promoted by indium surfactants. Furthermore, this model was able to describe the comprehensive behavior of V-defects such as their initiation at threading dislocations under In-rich conditions on the growing GaN surface.

All GaN films were later found to be unintentionally doped with silicon or oxygen that are typical n-type dopants in group III-nitrides, resulting in a maximum background electron carrier concentration of 2×10^{17} cm⁻³ in all samples. When the unintentional Si and O incorporation in the GaN films was controlled below 5×10^{16} cm⁻³, V-defect formation in the presence of indium surfactant was greatly reduced. Therefore, in order to identify the effect of n-type doping on the V-defect formation, intentional Si doping into 1.8 µm GaN films grown at 950 °C using SiH₄ was performed first. It turned out that Si can also induce V-defect formation on the GaN surface in the presence of indium. The origin of V-defect formation enhanced by Si doping may stem from the behavior of Si as an an anti-surfactant.²⁸ Tanaka et al. reported that heavy Si doping lead to a change in the growth mode from 2-dimensional (2D) to 3-dimensional (3D) growth, allowing for the fabrication of quantum dots.²⁹ They also observed that a high density of nano holes at TDs was created, which may originate from the formation of Si – N masking in their thin GaN film grown on AlGaN. Similarly, Si – N bonds seemed to form at the TD cores in the current study because the TD core has nitrogen dangling bonds that can easily capture Si, which may locally prevent GaN deposition. Once the nano-sized holes were created by Si – N masking, the size of the nano holes may increase by expanding this masking area and the additional indium surfactant makes the six $(10\overline{1}1)$ surfaces stable, thus leading to large V-defects. As a result, indium increased V-defect density at a constant Si doping level, and Si also drove more V-defects at a fixed amount of indium surfactant. Therefore, the use of indium surfactant combined with Si dopant was identified as the most favorable growth conditions for V-defect formation in GaN films grown on SiC.

The nucleation and growth model predicted that the energy barrier for V-defect formation approaches infinity in homoepitaxy, where there is no misfit stress. When the indium combined with Si doping was used, no V-defects formed during 1.8 µm thick GaN growth on bulk GaN substrates, as predicted by the proposed model. The growth stress change in GaN film grown on Si(111) substrate differs from that of GaN film grown on SiC.^{30,31} When GaN nucleates on the AlN buffer layer / Si(111), compressive stress is induced first. This compressive incremental stress changes to tensile incremental stress during coalescence between GaN islands and the mean stress also becomes tensile during 2D growth.³⁰ Thus, when post-growth tensile thermal stress, caused by the difference in coefficient of thermal expansion (CTE) between GaN and Si(111) substrate during cooling after growth, is added to the tensile growth stress, cracking occurs in the GaN films because cracking has been known to be a typical stress relaxation mechanism for tension.³⁰ This cracking had been an obstacle in utilizing Si(111) substrates for GaN growth until AlGaN graded buffer layers were used to induce more compressive growth stress that compensates the tensile thermal stress.³² Thus, the effect of indium surfactant on 1.8 µm thick Ga-polar GaN epilayers grown at 950 °C on Si(111) substrates are interesting if V-defect formation can relieve tensile growth stress elastically. However, the real-time stress measurements showed that additional tensile stress was induced in the GaN film grown on Si(111) by indium, as compared to the reference GaN, thus detrimental to GaN films which experience tensile thermal stress. A thickness interruption study revealed that the generation of tensile stress by indium appeared to correlate with the reduction of V-defects since a high density of V-defects were created under the initial compressive stress at the GaN nucleation stage and then the V-defect density was reduced during GaN growth. Although the initial misfit stress of GaN films on Si(111) was lower than that of GaN on SiC, a high density of V-defects was generated. X-ray rocking curve measurements estimated a high TD density of 3.5×10^{10} cm⁻² in the GaN films grown on Si(111) which is nearly one order higher than that of GaN films grown on SiC, providing more nucleation sites for V-defects. Therefore, the high density of TDs was believed to strongly drive V-defect formation under In-rich conditions during GaN growth.

V-defects become more critical in high indium composition InGaN alloys due to the highly In-rich environment that reduces the surface energy of $(10\overline{1}1)$ plane of GaN during epitaxy. Since blue light emitting diodes (LEDs) and laser diodes (LDs) utilizing In_xGa_{1-x}N (x ≈ 0.15) as active media were successfully realized in the early 1990's,¹ extensive research has been focused on improving the efficiencies of green LEDs and LDs requiring higher indium composition InGaN. However, the efficiencies of green LEDs and LDs are significantly lower than those of blue light emitting devices because of larger misfit stress, phase separation, and misalignment between conduction and valence bands in the high indium composition InGaN films.³³ Therefore, there exists a so-called 'green gap' due to the lower efficiency of green LEDs as compared to both highly efficient blue LEDs using InGaN and red LEDs utilizing AlInGaP.³³ In fact, current-injected green LDs, which have more complicated structures than LEDs, have not been commercialized yet due to the problems listed. In addition, a high density of Vdefects on the surface of InGaN hinders the development of stable green LDs with long lifetime because V-defects have been reported to provide a pathway for reverse leakage currents in LEDs.^{17,34} Thus, understanding the origin of V-defects is crucial to control these defects. From the experimental results on GaN growth under In-rich conditions using Si-face SiC, bulk GaN, and Si(111) substrates, it can be concluded that V-defect formation was driven by misfit stress, reduction of (1011) surface energy by indium surfactant, Si incorporation, and high TD density in the heteroepitaxially grown GaN whereas high quality bulk GaN substrates hindered V-defect formation. From the nucleation and growth model, the only way to reduce V-defect density in heteroepitaxy seemed to be minimizing the nucleation sites, i.e., reduction of TD density. These conclusions direct attention towards the N-polar group III-nitrides, where V-defects may not be preferred energetically as predicted by theoretical first-principles calculations.⁵ Therefore, the heteroepitaxially grown N-polar GaN films may solve the issues regarding a high density of V-defects in high indium composition InGaN film without using highly expensive bulk GaN substrates.

Group III-nitrides have a polar asymmetry along the c-axis of their hexagonal wurtzite crystal structure, which gives rise to spontaneous and piezoelectric polarizations along the polar axis.³⁵⁻³⁷ Most LEDs, LDs, and high electron mobility transistors (HEMTs) have been developed and realized based on Ga-polar GaN films grown on the c-plane of sapphire or SiC along the [0001] direction because Ga-polar GaN has excellent surface morphology. In general, group III-nitrides can be grown along either [0001] or [0001] directions of polar axis. Recently, N-polar GaN is attracting much attention because it has been reported that N-face GaN has advantages over Ga-polar GaN because the opposite polarity allows for heavy p-type doping along the N-polar direction and

novel design of high electron mobility transistor (HEMT) devices. N-polar GaN films heavily p-type doped with Mg showed much more stable surface, as compared to Gapolar GaN films which exhibited a rough surface due to Mg-induced polarity inversion.³⁸ In contrast to depletion mode operation (normally on) in Ga-polar HEMT, enhanced mode operation (normally off) with low gate leakage current in N-polar HEMT have been reported.^{37,39,40} Polarization-induced hole doping using opposite spontaneous and piezoelectric polarizations along the N-polar direction was demonstrated in compositionally graded N-polar AlGaN, which lead to high hole concentration and in turn gave rise to the higher internal quantum efficiency in LEDs.⁴¹ Thus, the opposite polarity that flips the spontaneous and piezoelectric polarizations can enable a more flexible design in optoelectronic devices. In addition, N-face InGaN films could be Vdefect free, as predicted by theoretical studies, thus allowing for more stable and efficient green LDs. By modifying the nitridation step of sapphire prior to GaN growths or using C-face SiC substrates, N-polar GaN films can be grown along the [0001] of the substrates. Even though growth of smooth N-polar GaN films has been demonstrated by MBE.⁴⁰ it has been challenging to grow smooth N-polar GaN films grown by MOCVD due to the surface defects, so-called hexagonal hillocks, that make N-polar GaN unsuitable for the device fabrication.^{35,42-44} This obstacle has been overcome by using misoriented substrates towards either $<10\overline{10}>$ or $<11\overline{20}>$ from the c-axis of bulk GaN, sapphire, and SiC substrates, suppressing the formation of hexagonal hillocks.^{36,45-47} However, despite the reduced hexagonal hillocks, the surface of epitaxially grown Npolar GaN film is typically rough at the macroscopic scale as compared to Ga-face GaN,

which may require two-step process composed of low temperature GaN layer and high temperature main GaN film.⁴⁷

Therefore, the indium surfactant effect on 1.9 μ m thick N-polar GaN films grown at 950 °C on the vicinal SiC substrates misoriented towards $<11\overline{2}0 >$ by 3.57 degree by MOCVD was investigated to verify whether the V-defect formations are not preferred and indium can improve the surface morphology of N-polar GaN films. AFM measurements showed that the use of indium and Si doping did not drive any V-defects on the N-polar GaN surface, proving that the V-defects are not preferred in the N-polar GaN films. This result suggests that the N-polar InGaN / GaN systems may be V-defect free even with high indium composition and Si doping, which may enable stable and highly efficient green LDs. In addition, indium surfactant dramatically improved the surface morphology and optical properties of N-polar GaN films. A variety of growth conditions for the N-polar GaN epilayers by varying growth temperature, two-step process, and AlN buffer layer thickness were exploited to optimize the surface morphology and structural properties of N-polar GaN films for the future N-polar InGaN growth.

1.2 Objective

The major goal of this thesis research is to experimentally investigate the effect of indium surfactants on the film stress and microstructure of GaN grown by MOCVD, and develop a theoretical model to explain the mechanism of stress relaxation due to indium.

First, a series of GaN films were grown on SiC by MOCVD with varying amounts of indium. The investigation utilizing in-situ and ex-situ stress measurements combined with various characterization tools revealed that compressive misfit stress was relaxed by V-defect formation under In-rich conditions whereas enhanced step-flow growth was simultaneously observed. Based on the experimental results, a nucleation and growth model was developed to explain the driving force for V-defect formation that was promoted by indium surfactant in GaN films grown on SiC. Since these GaN films were unintentionally doped with Si, the investigation into the effect of intentional doping at a constant amount of indium surfactant was also conducted to clarify the driving force for V-defect formation. This study revealed that Si is another important factor in creation of V-defects in addition to indium surfactant.

Based on the proposed model, GaN film growth on bulk GaN substrates using indium surfactant and Si doping were performed to verify the hypothesis that V-defects are not energetically favored in homoepitaxy. As predicted by the nucleation and growth model, homoepitaxially grown GaN films did not show any V-defects due to zero misfit stress. GaN growth on Si (111) under In-rich conditions showed that V-defects were driven by a high density of TDs. To clarify the observed additional tensile stress promoted by indium, a thickness interruption study was employed. This study demonstrated that a reduction of V-defects may give rise to the generation of tensile stress.

From these experimental results and the developed nucleation and growth model, it was concluded that V-defects cannot be avoided in Ga-polar GaN films grown on lattice-mismatched substrates. Thus, N-polar GaN films, which have opposite polarity, were investigated since theoretical study utilizing first-principles calculations predicted that V-defects are not energetically favored along the N-polar direction regardless of misfit stress. N-polar GaN growth on vicinal C-face SiC demonstrated that V-defects did not form on the N-face GaN. These results strongly suggest that high indium composition N-polar InGaN films can be grown without any V-defects. Thus, optimization of growth conditions for N-polar GaN films were exploited in order to grow the N-polar InGaN alloys which will be investigated in the future.

1.3 Thesis Outline

This thesis research presents a systematic study of GaN growth by MOCVD and the effect of indium surfactant on the V-defect formation and physical properties of GaN epilayers grown on a variety of substrates such as Si-face SiC, bulk GaN, Si(111), and Cface SiC.

Chapter 2 reviews literatures starting from an overview of group III-nitrides for LEDs and LDs. Stress relaxation mechanisms, indium surfactant, V-defects, polarity of GaN films, and issues in N-polar GaN growth are discussed.

Chapter 3 provides a description on the experimental methods used in this work. MOCVD system, MOSS, substrates, growth process and various characterization techniques are described in detail. Chapter 4 presents the experimental results obtained from Ga-polar GaN films grown on Si-face SiC substrates with indium surfactant. Then, a nucleation and growth model is developed to explain driving force for V-defect formation promoted by indium. The effect of intentional Si doping at a constant TMIn flow rate on the formation of Vdefect is also investigated.

Chapter 5 contains the results of GaN growth on bulk GaN and Si(111) substrates with indium surfactant. The driving force for V-defects in GaN films are discussed in terms of misfit stress and threading dislocation density.

Chapter 6 presents the results of N-polar GaN films grown on vicinal C-face SiC substrates grown with indium surfactant. The details of development in optimizing growth conditions of N-polar GaN are also presented.

Chapter 7 summarizes all results in this thesis research. Future works are suggested to optimize the physical properties of N-polar GaN films for the future N-polar InGaN growth.

Chapter 2

Literature Review

This chapter reviews the literature related to the current thesis research. The review begins from the historical overview of group III-nitrides for the applications of light emitting devices. The comprehensive study on the stress relaxation mechanisms of GaN films will be covered. Then, the kinetics of adsorbed adatoms and surface energies of GaN films, modified by indium surfactant, will be discussed. The driving force for V-defect formation will be discussed based on the two models suggested by Northrup *et al* ⁵ and Song.¹⁶ We will review the 'green gap' which originates from the low efficiency of high indium content In_xGa_{1-x}N films ($x \approx 0.32$) in green LEDs and LDs,³³ where V-defects become more critical. Lastly, the motivation and issues pertinent to N-polar GaN growth will be presented.

2.1 Overview of Group III-Nitrides for Light Emitting Devices

The group III-nitrides, GaN, InN, and AlN, and their alloys, have been the most important materials for optoelectronic devices such as blue, green, and ultraviolet (UV) semiconductor LEDs and LDs because of the widely tunable direct band gaps of their continuous alloy systems (0.7 eV for wurtzite InN, 3.4 eV for wurtzite GaN, and 6.2 eV for wurtzite AlN)⁴⁸⁻⁵¹ ranging from infrared (IR) to ultraviolet (UV), as shown in Fig. 2.1.



Figure 2.1. Bandgap energies and lattice constants of AlN, GaN, InN, and related alloys at room temperature. [Ref. Y. A. Xi and E. F. Shubert, Retrieved from <u>http://www.ecse.rpi.edu/~schubert/Course-Teaching-modules/A39-Measurement-of-Al-content-in-AlGaN-by-X-ray-diffraction-&-transmittance.pdf</u>, (2006).]

In particular, GaN and In_xGa_{1-x}N ternary alloys have been studied extensively because the GaN film is the base material in LEDs and LDs, and the InGaN, which is typically grown on the smooth high quality GaN epilayers, is the active material. Until the 1970s, epitaxy of group III-nitrides had been challenging due to the lack of suitable substrates. Bulk GaN substrates were not readily available because of the difficulty in growth and extremely high cost because conventional methods such as Czochralski or Bridgman growths from stoichiometric melts are practically impossible due to the high melting point of GaN and huge partial pressure of nitrogen at elevated temperature.⁵²⁻⁵⁴ Thus, heteroepitaxial growths of III-nitrides on lattice-mismatched substrates such as sapphire and SiC were the common methods using MOCVD and MBE. However, the direct epitaxy of GaN films on those foreign substrates resulted in the 3-dimensional islanding of GaN films due to the incoherency in lattice constants and thermal expansion coefficients between the GaN film and the substrate. This poor surface morphology was a limit to development of devices using GaN films until an AlN buffer layer was used in the 1980s, which lead to smooth GaN films.^{55,56} Later, a low temperature (~ 600 °C) thin GaN buffer layer was used, also leading to smooth surface morphology and improved crystal quality of high temperature GaN films.⁵⁷ The atomically smooth high quality GaN films were able to provide the base materials for the InGaN alloys that can be utilized in blue LEDs. Nowadays, the use of buffer layers has become a standard process in GaN epitaxy.

In general, LED devices are fabricated based on a p-n junction. Thus, it is essential to obtain n-type and p-type nitrides in a controllable way. For n-type doping, it was demonstrated in early 1990s that silicon using SiH₄ (silane) and germanium using GeH₄ (germane) can be used as n-type dopants in GaN films grown with GaN buffer layer without causing cracking.⁵⁸ Silicon resulted in a higher electron concentration in GaN films due to the relatively lower ionization energy at room temperature, as compared to Ge. Also, Ge caused surface roughening of GaN at high doping levels (~ 10^{19} cm⁻³). Thus, Si became the suitable n-type dopant for GaN. In p-type doping, although Mg was predicted to be an acceptor, Mg doping had been problematic because it did not lead to hole carriers in GaN films.¹ In addition to high ionization energy of Mg, the main reason for the low efficiency in Mg doping turned out to be hydrogen that passivates Mg, which was overcome by low energy electron beam irradiation of the
GaN.⁵⁹ Later, thermal annealing in N₂ atmosphere turned out to be more efficient to activate Mg dopants.⁶⁰ Both processes allowed H to diffuse out, enabling Mg to be electrically active. In the 1990s, while highly efficient red LEDs were demonstrated with AlInGaP, SiC blue LEDs had very poor efficiency. The breakthrough using InGaN multiple quantum wells for highly efficient blue LEDs was finally made with properly controlled n-type and p-type doping, which was exploited by Shuji Nakamura of Nichia Chemical, Inc. in 1993.^{61,62} Since the advent of highly efficient blue LEDs made of group III-nitrides, the development in this area has been rapidly made mainly due to progress in the material growth techniques such as MOCVD and MBE which make it possible to manipulate and improve the structural, electrical, and optical properties of the group IIInitrides. However, even with these successes, the understanding of the various defects in nitride thin films, stemming from the relaxation of misfit stress in the heteroepitaxy, have not been mastered completely. Thus, it is essential to understand the fundamental material characteristics correlated with film stress and imperfections in order to exploit various applications by using these nitrides. In the next section 2.2, we will start reviewing the basic physical properties of group III-nitrides and substrates, and will be studying the stress relaxation mechanisms in section 2.3.

2.2 Physical Properties of Group III-Nitrides and Substrates

2.2.1 Structural, Electrical, and Optical Properties of GaN, AlN, and InN

The thermodynamically stable crystal structure of group III-nitrides is the hexagonal wurtzite structure (space group: P6₃mc) whereas the cubic zinc blende is the metastable phase.^{50,51} They all have direct band gaps except cubic AlN which has an indirect gap.⁶³ The stacking sequence of group III and N layers is *AB* along the c-axis of the wurtzite phase, and *ABC* along [111] of the zinc blende structure, as shown in Fig. 2.2. Both phases lack inversion symmetry. Polar axes exists along [0001] in the hexagonal wurtzite and along [111] in the cubic zinc blende. This anisotropy results in spontaneous polarization along the polar axes. In addition, large piezoelectric polarization



Figure 2.2. The stacking sequence of group III and N layers along the polar axes follows (a) *ABAB* in the wurtzite structure, and (b) *ABC* in the zincblende structure. [Ref. B. Gil, *Group III Nitride Semiconductor Compounds: Physics and Applications* (Oxford University Press Inc., New York, NY, 1998)].

of AlGaN combined with spontaneous polarization affects the electronic band structures and carrier distributions due to electric fields in the nitrides. The polarization engineering with AlGaN/GaN heterostructures allow for various applications such as high electron mobility transistors (HEMTs) utilizing two dimensional electron gas (2DEG) because the impurity ions incorporated by intentional doping do not scatter carriers in a HEMT.

GaN is a base material in light emitting devices as well as high power devices. Therefore, GaN films have been the most extensively studied. Wurtzite GaN has lattice constants a = 3.1888 Å and c = 5.185 Å,⁶⁴ and its bandgap is 3.4 eV at room temperature.^{50,51} Polytype cubic zinc blende GaN has lattice constant a = 4.52 Å and the bandgap is known to be 3.2 eV.⁵¹ GaN has excellent thermal stability due to its wide band gap, allowing for GaN-based high power devices operating at the elevated temperatures. Since there has been no suitable wet etchant due to the excellent chemical stability of GaN, dry etching is used in lithography.⁶⁵ In order to grow high quality GaN, the proper growth temperature has been reported to be 1030 ~ 1080 °C in MOCVD, using low temperature GaN buffer layer on sapphire substrate and high temperature AlN buffer layer on SiC substrate.⁶⁶ Nowadays, the threading dislocation density in the GaN films is as low as the order of 10^8 cm⁻² in the heteroepitaxy, and ~ 10^6 cm⁻² in the epitaxial lateral overgrowth (ELOG) technique. Electrical and optical properties of GaN are greatly affected by point defects associated with native defects or impurities. For a long time, autodoping in GaN has been reported, and as-grown GaN films are typically n-type. The origin of n-type doping has been attributed to either nitrogen vacancies or unintentional impurity doping.

Wurtzite AlN has lattice parameters a = 3.112 Å and c = 4.982 Å, and the direct band gap is 6.2 eV (300 K).⁵¹ Cubic phase AlN has lattice constant a = 4.38 Å,⁵¹ and its indirect band gap is 5.34 eV (300 K).⁶⁷ The binding energy of AlN is 2.88 eV, the highest value among the III-nitrides (2.20 eV for GaN and 1.98 eV for InN).⁵⁰ AlN has excellent thermal and chemical stability. Also, AlN has very wide band gap and nearly acts as an insulator, which makes AlN popular for packaging material.⁶⁵ For the optoelectronic and high power electronic devices, however, the alloy with GaN is much more attractive because AlGaN, which has lower resistivity than AlN, can be used as barrier layer that can confine carriers in GaN or InGaN. The difficulty in achieving p-type doping due to high activation energy of Mg in AlN is a limit to the direct use of AlN in devices. AlN has large spontaneous and piezoelectric constants, as compared to GaN and InN. Therefore, AlGaN can be used in high power devices such as HEMT using AlGaN / GaN heterostructures, where 2DEG formation is assisted by the total polarizations.⁶⁵

InN is the most challenging to grow among group III-nitrides due to its thermal instability. In order to grow high quality InN, higher growth temperature is desirable. However, InN dissociates above approximately 500 °C. High N₂ pressure is necessary to suppress the dissociation of InN at the growth temperature. This behavior of InN is well illustrated in the Fig. 2.3. Wurtzite InN has lattice parameters a = 3.539 Å and c = 5.708 Å.⁶⁸ The band gap of InN was assumed to be 1.89 eV for long time. This value was corrected in the early 2000s since improved growth techniques lead to significant improvement of the crystal quality of InN. The revised band gap of InN is 0.7 eV (300 K),⁴⁹ and thus group III-nitride and their alloy systems can cover from the near infrared (IR) to UV. As mentioned earlier, the In_xGa_{1-x}N alloy is of interest in light emitting



Figure 2.3. Equilibrium N_2 pressure over the MN (s) + M (l). M indicates group III metals such as Ga, Al, and In. [Ref. O. Ambacher, J. Appl. D: Appl. Phys. **31**, 2653 (1998).]

devices due to the tunable band gaps ranging from blue ($x \approx 0.15$) to green ($x \approx 0.42$). However, high indium content InGaN alloys are very difficult to grow, resulting in lower quantum efficiency in green LEDs and LDs. This phenomenon leads to so-called 'green gap' in the solid state semiconductor light emitting devices, which will be reviewed in section 2.6. Physical properties of GaN, AIN, and InN are summarized in Table 2.1.

Properties	GaN	AlN	InN
Band gap at 300 K (eV)	3.4 3.2 (zincblende)	6.2 5.34 ^a (zincblende, indirect)	0.7 ^b
Lattice constants at 300 K (Å)	$a = 3.1888^{\circ}$ c = 5.185 a = 4.52 (zincblende)	a = 3.112 c = 4.982 a = 4.38 (zincblende)	$a = 3.539^{d}$ $c = 5.708^{d}$
Thermal expansion coefficient at 300 K (10 ⁻⁶ K ⁻¹)	$\Delta a/a = 5.59$ $\Delta c/c = 3.17$	$\Delta a/a = 4.2$ $\Delta c/c = 5.3$	$\Delta a/a = 3.6^{\rm e}$ $\Delta c/c = 2.6^{\rm e}$
Thermal conductivity (W/cm·K)	<i>k</i> = 1.3	<i>k</i> = 2.0	$k = 0.43^{\rm f}$ $k = 1.08^{\rm g}$
Static dielectric constant	8.9	8.5	15.3 ^h
Density (g/cm ³)	6.07 ⁱ	3.29 ⁱ	6.81 ⁱ
Index of refraction	n (1 eV) = 2.33 n (3.4 eV) = 2.67	<i>n</i> (3.0 eV) =2.15	$n = 2.8 \sim 3.05$
Electron effective mass	$m_e^* = 0.20 m_0^{j}$	$m_e^* = 0.48 m_0^{\rm h}$	$m_e^* = 0.11 m_0^k$
Biaxial modulus (GPa)	478 ¹	508 ¹	308 ^m
^a Reference. ⁶⁷ ^b Reference. ⁴⁹ ^c Reference. ⁶⁴ ^d Reference. ⁶⁸ ^e Reference. ⁶⁹ ^f Reference. ⁷⁰ ^g Reference. ⁷¹		^h Reference. ^{72,73} ⁱ Reference. ⁵⁰ ^j Reference. ⁷⁴ ^k Reference. ⁷³ ¹ Reference. ^{75,76} ^m Reference. ⁷⁷	

Table 2.1. Physical properties of wurtzite GaN, AlN, and InN.⁵¹

2.2.2 Substrates

For group III-nitride growth, the most commonly used foreign substrates are sapphire and SiC since bulk GaN substrates for homoepitaxy of GaN are difficult to grow due to the high melting temperature of GaN $(2791 \text{ K})^{50}$ and high vapor pressure of nitrogen at that temperature as briefly reviewed in section 2.1.

Sapphire (Al_2O_3) has been the most frequently used materials for GaN growth mainly due to its low cost, wide availability of large area wafers, and stability at high temperature due to wide bandgap of 8.8 eV.⁵⁰ Sapphire has a rhombohedral corundum crystal structure which has lattice constants a = 4.759 Å and c = 12.991 Å at room temperature.^{51,78} Thus, in-plane lattice mismatch between GaN basal and sapphire basal planes in the wurtzite GaN growth is 32.3 %, which is very high. To reduce high lattice mismatch, actual GaN growth occurs with 30° rotation in-plane with respect to the basal plane of sapphire, resulting in less lattice mismatch of -16 % because the atomic spacing of sapphire parallel to the lattice constant a of GaN becomes 2.75 Å.^{78,79} Although the lattice mismatch is reduced to -16 %, misfit stress is high enough to cause high density of threading dislocations and poor surface morphology in GaN grown sapphire, which implies that properly engineered buffer layers are necessary for the main GaN growth. Although a compressive misfit stress was expected in GaN films grown on sapphire substrates due to the lattice mismatch, in-situ stress measurements revealed that the growth stress of GaN grown sapphire is tensile due to coalescence between highly misoriented GaN nuclei on sapphire substrates.80 Thermal expansion coefficients of sapphire are $\Delta a/a = 7.5 \times 10^{-6} \text{ K}^{-1}$ and $\Delta c/c = 8.5 \times 10^{-6} \text{ K}^{-1.81}$ Thus, thermal mismatch

between GaN and sapphire induces a compressive thermal stress in GaN films after epitaxy. Thermal conductivity of sapphire is 0.5 W/cm·K, which is smaller than 1.3 W/cm·K of GaN.⁸¹ For high power optoelectronic devices at elevated temperature, sapphire substrate is inappropriate due to poorer heat dissipation. Therefore, SiC has advantage over sapphire due to its exellent thermal conductivity of 4.9 W/cm·K.

SiC has better characteristic than sapphire in terms of the lattice mismatch with GaN. SiC has many polytypes depending on bilayer stacking sequence such as 4H (*ABCB*) and 6H SiC (*ABCACB*) which have a hexagonal structure.⁸² 6H-SiC has lattice constants a = 3.08 Å and c = 15.12 Å at room temperature.^{50,81} In contrast to the lattice mismatch of -16 % between GaN and sapphire, the difference in lattice parameters between GaN and 6H-SiC is -3.5 %, which induces a compressive misfit stress in GaN films grown on 6H-SiC. Thermal expansion coefficients of 6H-SiC are $\Delta a/a = 4.2 \times 10^{-6}$ K⁻¹ and $\Delta c/c = 4.7 \times 10^{-6}$ K^{-1,81} resulting in tensile thermal stress due to the difference in coefficient of thermal expansion (CTE) between GaN and 6H-SiC. Since 6H-SiC has wide bandgap of 2.9 eV and excellent thermal conductivity of 4.9 W/cm·K,^{81,82} 6H-SiC substrates are suitable for high power devices at elevated temperature because this material is thermally stable up to 1580 K at which the intrinsic carrier concentration becomes 5×10^{15} cm^{-3.82} The disadvantage of SiC is relatively high cost in comparison to sapphire.

Si(111) substrates have been attracting great attention primarily due to its low cost, high quality, and availability of large size wafers. Furthermore, the most attractive advantage arises from the possibility of integration of well established Si-based

technologies with III-nitrides. Si has a diamond cubic crystal structure with a lattice constant a = 5.4309 Å.⁵⁰ For hexagonal wurtzite GaN growth, Si(111) wafer can be used since Si has hexagonal closed packing structure along the [111] direction with the apparent atomic spacing of 3.84 Å, resulting in 17 % lattice mismatch with GaN.^{66,83} CTE of Si is 3.6×10^{-6} K^{-1,50} which gives rise to tensile thermal stress during cooling after GaN growth. Since the growth stress in GaN films grown on Si(111) using an AlN buffer layer is also tensile, cracking has been a limit to the use of Si(111) substrates since large tensile stress in GaN is typically relaxed by cracking.³⁰ Thus, Si(111) substrates the tensile thermal stress by inducing compressive growth stress in the GaN films grown on Si(111).³²

2.2.3 Buffer Layers

Poor surface morphology due to 3D islanding in GaN films grown on sapphire was a major obstacle in developing high quality smooth GaN epilayers in heteroepitaxy until AlN buffer layer was used in the 1980s by Yoshida *et al.* and Amano *et al.*,^{55,56} which lead to smooth surface of GaN, as reviewed in section 2.1. The use of AlN buffer layers were studied extensively,^{84,85} and later Nakamura demonstrated that low temperature GaN buffer layer can be also employed to realize high quality smooth GaN films.⁵⁷ Without buffer layers, direct growth of GaN on sapphire lead to rough surface due to co-existence of two polarity, i.e., Ga- and N-polar GaN films.⁴⁴ Inversion domains

of Ga-polarity embedded in N-polar GaN matrix turned out to have much faster growth rate than the matrix, which caused surface defects like hexagonal hillocks.⁴³ The use of low temperature AlN or GaN buffer layers provides the Ga-polar GaN epilayers because these amorphous buffer layers were converted to crystals oriented along the [0001] direction during annealing at high temperature, thus serving as a nucleation layer for the following high temperature Ga-polar GaN growth.⁸⁴ In addition, the buffer layer promoted lateral growth of GaN films, thus leading to the smooth surface morphology of GaN films.^{84,85} Consequently, the use of low temperature AlN or GaN became a standard process for the heteroepitaxy of GaN films using sapphire substrates.

Although 6H-SiC has less lattice mismatch in comparison to sapphire, direct growth of GaN on 6H-SiC showed rough surface due to 3D islanding of GaN arising from poor wetting.⁸⁶ Thus, AlN buffer layer has been used for GaN growth on SiC to promote 2D growth of GaN. Unlike the low temperature buffer layers on sapphire substrates, low temperature AlN on SiC resulted in random polycrystalline materials, which subsequently lead to polycrystalline GaN.⁸¹ Thus, high temperature (> 1100 °C) AlN buffer layer has been developed for the following main GaN growth to provide smooth surface morphology and high crystallinity of GaN films. In this thesis research, high temperature AlN buffer layers were used for all GaN growths on SiC.

2.2.4 Hexagonal Lattice

The wurtzite crystal structure of group III-nitrides belongs to the hexagonal crystal system. The hexagonal lattice uses different indexing system from the cubic or tetragonal structures where the directions and planes are represented by Miller indices, i.e., 3 indices (*hkl*) for a plane and [*hkl*] for a direction. Since the crystallographic axes in the hexagonal lattice are not orthogonal and two axes a_1 and a_2 on the basal plane are at 120° to one another, the planes are defined more commonly by the Miller-Bravais indices using (*hkil*). The index *i* refers to the reciprocal of the fractional intercept on the a_3 axis, and the value of *i* is given by⁸⁷

$$h + k = -i. (2.1)$$

Therefore, (100), (010), (110), and (101) planes become $(10\overline{10})$, $(01\overline{10})$, $(11\overline{20})$, $(10\overline{11})$ for instance. For direction in the hexagonal lattice, the relationship between three axes [*hkl*] indices and four axes [*uvtw*] indices is given by the following:

$$h = u - t , \qquad (2.2)$$

$$k = v - t , \qquad (2.3)$$

$$l = w, \tag{2.4}$$

$$u = (2h - k)/3$$
, (2.5)

$$v = (2k - h)/3,$$
 (2.6)

$$t = -(u+v) = -(h+k)/3, \qquad (2.7)$$

$$w = l . (2.8)$$

Thus, for example, [100], [110], and [210] become $[2\bar{1}\bar{1}0]$, $[11\bar{2}0]$, and $[10\bar{1}0]$. For planes, the conversion of three indices to Miller-Bravais indices is straightforward, but the conversion of direction should be carefully done. In a crystal system, there are sets of equivalent lattice planes and directions. These sets of equivalent planes are represented by {*hkl*} and {*hkil*} instead of (*hkl*) or (*hkil*). For the direction, sets of equivalent directions are referred to an *<hkl>* and *<uvtw>* instead of [*hkl*] and [*uvtw*]. Frequently, some important planes are named without using indices. For instance, {111} planes in the cubic crystal are sometimes called 'octahedral planes'. In the hexagonal structure, (0001)



Figure 2.4. The crystallographic orientations of the basal plane in the hexagonal lattice. The directions are represented by four indices. The c-axis is normal to this page. [Ref. J. D. Acord, Thesis, The Pennsylvania State University, 2007.]

27

plane, {1011} planes, and {1011} planes are often called 'basal plane', 'prismatic planes', and 'pyramidal planes', respectively. The principle crystallographic orientations in the hexagonal lattice using the [*uvtw*] idices are illustrated in Fig. 2.4.

2.3 Stress Relaxation Mechanisms in Heteroepitaxial Growth of Nitrides

The heteroepitaxial growths of nitrides on the lattice-mismatched substrates introduce misfit stress in the films. The strain energy builds up, and relaxes through particular stress relaxation mechanisms, resulting in various defects in III-nitrides. The most common mechanism for plastic stress relaxation is the formation of misfit dislocations. Another important plastic mechanism is dislocation slip. These two mechanisms are discussed in the following sections briefly and other mechanisms such as threading dislocation bending, cracking, and surface defects will be also discussed shortly.

2.3.1 Misfit Dislocations

As stated earlier, wurtzite GaN has lattice constants a = 3.1888 Å and c = 5.185 Å.⁶⁴ The most popular substrates in heteroepitaxy are sapphire and 6H-SiC which have lattice constants a = 4.758 Å and 3.08 Å, respectively.^{50,51} For the GaN epilayers grown on sapphire, GaN film rotates by 30° in-plane with respect to sapphire substrate.^{78,79} The

atomic spacing of sapphire substrate parallel to a_1 axis of GaN is 2.75 Å. Thus, GaN films on both sapphire and SiC substrates experience compressive misfit stress although the compressive stress changes to tension in the GaN films grown on sapphire during coalescence and the following step flow growths.^{80,88} In the GaN films, this misfit stress accumulates, and relaxes by creating misfit dislocations at the heterointerface between the film and substrate when the film reaches a critical thickness. Dislocations are line defects in materials, and the formation of dislocations increase the system energy in principle. Thus, when the relief of strain energy by misfit dislocations is larger than the dislocation energy, the misfit dislocation formation becomes energetically favorable beyond the critical thickness (*h_c*) which is given by the following:^{2,16}

$$h_{c} = \frac{b(1 - v\cos^{2}\alpha)}{4\pi\varepsilon(1 + v)} \left[\ln\left(\frac{h_{c}}{b}\right) + 1 \right],$$
(2.9)

where *b* is the magnitude of the Burgers vector, *v* is Poisson's ratio, α is the angle between the misfit dislocation line and Burgers vector *b*, and ε is the strain in the film. In general, the formations of misfit dislocations at the heterointerface are the major mechanism in the stress relaxation, as reported by Moran *et al.* who observed that more than 90% misfit strain was relieved by misfit dislocations in the GaN growths on AlN / SiC.⁸⁹

2.3.2 Slip Systems in Hexagonal Lattice

In cubic materials such as Si and GaAs, the misfit stress relaxes along the primary slip system, {111} <100>.^{2,90} In contrast, the stress relaxation mechanisms in hexagonal wurtzite GaN are complicated due to the limited slip systems since the resolved shear stress is zero along the primary slip systems on the basal {0001}, and prismatic {1100} and {1120} planes.¹⁶ In order to identify the active slip systems in hexagonal GaN system, Srinivasan *et al.* considered three forces acting on the dislocation to slip such as resolved shear stress arising from misfit stress, the dislocation line tension opposing the motion of the dislocation, and Peierls force limiting the dislocation motion by friction.²⁷ The shear stress (*F_a*) acting on the slip plane and in the slip direction is given by²

$$F_a = 2Gbh\varepsilon \frac{1+\nu}{1-\nu} \cos\lambda, \qquad (2.10)$$

where G is the shear modulus of the film, b is the magnitude of the Burgers vector of the misfit dislocation, h is the film thickness, v is the Poisson's ratio, λ is the angle between the Burgers vector and the direction on the interfacial plane that is perpendicular to the dislocation line, and ε is the lattice mismatch strain, which is $(a_f - a_s)/a_s$ where a_s and a_f are the lattice constants of the substrate and the film. Thus, in Eq. (2.10), $\cos \lambda$ is zero on the basal {0001}, and prismatic {1100} and {1120} planes in Fig. 2.5(a), (b), and (c), making these primary slip systems inactive.²⁷ The secondary slip systems on the

pyramidal planes such as $\{11\overline{2}2\} < 11\overline{2}3 >$, $\{1\overline{1}01\} < 11\overline{2}3 >$, and $\{1\overline{1}02\} < 1\overline{1}01 >$ in Fig. 2.5(d), (e), and (f), have non-zero cos λ . The line tension (*F_l*) is given by²⁷

$$F_{l} = \frac{Gb^{2}}{4\pi} \frac{1 - v \cos^{2} \alpha}{(1 - v)} \left[\ln \left(\frac{h}{b} \right) + 1 \right], \qquad (2.11)$$

where α is the angle between the misfit dislocation line and its Burgers vector. The Peierls force (*F_P*) is given by²⁷

$$F_{p} = 2Gbh \sec \phi \left(\frac{1 - v \cos^{2} \alpha}{1 - v}\right) \omega \times \exp \left(\frac{-2\pi d (1 - v \cos^{2} \alpha) \omega}{(1 - v)b}\right), \qquad (2.12)$$

where ϕ is the angle between the film surface and the normal to the slip plane, *d* is the interplanar spacing corresponding to the slip plane, and ω is a material constant given by

$$\omega = \exp\left(\frac{4\pi^2 nkT}{5GV}\right),\tag{2.13}$$

where *n* is the number of atoms per unit cell, *V* is the volume of the unit cell, and *T* is the growth temperature. Therefore, the net driving force (F_{net}) for dislocation slip is

$$F_{net} = F_a - F_l - F_P. (2.14)$$



Figure 2.5. Slip systems in a hexagonal lattice. [Ref. Srinivasan *et al.*, Appl. Phys. Lett. **83**, 5187 (2003).]

From Eq. (2.14), the energetically favorable systems among secondary slip systems can be predicted, depending on the misfit stress and growth condition. In order for the dislocation slip to occur, larger misfit stress and smaller Peierls force are required. However, the plastic relaxation along the secondary slip systems, $\{11\overline{2}2\} < 11\overline{2}3 >$, $\{1\overline{1}01\} < 11\overline{2}3 >$, and $\{1\overline{1}02\} < 1\overline{1}01 >$, typically requires high activation energy. If another stress relaxation mechanism is available, the dislocation slip does not take place.¹⁶

2.3.3 Other Stress Relaxation Mechanisms

The threading dislocation (TD) is a dislocation propagating towards the film surface, which does not contribute to the stress relaxation unlike the misfit dislocations. Also, TD density is reduced only by the reaction between TDs.^{91,92} Since the TD is

known to be detrimental to device performance, it is critical to minimize the TD density in order to obtain high quality nitride films. Usually, the TD bending does not take place, but the inclination can be activated by the surface roughness which makes the resolved shear stress non-zero⁹³ or Si doping into AlGaN films without surface roughening.^{94,95} The misfit stress can be relaxed by such an inclination of edge type TDs because the projected length of the inclined dislocation acts as a misfit dislocation segment that can contribute to the relaxation of misfit stress. This mechanism has been termed as "effective climb" of edge TDs since this inclination process does not require vacancy diffusion that is necessary in a typical climb process of dislocation.⁹⁶ The relaxation associated with this inclination of TD is given by the following:⁹⁶

$$\varepsilon = \frac{1}{2} b \rho_{TD} h_f \tan \alpha \tag{2.15}$$

where *b* is the magnitude of dislocation Burgers vector, ρ_{TD} is the density of inclined TD, h_f is the film thickness, and α is the angle of inclination with respect to the original line direction (projected length L is equal to h_f tan α). Further inclination of TD can lead to creating the misfit dislocation segment whose dislocation line is parallel to the basal plane, thus contributing to the plastic stress relaxation.^{97,98}

Cracking is another important mechanism in stress relaxation. In general, the tensile stress in nitrides can relax by cracking that makes device fabrication impossible. The large tensile stress is typically induced during cooling from the growth temperature to room temperature in the epitaxy when the coefficient of thermal expansion (CTE) of

substrate is smaller than that of thin film.⁹⁹ Thus, in addition to the film stress during growth, thermal stress induced by the difference in CTE should be taken into account in designing heterostructures using multiple nitride epilayers.³² The CTE of GaN film and 6H-SiC along *a* axis is 5.6×10^{-6} K⁻¹ and 4.3×10^{-6} K⁻¹,⁵⁰ respectively, which leads to the tensile stress during cooling from the growth temperature. If the GaN film is under tension during growth at the growth temperature, then cracking may occur due to the thermal stress during cooling in the GaN film grown on 6H-SiC substrate. Therefore, compressive stress in epilayers grown on SiC is highly desirable. Silicon has the CTE of 2.6 × 10⁻⁶ K⁻¹.¹⁰⁰ Although Si(111) can serve as a substrate for the heteroepitaxy of GaN, the cracking usually takes place due to the tensile stress induced by both thermal and growth stresses in GaN growths, which makes Si(111) substrates more difficult to use. This cracking issue can be reduced by the AlGaN graded buffer layer, which leads to more compressive stress during growth.³²

In contrast to the plastic relaxation of stress where dislocation motion occurs, the surface defect such as V-defect can relax the film stress in an elastic way.^{16,27} In the InGaN / GaN system, the V-defects are the most commonly observed extended surface defects formed on the surface of InGaN films, which leads to the relaxation of compressive stress in InGaN. The details of V-defect formations will be reviewed in section 2.5 since these defects are the main focus of the current thesis research.

2.4 Indium Surfactant

Indium can act as a surfactant on the growing GaN surface without being incorporated into GaN films due to its high vapor pressure at growth temperatures of 900 – 1000 °C. Thus, indium surfactant can modify the growth mode by changing surface energy and surface diffusivity of adsorbed adatoms.^{5,101} Shu *et al.* reported that isoelectronic indium doping into GaN leads to improved surface morphology and enhaced optical properties.⁶ Although they described indium as an isoelectronic dopant, their SIMS results showed that 0.2 % indium existed in the 1.7 μ m thick GaN films grown on sapphire at 1000 °C by MOCVD, which was surfactant effect rather than isoelectronic doping. Figure 2.6 indicates the scanning electron microscopy (SEM) pictures of GaN surface grown with indium surfactant, reported by Shu *et al.* As the



Figure 2.6. (a) – (e) are the SEM micrographs of undoped and In-doped GaN films for different TMIn flow rates of 0, 0.22, 0.44, 1.1, and 2.12 μ mol/min, reported by Shu *et al*. The doping level of indium into GaN was less than 0.2 % at the 2.12 μ mol/min, thus indium was used as a surfactant. Dramatic reduction of nanopits and improved surface morphology are evident when In was introduced during growth. [Ref. Shu *et al.*, Appl. Phys. Lett. **73**, 641 (1998).]

molar flow rate of trimethylindium (TMIn) increases from 0 to 2.12 µmol/min at the trimethylgallium (TMGa) flow rate of 10.3 µmol/min (TMIn / TMGa = 0.21), many dark spots (pits with diameter of about 100 ~ 200 nm) disappear, and the GaN surface becomes smoother. They also presented that the full width at half maximum (FWHM) of I_2 peak (recombination of excitons bound to shallow neutral donor) in PL spectra measured at 15 K decreased from 16 meV to 10 meV, and the linewidth of rocking curves on (1010) plane was reduced from 2040 arcsec to 1560 arcsec, indicating the improvement of optical and structural properties in the GaN epilayers. From the PL and Raman scattering spectroscopy, they observed that the film stress remained unchanged with an indium surfactant. However, there are other studies reporting that indium surfactant lead to the strain relief of GaN films,⁷ and the structural properties of GaN remained unchanged while the PL characteristics was enhanced by indium.¹⁵ Thus, the smoother surface morphology of GaN was the common observation, but the experimental results on the film stress and structural properties have been inconsistent, which lead to one of the motivations in the current thesis study.

2.4.1 Surface Diffusion of Ga and N Modified by Indium Surfactant

Experimental results from other studies indicated that indium surfactants lead to an enhancement of the step-flow growth on the GaN (0001) surface.^{6,8,11,15} Neugebauer *et al.* utilized first-principle calculations to investigate the mechanism of the enhanced surface diffusion that leads to a smooth GaN surface with indium.¹⁰¹ In the hexagonal wurtzite GaN, they considered migration pathways and diffusion energy barriers for Ga and N adatoms when an indium monolayer exists on the GaN (0001) surface. When a Ga adatom is adsorbed on the In monolayer, the calculations showed that the diffusion barrier of the Ga adatom is reduced to 0.12 eV, as compared to 0.7 eV in the absence of In adlayer. Thus, the surface mobility of Ga adatom is enhanced due to the lowered barrier energy. For N adatom, they found that the N atom is adsorbed and tends to sit below the In adlayer, generating a diffusion channel underneath the In. The diffusion barrier energy for N is 0.5 eV, which is lowered from 1.3 eV on a bare GaN (0001) surface. Therefore, the surface migrations of both Ga and N adatoms can be enhanced when In segregates on the GaN surface.

2.4.2 Surface Energies of GaN Modified by Indium Surfactant

Indium surfactants also lead to an alteration of the surface energies of the various crystalline orientations of GaN. Northrup *et al.* simulated the surface energy reduction by indium, using first-principle calculations.⁵ Figure 2.7 shows a two dimensional schematic representation of GaN (0001) and (1011) surface configurations. The A1 site represents the adlayer on GaN (0001), and S3, B2, and T1 indicate the threefold, twofold, and onefold sites in terms of bonding to N atoms. One of the reasons for the differential change of surface energies is that the length of In-N bond is 11 % longer than that of Ga-N, leading to a site-dependent reduction of surface energies. The decrease of energy by substituting indium into A1, B2, and T1 sites is higher than that for S3 sites. This leads to

less energy required to create the $(10\overline{1}1)$ when indium is present. The calculation result suggests that both (0001) and $(10\overline{1}1)$ surface energies are reduced, but the energy of $(10\overline{1}1)$ decreases significantly under In-rich conditions, as compared to $(10\overline{1}1)$ surface energy. Therefore, this relative change of surface energies can induce the driving force to create (10\overline{1}1) surfaces, which gives rise to a high probability to form V-defects on GaN (0001) surfaces with indium surfactants as well as on the surface of InGaN / GaN systems. The next section will review these V-defects which are the important stress relaxation mechanism which is typically observed in the InGaN / GaN systems and GaN films grown at the low growth temperature.



Figure 2.7. Schematic representation of GaN surfaces. Solid circle indicates Ga atom and hollow circle indicates N. S3, B2, and T1 have 3, 2, and 1 bonds to N, and each site can be occupied by Ga or In. [Ref. Northrup *et al.*, Phys. Rev. B **60**, R8473 (1999).]

2.5 V-defect

V-defect is an extended surface defect, also known as V-pit or inverted hexagonal pyramid defect, which typically forms at the terminated threading dislocation in group III – nitrides, as schematically represented in Fig. 2.8. The origin of V-defect formation has been studied extensively. In the GaN films grown at low temperature below about 1050 °C, V-defect can form when the surface migration of adsorbed adatoms is limited. Also, V-defects are often observed in the InGaN films grown on GaN when indium is involved in heteroepitaxial growths at low growth temperatures below 800 °C,¹⁶⁻²⁶ where the accumulated misfit strain energy relaxes by V-defects instead of plastic motion of dislocation that is restricted at such a low growth temperature. Theoretical studies found that the differential behavior of indium in the reduction of surface energies of (0001) and (1011) gives rise to the formation of V-defect since the decrease of surface energy of (1011) is higher as compared to that of (0002), as explained in section 2.4.2. Thus, V-



Figure 2.8. Schematic representation of V-defect, also known as inverted hexagonal pyramid defect, in the nitrides.

defect, consisting of six (1011) planes, can be stabilized under In-rich condition on the growing GaN surface.

2.5.1 Driving Force for V-defect Formation

In order to understand the origin of V-defect formation in the InGaN films grown on GaN, a couple of models have been suggested by Northrup *et al.*⁵ and Song.¹⁶ We will review these two models in the current section. For convenience, here we denote each model as Northrup's model and Song's model.

2.5.1.1 Northrup's Model

Northrup *et al.* attempted to calculate the formation energy of V-pits formed over a screw threading dislocation in the InGaN films, taking the change of surface, strain, and screw dislocation energy into account.^{5,102} The formation energy of a V-defect is given by

$$\Delta E(x) = \gamma_0 r^2 \{ Sx^2 - Cx \ln x \}, \qquad (2.16)$$

where γ_0 is the surface energy of the (1010) surfaces, i.e., sidewalls of the small open core of screw threading dislocation, r is the radius of a small core of screw threading dislocation, x is given by a/r, a and h are the lateral size and depth of V-pit, as shown in Fig. 2.9(a), C is a geometrical factor equal to $2\pi h/a$ [C = 10.26 for (1011) facets], and the S is the projected difference in surface energies of the (0001) and the (1011) surfaces:

$$S = (3\sqrt{3})/2[\gamma(1011)/\alpha - \gamma(0001)]/\gamma_0, \qquad (2.17)$$

where $\gamma(10\overline{1}1)$ and $\gamma(0001)$ are the surface energies of the (1011) and (0001) surfaces, respectively. The α is $\cos\theta = 0.468$ at the interplanar angle of 62.1° between the (0001) and the (1011) surfaces. Figure 2.9(b) shows the V-pit formation energy as a function of



Figure 2.9. (a) Schematic representation of V-pit with a lateral size of a and depth of h, formed on the terminated threading dislocation. (b) V-pit formation energy as a function of the diameter of V-pit. When In atom is absent, S is larger than 3.0, and S factor decreases as the indium amount increases on the GaN surface. [Ref. Northrup *et al.*, Phys. Rev. B **60**, R8473 (1999).]

diameter of V-pit with varying S factor given in Eq. (2.17). When indium is absent, i.e., the S factor is larger than 3.0, there is no driving force for V-defect formation because the formation energy for V-defect keeps increasing. As the S factor decreases from 0.3 down to 0.1, i.e., the GaN surface becomes more indium-rich, the formation energy for Vdefect begins to decrease, which enables the V-defect to be energetically favorable. The equilibrium diameter of V-defect can be obtained by setting the first derivative of Eq. (2.16) to zero. The equilibrium size of V-defect increases from ~ 40 nm to ~ 140 nm as the S factor decreases from 0.3 to 0.1, as seen in Fig. 2.9(b). Consequently, this model shows that the presence of indium atoms can drive V-defect nucleation that is energetically preferable. However, this model is incomplete in a couple of aspects as follows. In Fig. 2.9(b), the formation energy for V-pit is predicted to reach a minimum at the equilibrium diameter and then increase, which should suppress the growth of Vdefect beyond the equilibrium diameter. However, our experimental observations showed that the V-defect size keeps increasing to the maximum size of $\sim 1 \,\mu\text{m}$ under the In-rich conditions as the GaN film grows to 1.8 µm. In addition, this model does not present the energy barrier for V-defect formation. Thus, under In-rich conditions, the V-defect should form at all threading dislocations, which is not observed in experiments. Lastly, in Eq. (2.16), this model considered the strain energy around the local region surrounding dislocation based on Frank model.¹⁰³ However, the V-pit size is typically much larger than a few tens of nanometers. Thus, bulk strain energy should be considered in the energy balance equation.

2.5.1.2 Song's Model

Song assumed that the V-pit is an inverted cone, using the cylindrical coordinate system, as shown in Fig. 2.10(a).¹⁶ By considering strain, dislocation, surface and mechanical energies to create the inverted facets in the $In_xGa_{1-x}N / GaN$ system ($x = 0.10 \sim 0.15$), the initial state without V-defects can be compared to the final state with V-defects in a given system, yielding the change of total system energy, as plotted in Fig. 2.10(b). The misfit strain between the InGaN and GaN films was assumed to be 5×10^{-3} in this calculation. As the film thickness increases, the system energy is reduced, suggesting that there is a strong driving force for V-pit formation on the InGaN surface under In-rich conditions on the GaN surface. However, this model is also incomplete because the surface energy of GaN (0001) was not considered. In addition, there is no energy barrier for V-pit nucleation, similar with Northrup's model. The concept of a thermal energy barrier, which is not a well defined term, had to be introduced in this



Figure 2.10. (a) Schematic representation of V-pit that is assumed to be an inverted cone. Z=rd, where the ideal *d* value is 1.63. (b) The change of total system energy as a function of thickness with increasing V-pit density. The *f* is the initial misfit strain between the InGaN and GaN. [Ref. T. L. Song, J. Appl. Phys. **98**, 084906 (2005).]

model to explain that the V-defects do not form at all threading dislocations. Therefore, in the current thesis study, a nucleation and growth model, modified from both Northrup and Song's models, will be developed in Chapter 4 to provide a better description of the V-defect formation under indium rich conditions on the growing GaN films.

2.6 Green Gap in the Solid State Laser Diodes

V-defects become more crucial in high indium composition InGaN films for green light emitting devices due to the highly In-rich conditions that reduce surface energy of the ($10\overline{1}1$) plane during epitaxy. Since the blue LED was demonstrated using InGaN active quantum well layer by Shuji Nakamura in 1993, rapid progress has been made in the solid state lighting devices. The internal quantum efficiency of blue LEDs has been increased significantly. InGaN-based blue LDs also have been commercialized successfully. However, the quantum efficiency of InGaN-based green LED is still much lower than that of blue LED. Furthermore, the green LD made of InGaN has not been commercially available yet because of defects and misalignment between conduction and valence bands in the high indium composition InGaN film.³³ For blue LEDs and LDs, the indium composition should increase to ~ 0.32, which leads to defects in the InGaN films such as phase separation and high density of V-defects originating from the misfit stress at the low growth temperature to have higher indium content.¹⁷ Solid state LDs operating by current injection have more complicated structures than LEDs because they must

obtain the optical gain with a resonant cavity for the coherency of emitted light.¹ Hence, high quality active medium is required to realize continuous lasing at room temperature with long lifetime. Since highly efficient red LEDs and LDs have been successfully realized with AlGaInP, there is so-called 'green gap' in the efficiency of current-injection solid state light emitters because the quantum efficiency decreases when the light emission wavelength approaches green from either red or blue, as seen in Fig. 2.11.³³

For the application of green LDs using high indium composition of InGaN films, V-defects become more critical factor in addition to the composition fluctuation of InGaN because V-defects may give rise to the path for reverse leakage currents.^{17,34} Thus, in order to realize the reliable green light emitting devices, it is important to identify and understand the V-defect formation mechanism to control these defects. Since these V-defects always form at the threading dislocations, the efforts to minimize these defects



Figure 2.11. Quantum efficiency of InGaN and AlGaInP LEDs as a function of emission wavelength. As the peak wavelength approaches green from either red or blue, the efficiency decreases, resulting in 'green gap'. [Ref. A. Khan, Nature Photonics **3**, 432 (2009).]

have been made using a bulk GaN substrate which has low threading dislocation density.¹⁷ Figure 2.12 shows AFM images of Mg-doped InGaN layers in two green LEDs grown on bulk GaN and sapphire substrates. Although V-defects are still observed at the order of 10⁷ cm⁻² on the bulk GaN, minimizing V-defects is successful on the bulk GaN substrate.

Recently, Nichia Corp. reported that they succeeded in fabricating stable green laser diode emitting 515 nm at room temperature by improving MOCVD growth condition of epitaxial layers.¹⁰⁴ Although they did not provide the details of epitaxy conditions in the InGaN / GaN multiple quantum well growths, the free-standing bulk GaN substrates used for their green LD were prepared in a complicated way.¹⁰⁵ First, they grew 2.5 µm thick GaN on the c-plane of sapphire substrates. Using SiO₂ stripe mask, 15 µm thick GaN was grown by the epitaxial lateral overgrowth (ELOG) to reduce the threading dislocation density. Then, 200 µm thick GaN was grown by the conventional hydride vapor phase epitaxy (HVPE). In the next step, they removed sapphire substrate by polishing, leaving only bulk GaN. Then, another ELOG was done on 150 µm thick bulk GaN to get the free-standing bulk GaN substrate for the epitaxy of the green LD. Therefore, a lot of efforts were made from the substrate preparation stage. However, if the V-defect is a concern in achieving high quality InGaN film which has the high indium composition, nitrogen-polar (N-polar) InGaN and GaN films may provide V-defect free surface morphology. The first principle calculations predict that the V-defect is not energetically preferred in the N-polar GaN which has opposite growth direction [0001] to the normal growth direction [0001].⁵ Most high power and optoelectronic devices have



Figure 2.12. AFM images of InGaN:Mg films grown on (a) bulk GaN and (b) sapphire substrates. The bulk GaN substrate has lower threading dislocation density, resulting in the lower V-defect density in the green LED. [Ref. Liu *et al.*, J. Cryst. Growth **310**, 5166 (2008).]

been fabricated on the Ga-polar GaN grown on the c-plane sapphire or SiC substrates along [0001] direction because Ga-polar GaN has excellent surface morphology, although the GaN growths can be done along [0001] basically. Hence, the N-polar InGaN and GaN films grown on sapphire or SiC could be an alternative for the V-defect free InGaN films in green LDs without using the expensive bulk GaN substrates prepared in a complicated manner. To grow N-polar InGaN films, high quality smooth N-polar GaN growths should be realized first. Thus, in the next section 2.7, we will review the basic physical properties of N-polar GaN films as well as the issues in the N-polar GaN growths.

2.7 N-polar GaN

Group III-nitrides have the polar nature along the c-axis in the wurtzite crystal structure. The polarity of GaN is a critical parameter in designing devices with heterostructures. Since Ga-polar GaN has excellent surface morphology, most optoelectronic and power devices have been developed and realized on the c-plane of sapphire or SiC substrates, which has the heteroepitaxial growth direction of nitrides along the [0001] of substrates. As compared to Ga-Polar GaN, N-polar GaN grown along [0001] of substrates has advantages such as stable surface morphology against Mg,³⁸ heavy p-type doping with



Figure 2.13. $30 \times 30 \text{ }\mu\text{m}^2$ AFM amplitude images of N-polar GaN (a – e) and Ga-polar GaN (f – j) with increasing Mg doping level. The height scale is 0.0 – 0.5 V for a – e and j, and 0.0 – 0.1 V for f – i. [Ref. Brown *et al.*, Appl. Phys. Lett. **94,** 153506 (2009).]

enhanced mode operation and lower gate leakage current of N-polar HEMT,^{37,39} and novel design of devices using opposite spontaneous and piezoelectric polarizations.⁴¹

Figure 2.13 shows the AFM amplitude images of N-polar and Ga-polar GaN films with increasing Mg doping.³⁹ As the bis-cyclopentadienyl magnesium (CP₂Mg) flow rate increases, the surface of N-polar GaN remains unchanged as compared to the roughened

surface of Ga-polar GaN that contains hexagonal domain inversions caused by heavy Mg doping. Hence, the N-polar GaN shows better surface properties against heavy Mg doping in comparison with Ga-polar GaN.

One of the biggest issues in III-nitrides has been a high resistivity of p-type due to high ionization energy of Mg dopants at room temperature since the advent of blue LEDs using nitrides. For n-type doping, Si dopant has ionization energy of ~ 15 meV for GaN and 282 meV for AlN at room temperature.^{41,106,107} In contrast, Mg acceptor dopant has 200 meV for GaN and 630 meV for AlN.¹⁰⁶ Therefore, achieving high concentration of holes with low resistivity has not been an easy process especially in AlGaN alloys that are employed for deep UV light emitters. Recently, Simon *et al.* developed compositionally graded AlGaN / GaN heterostructures along N-polar direction with polarization-induced hole doping, demonstrating highly conductive p-type AlGaN layer by creating three-dimensional hole gas.⁴¹ N-polar nitrides, thus, can allow for a novel approach to the issues related to the high resistivity of p-type nitrides in many devices including HEMT.

In addition to these advantages of N-polar nitrides, theoretical study predicts that the V-defect, frequently observed in the In-polar InGaN films, may not form in the Npolar InGaN and GaN films.⁵ Since the high indium composition InGaN film for green LEDs and LDs typically has high density of V-defects, as explained in the section 2.5, Npolar InGaN grown on GaN may provide superior surface morphology over Ga-polar InGaN / GaN system at the high indium composition. However, there is another type of surface defects, commonly called 'hexagonal hillocks', frequently observed in the N- polar GaN films. Therefore, inn the following sections, we will study the origin of these defects and how these hillocks could be minimized.

2.7.1 Hexagonal Hillock

Although V-defect formation in In-polar InGaN may not be preferred along the [0001] orientation according to the theoretical prediction, it is well known that the high density of surface defects, so-called the hexagonal hillocks, has been a main obstacle in fabricating optoelectronic devices utilizing N-polar GaN. These surface defects are observed in the homoepitaxy⁴³ as well as the heteroepitaxy of GaN.^{36,44} Since these surface defects form during homoepitaxy, the formation mechanism is irrelevant to the misfit stress. Figure 2.14 shows the typical hexagonal hillocks on N-polar GaN grown on



Figure 2.14. (a) Differential interference contrast optical micrograph of MOCVDgrown homoepitaxial GaN on an N-polar GaN substrate and (b) optical micrograph of a 1 μ m thick GaN film grown on an on-axis [0001] SiC substrate. High density of hexagonal hillocks (~ 50 μ m size) is observed in both homoepitaxy and heteroepitaxy. [Ref. Weyher *et al.*, J. Cryst. Growth **204**, 419 (1999), and D. F. Brown *et al.*, Appl. Phys. Lett. **93**, 042104 (2008).]

(a) bulk N-face GaN and (b) C-face SiC. 36,43 The size of the hillocks ranges from 10 μm to 50 µm. It has been reported that the precursor input ratio of group V to III has the influence on the density of these hillocks. Higher V/III ratio resulted in the smaller size of hexagonal hillocks with higher density, as reported by Sumiya et al.³⁵ The important nature of the hillock was investigated by Weyher et al. using TEM analysis.⁴³ Figure 2.15 indicates the cross-sectional TEM image in the region near the core of hexagonal hillocks. The columnar defect exists from the plate-like nucleation layer to the top of the hexagonal hillocks along the growth direction of [0001]. Convergent beam electron diffraction (CBED) revealed that the columnar defect is Ga-polar GaN. Thus, the core of the hexagonal hillock is the inversion domain embedded in the N-polar GaN matrix. Another important observation is that the Ga-polar inversion domain has a higher growth rate than the N-polar matrix, resulting in the faceted hillocks. The increased surface roughness associated with these hillocks makes the N-polar GaN not suitable for the application of optoelectronic and power devices although it may allow for novel devices. However, these hillock defects can be minimized by using the vicinal substrates, which will be discussed in the next section.

2.7.2 Effect of the Substrate Misorientation on the N-polar GaN

The obstacle caused by hexagonal hillocks in N-polar GaN has been overcome by using misoriented substrates which lead to the suppression of hillock formation. By increasing the misorientation towards $(11\overline{2}0)$ plane (a-plane) or $(10\overline{1}0)$ plane (m-plane) of


Figure 2.15. TEM cross-sectional images of the columnar defect delineating the core of the hexagonal hillock. (a) Defect imaged with g in the growth direction close to the $<1\overline{100}>$ zone, and (b) weak beam image of the same defect revealing a thin planar nucleating site at the base of the column. [Ref. Weyher *et al.*, J. Cryst. Growth **204**, 419 (1999).]

sapphire and SiC substrates from on-axis [0001], it has been reported that the density of hexagonal hillocks could be reduced dramatically.^{36,45-47} Figure 2.16 shows the optical microscope images of N-polar GaN films grown by MOCVD with increasing the miscut of sapphire substrates.³⁶ As the misorientation increases from 0 to 2°, the density of hexagonal hillock was significantly reduced. The possible explanation would be the increased step edge of the substrate, caused by the miscut, which may be the preferred site in Ga adsorption. These behaviors may suppress the faster Ga adsorption on the nucleation of inversion domain. Consequently, in the current thesis study, misoriented SiC substrates will be used for the development of N-polar GaN growths.



Figure 2.16. Optical microscope images of 0.8 µm thick GaN films grown on (0001) sapphire substrates with misorientation angles of (a) 0.5° , (c) 1° , and (e) 2° toward the a plane ($11\overline{2}0$), and (b) 0.5° , (d) 1° , and (f) 2° toward the m plane ($10\overline{1}0$). The inserts in (a) and (b) are enlarged threefold. [Ref. Keller *et al.*, J. Appl. Phys. **102**, 083546 (2007).]

Chapter 3

Experimental Methods

This chapter describes experimental methods used in the current study. All GaN films were grown in the MOCVD system, so we will briefly review the components of MOCVD system first. Then, the *in-situ* stress measurement technique using multi-beam optical stress sensor (MOSS), which is integrated on the MOCVD system, will be described. The basic information of substrates such as wafer orientations will be described for the substrate preparations. Then, the cleaning procedure of substrates and typical MOCVD growth process will be reviewed. Ex-situ characterization techniques such as x-ray diffraction (XRD), atomic force microscopy (AFM), micro-Raman scattering spectroscopy, photoluminescence (PL), secondary ion mass spectroscopy (SIMS), mercury-probe capacitance-voltage (C-V) measurements, and transmission electron microscopy (TEM) were used to investigate the structural, optical, and electrical properties of GaN epilayers. Thus, the basic principles and measurement methods of these tools will be studied and reviewed. In the current thesis study, all epitaxial sample growths and characterizations were done by the author. However, TEM including specimen preparations was performed by Dr. Xiaojun Weng at Penn State University, and SIMS was done at the Evans Analytical Group by Dr. Wei Ou since SIMS is not available at Penn State University.

3.1 MOCVD System

The MOCVD system was originally manufactured by Thomas Swan, Inc., and modified by CVD Equipment Corporation. This system consists of the reactor, gas manifold cabinet, control computer, vacuum pump, and scrubber, as shown in Fig. 3.1.



Figure 3.1. Photograph of MOCVD system in 220 EE West bldg. Scrubber and rotary vane vacuum pump are behind the MOCVD system.

3.1.1 Reactor

The reactor has a cold wall design with vertical configuration, as shown in Fig. 3.2. It is made of quartz that enables the penetration of electromagnetic wave from the coil wrapped outside the quartz reactor, so that silicon carbide (SiC) coated graphite

susceptor can be heated by induction using remote radio-frequency (RF) generator. The susceptor is mounted on the quartz support shaft that also acts as a feedthrough for a thermocouple in contact with the end of shaft beneath the susceptor to monitor and control the growth temperature. The quartz shaft is capable of rotating because it passes through a ferrofluidic seal (Rigaku, Inc.). The susceptor rotation was kept typically at 30 rpm during epitaxial growths. In principle, the susceptor can hold 2" wafer, but typically a SiC substrate piece ($1 \times 1 \text{ cm}^2$) was loaded in the square pocket, which has 250 µm in depth, on the top of susceptor. Two coaxial quartz cones for group III and V are mounted at the top of the reactor, as seen in Fig. 3.2(b), which separates group III source precursors and group V ammonia to suppress the pre-reaction that does not contribute to



Figure 3.2. (a) Photograph and (b) schematic diagram of vertically configured quartz reactor.

the film growth. A removable quartz liner tube is located inside the reactor, which prevents the deposition of film on the reactor wall and enables easy cleaning of deposits resulted from the growth process. Carrier gas purges between the reactor and liner tube from the bottom to the top for further cooling in addition to water cooling in the water jacket of the reactor. Two exhaust lines are connected from the bottom of reactor through the trap and butterfly valve to the rotary vane vacuum pump. The butterfly valve controlled the reactor pressure typically at 50 \sim 100 Torr for GaN growths by adjusting the angle of disk that controls gas flows. MOSS system is integrated onto the top of reactor, and two optical ports provide the laser beam path for the MOSS system. This MOSS system will be described in detail in section 3.3.

3.1.2 Gas Manifold Cabinet

The gas manifold cabinet is composed of bubblers, mass flow controllers (MFCs), pressure controllers, and pneumatic valves. Ultra high purity (UHP) H₂ (99.999 %) purchased from general stores at Penn State University was the choice for carrier gas during GaN growths. Two H₂ gas cylinders were installed in a separate cabinet. N₂ was used for purging gas lines and reactor before and after CVD processes. N₂ was supplied from the liquid nitrogen tank at Electrical Engineering West building. The liquid nitrogen was periodically refilled by Air products and Chemicals, Inc. Both H₂ and N₂ were purified by SAES ambient purifier (MC3000 series) to further reduce impurity levels.

The source precursors were trimethylgallium (TMGa), trimethylaluminum (TMAl), trimethylindium (TMIn), and ammonia (NH₃) for Ga, Al, In, and N, respectively. TMGa, TMAl, and TMIn bubblers, purchased from Epichem (currently SAFC Hitech, Inc.), were placed in Lauda baths which control the bubbler temperature to provide proper equilibrium vapor pressures of source precursors. TMGa bubbler temperature was kept at - 13 °C in ethylene glycol and water, covered by Styrofoam to help thermal isolation from the ambient. TMAl and TMIn bubblers were typically controlled at 25 °C in water. The equilibrium vapor pressures of TMGa, TMAl, and TMIn at the given bubbler temperatures are determined by the following equations provided by the manufacturer:

$$\log_{10} P_{TMGa} = 8.07 - \frac{1703}{T_{TMGa}}, \qquad (3.1)$$

$$\log_{10} P_{TMAI} = 8.224 - \frac{2134}{T_{TMAI}}, \qquad (3.2)$$

$$\log_{10} P_{TMIn} = 10.52 - \frac{3014}{T_{TMIn}}, \qquad (3.3)$$

where P (Torr) is the equilibrium vapor pressure of source precursor, and T (K) is the bubbler temperature. The pressure controllers, which adjust total vapor pressure of source precursors, were also installed on the downstream from the bubblers. MFCs were installed on the upstream of the group III bubblers to control flow rates of H₂ carrier gas that passes through these bubblers. The molar flow rates of TMGa and TMIn source precursors can be determined by the following equation.

$$n_{metalorganic} = n_{carrier} \left(\frac{P_{vap}}{P_{total}} \left/ \left(1 - \frac{P_{vap}}{P_{total}} \right) \right),$$
(3.4)

where $n_{metalorganic}$ is the molar flow rate of TMGa or TMIn in standard cubic centimeter per minute (sccm), $n_{carrier}$ is the flow rate of carrier gas in sccm, P_{vap} is the equilibrium vapor pressure of TMGa or TMIn in the bubbler at the given temperature, and P_{total} is the total pressure controlled by pressure controllers. Unlike TMGa and TMIn, TMAI evaporates as dimers. Thus, for TMAI, the molar flow rate (n_{TMAI}) is given by

$$n_{TMAl} = 2 \times n_{carrier} \left(\frac{P_{vap}}{P_{total}} \middle/ \left(1 - \frac{P_{vap}}{P_{total}} \right) \right).$$
(3.5)

Ammonia was purchased from Praxair, Inc. as a liquefied gas form at the vapor pressure of 114.1 psi at 21 °C. Net weight 50 lbs NH₃ cylinder was purchased, and stored in a separate standalone cabinet. Initially, the purity grade of 5.5 (99.9995 %) was used, which contains 0.5 parts per million (ppm) oxygen and 1 ppm water. Although SAES ambient purifier was also used for NH₃, we later switched to higher grade of 6.5 (99.99995 %) with reduced oxygen (50 parts per billion (ppb)) and water (200 ppb) to further minimize the impurities originating from the ammonia.

The gas lines mostly consisted of $\frac{1}{4}$ " steel tubes in the gas manifold cabinet. The steel tubes on the downstream from group III bubblers to the reactor were wrapped by heating tape, which was controlled at 30 ~ 60 °C. The temperature of heating tape must

be higher than the bubbler temperature in order to prevent the condensation of metalorganic gas precursors in the steel tubes. Ammonia gas line was $\frac{1}{4}$ " steel line surrounded by coaxial outer $\frac{1}{2}$ " steel tube to prevent any possible leak. The entire gas line configurations are schematically represented on page 46 of Abhishek Jain's thesis.¹⁰⁸

3.1.3 Vacuum Pump and Scrubber

The vacuum pump used in the MOCVD system is a mechanical rotary vane vacuum pump, Leybold Trivac B series. The lubricant for this pump was fomblin, perfluorinated polyether (PFPE), which is inert oil in high oxygen and corrosive environments. This oil has advantages such as low vapor pressure, chemical inertness, and thermal stability. Thus, possible contaminations caused by oil oxidation or by-products from the reaction between oil and gases are minimized. The exhaust gases were diluted with N₂, and then directed to chemical scrubber (Misonix, Inc.) which can neutralize the alkaline gases due to the excess ammonia or metalorganic sources by acid before discharging. The acid solution was 50 weight percent sulfuric acid (H₂SO₄) in water. The reaction between sulfuric acid and water is thermodynamically preferred and highly exothermic. Thus, for safety, it is highly desirable to add sulfuric acid to water in the reservoir equipped in the scrubber since this makes sure that the acid is a limiting reagent. Therefore, refilling sulfuric acid to the reservoir should be done slowly to allow for heat dissipation.

3.2 Multi-beam Optical Stress Sensor (MOSS)

MOSS system, developed by K-space Associates, Inc. and Sandia National Laboratories, was used in the MOCVD system for the *in-situ* stress measurements of epitaxially grown GaN films. In principle, MOSS utilizes an array of laser beams which are reflected off on the growing film surface. The change of spacing between laser beams, detected by the charge-coupled device (CCD) camera, corresponds to a change in the curvature of the film, as schematically represented in Fig. 3.3. A single beam light source was AlInGaP-based semiconductor laser emitting 658 nm, which has the maximum power of 13 mW. The power of this laser can be adjusted by the integrated current controller in the MOSS control computer. For stable operation, the temperature of this laser package was controlled at 13 °C by Peltier device. This laser light was coupled



Figure 3.3. Schematic diagram of MOSS system equipped in the MOCVD system. The real-time change of beam spacing, corresponding to the film curvature, allows for the *in-situ* stress measurements.

into an optical fiber, and guided towards a focal length adjustable lens. Etalon was placed to generate one-dimensional array of laser beams from the single laser light. These multiple lights were focused on the film surface by the focal length adjustable lens. The spacing change of reflected beams from the sample was monitored by CCD camera, which has sensor size of 8.8 mm \times 6.6 mm with the resolution of 768 \times 480 pixels. The CCD camera was wired to the frame grabber in the control computer in order to capture the real-time image of beam spots, and determine the beam position at the trigger pulses generated by the susceptor rotation.

The differential change of beam spacing correlates to the film curvature, which provides the stress-thickness products ($\sigma_f h_f$) by Stoney's equation as follows:⁸⁰

$$\sigma_f h_f = \frac{M_s h_s^2 \kappa}{6} = \left[\frac{\delta d}{d_0}\right] \frac{(M_s h_s^2 \cos \theta)}{12L},$$
(3.6)

where subscripts f and s refer to the film and substrate, σ_f is the film stress, h is the thickness, κ is the curvature, M is the biaxial modulus, d_0 is the reference spacing of laser spots, δd is the change of laser spot spacing during growth, θ is the incident angle of the laser beams, and L is the distance between the substrate and CCD camera. Thus, MOSS system enables the real-time stress monitoring of GaN films at the growth temperature. In addition to the film stress, the reflectivity data, recorded as a function of time, can determine the growth rate since the reflected light oscillates due to the constructive and destructive interferences as the film grows. When the incident laser beam penetrates the sample and gets reflected on the underlying interface, this beam travels additional path

with respect to the reflected light on the surface. Thus, the film thickness (*d*) can be correlated with this extra beam path by the following equation:¹⁰⁸

$$d = \frac{\lambda}{2\cos\theta n_f},\tag{3.7}$$

where λ is the laser wavelength (658 nm), θ is the incident angle of the laser (10°), and n_f is the refractive index of the films at 658 nm ($n_{GaN} \approx 2.37$ and $n_{AlN} \approx 2.06$).¹⁰⁹ Therefore, one oscillation in the reflectivity data corresponds to approximately 140 nm for GaN and 160 nm for AlN, respectively, and the growth rate can be determined.

3.3 Substrate Preparation and Growth Process

For hexagonal wurtzite GaN growths, SiC, Si(111) and bulk GaN substrates were used in the current study to investigate the indium surfactant effect on the GaN epilayers. This section describes the basic information of these substrates such as wafer orientations, provided by the manufacturers, which is important for the preparation of different polarity GaN growths. Also, the cleaning process of substrates prior to epitaxy and actual process steps in GaN growths are briefly described.

3.3.1 Orientations of SiC, Si(111), and Bulk GaN Substrates

Among many polytypes of SiC, 6H-SiC substrates were used in this study. All 2" 6H-SiC wafers were purchased from Cree, Inc. For Ga-polar GaN, the substrates were research grade, on-axis (0001) (\pm 0.5 degree), n-type (nitrogen dopant), semi-conducting (0.02 ~ 0.09 Ohm-cm), chemical mechanical polish (CMP) finished Si-face, and approximately 250 µm thick 6H-SiC wafers. In contrast, vicinal C-face 6H-SiC substrates, misoriented towards <1120 > by 3.57 degree, were used for N-polar GaN growths since the polarity of SiC substrate can determine the polarity of GaN film. These wafers were also research grade, n-type, semi-conducting, and approximately 390 µm thick wafers, and the C-face was CMP-finished for epitaxy. Since the SiC wafers were double side polished by the manufacturer, it is important to identify the polarity and misorientation direction of SiC wafers. The definitions of flat orientation, polarity, and misorientation of 6H-SiC wafers are shown in Fig. 3.4. The primary flat is always



Figure 3.4. Diameter, primary and secondary flat orientations, and wafer ID number of (a) carbon face up for silicon face polished wafer and (b) silicon face up for carbon face polished wafer. Primary flat is one of $\{10\overline{1}1\}$ planes and parallel to $<11\overline{2}0>$. Wafer ID is scribed on the face which is not used for epitaxy.

{1010} plane and parallel to $<11\overline{20}>$ regardless of the wafer polarity. Therefore, the miscut direction of $<11\overline{20}>$ in the C-face SiC wafers used here is parallel to the primary flat, as shown in Fig. 3.4(b). The simplest way to identify the polarity of SiC substrates was the wafer ID number which is scribed on the face that is not used for epitaxy.

Bulk GaN substrates were provided as square pieces by Kyma Technologies, Inc. All bulk GaN substrates were sized to about $1 \times 1 \text{ cm}^2$ to fit the pocket of the susceptor. They were typically double side polished, nominally undoped, and approximately 380 µm thick substrates. Two flats are required to identify the polarity of double side polished GaN substrates, as shown in Fig. 3.5. Silicon (111) wafers were purchased from Nitronex, Inc. They were 2", 500 µm thick, highly resistive (2,000 ~ 10,000 ohm-cm), and undoped intrinsic single-side polished Si wafers.

For double side polished 6H-SiC substrates, intentional roughening of one side of the wafer had to be done to prevent the laser light reflection from the bottom surface of substrate, which causes problems in tracking the laser spots reflected from the epilayers in the MOSS system. 6H-SiC and Si(111) wafers were diced to $1 \times 1 \text{ cm}^2$ pieces which



Figure 3.5. Two flats are necessary to identify the [0001] and [0001] of bulk GaN substrates.

can fit the pocket of the susceptor. Both intentional roughening and dicing of SiC wafers were done in Electro-Optics Center (EOC) at Freeport, PA by William Everson.

3.3.2 Substrate Cleaning Process

Prior to group III-nitride growths by MOCVD, all substrates were treated by a series of cleaning steps as follows:

- Dip in Opticlear solvent
- Ultrasonication in acetone for 10 min
- Ultrasonication in isopropanol for 10 min
- Rinse in de-ionized (DI) water
- Gentle wiping with cotton swab in acetone
- Ultrasonication in acetone for 5 min
- Ultrasonication in isopropanol for 5 min
- Rinse in DI water
- Dip in 10 % hydrofluoric acid (HF) for 10 min
- Rinse in DI water
- Drying with nitrogen

Intentional roughening and dicing of the SiC wafers require crystalbond or wax for mounting wafers. Thus, substrate cleaning process is critical to remove the wax residues and clean any organic contaminants on the substrate surface, which could be detrimental to epitaxially grown GaN films. In order to get rid of the residues, substrates were first dipped in the Opticlear (National Diagnostics) solvent for an hour. Opticlear is a nontoxic, nonflammable, and biodegradable solvent that can be used for the removal of wax, pitch, flux, grease, resin and solvent soluble resists. Then, substrates were ultrasonicated in an acetone and isopropanol (CMOS grade) for 10 min in each step, and rinsed in DI water. In order to make sure that wax residues are eliminated, substrates were cotton-swabbed gently in acetone, which turns out to be important step. Figure 3.6 shows AFM images of SiC substrates before and after cotton swab stage in the cleaning process. Even with dip in Opticlear and sonication in acetone and isopropanol, the wax residues were sometimes observed on the SiC substrate surface, as shown in Fig. 3.6(a). Gentle wiping with cotton swab in acetone removed the residues effectively, as seen in Fig. 3.6(b). Typically, SiC surface has thin contaminants layer arising from bonding to



Figure 3.6. $10 \times 10 \text{ }\mu\text{m}^2$ AFM images of (a) SiC substrate cleaned by dip in Opticlear, sonication in acetone and isopropanol, and rinse in DI water, and (b) SiC substrate further cleaned by wiping with cotton swab in acetone and additional sonication in acetone and isopropanol.

oxygen. Si wafers have thin native oxide layer on the surface. Thus, wet etching with HF was used to remove those layers prior to loading the substrate into the MOCVD reactor.

3.3.3 Growth Process

All growth processes were controlled by the MOCVD system computer which has a programmable recipe, consisting of sequential segments. The growth steps of typical recipe for GaN growths are as follows:

- Purge gas lines and reactor with N_2
- Adjust the reactor pressure to the desired growth pressure
- Set gas flow rates of MFCs at the desired values
- Switch N_2 to H_2 and heat the susceptor to the growth temperature
- Hold at the growth temperature
- AlN buffer layer growth
- Hold, and adjust gas flow rates and growth temperature if necessary
- GaN growth
- Cooling from the growth temperature to 300 °C
- Switch H_2 to N_2
- Purge gas lines and reactor with $N_{\rm 2}$
- Increase the reactor pressure to 650 Torr
- Shut all valves

It is important to change the reactor pressure slowly after loading and before unloading samples. Rapid change of the reactor pressure may cause dispersing of particles from the dish located below the susceptor, which spreads particles on the sample surface. The hold step prior to AlN buffer layer is for source gas flow rates to be stabilized and thermal cleaning of substrates at 1100 °C.

Prior to film growths, the reactor was baked at 1175 °C and about $7 \sim 10$ Torr in H₂ atmosphere to etch out the deposits on the susceptor and liner tube. To protect the pocket of susceptor and monitor the re-deposition from etching, a cleaned Si(100) piece was put on the susceptor, and the MOSS reflectivity data was monitored. Depending on the GaN thickness in the previous growth, the baking duration was determined to be between 40 min and 90 min, based on the MOSS reflectivity signal.

3.4 Characterization

3.4.1 X-ray diffraction (XRD)

Epitaxially grown semiconductors are nearly perfect single crystals, which necessitates high resolution in x-ray diffraction (XRD) experiments unlike highly defective polycrystalline thin films which can be analyzed by medium or low resolution XRD. Also, aligning a particular set of diffracted plane of a single crystal along 2θ , ω , ϕ , and κ angles requires a four-circle diffractometer. Therefore, to analyze the stress and

mosaic structures of GaN epilayers grown by MOCVD in this study, HRXRD measurements were performed in a Philips (currently PANanalytical) X'Pert PRO MRD four-circle diffractometer located in 164 MRI building at Penn State University. This diffractometer utilizes modular systems which allow for low, medium, and high resolution XRD measurements that can be easily re-configured, using Pre-aligned Fast Interchangeable X-ray (PreFIX) modules. In general, x-ray diffractometer is composed of three parts, i.e., incident beam optics, sample stage, and diffracted beam optics, as shown in Fig. 3.7. In order to configure the high resolution mode, a hybrid monochromator PreFIX module, consisting of a parabolic-shaped multilayer x-ray mirror and 2-crystal



Figure 3.7. Photograph of a Philips X'Pert PRO MRD four-circle diffractometer located in 164 MRI building at Penn State University. High resolution mode was configured, using hybrid monochromator PreFIX module in the incident beam optics, and the triple axis & rocking curve attachments module in the diffracted beam optics.

Ge(220) 4-bounce monochromator, was installed in the incident beam optics. In the hybrid monochromator, the x-ray mirror converts the divergent beam to quasi-parallel x-ray beam which in turn becomes the intense monochromatic beam (spectral range ~ 19 arcsec) through the monochromator. In contrast, the medium resolution XRD demands only a separate x-ray mirror module, and low resolution XRD does not even need x-ray mirror. The source x-ray was Cu K_{a1} radiation ($\lambda = 1.5406$ Å). Fixed divergence slit (1/4°) was used to control the equatorial divergence of the line focused beam generated from the x-ray tube. Divergence slit (1/4°) combined with hybrid monochromator produces 0.6 mm beam in height. The length of the line focused x-ray beam is approximately 2 cm, but was confined to 1 cm using incident beam mask, since the sample dimension was typically 1 × 1 cm² piece.

In the diffracted beam optics, triple axis & rocking curve attachments PreFIX module, which provides two different beam paths, was configured for HRXRD rocking curves and $2\theta - \omega$ measurements, as seen in Fig. 3.7. In the triple axis path, the diffracted x-ray from samples passes through the analyzer crystal, a channel cut Ge(220) crystal, which provides ~ 12 arcsec acceptance angle for the detector #1. This triple axis mode is generally used for reciprocal space mapping. For the rocking curves and $2\theta - \omega$ measurements in the current study, the rocking curve path was used with detector #2. Since the resolution in rocking curve measurements (ω - scans) are determined by the incident beam monochromator and sample, the receiving slit (1/2°) was placed in front of the detector #2 only for the reduction of background radiation. However, for the $2\theta - \omega$ scans, the receiving slit (1/2°) was used to reduce the acceptance angle for the detector.

X-ray diffractions occur in crystals at particular incident angles which satisfy the Bragg law given by⁸⁷

$$\lambda = 2d\sin\theta, \qquad (3.8)$$

where λ is the wavelength of incident x-ray, d is the spacing between the adjacent (hkl) planes, and θ is the Bragg angle between the incident x-ray and atomic planes under consideration. Basically, lattice parameters of crystals can be calculated by the Bragg law if we measure any diffraction on an atomic plane, for instance, in a cubic crystal. However, precise measurements of lattice constants require diffractions at higher Bragg angle θ near 90° because the variation of sin θ becomes smaller as θ approaches 90°, as indicated in Fig. 3.8, giving rise to the reduced error in $\sin\theta$ that arises from the error in the experimental measurements of θ . Therefore, the extrapolation technique by measuring multiple diffracted planes including higher Bragg angle near 90° is a preferred and more accurate method in determining lattice constants. For the extrapolation, $\cos^2 \theta$ can be used when only high Bragg angles are considered in 2θ - ω measurements. However, Nelson-Riley function, $(\cos^2 \theta / \theta + \cos^2 \theta / \sin \theta)$, ^{87,110,111} typically works better when the diffractions are measured at the low Bragg angles as well as high angles due to the better linearity of Nelson-Riley function at the lower angles. Thus, in this study, the lattice parameters of GaN epilayers were determined by measuring multiple 2θ - ω scans, using Nelson-Riley function, for precise measurements.



Figure 3.8. The change of $\sin\theta$ with θ . The error in $\sin\theta$ caused by the same error of $\Delta\theta$ becomes smaller when θ approaches 90°. The experimental error of $\Delta\theta$ is exaggerated.

3.4.2 Raman Scattering Spectroscopy

When light is illuminated on molecules or lattice of materials, the majority of light is elastically scattered, which is called Rayleigh scattering. This scattered light has the same wavelength of the light source. However, small portion of light can excite the molecules or lattice to higher energy states in vibrational modes. In this case, the light is inelastically scattered, which was found by Raman, thus termed as Raman scattering. The inelastically scattered light has different photon energy from the source light. Raman scattering spectroscopy probes this energy shift of inelastically scattered light corresponding to a specific resonant frequency of molecule vibrations or lattice vibrations, i.e., phonons, providing the information on the material characteristics.¹¹²

Infrared (IR) spectroscopy can also probe vibrations of molecules. However, Raman spectroscopy differs from IR spectroscopy in that Raman detects the change of polarizability whereas IR detects the change of dipole moment, when the light interacts with molecules or lattice.¹¹² Thus, Raman and IR techniques are complementary tools.

Since the intensity and frequency of phonon modes can vary, depending upon the composition, impurity, quality, and stress of materials, Raman scattering spectroscopy was employed in the current study to characterize the film stress and examine the change of electron carrier concentration in GaN epilayers, using Renishaw inVia spectrometer in 13 Hosler building. This spectrometer is a micro-Raman system which equips the optical microscope that allows for about $\sim 1 \ \mu m$ spatial resolution. For the monochromatic excitation source light, 514 nm Ar+ ion laser was used. All measurements were done in a backscattering geometry of $z(x, x)\overline{z}$ along c-axis of hexagonal wurtzite GaN at room temperature. In the $z(x, x)\overline{z}$ geometry, E₂(high) and A₁(LO) phonon modes in GaN are observed, obeying Raman selection rules. $z(x,x)\overline{z}$ is a Porto's notation, which implies that the source and scattered light propagates along z and \overline{z} direction (z is parallel to the c-axis of hexagonal wurtzite GaN), and the incident and scattered lights are polarized along x direction. In the hexagonal GaN crystal, there are 6 Raman-active phonon modes such as $E_2(low)$, $A_1(TO)$, $E_1(TO)$, $E_2(high)$, $A_1(LO)$, and $E_1(LO)$. The selection rules of allowed phonon modes which depend upon the scattering geometries and polarization directions of incident and scattered lights are summarized in Table 3.1.¹¹³ The frequencies of each phonon modes are summarized in Table 3.2.^{113,114}

Scattering geometry	Allowed Raman modes
$z(x,x)\overline{z}$	$E_2, A_1(LO)$
$z(x,y)\overline{z}$	E_2
$x(y, y)\overline{x}$	$E_2, A_1(TO)$
$x(z,z)\overline{x}$	$A_1(TO)$
$x(z,y)\overline{x}$	$E_1(TO)$
x(y,z)y	$E_1(TO), E_1(LO)$
x(y,y)z	E ₂

Table **3.1.** Selection rules of the allowed phonon modes, depending on the Raman scattering geometries, for the hexagonal wurtzite GaN.¹¹³

Table 3.2. Typical phonon frequencies of the heteroepitaxially grown hexagonal wurtzite GaN (50 ~ 70 μ m) at room temperature. The values in brackets derive from bulk GaN.^{113,114}

Phonon modes	Frequencies (cm ⁻¹)
E ₂ (low)	144.0 (144)
$A_1(TO)$	531.8 (531)
$E_1(TO)$	558.8 (560)
E ₂ (high)	567.6 (568)
$A_1(LO)$	734.0
E ₁ (LO)	741.0

3.4.3 Atomic Force Microscopy (AFM)

For the investigation of surface morphologies in GaN films, AFM measurements were done on a Digital Instruments Dimension 3100 in 13 Hosler building. In the AFM,

sample surface is scanned by a tip on cantilever that is deflected by forces such as van der Waals force, capillary force, electrostatic force, and magnetic force between sample and tip. To measure this deflection, a laser light is focused on the cantilever that deflects the light towards an array of photodiodes, which also enables feedback mechanism to make the distance between tip and sample constant. All measurements in this study utilized tapping mode, which drives oscillation of cantilever at the resonant frequency (about 330 kHz). The used silicon tip (Nanosensors) had height of $10 \sim 15 \,\mu\text{m}$ and radius curvature of about 10 nm, providing enhanced resolution.

3.4.4 Photoluminescence (PL)

Photoluminescence (PL) measurements were performed at room temperature to investigate the optical properties of GaN epilayers. When the light which has higher photon energy than the band gap of semiconductor is illuminated on the sample, the electrons are excited from valence band to conduction band, creating the photoexcited electron-hole pairs. When the electrons recombine with holes, the light is generated corresponding to the band gap of the semiconductor, giving rise to PL. When impurities are incorporated into semiconductors, the electronic energy states due to impurities are introduced within the forbidden band gap, emitting the light which has lower photon energy than the band gap because of the defect-assisted recombinations of electrons and holes. The intensity and peak positions of PL signals vary with the crystal quality, impurities, and film stress, thus providing optical characteristics of GaN films. PL system consists of the source light, monochromator, and detector. The source excitation laser was fourth harmonic generated 266 nm from 1064 nm neodymium-doped yttrium aluminum garnet (Nd:YAG, Nd:Y₃Al₅O₁₂) laser. This light was chopped at approximately 101 Hz to provide trigger pulses, and then illuminated on the samples. The PL signals from samples were collected by a lens, and directed towards the input slit of the monochromator which has diffraction gratings. Rotation of gratings separates the colors of lights spatially. The intensity of the separated light is detected at the output slit of monochromator by photomultiplied tube (PMT) which has a series of dynodes that can amplify the electrical signal converted from light signal. The spectral range in PL measurements was typically from 275 nm to 650 nm every 0.2 nm step size.

3.4.5 Mercury Probe Capacitance-Voltage (C-V) Measurements

Mercury probe C-V measurements were done on Lehighton model 2017B Hg probe station to estimate the electron concentration in GaN films. In this technique, mercury electrode forms the Schottky contact on the GaN surface, which leads to the depletion of majority carriers due to the difference in work functions between mercury and sample. This technique basically measures the capacitance of depletion layer (space-charge region). The capacitance varies due to the changes of depletion region width driven by the applied reverse bias. Thus, the electron concentration (n) can be calculated from the differential C-V measurements by the following equation:¹¹⁵

$$n(W) = -\frac{C^3}{qK_s\varepsilon_0 A^2 dC/dV} = \frac{2}{qK_s\varepsilon_0 A^2 d(1/C^2)/dV},$$
(3.9)

where *C* is the measured capacitance, *q* is the charge, K_s is the dielectric constant of semiconductor, ε_0 is the vacuum permittivity, *A* is the area of electrode, *V* is the applied external bias, and *W* is the depletion region width given by

$$W = \frac{K_s \varepsilon_0 A}{C} \,. \tag{3.10}$$

In the Hg probe station, two mercury electrodes are formed on the sample surface, resulting in two Schottky barriers which do not allow for proper C-V measurements in principle. However, one electrode has much larger area than the other, which leads to an ohmic contact due to the leakage current through the large area. All C-V measurements were done at 1 MHz of AC voltage superimposed on the DC voltage ranging typically between -3 and 0 V for the n-type GaN films.

3.4.6 Transmission Electron Microscopy (TEM)

Cross-sectional and plan-view TEM specimens were prepared using conventional mechanical thinning followed by argon ion milling. Cross-sectional TEM was carried out on a JEOL 2010F field emission microscope operated at 200 keV to investigate the microstructure of the GaN epilayers. Plan-view TEM was performed on a Philips

78

EM420T operated at 120 keV to determine the TD density. All TEM work was done by Dr. Xiaojun Weng.

3.4.7 Secondary Ion Mass Spectroscopy (SIMS)

All SIMS analyses were done using primary Cs ion beams at Evans Analytical Group (EAG) to probe the impurities incorporated into the GaN epilayers. SIMS is the most sensitive tool that can profile the composition and impurities in materials. SIMS sputters samples by primary ion beams, and secondary ions formed from the samples are detected by a mass spectrometer. The SIMS equipment had the depth resolution of 5 Å and typical probe area of $500 \times 500 \ \mu\text{m}^2$. The detection limit for various elements in GaN films, provided by EAG, is summarized in Table 3.3.

Elements	Detection limit (cm ⁻³)
Si	5×10^{16}
Ο	5×10^{16}
С	5×10^{16}
Н	5×10^{17}
In	0.0001 (atomic fraction of Ga atoms)

Table **3.3.** Detection limits for selected elements of GaN films in SIMS analysis, provided by EAG.

Chapter 4

GaN Growth on SiC Substrates

4.1 Introduction

As reviewed in section 1.1 and 2.4, indium can act as a surfactant on the growing GaN surface without being incorporated into GaN films due to its high vapor pressure at growth temperatures of 900 – 1000 °C. Thus, indium surfactant can modify the growth mode of GaN films by changing the surface energy and surface diffusivity of adsorbed Ga and N adatoms.^{5,101} It has been reported that indium lead to the smoother surface morphology of GaN films.^{6,8-11} However, there have been conflicting reports in the stress relaxation and crystallinity of GaN films grown with indium surfactant,^{14,15} as described in section 1.1.

In this chapter, therefore, the main focus is to investigate the effect of indium surfactant on the stress evolution and structural properties of GaN epilayers grown on SiC substrates by MOCVD. First, a series of 1.8 µm thick GaN films were grown on SiC at 950 °C as a function of TMIn flow rate as described in section 4.2. *In-situ* and *ex-situ* stress measurements, AFM, and TEM revealed that the compressive stress induced by the misfit strain between the GaN epilayer and SiC substrate relaxed elastically by the formation of V-defects promoted by indium surfactant. Simultaneously improved step-flow growth was observed, which appears to be contradictory because the enhanced surface diffusion of adatoms may remove surface defects like V-defects. Therefore, in order to explain the driving force for V-defect formation in the presence of indium, a

nucleation and growth model was developed as described in section 4.3, taking into account the surface, dislocation, and strain energies of the GaN film. This model explains that the V-defects can be energetically favorable to form under In-rich conditions, resulting in a smoother GaN surface. Furthermore, the initiation of V-defects at the terminated edge and screw type threading dislocations are discussed based on this model. Mercury probe C-V measurements showed that all GaN films discussed in section 4.2 were unintentionally doped with Si, resulting in a background electron carrier concentration of 2×10^{17} cm⁻³. Thus, in section 4.4, an investigation into the effect of intentional Si doping on V-defect formation in the GaN films grown on SiC is reported using the same TMIn flow rate and identical growth conditions used in section 4.2. As the SiH₄ flow rate was raised at the fixed amount of indium, V-defect density increased, which lead to the relaxation of compressive misfit stress. On the other hand, V-defects were not strongly preferred in the presence of indium when unintentional Si incorporation into GaN film was limited. Therefore, Si turned out to be another important factor for Vdefect formation other than misfit strain energy, reduction of (1010) surface energy, and threading dislocation energy.

4.2 Unintentionally Si-doped GaN Grown with Indium Surfactant

In this section, the study focuses on the 1.8 µm thick nominally undoped GaN films grown on 6H-SiC substrates at 950 °C as a function of TMIn flow rate. The stress change was monitored *in-situ* using MOSS. HRXRD was used to confirm the stress

relaxation and examine the crystallinity of the GaN epilayers. AFM and TEM were employed to reveal the stress relaxation mechanisms modified by indium.

4.2.1 Experimental Details

All GaN samples were prepared by MOCVD in a vertical reactor equipped with an inductively heated rotating susceptor, as described in section 3.1. The source precursors were TMGa, TMAI, TMIn, and NH₃ for Ga, Al, In, and N, respectively. H₂ carrier gas transported these source precursors into the reactor where the pressure was maintained at 100 Torr. Chemical mechanical polished (CMP) Si-face 6H-SiC wafers were diced into 1 cm × 1 cm squares and cleaned through a series of sonication in acetone, isopropanol, and DI water, followed by a dip in 10% HF solution and rinse in DI water, prior to growths. AlN buffer layers (~ 90 nm) were grown on the *c*-plane of 6H-SiC at 1100 °C. Molar flow rates of TMAI and NH₃ were 10.3 µmol/min and 89.3 mmol/min (V/III ratio = 8670), respectively. 1.8 µm thick GaN epilayers were grown on the AlN buffer layer at 950 °C and TMIn (0, 2.2, 3.7 and 4.5 µmol/min) was added to the inlet gas, while the total flow rate of the group III species and other process variables were kept constant to observe the effect of indium surfactant on the GaN layers. TMGa and NH₃ were controlled at 9.2 µmol/min and 35.7 mmol/min (V/III ratio = 3880), respectively, for the GaN growths.

MOSS system, integrated in the MOCVD reactor, was employed using multiple laser beams to monitor the real-time stress change of GaN films, as described in section

3.2. The growth rate of all GaN films were approximately 0.46 nm/s, determined from oscillations in the laser intensity of the MOSS system, which arises from interference between the surface and underlying interface of GaN. Ex-situ HRXRD measurements were performed in a Philips MRD four-circle diffractometer with Cu K_{α} radiation (λ = 1.5406 Å) to evaluate mosaic structures and determine lattice parameters of the GaN films. AFM measurements were done to correlate the changes in film stress with surface morphology evolution. Cross-sectional and plan-view TEM specimens were prepared by conventional mechanical polishing and argon ion milling. Cross-sectional TEM was done on a JEOL 2010F field emission microscope operated at 200 keV to examine the microstructure of the GaN epilayers. Plan-view TEM was performed on a Philips EM420T operated at 120 keV to determine the TD density. Mercury-probe C-V measurements revealed that all GaN samples had the background electron concentration of about 2×10^{17} cm⁻³, which was presumably caused by unintentional Si and O incorporations, which are known to be n-type dopants in GaN films, because other GaN samples grown in the same MOCVD system showed unintentionally doped Si and O concentrations of approximately 1.0×10^{17} cm⁻³ to 4.0×10^{17} cm⁻³ in SIMS analysis (not shown here).

4.2.2 In-situ Stress Measurements

The stress-thickness product versus film thickness of GaN films grown with varying TMIn flow rate was obtained from the MOSS, as shown in Fig. 4.1. The



Figure 4.1. Stress-thickness vs. thickness as a function of TMIn molar flow rate during GaN growths at 950 °C, obtained from MOSS. The oscillation feature arises from an artifact caused by non-uniformity of the GaN film thickness across the sample.

incremental stress, the slope at any point on the stress-thickness curve, represents the incremental change of strain. Negative and positive slopes indicate compressive and tensile incremental stress, respectively. Thus, all GaN epilayers here experience only compressive incremental stress during growth due to lattice mismatch. The initial stress of all the GaN films is about -0.9 GPa. This reflects 93% relaxation of the theoretical misfit stress (-12.5 GPa) between GaN and 6H-SiC, assuming that the AlN buffer layer is pseudomorphically grown on SiC. This immediate relaxation concurs with Moran *et al.* who observed more than 90 % relaxation of compressive stress in GaN on AlN / SiC by misfit dislocations at the heterointerface.⁸⁹ Up to ~ 100 nm in Fig. 4.1, the stress-thickness curves are nearly identical regardless of the TMIn flow rate, indicating that indium incorporation into the GaN films is negligible even with TMIn = 4.5 μ mol/min

(TMIn / TMGa = 0.49) or is below the sensitivity of the MOSS because the larger mismatch of InGaN alloy would be expected to produce more compressive stress if indium was incorporated into the GaN. In the reference GaN grown without indium, the compressive stress gradually relaxes as the film grows beyond 400 nm. The GaN film with TMIn = 2.2 μ mol/min exhibits the similar tendency. However, at a TMIn flow rate equal to or higher than 3.7 μ mol/min, the GaN epilayers experience a reduction of compressive stress with respect to the reference GaN. The mean stress of each of the GaN layers at 1.8 μ m is -0.60, -0.57, -0.46, and -0.30 GPa for TMIn = 0, 2.2, 3.7, and 4.5 μ mol/min, respectively, which suggests that the presence of indium leads to more relaxation of compressive stress, depending upon the amount of indium surfactant on the growing GaN surface. The observed stress evolution also implies that indium surfactant does not affect the stress of GaN films thinner than ~ 300 nm, which explains contradictory observations that Yuan *et al.* found no stress change in the 200 nm thick GaN film grown with indium¹⁴ and Yamaguchi *et al.* observed stress relaxation in 1.8 and 2.7 μ m thick GaN films grown using indium surfactant.⁷

In addition to stress-thickness and growth rate, the measured reflectivity in MOSS provides information on the evolution of surface roughness. GaN growth consists of 3 stages, i.e., nucleation-islanding, coalescence, and 2-dimensional (2D) growth. At the nucleation stage, the intensity of the reflected light from the GaN surface decreases due to scattering, depending on the density and aspect ratio of the GaN nuclei. Once GaN islands combine during coalescence, the reflectivity begins to recover, and tends to saturate when the 2D growth starts. The reflectivity of both the reference and GaN grown



Figure 4.2. Reflectivity variations on the GaN films at TMIn of 0 and 4.5 μ mol/min during GaN growths at 950 °C, obtained from MOSS.

with TMIn = 4.5 μ mol/min, as shown in Fig. 4.2, well represents these growth steps. However, it should be noted that the recovering rate of reflectivity towards the saturation is slower in the GaN epilayer with TMIn = 4.5 μ mol/min, implying that either delayed coalescence or surface defects play a role. In general, delayed coalescence leads to a bigger lateral grain size, which in turn is expected to give rise to a reduction of threading dislocation density in the GaN films. If coalescence process is delayed, improved crystallinity may be expected in GaN grown with indium, which can be probed by x-ray rocking curve measurements. However, since enhanced surface diffusion of adatoms has been commonly reported in other studies in the presence of indium adlayer,^{6,8-11} a faster recovery rate of the reflectivity may be expected here. The observed trend, therefore, suggests that surface defects like V-defects play a role in the slower recovery of the reflectivity rather than the delayed coalescence. Considering the stress-thickness curves in Fig. 4.1, the slower recovery of reflectivity appears to correlate with stress relaxation in the presence of indium. This will be discussed in more detail later when the x-ray rocking curves and AFM results are presented.

4.2.3 X-ray Diffraction Analysis

To supplement and confirm the stress relaxation observed in the MOSS, the lattice parameters *a* and *c* of the GaN films were determined by HRXRD at room temperature, employing the extrapolation method with Nelson-Riley function, $(\cos^2 \theta / \theta + \cos^2 \theta / \sin \theta)$,^{87,110,111} as described in section 3.4.1. $2\theta - \omega$ scans on the GaN (0002), (0004), and (0006) planes were performed to obtain the *c* lattice constants. Figure 4.3(a) shows the extrapolation of measured lattice constants *c* of the reference GaN film,



Figure 4.3. Extrapolations of measured lattice constants (a) c and (b) a of the reference GaN film against Nelson-Riley function.
for instance. The linear least-squares fitting determined the extrapolated value of 5.1854 Å. From the diffractions on the $(10\overline{1}1)$, $(20\overline{2}2)$, $(20\overline{2}1)$, $(21\overline{3}1)$, and $(21\overline{3}3)$ planes, the *a* lattice constants were determined by the following equation for a hexagonal lattice.⁸⁷

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2},$$
(4.1)

where *a* and *c* are lattice constants, *d* is the interplanar spacing, and *h*, *k*, and *l* are the Miller indices of a lattice plane. Figure 4.3(b) shows the extrapolation of measured lattice parameters *a* and the extrapolated value of 3.1889 Å for the reference GaN film.

By using this technique, the lattice constants of all GaN samples were determined as a function of TMIn flow rate, as presented in Fig. 4.4. The sign of the strain is based on $a_0 = 3.1888$ Å and $c_0 = 5.1850$ Å of fully relaxed GaN at room temperature.⁶⁴ All *a*



Figure 4.4. (a) Lattice constants c and (b) lattice constants a measured from HRXRD at room temperature. The sign of strain is determined with respect to the lattice parameters of GaN at room temperature.

values of GaN films indicate tension, but if we consider the differences in the coefficient of thermal expansion (CTE) between GaN and substrate, they are all compressively strained at the growth temperature, thus consistent with the MOSS results. Assuming that the contribution of the thin AlN layer is negligible, the thermal strain in the GaN film is given by¹¹⁶

$$\varepsilon_{thermal} = (\alpha_{SiC} - \alpha_{GaN})(T_{Growth} - T_{RT}), \qquad (4.2)$$

where α_{siC} and α_{GaN} are the CTE of 6H-SiC (4.2 × 10⁻⁶ K⁻¹) and GaN (5.6 × 10⁻⁶ K⁻¹), ^{50,51} and T_{Growth} and T_{RT} are the growth and room temperatures, respectively. Excluding the thermal stress upon cooling down from 950 °C allows the extraction of the biaxial stress at the growth temperature with the assumption that the induced thermal stress is identical in all samples. Hence, the biaxial stress of GaN at the growth temperature is given by¹¹⁷

$$\sigma_f' = M_f \varepsilon_a', \tag{4.3}$$

where M_f is the biaxial modulus of GaN (478 GPa),^{75,76} and ε_a ' is the biaxial strain at the growth temperature. Figure 4.5 shows the change of biaxial stress obtained from HRXRD and the mean stress calculated from MOSS at the growth temperature of 950 °C. The trend shows good agreement between HRXRD and MOSS, confirming that the addition of indium surfactant allows the compressive stress of the GaN films to relax.



Figure 4.5. Biaxial stress change of GaN epilayers at the growth temperature of 950 °C, calculated from XRD and MOSS as a function of TMIn flow rate.

The differences in the magnitude of the film stress between HRXRD and MOSS are likely due to using the room temperature coefficient of the biaxial modulus, and possible errors in the calibration of the distance L between the film and CCD camera in the MOSS.

4.2.4 Crystallinity of GaN Films

Rocking curve measurements (ω - scans) in HRXRD were performed to examine the mosaic structure of the GaN films. The angle distributions of sub-grains out-of-plane and in-plane define the mosaicity, i.e., tilt and twist. In the GaN system, the coalescence process of each GaN nuclei during growth is known to initiate TDs to accommodate misorientations between GaN islands.⁸⁹ Thus, TD density is a strong function of the mosaicity in GaN films. Since broadenings in rocking curves of (0002) and (1010) planes are mainly associated with tilt and twist, screw and edge TD density can be estimated from the full width at half maximum (FWHM) of ω -scans on GaN (0002) and (1010), respectively. The rocking curve measurement on the (0002) plane is straightforward. However, the ω -scan on (1010) typically requires grazing incidence angle x-ray diffraction (GIXRD) with a high intensity x-ray source. Several models have been developed to indirectly determine the twist by measuring symmetric ω - scans in skew geometry with increasing inclination angle (χ) of reflecting planes¹¹⁸⁻¹²¹ since GIXRD is not readily available. The author used here an empirical model considering crystallite rotations and convolutions of two Pseudo-Voigt functions that reflect tilt and twist with inter-dependence parameter *m* between them, which was developed by Srikant *et al.*¹¹⁸

Figure 4.6 shows the measured FWHMs of ω - scans on (0002), (1015), (1013), (1012), (2023), (1011), and (3032) in the reference GaN film. The FWHM of (1010) at the inclination angle of 90° can be obtained from the fit (solid line), yielding the twist of GaN. Then, the screw and edge TD density can be estimated from the classical model for randomly distributed dislocations:^{64,122,123}

$$\rho_{screw} = \frac{\Gamma_{tilt}^2}{4.36b_{screw}^2},\tag{4.4}$$

$$\rho_{edge} = \frac{\Gamma_{twist}^2}{4.36b_{edge}^2},\tag{4.5}$$



Figure 4.6. FWHMs of (0002), $(10\overline{1}5)$, $(10\overline{1}3)$, $(10\overline{1}2)$, $(20\overline{2}3)$, $(10\overline{1}1)$, and $(30\overline{3}2)$ ω -scans in the reference GaN film and the fit (solid line) based on the Srikant's model.

where Γ_{tilt} and Γ_{twist} are the FWHMs of the (0002) and (1010) ω -scans, and b_{screw} (5.1850 Å) and b_{edge} (3.1888 Å) are the Burgers vectors along [0001] and $1/3 < 11\overline{20} >$, respectively. The calculated TD density in all GaN samples is plotted as a function of TMIn flow rate in Fig. 4.7. The screw TD density is slightly reduced from 2.8×10^8 cm⁻² to 1.8×10^8 cm⁻² while the edge TD density remains nearly unchanged. The total TD density, the summation of screw and edge TD density, does not indicate any significant variation with increasing TMIn flow rate. To validate the dislocation density estimated by rocking curves, plan-view TEM was performed on the reference and GaN grown at TMIn = 4.5 µmol/min by Dr. Xiaojun Weng. HRXRD estimated total TD density of 4.2×10^9 cm⁻² and 4.1×10^9 cm⁻² on both samples while TEM results were $(3.7 \pm 0.31) \times 10^9$ cm⁻² and $(3.9 \pm 0.44) \times 10^9$ cm⁻² over ten randomly selected regions. ρ_{XRD} / ρ_{TEM} is about 1.14 and 1.05, indicating good agreement between XRD and TEM. The other reported studies of indium surfactants in GaN grown on sapphire and silicon revealed that the crystallinity was improved by the introduction of indium.⁷ Therefore, the result here implies that the indium surfactant has less of an effect on the crystallinity of GaN grown on SiC substrates. One of the possible reasons may be the characteristic of GaN epilayers on SiC which have fewer misorientations between sub-grains due to the relatively smaller lattice mismatch in comparison with sapphire and Si(111) substrates, resulting in less effect of indium on the coalescence between GaN nuclei during growths.

Since the crystallinity of GaN films remained nearly constant as a function of indium, the results here suggest that the slower recovery of reflectivity observed in Fig. 4.2 was affected by surface defects other than the delayed coalescence. Thus, the stress relaxation induced by indium surfactant, as seen in Fig. 4.1, may be correlated to surface defects, which is discussed in the next section.



Figure 4.7. The estimated TD density of GaN films from XRD as a function of TMIn flow rate.

4.2.5 Surface Morphology and Microstructure

AFM measurements were carried out to investigate the surface morphology of GaN films due to the presence of indium. The AFM images from Fig. 4.8(a) to 4.8(d) show the change of step-terrace structures over $2 \times 2 \mu m^2$ in GaN epilayers. As the TMIn flow was raised from 0 up to 4.5 µmol/min, the root mean square (RMS) roughness changed as 0.49, 0.30, 0.19, and 0.15 nm. This reduction in the surface roughness of GaN epilayers is consistent with other reported studies that demonstrated enhanced step-flow growth.^{6,8-11,13} In the meantime, however, in the AFM images on $50 \times 50 \ \mu\text{m}^2$ areas from Fig. 4.8(e) to 4.8(h), the density of large pits increased significantly with increasing amounts of indium. The observed pits are inverted hexagon-shaped surface defects, i.e., commonly called V-defects or V-pits. Thus, the delayed recovery of reflectivity in Fig. 4.2 appears to be caused by these V-defects on the GaN surface grown with indium surfactant. Since the V-defect formation correlated with stress relaxation of GaN epilayers grown with indium surfactant, the author quantified the density and area fraction of the V-defects from five different $50 \times 50 \ \mu\text{m}^2$ regions in each of the samples, as plotted in Fig. 4.9. The density of V-defects is at the level of 10^6 cm⁻² without indium, but it reaches about 10⁷ cm⁻² at TMIn flow rates higher than 3.7 µmol/min. The area fraction of V-defects on the GaN surface is less than 1 % in the reference GaN, but increases to 7.2 % at TMIn = 4.5 μ mol/min. Because the variation of area fraction correlates with changes in the stress shown in Fig. 4.5, it can be concluded that the



Figure 4.8. AFM images of GaN epilayers grown with increasing TMIn flow rate. (a), (b), (c), and (d) on the first column indicates AFM images over $2 \times 2 \mu m^2$ area, and (e), (f), (g), and (h) on the second column shows images over $50 \times 50 \mu m^2$ area.



Figure 4.9. The density and area fraction of V-defects with increasing TMIn flow rate, measured from AFM images over five randomly selected $50 \times 50 \ \mu\text{m}^2$ area.

compressive stress of the GaN epilayers relaxes elastically through V-defects that were promoted by the indium surfactant.

In Si-doped and undoped AlGaN films, inclination of TDs with respect to the growth direction has been reported to relax compressive stress.^{94,95,97,98,124} To investigate the possible contribution of TD inclination to the stress relaxation, cross-sectional TEM analysis was performed. Figure 4.10 shows the bright field images of two regions near a V-defect and next to the V-defect in the GaN film grown at TMIn = 4.5 μ mol/min. Both images were collected along the GaN [1100] zone axis under the multi-beam diffraction condition to reveal all types of TDs. In Fig. 4.10(a), TDs bend towards the center of the V-defect and create misfit dislocation segments by further inclination toward the basal plane. The observed TD bending originates from the side walls of the V-defect which consist of six {1011} planes that lead to the non-zero resolved shear stress, as observed in



Figure 4.10. Bright field cross-sectional TEM images of (a) V-defect and (b) area next to V-defect.

the facet controlled GaN growth.⁹³ On the other hand, as exemplified in Fig. 4.10(b), no significant inclination of TDs was observed away from the V-defect. The inclination of TDs here was localized near the V-defect, thus not indicating systematic bending of TDs as observed in Si-doped AlGaN layers. No evidence of TD inclination was found elsewhere away from the V-defect throughout the TEM specimen. Therefore, the contribution of localized TD bending, followed by misfit dislocation formation, on the plastic stress relaxation is considered to be minor.

4.2.6 Discussion

The heteroepitaxial growth of GaN results in misfit stress due to differences in the lattice constants of GaN and SiC. The strain energy accumulates, and relaxes

immediately by generating misfit dislocations at the heterointerface as the film grows beyond a critical thickness. Further relaxation may occur by the creation of misfit dislocations arising from bending of TDs and interaction between TDs.^{3,96} In cubic materials such as Si and GaAs, the misfit stress relaxes along the primary slip system, {111} <100>.^{2,90} In contrast, the stress relaxation mechanisms in hexagonal wurtzite GaN are complicated due to the limited slip systems since the resolved shear stress is zero along the primary slip systems on the basal {0001}, and prismatic {1100} and $\{11\overline{2}0\}$ planes.^{16,27} Thus, plastic relaxation may take place along the $\{11\overline{2}2\} < 11\overline{2}3 >$ secondary slip system which requires higher activation energy.²⁷ Other relaxation mechanism such as dislocation climb is limited because this involves the diffusion of both group III and V vacancies that does not occur easily at the low growth temperature of 950 °C for GaN.^{125,126} Therefore, the elastic V-defect formation can be favored over the restricted plastic dislocation motions in order to relax the compressive misfit stress. However, V-defect formation could be contradictory to the fact that indium surfactant lead to enhanced step-flow growth, as observed in Fig. 4.8(a) - (d). In the next section, a nucleation and growth model will be developed to explain the energetically favored Vdefect formation under In-rich growth conditions in GaN films.

4.3 Nucleation and Growth Model for V-defect Formation

From the results on the nominally undoped GaN films grown on SiC with indium surfactant in section 4.2, a simple model was developed as presented in this section to

describe the driving force for V-defect formation in the presence of indium on the GaN surface. As described in section 2.5, two models suggested by Northrup *et al.*⁵ and Song¹⁶ were not complete in describing V-defect formation in their InGaN / GaN systems. Thus, the author develops here a nucleation and growth model, modified from two models, by considering strain, surface and dislocation energies.

4.3.1 Development of Nucleation and Growth Model

V-defects are frequently observed in InGaN films grown on GaN or InGaN/GaN multiple quantum wells at temperatures below 800 °C where plastic relaxation of compressive stress is limited and indium is involved in heteroepitaxial growth. In typical GaN growth without indium, V-defect size and density tend to increase due to the reduced surface mobility of adatoms when the growth temperature is lowered or V/III source input ratio increases. By introducing an indium surfactant that improves two-dimensional (2D) growth, one may expect that the size and density of V-defects in the GaN films should be reduced. However, this prediction is opposite to the observed AFM results at large scale [Fig. 4.8(e) - 4.8(h)] although the enhanced surface diffusion of adatoms is evident in AFM images over $2 \times 2 \mu m^2$ [Fig. 4.8(a) - 4.8(d)]. In order to understand the origin of V-defects promoted by indium and describe the stress relaxation, a simple model was developed to describe the driving force for V-defect formation, modified from two models suggested by Song¹⁶ and Northrup *et al.*^{5,102} The V-defect is assumed to be cone-shaped rather than hexagonal for simplification, ^{5,16,102} as schematically illustrated in Fig. 4.10. However, unlike Song's model, the GaN (0001)



Figure 4.10. V-defects are assumed to be a cone which has the radius of r and the height of h. One side length of the given system is a (a >> r).

surface energy is considered, and the mechanical energy associated with the creation of the V-defect is excluded because the V-defect forms as the threading dislocation core opens up. The author considers a system that has a TD as the initial state and a V-defect at the terminated TD for the final state. By comparing two states, the energy balance equation can be established in terms of strain, surface, and TD energies. In Northrup's model, the integrated strain energy density over the cone was used for the strain energy term based on Frank's model,¹⁰³ but bulk misfit strain energy per unit volume was used here, which can be deduced from the stress-thickness data. From the AFM results, the average radius of the V-defect was about 500 nm and the maximum radius was ~ 1 μ m. Thus, the relief of bulk misfit stress has to be considered in the energy balance rather than the strain energy in the local region surrounding the dislocation which was considered in Northrup's model. The total system energy (E_1) associated with a TD prior to V-defect formation is then given by

$$E_1 = E_{s1} + \gamma_1 + E_D, (4.6)$$

where E_{s1} is the bulk strain energy, γ_1 is the surface energy, and E_D is the dislocation energy consisting of elastic and core energy. E_{s1} , γ_1 and E_D^{-127} are given by

$$E_{s1} = M\varepsilon^2 a^2 h, \qquad (4.7)$$

$$\gamma_1 = \gamma_{(0001)} a^2, \tag{4.8}$$

$$E_D = (E_{elastic} + E_{core})h = \left[A_0 \ln\left(\frac{R}{r_{core}}\right) + E_{core}\right]h, \qquad (4.9)$$

where *M* is the biaxial modulus of the film, *h* is the film thickness (equivalent to 1.63*r* for the ideal V-defect, where *r* is the cone radius), *a* is the length of one side of the given system (a >> r) in Fig. 4.10, ε is the misfit strain of the film, $\gamma_{(0001)}$ is the surface energy of GaN (0001), A_0 is the prelogarithmic factor, *R* is the radius of a cylinder containing the dislocation line, r_{core} is the dislocation core radius, and E_{core} is the dislocation core energy. Once a V-defect initiates, the TD stops propagating, the GaN (0001) surface of the cone disappears, and GaN (1011) surfaces are created on the sidewalls of the cone. Thus, the total system energy (E_2) for the final state is expressed as:

$$E_2 = E_{s2} + \gamma_2, \tag{4.10}$$

where, E_{s_2} and γ_2 represent the strain and surface energies when the V-defect formed, which are given by

$$E_{s2} = M\varepsilon^2 a^2 h - \frac{1}{3}M\varepsilon^2 \pi r^2 h, \qquad (4.11)$$

$$\gamma_2 = \gamma_{(0001)} a^2 - \gamma_{(0001)} \pi r^2 + \gamma_{(10\bar{1}1)} \pi r \sqrt{h^2 + r^2} , \qquad (4.12)$$

where $\gamma_{(10\overline{1}1)}$ is the surface energy of GaN (10 $\overline{1}1$). Then, the change in the total system energy is expressed as follows:

$$\Delta E = E_2 - E_1 = \left(-\frac{1}{3} M \varepsilon^2 \pi r^2 h \right) + \left(\gamma_{(10\bar{1}1)} \pi r \sqrt{h^2 + r^2} - \gamma_{(0001)} \pi r^2 \right) - \left[A_0 \ln \left(\frac{R}{r_{core}} \right) + E_{core} \right] h$$
(4.13)

When the V-defect forms, the first two terms in Eq. (4.13) implies that the reduction of bulk strain energy competes with the increase of surface energy arising from the increased surface area of six (1011) in the V-defect. Thus, if the surface energy of the (1011) plane can be reduced by indium surfactant, the reduction of bulk strain energy may be dominant, leading to V-defect formation. From the theoretical study of the modified surface energy by indium, $\gamma_{(0001)}$ and $\gamma_{(1011)}$ are reduced from 12.3 eV/nm² and 12.5 eV/nm² on the Ga-terminated surfaces (Ga-rich condition) down to 10.3 eV/nm² and 5.9

eV/nm² under indium-rich conditions, as indium atoms replace Ga adatoms on the Gaterminated surface in order to have $x \approx 0.125$ in the In_xGa_{1-x}N film.⁵ The surface energy reduction could be higher under more indium-rich conditions, but the author regards 10.3 eV/nm² and 5.9 eV/nm² as an extreme, as opposed to the Ga-rich condition since the surface energies for more indium-rich conditions than these values were not available. For the bulk strain energy of GaN, ε was extracted from the initial slope of -0.9 GPa in the stress-thickness curves in Fig. 4.1 instead of the theoretical stress of -12.5 GPa because the theoretical misfit stress, which was relaxed by 93 % due to the misfit dislocations at the heterointerface, does not fully affect the V-defect nucleation. For the edge TD energy in anisotropic wurtzite GaN, 7.9 eV/nm for A_0 , 0.67 nm for r_{core} , and 14.6 eV/nm for E_{core} , simulated on the 5/7-coordinated atom rings, were employed.¹²⁸ For the screw dislocation, 13.5 eV/nm for A_0 , 0.67 nm for r_{core} , and 28.2 eV/nm for E_{core} , based on the open core type, were used.¹²⁸ *R* was assumed to be 2 nm for both edge and screw TDs.

4.3.2 System Energy Change by V-defect Formation

For the Ga-rich and In-rich conditions, ΔE is plotted in Fig. 4.11 as a function of V-defect radius when the V-defect forms on the terminated edge TD. Since the majority of TDs are edge type, the edge dislocation energy was considered first. The energy barrier (E_b) for V-defect formation can be obtained by setting the first derivative of Eq. (4.13) equal to zero. For GaN in the absence of indium, E_b is 2.2×10^7 eV [Fig. 4.11(a)].



Figure 4.11. The change of total system energy as a function of V-defect radius (a) under Ga-rich, and (b) under In-rich conditions. In both cases, the edge dislocation energy was considered. E_b represents the barrier energy for the V-defect formation. The calculation was performed with Eq. (4.13).

The V-defect growth is greatly limited because the system energy keeps increasing up to the V-defect radius of 1.35µm. In contrast, the E_b is significantly reduced to 9.2×10^3 eV at the radius of 108 nm under the In-rich condition, as seen in Fig. 4.11(b). This lowered E_b demonstrates that the probability of V-defect formation dramatically increases under the In-rich condition, supporting the AFM results observed in the 50 × 50 µm² scan image of Fig. 4.8. The author obtained E_b of 5.9×10^3 eV at 101 nm in the case of V-defect formed at the screw TD, where V-defect nucleation may be preferred over edge type due to a relatively lower E_b . In fact, the predicted change of system energy in Fig. 4.11(b) is analogous to the thermodynamic theory for the nucleation and growth of nuclei in solidification of a vapor phase.^{129,130} In the same context, the radius at the energy barrier here is denoted as the *critical radius*. As the GaN film grows, if V-defect nucleates and its size exceeds the critical radius during coalescence of each GaN nuclei, the V-defect will keep growing in order for the system to achieve the more stable state by lowering the system energy, giving rise to the relaxation of compressive strain energy. Thus, although the step-flow growth can be kinetically improved by indium, thermodynamically driven V-defect formation is simultaneously enhanced by the modified surface energy arising from indium on the surface of GaN grown on SiC. In the current model, the author considered only energetics. Therefore, the calculated critical radius and energy barrier should be understood in a qualitative manner because the actual V-defect size and density can vary depending on the kinetics such as modified adsorption of Ga by indium and different growth rates of GaN along [0001] and <1011 > . Also, the calculated energy barriers for an extended surface defect in the present model are significantly higher than typical bond energies and consequently should only be considered in a comparative manner. In actuality, when (1011) planes of each GaN islands are stabilized by indium surfactant during the coalescence prior to 2D growth, the initial size of the V-defect may become larger than the critical radius, which does not require the high activation energy corresponding to the energy barrier.

4.3.3 Initial Nucleation of V-defect

The suggested model provides additional predictions concerning the initiation of V-defects and the role of TDs. The change of system energy at the initial stage of V-defect formation is shown in Fig. 4.12, replotted using a different scale from Fig. 4.11. In the Ga-rich condition, the small sized (equilibrium radius of ~ 0.7 nm) V-defect can initiate although the formation energy is weak, but the growth of this nano-sized V-defect



Figure 4.12. The system energy change under Ga-rich and In-rich conditions as a function of V-defect size that forms on edge TD. To illustrate the initiation of nano-sized V-defect, this figure was replotted at different scale from Fig. 4.11.

is restricted by the increase of system energy up to the critical size of 1.35 μ m. In contrast, a relatively higher driving force exists in the In-rich environment, where the V-defect at the equilibrium radius of ~ 6.5 nm can be stabilized. This behavior in the initial nucleation can assist the V-defect to easily grow beyond the critical radius of 108 nm under In-rich condition.

Figure 4.13 illustrates the role of TDs in V-defect initiation under the In-rich condition. In the absence of TDs, there is no reduction of system energy for the initial nano-sized V-defect. As a result, the V-defect growth directly above the critical radius becomes unfeasible. In contrast, the local dislocation energy plays a critical role in the initiation of V-defects by reducing the system energy prior to V-defects growing over the critical radius. It has been reported that V-defects formed on the screw TD not on the edge type or vice versa.^{27,131} However, the current model suggests that V-defects can



Figure 4.13. The system energy change as a function of V-defect radius when V-defect forms at the terminated screw TD, edge TD and bulk region without any TD.

initiate at either screw or edge TDs. Generally, a screw TD has higher defect energy than an edge TD, hence the screw TD may be a favored site over edge type. However, this does not imply that V-defect cannot start from the edge TDs that dominate in GaN films. Other defect such as a stacking mismatch boundary has been reported to be connected to V-defects in InGaN/GaN multiple quantum wells grown on GaN.²³ The initiation mechanism due to the local defect energy seems to be similar with the case of TDs. Thus, the V-defect is expected to initiate at any local defect site, considering the results of the system energy calculations in the current model.

4.3.4 Discussion

In the presented nucleation and growth model for V-defect formation, the key factors are compressive misfit stress and differentially reduced surface energies induced by indium surfactant. The higher effective compressive stress and the more In-rich condition will lead to a greater driving force for V-defect nucleation. The author developed the nucleation and growth model, considering the formation energy of the Vdefect per unit dislocation. Under identical misfit stress and amount of indium, the model predicts that reduced TD density may not lower the V-defect formation energy per unit dislocation according to Eq. (4.13), but will decrease the number of nucleation sites for V-defects. If the compressive misfit stress in a given heterostructure cannot be lowered under an In-rich environment, the only way to decrease V-defect density is by minimizing the nucleation sites by reducing TD density, which may activate other plastic relaxation mechanisms such as systematic misfit dislocations observed in InGaN growth on high quality GaN (TD density of mid 10⁶ cm⁻²).²⁷ Since InGaN films can be grown at temperatures below 800 °C in MOCVD under In-rich and Ga-poor conditions, this model can also explain the origin of V-defects in InGaN/GaN systems, where compressive strain energy is induced by the epitaxial mismatch between InGaN and GaN. The author also expects that the energy barrier E_b for V-defect formation in GaN films should approach infinity for homoepitaxy, where the misfit stress does not exist since the GaN film is grown on bulk GaN substrate. Thus, V-defect formation should not be energetically favored in the case of homoepitaxy even though an In-rich growth condition is employed in the GaN growth. To verify this hypothesis, homoepitaxial GaN growths

on high quality bulk GaN substrates using excessive indium surfactant were conducted as described in section 5.3.

4.4 Intentionally Si-doped GaN Grown with Indium Surfactant

In section 4.2, while improved 2D layer-by-layer growth was observed, it was found that the V-defect size and density increased in nominally undoped GaN films grown on SiC substrates with increasing TMIn flow rate, which gave rise to the relaxation of compressive stress in an elastic way. The nucleation and growth model which was rigorously developed in section 4.3 explained that thermodynamically driven V-defect formation on the GaN surface under an In-rich environment can be favored although the step-flow growth mode is kinetically improved by indium that increases the surface migration of Ga and N adatoms.

All GaN films grown with indium surfactant were found to be unintentionally doped with either Si or O in section 4.2, and the background electron carrier concentration was about 2.0×10^{17} cm⁻³. In general, unintentional auto-doping in GaN films commonly occurs, which leads to n-type conductivity.^{51,107,132-135} The source of n-type doping has been extensively studied, but the reason has not been clearly revealed yet. Two factors have been reported to be possible sources of auto-doping. One is nitrogen vacancies, ^{133,135,136} and the other is impurities such as silicon and oxygen.^{107,132,137} Since GaN growths are usually performed under N-rich conditions (high V/III ratio) in MOCVD, which may not lead to N vacancies, Si and O are believed to be

unintentional n-type dopants in MOCVD-grown GaN films. In contrast, GaN growths by MBE typically utilizes slightly Ga-rich growth conditions, thus n-type auto-doping appears to be correlated to the generation of N vacancies in MBE-grown GaN films. Although the background electron carrier concentration of $\sim 10^{17}$ cm⁻³ is common in many other studies, the effect of unintensional Si doping may not be neglected since Si has been reported as an anti-surfactant on the growing GaN surface. This enabled fabrication of GaN quantum dots by MOCVD,^{28,29} although Si may not degrade the GaN surface under Ga-rich conditions which are characteristic of the MBE process.¹³⁸

Therefore, the effect of intentional Si doping combined with indium surfactant on V-defect formation and stress relaxation was investigated in 1.8 μ m thick GaN films grown at 950 °C by MOCVD. SiH₄ was introduced for intentional Si doping into GaN films at a fixed TMIn flow rate of 4.5 μ mol/min which was the highest TMIn flow rate used in section 4.2. *In-situ* stress measurements and AFM results revealed that V-defects were not strongly preferred when the unintentional Si incorporation was reduced in the GaN film. However, when the SiH₄ flow rate was raised at a constant TMIn flow rate, V-defect size and density increased, which relaxed the compressive misfit stress of GaN films on SiC. This observation indicates that Si is one of the critical factors in the generation of V-defects on the GaN surface.

4.4.1 Experimental Details

All GaN epilayers were grown by MOCVD on 6H-SiC substrates with AlN buffer layers, using TMGa, TMAl, TMIn, silane (SiH₄) and ammonia as source precursors for Ga, Al, In, Si, and N, respectively. Basically, the identical growth conditions used for growth of unintentionally n-type doped GaN films in section 4.2 was used except intentional Si doping was added. The reactor pressure was 100 Torr and H₂ was used as a carrier gas. CMP finished Si-face 6H-SiC wafers were diced into $1 \text{ cm} \times 1 \text{ cm}$ pieces and cleaned through a series of sonication steps in acetone, isopropanol, and DI water, followed by a dip in 10% HF acid solution and rinse in DI water. AlN buffer layers (~ 90 nm) were grown on the c-plane of 6H-SiC at 1100 °C prior to the GaN growths. Molar flow rates of TMA1 and NH₃ were 10.3 µmol/min and 89.3 mmol/min (V/III ratio = 8670), respectively. GaN epilayers of 1.8 μm were then grown at 950 °C on the AlN buffer layer. TMGa and NH₃ were controlled at 9.2 µmol/min and 35.7 mmol/min (V/III ratio = 3880). TMIn of 4.5 µmol/min was used during GaN growth as a surfactant, while the total flow rate of the group III species was kept constant. For Si doping, SiH₄ was introduced during GaN growth at the fixed TMIn flow rate of 4.5 µmol/min in order to observe the effect of Si doping combined with indium surfactant on V-defect formation and stress change in the GaN epilayers. The SiH₄ flow rate varied from 2.3 nmol/min to 9.2 nmol/min. The source input ratio of SiH₄ to TMGa was 2.5×10^{-4} and 1.0×10^{-3} , respectively. Although the identical growth condition was used here, the growth rate of all GaN samples turned out to be about 0.54 nm/s, which is faster than 0.46 nm/s of unintentionally Si-doped GaN films in section 4.2.

For the real-time stress measurements, the MOSS system was employed using multiple 658 nm laser beams and CCD camera. Micro-Raman scattering spectroscopy was performed at room temperature in a Renishaw Invia spectrometer to examine the film stress and electron carrier concentrations *ex-situ*, using a 514 nm Ar^+ laser as a source laser. PL measurements utilizing 266 nm source laser were done at room temperature to investigate the optical properties of GaN epilayers modified by Si doping combined with indium. AFM measurements were conducted to examine the change of surface morphology caused by Si doping and indium surfactant.

4.4.2 In-situ Stress Measurements

Figure 4.14 shows the stress-thickness versus film thickness of GaN films obtained from *in-situ* stress measurements at the growth temperature of 950 °C, using MOSS. As stated in section 4.2, the incremental stress, the slope at any point on the stress-thickness curve, represents the instantaneous change of strain, and negative and positive slopes indicate compressive and tensile incremental stress, respectively. In all samples, the initial slope exhibits similar values of about -0.8 GPa, which is slightly lower than -0.9 GPa of the unintentionally n-type doped GaN film. Although the difference is not significant, the slightly lowered initial incremental stress seems to originate from the different growth rates. Typically a lower V/III ratio at a constant group III flux results in a faster growth rate and lower misfit stress. Thus, a possible reason for the growth rate difference could be a lowered effective V/III ratio due to small changes in



Figure 4.14. Stress-thickness vs. thickness of GaN films grown at 950 $^{\circ}$ C by MOCVD, obtained from the MOSS. Compressive stress relaxes in the presence of indium surfactant and further relaxation occurs when SiH₄ was introduced for Si doping at the fixed TMIn flow rate 4.5 μ mol/min.

the MOCVD environment. In all samples in Fig. 4.14, the stress-thickness changes are linear and nearly similar up to ~ 200 nm. In the GaN film grown with TMIn = 4.5 μ mol/min, the compressive stress, originally arising from the misfit stress between GaN and the substrate, gradually relaxes with respect to the reference undoped GaN film grown without indium, similar to the results on the unintentionally n-type doped GaN films but with reduced relaxation of compressive stress. Mercury probe C-V measurements on the reference GaN and GaN grown with TMIn = 4.5 μ mol/min could not be used to measure the electron concentration because the films were fully depleted. The estimated Si or O concentrations were below mid 10¹⁶ cm⁻³, which is smaller than the 2 × 10¹⁷ cm⁻³ level of the untintentionally doped GaN films. This reduced impurity incorporation appears to correlate to the reduced relaxation of compressive stress in the

GaN film grown in the presence of indium. In order to observe the intentional Si doping effect in the presence of indium surfactant, SiH₄ was introduced using a fixed TMIn flow rate of 4.5 μ mol/min. Further relaxation of compressive stress was observed when the GaN film was doped with Si at SiH₄ = 2.3 nmol/min. As the SiH₄ flow rate increased to 9.2 nmol/min, the incremental stress changed from compressive to tensile beyond 1.1 μ m and more compressive stress was relaxed, suggesting that Si plays an important role in the relaxation of compressive stress. The mean stress of each GaN layers at 1.8 μ m is - 0.55, -0.41, -0.30, and -0.16 GPa, respectively.

4.4.3 Raman Scattering Spectroscopy Analysis

Ex-situ micro-Raman spectroscopy was employed to supplement and confirm the stress relaxation in the GaN epilayers grown with indium surfactant and Si doping, using a Renishaw Invia spectrometer in a backscattering geometry of $z(x, x)\overline{z}$ along the c-axis of hexagonal wurtzite GaN at room temperature. The 514 nm Ar⁺ laser was used as an excitation source and the incident light power was 1 mW. A 50× objective lens (N.A. = 0.75) was used, giving a spot size of 0.8 ~ 1.3 µm. Due to variations of the local stress state, Raman spectra were collected from five randomly selected regions in each sample. As described in section 3.4.2, among 6 Raman-active phonon modes such as E₂(low), A₁(TO), E₁(TO), E₂(high), A₁(LO), and E₁(LO),^{113,114,139} only E₂(high) and A₁(LO) modes are excited in the given $z(x, x)\overline{z}$ geometry due to the anisotropy in GaN, as seen in

Fig. 4.15. LO and TO represent longitudinal optical and transverse optical phonon modes, respectively. Since the E₂(high) mode centered around 568 cm⁻¹ is known to be the most sensitive to the biaxial stress of GaN, the frequency change of the E₂(high) mode can be indicative of the film stress.¹¹³ A higher wavenumber indicates more compressive stress and vice versa. Figure 4.16 shows E₂(high) mode and fitted curves with pseudo-Voigt function in Raman spectra of all GaN films. The peak position of E₂(high) mode red-shifts as 567.8 \pm 0.2 cm⁻¹, 567.2 \pm 0.2 cm⁻¹, 566.8 \pm 0.3 cm⁻¹, and 566.2 \pm 0.2 cm⁻¹, when indium surfactant was used and the Si doping level was increased at a constant TMIn = 4.5 µmol/min, suggesting that the film stress becomes more tensile. Based on 568 cm⁻¹ of E₂(high) mode in fully relaxed bulk GaN at room temperature, ^{113,114} the film stress can be obtained from the relative shift of the E₂(high) mode in the linear approximation by the following:¹⁴⁰



Figure 4.15. Raman scattering spectra of GaN films with indium surfactant and Sidoping. E₂(high) and A₁(LO) are excited in the given configuration of $z(x, x)\overline{z}$.



Figure 4.16. Frequency change of E_2 (high) mode in GaN films corresponding to the film stress. Solid curves indicate the fitted data by pseudo-Voigt function.

$$\Delta \omega_{\gamma} = \mathbf{K}_{\gamma} \boldsymbol{\sigma}_{xx}, \tag{4.14}$$

where $\Delta \omega_{\gamma}$ is the deviation in frequency of a given phonon mode γ , K_{γ} is the stress coefficient for a phonon mode γ , and σ_{xx} is the biaxial stress of GaN. For the E₂(high) mode, the stress coefficient in the literature varies as 2.7, 2.9, 4.2, 6.2 and 7.9 cm⁻¹/GPa.¹³⁹⁻¹⁴³ Here 4.2 cm⁻¹/GPa was employed. The calculated biaxial stress of the GaN epilayers from Eq. (4.14) is 0.04, 0.19, 0.29, and 0.43 GPa at room temperature, respectively. In order to directly compare these values to the mean stress obtained from the MOSS at the growth temperature of 950 °C, thermal stress induced by cooling from growth temperature to room temperature was taken into account, assuming that the contribution of the thin AlN buffer layer is negligible, which was already described in



Figure 4.17. Biaxial stress obtained from Raman and MOSS at the growth temperature of 950 °C.

section 4.2. Figure 4.17 presents the biaxial stress obtained from the Raman and MOSS at the growth temperature of 950 °C. The tendency of stress relaxation shows excellent agreement between Raman and MOSS, confirming that Si doping in the presence of indium induces more relaxation of compressive stress in the GaN epilayers.

In addition to the film stress, Raman scattering spectroscopy can provide additional information on the electron concentration in GaN films. The free carriers in GaN interact with LO phonon modes when the plasmon frequency becomes close to the LO phonon frequency, resulting in a coupling between the LO phonons and collective excitations of free electrons, i.e., plasmon. Due to plasmon's large collision damping in GaN, the intensity of the A₁(LO) phonon mode in the Raman spectrum is reduced by the coupled overdampened plasmon, as the electron concentration increases.^{144,145} This intensity reduction becomes significant when the electron carrier concentration increases over 7.5×10^{17} cm⁻³.^{113,145,146} Therefore, the coupled LO-phonon-plasmon mode can be



Figure 4.18. Intensity ratio of $A_1(LO)$ mode to $E_2(high)$ mode in all GaN epilayers.

indicative of the electron concentration. Figure 4.18 shows the intensity ratio of $A_1(LO)$ to $E_2(high)$, $I_{A_1(LO)}/I_{E_2(high)}$ of the GaN films. When indium surfactant was used without Si dopants, the intensity ratio becomes higher than that of the undoped GaN, implying that indium does not enhance unintentional Si or O incorporations into the GaN film. Thus, the observed stress relaxation of GaN grown with indium (TMIn = 4.5 µmol/min), as seen in Fig. 4.14, was found to be due to only the surfactant effect without the influence of unintentional auto-doping. Although the damping effect is not strong in the Si-doped samples because the electron concentration in all GaN samples is below 7.5×10^{17} cm⁻³, intensity reduction of the A₁(LO) modes was observed as the SiH₄ flow rate was increased up to 9.2 nmol/min, confirming that the further relaxation of compressive stress in Fig. 4.14 was done by additional intentional Si doping into the GaN films.

4.4.4 Optical Properties of GaN Films

Indium surfactant and Si doping affect the optical properties of GaN epilayers as well as the film stress. Figure 4.19 shows photoluminescence (PL) spectra measured at room temperature, using the fourth harmonic generated 266 nm line from a 1064 nm Nd:YAG laser excitation source. The reference undoped GaN does not show either nearband-edge (NBE) emission around 365 nm or yellow luminescence (YL) around 520 \sim 570 nm. At the low growth temperature of 950 °C, the carbon incorporation is significant in typical MOCVD-grown GaN films. Tang *et al.* has reported that carbon can quench NBE emission in GaN epilayers because carbon may capture the created excitons, providing non-radiative trap sites.¹⁴⁷ Hence, the quenched NBE emission in the reference GaN in Fig. 4.19 could be due to carbon impurities. The origin of YL, which arises from the defect states in the band gap, has been studied for a long time since YL has been



Figure 4.19. Photoluminescence spectra obtained from GaN films at room temperature.

universally observed in epitaxially grown GaN using MOCVD and MBE, thus regardless of growth techniques. Theoretical and experimental studies found that the native defects such as Ga vacancy and Ga vacancy related complex can act as deep acceptors, giving rise to the YL by introducing defect energy states in the bandgap.¹³⁷ First-principle calculations predict that the incorporation of Si can form a stable complex between Si on Ga site (Si_{Ga}) and vacancy on Ga site (V_{Ga}) , i.e., $Si_{Ga} - V_{Ga}$, and the equilibrium concentration of V_{Ga} related defects increases as the Fermi level increases by Si doping, which is consistent with the fact that n-type GaN typically shows strong YL.¹³⁷ Since carbon has been reported not to reduce YL,¹⁴⁷ the unintentional Si incorporation seems to be low in the undoped reference GaN here, as observed by Raman scattering spectroscopy. When only indium surfactant (4.5 µmol/min) was used during GaN growth, the NBE emission begins to appear with low efficiency. It appears that indium surfactant may reduce non-radiative recombination centers such as possibly carbonrelated complexes, leading to enhanced NBE transition of excitons. Also, there is a weak emission around 440 nm, which is commonly called blue luminescence (BL). BL is often observed in Mg-doped GaN films because of deep donor defects compensating p-type dopants.¹⁴⁸ Since neither Si nor Mg was doped into the GaN grown with only indium, a possible reason for BL could be the native defects behaving as deep donors, which may also explain that the intensity of the $A_1(LO)$ mode increased by compensating unintentional Si doping in Fig. 4.18. However, further study is necessary to find the origin of the BL.

As SiH₄ was added for n-type doping in the presence of indium, both NBE radiation and YL are amplified, as seen in Fig. 4.19. The higher efficiency of YL appears

to be due to the increased Si doping level that induces a higher density of Ga vacancy related defects behaving as deep acceptors. Also, the observed improvement of NBE emission by Si doping is caused by the increase of the electron concentration. Assuming that the trap density for non-radiative recombination is independent of doping, the radiative recombination rate of excitons is proportional to the donor concentration, leading to higher efficiency of VBE transitions. In three GaN samples except the undoped GaN, the peak position of the NBE emission red-shifts as 364.4 ± 0.03 nm, 365.3 ± 0.03 nm, and 365.9 ± 0.02 nm. This supports that the film stress changes to tensile relatively, as observed in the MOSS and Raman.

In section 4.2, the use of indium surfactant on the GaN films grown on SiC did not improve the crystallinity. To examine the effect of intentional Si doping on the mosaic structure of GaN films, x-ray rocking curve measurements were conducted in a Philips MRD four-circle diffractometer. As described earlier, the angle distributions of sub-grains out-of-plane and in-plane causes tilt and twist, which can be determined from the FWHMs of (0002) and (1010) in rocking curves. Screw and edge threading dislocation density can be estimated from the measured tilt and twist. Here the FWHM of (3032) was taken as a figure of merit for the twist to estimate edge TD density in a simpler manner instead of using Srikant's model employed in section 4.2 because the twist can be 1.14 times the FWHM of (3032) in GaN films grown on SiC.¹⁴⁹ The estimated total TD density was 3.8×10^9 , 5.2×10^9 , 6.2×10^9 , and 8.9×10^9 cm⁻², respectively, showing that the Si doping increased the TD density which may decrease the efficiency of the NBE emission in PL spectra. Thus, the observed trend in PL measurements seems to be affected by only point defects such as native and Si dopant related defects in the GaN films.

4.4.5 Surface Morphology

The compressive stress relaxation in unintentionally Si-doped GaN grown with increasing TMIn flow rate was due to V-defect formation, as discussed in section 4.2. Under similar unintentional Si or O incorporation into GaN films, the size and density of V-defects increased with increasing amount of indium surfactant. Thus, in the current study, the morphological change in the GaN films was examined to investigate the stress relaxation mechanism and the effect of intentional Si doping on V-pit formation as well as the improved surface smoothness caused by the indium surfactant. Figure 4.20(a) - (d)show AFM images over $2 \times 2 \mu m^2$ area. Once indium surfactant (4.5 μ mol/min) is introduced during GaN growth, improved surface step-terrace structures were observed in Fig. 4.20(b), as compared to the undoped reference GaN. Si doping under a constant TMIn flow rate does not change the surface morphology of the GaN films in the given 2 \times 2 um² area [Fig. 4.20(c) and (d)]. The RMS roughness was estimated as 0.55 nm, 0.15 nm, 0.18 nm, and 0.16 nm, respectively. This confirms that indium surfactant leads to enhanced 2D growth by improved surface migration of adsorbed adatoms on the growing GaN surface, thus consistent with the results on unintentionally doped GaN films. Figure 4.20(e) - (h) indicate AFM measurements over $50 \times 50 \ \mu\text{m}^2$ area. The undoped GaN film does not show any V-defect on the surface unlike the unintentionally doped GaN grown



Figure 4.20. AFM images of GaN eplilayers. (a), (b), (c), and (d) show AFM images over $2 \times 2 \ \mu m^2$ and (e), (f), (g), and (h) show AFM images over $50 \times 50 \ \mu m^2$.
without indium which showed V-defects on the surface. Also, when indium surfactant was used during growth, V-defects do not form, as shown in Fig. 4.19(f), in contrast to the observations with unintentionally doped GaN films grown with indium. However, when Si dopants are incorporated into GaN films in the presence of indium, the size and density of V-defects increases as the SiH₄ flow rate was raised, as can be seen in Fig. 4.20(g) and 4.20(h). The estimated V-defect density in the GaN films is 1.2×10^6 cm⁻² and 3.2×10^6 cm⁻², respectively. In the GaN film grown with only indium, the stress relaxation may be done by the enhanced step-flow growth, which expedites GaN islands to reach each other during coalescence and reduces surface roughness in the following 2D growth. The other possibility may be removal of V-defects which may form under the initial compressive stress and then disappear as the film grows, which will be discussed in section 5.3.3. The stress relaxation in the GaN films doped with Si appears to be done by V-defect formation in addition to the indium surfactant effect, which is consistent with the previous observations in the unintentionally doped GaN films grown with indium where V-defect formation was the stress relaxation mechanism. In addition, V-defect formation due to the intentional Si doping combined with indium demonstrates that Vdefect formation as reported in section 4.2 was affected by the unintentional Si doping other than O incorporation. From the current results combined with the previous studies, it can be concluded that V-defect formation is not preferred under only indium surfactant at the given growth condition when unintentional Si incorporation is well controlled. However, when Si is doped into GaN at a constant rate, the size and density of V-defects increases with increasing amounts of indium. Also, at a fixed TMIn flow rate, the size

and density of V-defects increases as the Si doping level increases. Thus, it turns out that Si is another important factor in V-defect formation in addition to indium.

4.4.6 Discussion

Since the surface energies of GaN films modified by Si were not available in the literature, the change of surface energy could not be introduced to the nucleation and growth model. However, Si seems to decrease at least the surface energy of (1010) which makes V-defect formation favorable thermodynamically or decreases the surface migration of adatoms on (1010) planes. The other possible origin of V-defect formations enhanced by Si doping may be the behavior of Si as an anti-surfactant.²⁸ As briefly reviewed in the introduction of section 4.4, Tanaka et al. reported that Si acted as an antisurfactant, which enabled 3-dimensional (3D) growth from 2D growth mode of GaN for the fabrication of quantum dots.²⁹ When Si was introduced on the AlGaN surface for GaN quantum dots, a high density of nano holes was created by the formation of Si - N masking the thin GaN film grown on AlGaN. A similar mechanism could be employed here to explain the initiation of V-defects. When Si is incorporated into the GaN film, the TD core can be a preferred incorporation site because the TD core has nitrogen dangling bonds that can easily capture Si. Thus, Si - N bonding can be formed at the TD cores, acting as a mask that locally prevents GaN deposition. Once the nano-sized holes, which can be the initiation of V-defects, are created by Si - N masking at the terminated TD

cores, the size of nano holes may increase by expanding this masking area and additional indium surfactant which makes $six(10\overline{10})$ surfaces stable, thus leading to a large V-defect.

From the results on the intentional Si doping, the energy barrier for V-defect formation, introduced in the nucleation and growth model in section 4.3, seems to be lowered by the presence of Si in addition to indium surfactant. Although the effect of Si cannot be considered, the nucleation and growth model still predicts that the V-defect formation should not be energetically preferred since there is no misfit stress in the homoepitaxy. Thus, in next chapter, the author will investigate the V-defect formation in GaN growth on bulk GaN substrates.

4.5 Conclusions

In this chapter, the author investigated the effect of indium surfactant on the stress change of nominally undoped GaN films on 6H-SiC substrates grown at 950°C by MOCVD. The *in-situ* wafer curvature measurements revealed that the indium surfactant induced the relaxation of compressive stress in the GaN epilayers. $2\theta - \omega$ scans in HRXRD confirmed the stress relaxation observed in the real-time stress evolution monitored by MOSS. The x-ray rocking curve measurements showed that the mosaicity of GaN films was unchanged by introducing indium. AFM measurements revealed that the step-flow growth was enhanced by the presence of an indium surfactant, but simultaneously V-defect formation was promoted on the GaN surface. Cross-sectional TEM showed localized threading dislocation bending towards the center of the V-defect, which may be a minor contribution to the plastic relaxation of compressive stress.

A nucleation and growth model was proposed to explain the conflicting results that surface defects like V-defects formed during GaN growth using indium surfactant that simultaneously lead to the enhanced step-flow growth mode of GaN films. This model predicts that indium can reduce the energy barrier for V-defect formation from 2.2 $\times 10^7$ eV down to 9.2×10^3 eV when the V-defect forms at an edge TD, and to 5.9×10^3 eV when the V-defect nucleates at a screw TD. This lowered energy barrier gives rise to a high probability of V-defect formation under an indium-rich environment on the growing GaN surface, leading to the elastic relaxation of compressive stress in the GaN epilayers. Also, the presented model well describes the comprehensive behaviors of Vdefect formation under In-rich conditions including the initiation of V-defects.

Since the nominally undoped GaN films turned out to be unintentionally doped with Si or O, the effect of intentional Si doping combined with indium surfactant on Vdefect formation and the stress relaxation mechanism was investigated. MOSS and Raman scattering spectroscopy showed that the compressive misfit stress was relaxed by the indium surfactant and further relief occurred when Si was doped into GaN films with indium. From PL measurements, indium surfactant was found to improve the optical properties of GaN by increasing NBE transitions of excitons. Si doping increased the efficiency of both NBE emission and YL in the PL spectra. AFM measurements revealed that V-defect formation was not preferred in the undoped GaN films using indium surfactant unlike unintentionally Si or O doped GaN films grown with indium surfactant. However, when Si was intentionally doped into GaN with indium surfactant, the size and density of V-defects increased as a function of Si dopants. The relaxation of compressive stress by V-defect formation was observed in GaN films grown with Si doping in the presence of indium, consistent with the results on the unintentionally Si-doped GaN epilayers. The critical factors for V-defect formation are known to be misfit stress, reduced surface energy of $(10\overline{10})$ by the presence of indium, and threading dislocation density. From the studies of intentional Si doping, Si was identified as another important factor in V-defect formation. Although the surface energies of GaN (0002) and ($10\overline{11}$) modified by Si were not available in the literature, the presence of Si is believed to reduce the ($10\overline{11}$) surface energy or decrease the surface migration of adatoms on ($10\overline{11}$) planes that can lead to V-defect formation, which induces the relaxation of compressive misfit stress in GaN films grown on SiC. The other possible origin may be the anti-surfactant behavior of Si. Due to N dangling bonds at the TD cores, Si can be easily captured at these sites, creating Si – N masking that locally prevents GaN deposition. This masking effect can give rise to nano-sized holes which initiate nano-sized V-defects. Thus, these small V-defects can become larger by expanding the masking area or additional indium surfactant effect that makes ($10\overline{11}$) planes of V-defects stable.

Chapter 5

GaN Growth on Bulk GaN and Si(111) Substrates

5.1 Introduction

As discussed in the previous chapter, the effects of indium surfactant and Si doping on GaN epilayers grown on SiC substrates have been investigated to study the stress relaxation mechanism of GaN films. The results showed that compressive misfit stress relaxed through V-defect formation that was promoted by the indium surfactant and Si doping while step-flow growth was enhanced under In-rich conditions at the same time. Since the initial compressive misfit stress was one of the crucial factors to drive V-defects, the studies of GaN epilayers grown on different substrates such as bulk GaN and Si(111) are of great interest because the sign and magnitude of misfit stress vary. Thus, in order to observe the V-defect formation under reduced misfit stress and with different growth stress evolution, GaN growths were conducted as reported in this chapter, using bulk GaN and Si(111) substrates under In-rich condition.

Homoepitaxial growth of GaN on bulk GaN has advantages in terms of lattice and CTE matches, which gives rise to a low density of defects such as TDs, stacking faults and crackings.^{150,151} In addition, it is possible to simplify the growth process due to the omission of buffer layer growth prior to GaN growth. The improved film quality directly enhances the performance of optoelectronic and high-power electronic devices by reduction of non-radiative recombination centers and electron trap sites. Since there is no

misfit stress in homoepitaxy, the nucleation and growth model predicts that the energy barrier for V-defect formation approaches infinity. Furthermore, the bulk GaN substrates, provided by Kyma technologies, Inc., have very low TD density (mid 10⁶ cm⁻²), thus reducing nucleation sites for V-defects. Therefore, the use of indium surfactant and Si doping in homoepitaxy may not cause V-defect formation, which will be investigated in this chapter.

Unlike the GaN films grown on SiC where compressive misfit stress is induced, a different stress relaxation may be observed if tensile stress is generated during GaN growth. For this purpose, Si(111) substrates were used to investigate stress evolution and V-defect formation in the GaN films grown with an indium surfactant. Since the lattice constant a of Si(111) is 3.84 Å as compared to 3.1888 Å of wurtzite GaN growth, GaN film stress becomes tensile. The evolution of growth stress in the GaN film grown on Si(111) substrate differs from that of the GaN film grown on SiC.^{30,31} When GaN nucleates on an AIN buffer layer / Si(111), compressive stress is induced first. This initial compressive incremental stress rapidly changes to tensile incremental stress during coalescence between GaN nuclei. When 2D growth starts, the tensile incremental stress becomes constant, and the mean tensile stress is not usually relaxed until cracking occurs.³⁰ Thus, tensile thermal stress, caused by the CTE difference between GaN and the Si(111) substrate during cooling after growth, is added to the tensile growth stress, causing the film cracking which is known to be a typical stress relaxation mechanism of GaN films under large tension.³⁰ This cracking had been an obstacle in utilizing Si(111) substrates for heteroepitaxy of GaN until AlGaN graded buffer layer and other techniques were suggested to induce more compressive growth stress which can compensate the

post-growth tensile thermal stress.³² Therefore, the use of indium surfactant in GaN grown on Si(111) is interesting if indium surfactant can elastically relax the tensile growth stress by V-defect formation. Furthermore, as compared to the GaN growth on SiC, GaN films grown on Si(111) substrates usually contains high TD density (~ 10^{10} cm⁻²), resulting in a high density of nucleation sites for V-defect formation.

Therefore, the aim of this chapter is to investigate stress relaxation mechanisms and V-defect formation in GaN epilayers grown on two different substrates (bulk GaN and Si (111) substrates) when indium is present during growth. In homoepitaxy, MOSS and AFM results demonstrated that V-defects did not form with the indium surfactant even when combined with Si doping, as predicted by the nucleation and growth model. In the case of GaN growth on Si(111) substrate, *in-situ* stress measurements revealed that more tensile stress was induced in the GaN films under In-rich conditions. AFM measurements showed that V-defects were created by adding indium during GaN growth, suggesting that V-defects did not relieve tensile stress. A thickness interruption study revealed that indium surfactant resulted in V-defect nucleation under the initial compressive stress prior to coalescence, and the additional tensile stress generation could be due to a reduction of the V-defect density. Thus, although the enhanced step-flow growth can be achieved by indium, the use of indium could be detrimental to GaN films grown on Si(111) substrates due to the larger tensile growth stress which will be added to the tensile thermal stress. From these results, it can be concluded that the V-defects in heteroepitaxial growth of GaN films cannot be completely suppressed in the presence of indium and Si dopants. In particular, when the misfit stress cannot be reduced in a given system such as InGaN/GaN, using high quality bulk GaN substrates is the only way to

reduce V-defects, which is not practical due to the high cost of bulk GaN. Therefore, this conclusion leads to the great interest towards the growth of N-polar GaN films on C-face SiC substrates which will be studied in chapter 6.

5.2 GaN Growth on bulk GaN Substrates with Indium Surfactant

As discussed in this section, preliminary experiments were conducted first to optimize the growth condition of homoepitaxy. Then, the system energy change associated with V-defect formation in homoepitaxy, will be discussed using the nucleation and growth model. The calculation results suggest that V-defects should not form with indium surfactant and Si doping because there is no misfit stress. To verify this hypothesis, indium surfactant and Si doping will be introduced during homoepitaxy of GaN.

5.2.1 Experimental Details

Bulk GaN substrates were provided by Kyma Technologies, Inc. All bulk GaN substrates were given as 1.0×1.0 cm² pieces to fit the pocket of the susceptor. They were double side polished, nominally undoped, and approximately 380 µm thick substrates. Bulk GaN pieces were cleaned through a series of ultrasonication in acetone, isopropanol, and DI water, followed by a dip in 10% HF solution and rinse in DI water. A preliminary

study optimizing growth condition was performed first at the growth temperature of 1100 °C. For 1.1 µm thick GaN film growth, molar flow rates of TMGa and NH₃ were controlled at 7.9 µmol/min and 62.5 mmol/min (V/III ratio = 7950), respectively. H₂ was used as a carrier gas, and the reactor pressure was set at 50 Torr. However, the intensity of reflected light from the sample in MOSS gradually decreased at 1100 °C during the hold step prior to GaN growth, suggesting that the surface of the bulk GaN substrates was degraded by hydrogen etching. To avoid this issue, N2 and was used as a carrier gas and NH₃ was introduced during heating and hold steps. At the actual GaN growth step after hold, N₂ was changed to H₂ 15 seconds before the introduction of TMGa to the reactor. No buffer layer was used since homoepitaxy does not require any nucleation layer. In order to observe the effect of indium surfactant and intentional Si doping on V-defect formation in the homoepitaxially grown GaN films, the growth temperature was reduced to 950 °C, and the reactor pressure was changed to 100 Torr. Molar flow rates of TMGa and NH₃ were 7.9 µmol/min and 30.4 mmol/min (V/III ratio = 3860), similar to the growth condition used in the GaN growths on SiC substrates. To study the effect of indium surfactant, TMIn of 6.8 µmol/min (TMIn/TMGa = 0.86) was added to the reactor during 1.8 µm GaN growth. Here the TMIn flux is higher than 4.5 µmol/min used in chapter 4. For Si doping combined with indium, TMIn of 6.8 µmol/min and SiH₄ of 9.2 nmol/min were introduced simultaneously for GaN growth since both indium and Si doping increased V-defect size and density in the GaN epilayers grown on SiC substrates.

The MOSS system was used to monitor the real-time curvature change of the GaN films. No oscillation in the reflectivity data was observed during GaN growth in the

MOSS because no buffer layer was used. Thus, the growth rate could not be determined during homoepitaxy. Instead, to grow 1.8 µm thick GaN, the growth time was estimated by the growth rate obtained from GaN grown on SiC under the identical growth condition, assuming that the growth rate of GaN in homoepitaxy is similar to that of GaN films grown on SiC. AFM measurements were performed to investigate the surface morphology of the GaN films.

5.2.2 Preliminary Results on the Homoepitaxy

A preliminary study on the homoepitaxial growth of GaN was carried out at 1100 °C in order to optimize growth conditions, and investigate the stress change and surface morphology prior to introducing indium at 950 °C. Figure 5.1 shows the curvature change



Figure 5.1. Curvature change of 1.1 µm thick GaN grown on bulk GaN at 1100 °C.

of 1.1 μ m thick GaN film obtained from the MOSS. In the curvature data, the slope at any given point represents the instantaneous change of stress, similar to the stressthickness data. Thus, negative and positive slopes indicate compressive and tensile incremental stress, respectively. As explained in the previous section, N₂ was used as a carrier gas and NH₃ was also employed prior to the GaN growth segment because the surface of the bulk GaN substrate was severely etched by hydrogen during the hold step at the growth temperature. In the MOSS system, the reflectivity and film curvature decreased when H₂ etching occurred on the bare GaN substrate. As shown in Fig. 5.1, no change in the curvature during hold was observed, which confirms that the surface of the bare GaN substrates was not degraded when N₂ and NH₃ were used during heating and hold segments. Therefore, the use of N₂ as a carrier gas prior to GaN growth step became standard for homoepitaxy. However, for the actual GaN growth, N₂ was changed to H₂, which causes the discontinuity of curvature at the onset of GaN growth in Fig. 5.1. During GaN growth, the film curvature remains nearly constant, confirming that there is no misfit stress and the homoepitaxially grown GaN epilayer is fully relaxed.

Figure 5.2 shows an AFM micrograph of the GaN epilayer over $2 \times 2 \ \mu m^2$. The nano-sized pits, associated with the TDs, are rarely observed in comparison to the heteroepitaxially grown GaN on SiC. This implies that the presented homoepitaxially grown GaN film has very low TD density (~ mid 10^6 cm^{-2}). Excellent step-terrace structures are also observed, as compared to GaN grown on SiC. Thus, MOSS and AFM results here confirm two factors for hindering V-defect formation in homoepitaxy, i.e., nearly zero misfit stress and low density of V-defect nucleation sites in the presence of indium.



Figure 5.2. AFM image of 1.1 μ m thick GaN grown on bulk GaN substrate at 1100 °C. The scanned area in the AFM micrograph is 2 × 2 μ m² and the RMS roughness is 0.16 nm.

5.2.3 V-defect Formation Energy in Homoepitaxy

Figure 5.3 presents the system energy change as a function of V-defect radius under In-rich condition when the misfit stress decreases from -0.9 GPa, which was the initial compressive misfit stress of GaN grown on SiC in section 4.2, down to 0 GPa for homoepitaxy, supposing that the V-defect forms at the edge type TD. This calculation was done based on Eq. (4.13) developed in the nucleation and growth model. Si doping was not considered in these predictions because the surface energy modified by Si dopant was not available in the literature. However, without misfit stress, V-defect formation always raises the system energy regardless of Si doping because the strain energy term in Eq. (4.13) vanishes for zero misfit stress. Thus, the energy barrier and critical radius for V-defect formation keep increasing in homoepitaxy. Furthermore, the bulk GaN substrate



Figure 5.3. System energy change as a function of V-defect radius. As the misfit stress is reduced from -0.9 GPa to 0 GPa (homoepitaxy), the energy barrier and critical radius for V-defect formation keep increasing.

used here has very low TD density (~ mid 10^6 cm⁻²), i.e., low density of nucleation sites for V-defects. Hence, the formation of V-defects should not be favored in the GaN growth on bulk GaN substrates with indium surfactant even combined with Si doping.

5.2.4 Homoepitaxy with Indium Surfactant and Intentional Si Doping

In order to observe the effect of indium surfactant and also to be consistent with the previous experiments, the GaN growth temperature was reduced to 950 °C and reactor pressure was raised to 100 Torr. Figure 5.4 shows the film curvature change during a series of homoepitaxial growth, acquired from the MOSS. All homoepitaxially grown GaN films here do not show curvature change with indium and Si doping. This



Figure 5.4. Curvature changes of 1.8 μ m thick GaN films grown on bulk GaN at 950 °C with indium surfactant and Si doping. During these homoepitaxial growths, no significant curvature changes are observed.

observation suggests that these films are fully relaxed and there is no misfit stress that has to be relieved. Here, a higher TMIn flow rate (6.8 μ mol/min) was used, as compared to the highest TMIn flow rate of 4.5 μ mol/min used in the GaN grown on SiC in chapter 4. For intentional Si-doping, a SiH₄ flow of 9.2 nmol/min was used in combination with the indium surfactant, which was the most favorable growth condition for V-defect formation, identified in chapter 4.

The MOSS results suggest that any kind of stress relaxation mechanism may not need to be activated in homoepitaxy, which implies that V-defects may not form. To examine this prediction, AFM measurements were performed on the reference GaN, GaN grown with indium, and GaN grown with indium and Si doping. Figure 5.5(a) - (c) shows $2 \times 2 \mu m^2$ AFM images of three samples. The reference GaN shows a relatively

rough surface due to the limited surface mobility of Ga and N adatoms at the growth temperature of 950 °C, resulting in an RMS surface roughness of 0.43 nm. However, once the indium surfactant is used, the GaN surface becomes smoother, reducing the RMS roughness from 0.43 nm down to 0.12 and 0.13 nm, respectively. Hence, this



Figure 5.5. AFM images of GaN eplilayers grown on bulk GaN substrates with indium surfactant and Si doping. (a), (b), and (c) show AFM images over $2 \times 2 \ \mu m^2$ and (d), (e), and (f) show AFM images over $50 \times 50 \ \mu m^2$.

improved surface morphology agrees with the results on the GaN films grown on SiC. However, in $50 \times 50 \ \mu\text{m}^2$ AFM images from Fig. 5.5(d) - (f), no V-defects were found in any of the samples even with excessive amount of indium combined with Si doping. Consequently, V-defects were suppressed by using high quality bulk GaN substrates which have low TD density and provide zero misfit strain, as predicted by the nucleation and growth model.

The substrates used here were all polished c-plane GaN for the epitaxy. However, the surface quality of each bare bulk GaN substrates was not consistent in terms of polishing and misorientation. In Fig. 5.5(d) and (e), the stripe patterns seem to be influenced by poor polishing during preparation of the substrates. Also, the anisotropic steps towards a particular direction suggest that these GaN substrates were miscut from the c-axis of wurtzite GaN.

5.3 GaN Growth on Si(111) Substrates with Indium Surfactant

In this section, the study focuses on stress change and V-defect formation in GaN growths on Si(111) substrates with indium surfactant. As discussed in section 5.1, the stress change of GaN films on Si(111) differs from that of GaN on SiC. Tensile growth stress is typically induced in the GaN / AlN / Si(111) system, which causes film cracking during cooling after growth. Thus, if indium can elastically relax the tensile stress of GaN by V-defect formation, the cracking may be reduced. However, MOSS and AFM measurements revealed that indium added more tensile growth stress by V-defect

formation. In order to find the origin of tensile stress generation enhanced by indium surfactant, a thickness interruption method was employed using excessive amount of indium (6.8 µmol/min).

5.3.1 Experimental Details

GaN epilayers grown on Si(111) substrates were prepared by MOCVD. The source precursors were TMGa, TMAl, TMIn, and NH₃ for Ga, Al, In, and N, respectively. H_2 carrier gas was used, and the reactor pressure was 100 Torr. Si(111) wafers were 2 inch, 500 µm thick, highly resistive (2,000 ~ 10,000 ohm-cm), and undoped single-side polished wafers (Nitronex, Inc.). They were diced into $1 \text{ cm} \times 1 \text{ cm}$ pieces and cleaned through a series of sonication in acetone, isopropanol, and DI water. Then, the thin native SiO₂ layer on the Si(111) was etched out by a dip in 10% HF, followed by a rinse in DI water, prior to buffer layer growth. AlN buffer films (~ 90 nm) were grown on the Si(111) at 1100 °C. The source fluxes of TMA1 and NH₃ were 10.3 μ mol/min and 89.3 mmol/min (V/III ratio = 8670), respectively. GaN epilayers of 1.8 μ m were grown on the AlN buffer layer at 950 °C. The molar flow rates of TMGa and NH₃ were 7.9 µmol/min and 5.4 mmol/min (V/III ratio = 680). This lowered V/III ratio resulted in zero V-defect density in the reference GaN film so that the origin of V-defect formation by adding indium could be easily identified. Since the film stress did not change significantly, an excessive amount of indium (6.8 µmol/min) was introduced during GaN growth with the thickness interruption method. Ex-situ HRXRD

measurements were performed in a Philips MRD four-circle diffractometer with Cu K_{α} radiation ($\lambda = 1.5406$ Å) to evaluate the crystallinity and estimate the threading dislocation density. AFM measurements were employed to correlate the variations in film stress with the surface morphology change.

5.3.2 Thickness Interruption Study

Figure 5.6 presents the stress-thickness data of the reference GaN and the GaN film grown on AlN / Si(111) substrates using a TMIn flow rate of 6.8 μ mol/min. Both GaN films show an initial incremental stress of approximately -0.4 ~ -0.5 GPa. In the reference GaN, the initial compressive stress changes to tensile incremental stress beyond



Figure 5.6. Stress-thickness data of GaN films grown on Si(111) substrates at 950 °C using 90 nm thick AIN buffer layers. For the indium surfactant effect, TMIn flow rate of 6.8 µmol/min was used during GaN growth.

 ~ 600 nm. In contrast, the incremental stress transition from compression to tension occurs around ~ 350 nm when indium was introduced during GaN growth. As mentioned in section 5.1, the tensile stress is usually generated in the GaN film grown on Si(111) due to the coalescence between misoriented GaN sub-grains. Hence, here the faster transition in the GaN film grown with indium might be correlated to the expedited coalescence promoted by indium surfactant which allows for the improved surface migrations of Ga and N adatoms. As both GaN films grow beyond $\sim 1.0 \mu$ m, the incremental tensile stress appears to be nearly constant, and the tensile stress extends to the end of the 1.8 μ m thick GaN growth without relaxation of tension. The mean stress of each GaN films is 0.09 and 0.16 GPa, respectively, showing that the indium surfactant leads to more tensile stress in the GaN film grown on the Si(111) substrate.

To examine the possible V-defect formation in the GaN grown on Si(111) substrates, AFM measurements were done over $50 \times 50 \ \mu\text{m}^2$. Figure 5.7 shows AFM



Figure 5.7. AFM images of 1.8 μ m GaN films grown (a) without indium surfactant and (b) with indium surfactant (TMIn = 6.8 μ mol/min). The scan area was 50 × 50 μ m².

images of both GaN films. The reference GaN has no V-defects. However, the GaN film grown with TMIn flow rate of 6.8 μ mol/min has V-defect density of 1.4×10^6 cm⁻². Therefore, the additional tensile stress generation by indium surfactant seems to be due to V-defect generation. It has been reported that V-defect is an elastic relaxation mechanism of compressive stress in InGaN films.^{16,27} Also, in chapter 4, the compressive stress of GaN films was relieved via V-defects induced by indium and Si doping. However, the GaN film here grown on Si(111) becomes more tensile in the presence of indium by Vdefects, which may be contradictory because V-defect generation should not be preferred thermodynamically if it adds more strain in the GaN film.

In order to investigate and understand the stress change of the GaN film grown on Si(111) through V-defect formation under In-rich conditions, the GaN growths were interrupted at various film thicknesses. Figure 5.8 shows $50 \times 50 \ \mu\text{m}^2$ AFM images of the reference sample and GaN grown with indium at the thicknesses of 0.5 μ m, 1.0 μ m, and 1.4 μ m. At the GaN thickness of 500 nm, the reference GaN shows nearly zero V-defects, and no V-defects were observed at 1.0 μ m, as can be seen in Fig. 5.8(a) and (b). Thus, 1.4 μ m thick GaN growth without indium surfactant was not conducted because 1.8 μ m thick GaN did not show any V-defects, as shown in Fig. 5.7(a). On the other hand, 500 nm thick GaN grown on Si(111) with TMIn of 6.8 μ mol/min shows a high density of small sized V-defects in Fig. 5.8(c). From the stress-thickness data in Fig. 5.6, the initial incremental compressive stress of the GaN film in the presence of indium becomes tensile beyond ~ 350 nm. Thus, the relative tension in the GaN grown with indium at 500 nm with respect to the reference GaN is believed to be due to V-defect generation which



Figure 5.8. AFM images of GaN eplilayer grown on Si(111) substrates using AlN buffer layers over $50 \times 50 \ \mu\text{m}^2$. (a) and (b) show GaN films without indium at 0.5 $\ \mu\text{m}$ and 1.0 $\ \mu\text{m}$. (c), (d), and (e) show GaN films grown with indium surfactant at 0.5 $\ \mu\text{m}$, 1.0 $\ \mu\text{m}$, and 1.4 $\ \mu\text{m}$.

relaxes the initial compressive stress of the GaN film, consistent with the results for the GaN films on SiC in chapter 4. However, V-defect density decreases when the film keeps growing, as shown in Fig. 5.8(d) and (e), and Fig. 5.7(b). To correlate the stress change to

the V-defect size and density, V-defects were quantified as a function of film thickness in terms of area fraction, density, and radius of V-defects, as seen in Fig. 5.9 and 5.10. As the GaN film grows in the presence of indium, V-defect density decreases from 1.4×10^8 cm⁻² to 1.4×10^6 cm⁻² and area fraction is reduced from 11.2 % down to 0.4 %. Simultaneously, the average V-defect radius increases from 110 nm to 330 nm, and the maximum radius of the V-defects does not increase significantly beyond the film thickness of 1.0 μ m [Fig. 5.10]. These results imply that some small sized V-defects disappear, but some V-defects survive as the GaN film grows. Therefore, it seems that there is a critical radius for V-defects that may allow some of the V-defects to survive, which was the main concept developed in the nucleation and growth model. Also, the more tensile stress generation in the presence of indium shown in Fig. 5.6 appears to be correlated to the reduction of V-defect density, which will be discussed in the next section.



Figure 5.9. Area fraction and density of V-defects in the GaN film grown on Si(111) with indium surfactant (6.8 μ mol/min) as a function of film thickness.



Figure 5.10. (a) Average radius and (b) maximum radius of V-defects in the GaN films grown on Si(111) substrate with indium surfactant as a function of film thickness, estimated from AFM images in Fig. 5.8(c) - (e) and Fig. 5.7(b).

From the nucleation and growth model, the critical radius for V-defect formation here was approximately 600 nm, assuming that all variables are the same with GaN growth on SiC except the misfit stress of -0.4 GPa that was measured from the stressthickness data in Fig. 5.6. Since the higher TMIn flow rate of 6.8 µmol/min was used in comparison with 4.5 µmol/min in the case of GaN on SiC, the critical radius should be smaller than 600 nm. As stated in section 4.3, the nucleation and growth model should be understood in a qualitative way. Thus, although this model cannot quantitatively describe the strong driving force for V-defects in the 500 nm thick GaN film grown on Si(111) with indium, the model can explain the reduction of V-defects based on the concept of a critical radius of the V-defect. Also, the high density of V-defects in the 500 nm thick GaN film grown with indium demonstrates that TD density is a critical factor for Vdefect generation. X-ray rocking curve measurements on both GaN films grown on Si(111) with and without indium surfactant estimated the TD density to be about 3.5×10^{10} cm⁻². This value is nearly one order higher than that of GaN grown on SiC. Thus, it appears that the high TD density leads to a high probability of V-defect formation although the misfit stress is relatively small.

5.3.3 Tensile Stress Generation by Reduction of V-defects

In the previous section, more tensile stress was found to be induced in the 1.8 µm GaN film grown at 950 °C on Si(111) substrate by indium surfactant, as compared to the reference GaN grown without indium. V-defect formations appeared to relax the initial compressive stress, as can be seen in Fig. 5.6 and 5.8(c). Furthermore, the generation of more tensile stress seemed to be correlated to the reduction of V-defects as the GaN film grew beyond 500 nm. This observation supports that the film stress is not returned to the original compression state by the removal of V-defects, implying that the creation and reduction of V-defects may not be reversible. The possible reason for tensile stress generation induced by reduction of V-defects may be similar to the mechanism of tensile stress generation during coalescence of each GaN nuclei at the initial stage of film growth, which was also observed on the stress-thickness data of both samples in Fig. 5.6.

The tensile stress generation at the coalescence stage has been observed in metal film and polycrystalline thin film growth.¹⁵²⁻¹⁵⁴ The proposed mechanism was a zipping process of each island during coalescence, as schematically represented in Fig. 5.11.^{153,155} The coalescing islands make contact with each other at their bases and zip up the



Figure 5.11. Zipping process of each GaN nuclei at the initial stage of film growth on substrate. GaN film becomes tensile due to the zipping process that reduces the volume between GaN nuclei. [Refs. Nix *et al.*, J. Mater. Res. **14**, 3467 (1999) and J. D. Acord, Thesis, The Pennsylvania State University, 2007].

interface between islands to form a continuous film. In this process, the islands become strained by reaching each other to fill the gap, resulting in the tensile stress. Here the driving force is the reduction of net surface energy, which is balanced by increasing strain energy. In general, the misorientation of GaN nuclei on Si(111) is much greater than that of the GaN film grown on SiC. Therefore, the coalescence of GaN islands on Si(111) generates more tensile stress corresponding to the volume between GaN islands, giving rise to the transition of initial compressive incremental stress to tensile incremental stress in Fig. 5.6, which was not observed in the GaN grown on SiC. A similar mechanism can be found in the reduction of V-defect density. Figure 5.12 shows a schematic representation in removal process of V-defects. To fill the V-defect, GaN films around V-defects try to reach each other, which may contribute to the generation of tensile stress, leading to the concave-up film with respect to the original state. Depending on the V-defect density and size, the magnitude of tensile stress generation may differ. Therefore, the tensile stress creation of GaN grown on Si(111) with indium surfactant is



Figure 5.12. Schematic representation of removal process of V-defects when the GaN film grows. Filling V-defects may lead to tensile stress generation because GaN films try to reach each other towards the center of V-defect, and fill the volume corresponding to V-defects. The film curvature due to tension on the right side is exaggerated.

substantial between 500 nm and 1.0 μ m, but negligible when the reduction of V-defect density and area fraction is small at the film thickness greater than 1 μ m, where the incremental stress in Fig. 5.6 becomes almost constant. Based on this observation in the thickness interruption study, the relaxation of compressive stress in GaN films grown on SiC with indium surfactant and Si doping as reported in chapter 4 may be also correlated with the generation of tensile stress associated with the reduction of V-defects. In fact, AFM images in figure 4.8(h) and 4.20(h) showed that V-defect radius varied from ~ 100 nm up to ~ 1.1 μ m. Therefore, it appears that some of the V-defects were disappearing while the V-defects beyond the critical radius survived, contributing to the relaxation of compressive stress.

Consequently, the indium surfactant in the GaN film grown on Si(111) induced more tensile stress by the creation and reduction of V-defects in comparison to the reference GaN. Since thermal stress induced in the GaN film is tensile due to the CTE difference, the use of indium could degrade the film quality because of cracking networks that are relaxation mechanisms for tensile stress. In addition, highly defective GaN film grown on Si(111) gave rise to the strong driving force for V-defect generation although the initial misfit stress of \sim -0.5 GPa was lower than -0.9 GPa of GaN grown on SiC. Without using thick AlGaN graded buffer or other techniques to induce more compressive growth stress and reduce TD density, therefore, indium surfactant should not be used in the given GaN / AlN / Si(111) system.

5.4 Conclusions

The nucleation and growth model predicted that the energy barrier for V-defect formation approaches infinity under In-rich conditions in homoepitaxy. The homoepitaxial growth of 1.8 µm thick GaN films on bulk GaN substrates demonstrated that no V-defects formed even with excessive amounts of indium (6.8 µmol/min) and intentional Si doping (9.2 nmol/min) which were the most favorable conditions for Vdefect formation observed in GaN growths on SiC. The bulk GaN substrates provided much lower TD density, i.e., less density of nucleation sites for V-defect formation. Also, the stress-thickness data confirmed that the homoepitaxially grown GaN film is fully relaxed, leading to zero misfit stress, which in turn makes V-defects energetically unfavorable.

The heteroepitaxial growth of 1.8 μ m thick GaN films on Si(111) substrates using an AlN buffer layer (~ 90 nm) were performed to investigate the effect of indium surfactant on V-defect formation and stress change. The *in-situ* stress measurements revealed that the initial compressive incremental stress changed to tensile during coalescence of GaN nuclei around 600 nm in the reference GaN grown without indium. In the case of the GaN film grown in the presence of indium (6.8 µmol/min), this transition occurred around 350 nm. The mean stress at 1.8 µm was 0.09 GPa and 0.16 GPa for the reference GaN and GaN film grown with indium surfactant, respectively, demonstrating that the presence of indium generated more tensile stress in the GaN film. AFM measurements showed that 1.8 µm thick GaN film grown with indium had a Vdefect density of 1.4×10^6 cm⁻². The thickness interruption study indicated that V-defect density decreased from 1.4×10^8 cm⁻² to 1.4×10^6 cm⁻² and the area fraction of V-defects was reduced from 11.2 % to 0.4 % as the GaN film grew under In-rich conditions. Reduction of V-defect density appeared to be correlated to increased tensile stress generation. Therefore, the creation of V-defects seemed to relax the initial compressive stress during coalescence, which may lead to the early transition of compressive incremental stress to tension in comparison to the reference GaN. The possible mechanism for more tensile stress generation could be correlated to the volume reduction of V-defects when the films try to reach each other to close the V-defect in the presence of indium, as the GaN film grew beyond 500 nm. This process appeared to be similar to the tensile stress generated by the coalescence of GaN islands at the initial stage of film growth.

From these results, it can be concluded that V-defects can be energetically favorable in the heteroepitaxial growth of highly defective GaN films on Si(111) with indium surfactant, where misfit stress exists. High TD density resulted in the strong

driving force for V-defect formation in the GaN films grown on Si(111) under In-rich conditions, although the misfit stress was relatively small, compared to that of GaN films on SiC. Thus, homoepitaxy using high quality bulk GaN substrates seems to be the only way to suppress V-defect formation under In-rich conditions even accompanied with intentional Si doping, as predicted by the nucleation and growth model and demonstrated by the experimental results in this chapter. In other words, the only way to minimize the V-defect density in heteroeptiaxy using foreign substrates is reduction of TD density, i.e., reduction of V-defect nucleation sites, but this still cannot remove V-defects completely when Si dopants are present with indium surfactant. As a result, there was interest in studying N-polar GaN films where V-defects are not preferred energetically, which is predicted by first-principles calculations.⁵ Hence, the next chapter focuses on the heteroepitaxial growth of N-polar GaN on C-face misoriented SiC substrates in the presence of indium surfactant combined with intentional Si doping.

Chapter 6

N-polar GaN Growth on C-face Vicinal SiC Substrates

6.1 Introduction

In chapter 4 and 5, indium surfactant and Si doping lead to V-defect formation in heteroepitaxial growth of GaN epilayers on lattice-mismatched substrates such as SiC and Si(111) while the enhanced step-flow growth was simultaneously observed due to the kinetically improved surface migrations of Ga and N adatoms by indium. Misfit stress, reduction of $(10\overline{1}1)$ surface energy by indium surfactant. Si incorporation, and threading dislocations (TDs) drove V-defect formation in GaN heteroepitaxy, as evidenced by the experimental results in previous chapters. In contrast, homoepitaxial growth of GaN on bulk GaN substrates did not show any V-defects under In-rich conditions and even with Si doping due to zero misfit stress and low TD density. Despite using high quality bulk GaN substrates, the nucleation and growth model predicts that it may not be possible to fully hinder V-defects in a system where misfit stress cannot be avoided, such as InGaN growth on GaN, since misfit stress between InGaN and GaN can drive V-defect formation under In-rich conditions. Liu et al.¹⁷ observed that the V-defect density in their Mg-doped InGaN films in green LEDs dramatically decreased to 10^7 cm⁻² on high quality bulk GaN substrates, as compared to a V-defect density of mid 10^8 cm⁻² on sapphire substrates, supporting the prediction made by the nucleation and growth model. Thus,

even with bulk GaN substrates, it is challenging to control V-defects especially in high indium composition InGaN films for green and deep green light emitting devices.

As indium composition increases in InGaN films for green LEDs and LDs, Vdefects become more critical because V-defects have been reported to provide a pathway for leakage currents, degrading the lifetime of devices.^{17,34} More seriously, phase separation, composition fluctuations, and high misfit stress in the high indium composition InGaN films reduces the quantum efficiency of green LEDs and LDs, leading to the 'green gap' which arises from the efficiency drop when the emission wavelength in LEDs and LDs approaches green from either the red or blue light.³³ Thus, green LDs, which require a much more complicated device structure with a cavity in comparison to LEDs, have not been commercialized yet. Recently, a green LD (513 nm), which was realized by utilizing high quality GaN substrates and optimizing growth conditions of InGaN/GaN multiple quantum wells, has been demonstrated by Nichia Corp.¹⁰⁴ Although they did not report the details of InGaN growth conditions, their high quality bulk GaN substrates seemed to be prepared in a very complex way utilizing patterning, several epitaxial lateral overgrowth (ELOG) steps, polishing, removal of the sapphire substrate, and etc.¹⁰⁵ Therefore, if V-defect free InGaN films for green LDs can be obtained with reduced defects on foreign substrates such as sapphire and SiC, then heteroepitaxy of GaN for InGaN growth will be the practically preferred method due to the high cost of bulk GaN substrates.

GaN epilayers, which have been so far studied in chapter 4 and 5, were all Gapolar films grown along the [0001] direction of hexagonal wurtzite GaN. However, firstprinciples calculations predict that V-defects are not energetically preferred along N- polar directions unlike Ga-polar GaN,⁵ thus directing great attention towards the heteroepitaxy of N-polar GaN films. Basically, growth of GaN films along the $[000\bar{1}]$ direction can be done by using C-face SiC substrates and modifying the nitridation step of sapphire, as shown in Fig. 6.1.¹⁵⁶ However, most optoelectronic devices have been by far developed on Ga-polar GaN films because Ga-face GaN provided a very smooth surface for InGaN growth in blue LEDs and LDs. The crucial factor that makes N-polar GaN inappropriate for device fabrication has been another type of extended surface defect, a so-called hexagonal hillock.^{43,44} As reviewed in section 2.7, these hexagonal hillocks are typically 10 ~ 50 µm in width and 1 ~ 2 µm in height [see Fig. 2.14]. The formation of these hillocks has been observed in homoepitaxy as well as heteroepitaxy of N-polar GaN by MOCVD, which suggests that the origin of hexagonal hillock is irrelevant to misfit stress.^{35,42-44,157} TEM analysis revealed that a 100 ~ 200 nm wide Gapolar column is embedded in the N-polar matrix at the center of the hexagonal hillock.



Figure 6.1. Wurtzite crystal structures of (a) Ga-polar GaN and (b) N-polar GaN. The arrow indicates the growth direction. [Ref. Sumiya *et al.*, MRS Internet Journal of Nitride Semiconductor Research **9**, 1 (2004).]

[see Fig. 2.15].^{43,44} Thus, these surface defects have inversion domains which have opposite polarity and faster growth rate in comparison to the N-polar matrix. To overcome this issue, the use of vicinal substrates has been suggested. By increasing the misorientation of the substrate from the c-axis, hexagonal hillock density was dramatically reduced in both homoepitaxy and heteroepitaxy of N-polar GaN films.^{36,45-47} However, although the hexagonal hillocks can be suppressed, the surface of N-polar GaN is typically rough, as compared to that of Ga-polar GaN.

Therefore, the first goal as described in this chapter was N-polar GaN growths on vicinal C-face SiC substrates misoriented towards $<11\overline{2}0 >$ by 3.57 degree from the c-axis, using indium surfactant and Si doping, in order to verify whether V-defects are energetically unfavorable and indium surfactant can lead to the improved surface morphology on N-face GaN. *In-situ* stress measurements revealed that no stress was changed during the 1.9 µm N-polar GaN growths with indium and Si doping with respect to the reference N-polar GaN, suggesting that modification of stress change associated with V-defects did not happen. AFM measurements confirmed that no V-defects formed and indium significantly improved the surface morphology of N-polar GaN. PL measurements indicated that indium surfactant lead to an enhancement of NBE emission and reduction of defect-related YL. Hence, indium turned out to be an effective strategy to improve the surface morphology and optical properties of N-polar GaN films.

The second goal described in this chapter was to optimize growth conditions of N-polar GaN films for future InGaN growth. Effects of growth temperature, a two-step process, and AlN buffer layer thickness on the surface morphology and structural properties of 1.1 μ m N-polar GaN films were investigated. Unlike Ga-polar GaN films, AFM measurements showed that an increase of growth temperature did not improve the surface morphology of N-polar GaN films. Therefore, a two-step process, utilizing a low temperature thin GaN layer followed by high temperature GaN growth, was studied. AFM and HRXRD ω - scans showed promising results from two-step processed N-polar GaN film in terms of crystal quality and surface morphology. As compared to a 90 nm AlN buffer film that was normally used for GaN growths in this thesis study, the use of a thinner AlN buffer layer (~ 30 nm) increased surface roughness, but reduced edge type TD density of the N-polar GaN film. Thus, a combination of a thinner AlN buffer layer with the two-step process for N-polar GaN is expected to provide lower TD density as well as improved surface morphology, which is suggested for future studies of N-polar InGaN growth.

6.2 N-polar GaN Growth with Indium Surfactant and Si Doping

As described in this section, the study focused on 1.9 μ m N-polar GaN growths on vicinal C-face SiC substrates at 950 °C by MOCVD to examine the driving force for V-defect formation along the [0001] growth direction, utilizing indium surfactants and Si doping. The MOSS system was employed to monitor real-time stress changes. AFM measurements will be performed to investigate the surface morphology modified by indium surfactant and Si doping. HRXRD rocking curves were used to measure the crystallinity of N-polar GaN films. SIMS analysis was done to probe impurities in N- polar GaN films which have highly reactive surfaces. PL measurements were employed to characterize the optical properties of N-polar GaN films modified by indium surfactants and Si doping.

6.2.1 Experimental Details

The polarity of the SiC substrate along the c-axis can determine the polarity of the GaN film. Thus, N-polar GaN epilayers were grown by MOCVD, using carbon-face 6H-SiC substrates. These C-face SiC wafers were purchased from Cree, Inc., and they were 380 µm thick, semi-conducting (n-type doped with N), C-face CMP finished, and misoriented towards $< 11\overline{20} >$ by 3.57 degree from the c-axis of SiC. The relationship between wafer flat and misorientation direction was already described in section 3.3.1. Prior to epitaxy, the surface morphology of bare C-face SiC wafer was examined by AFM, as shown in Fig. 6.2. Although C-face SiC wafers do not have the step-terrace structures which bare Si-face SiC wafers show, RMS surface roughness of 0.10 nm in Cface SiC wafer was comparable to or slightly better than 0.12 nm in Si-face SiC wafer. Therefore, a rough surface of N-polar GaN in comparison to Ga-polar GaN may not originate from the surface quality of the substrates. Source precursors were TMGa, TMAI, TMIn, and NH₃ for Ga, Al, In, and N, which were carried by H₂ into the reactor where the pressure was maintained at 100 Torr. C-face 6H-SiC wafers were diced into 1 \times 1 cm² pieces and loaded onto the rotating susceptor that was inductively heated by a remote RF generator. AlN buffer layers (~ 90 nm) were grown on the substrate at 1100


Figure 6.2. $10 \times 10 \text{ }\mu\text{m}^2$ AFM images of (a) Si-face SiC (on-axis) for Ga-polar GaN growth and (b) C-face vicinal SiC substrate misoriented towards $<11\overline{2}0 > by 3.57$ degree from the c-axis for N-polar GaN growth. The RMS surface roughness is 0.12 nm and 0.10 nm, respectively.

°C first. Molar flow rates of TMAl and NH₃ were 10.3 μ mol/min and 89.3 mmol/min (V/III ratio = 8670). GaN epilayers of 1.9 μ m were then grown on the AlN buffer layer at 950 °C. TMGa and NH₃ were controlled at 9.2 μ mol/min and 35.7 mmol/min (V/III ratio = 3880), respectively. To investigate the effects of indium surfactant and intentional Si doping on the N-polar GaN films, TMIn of 4.5 μ mol/min and SiH₄ of 9.2 nmol/min were introduced during N-polar GaN growth.

For *in-situ* stress measurements, MOSS was used using multi-beam laser spots which were reflected on the sample surface to measure the film curvature change. The growth rate of all N-polar GaN films was approximately 0.45 nm/s, determined from the oscillations of reflected light intensity, which was slower than 0.49 nm/s of Ga-polar GaN films under identical growth conditions. AFM measurements were done in tapping mode on a Digital Instruments Dimension 3100. HRXRD measurements were performed in a Philips MRD four-circle diffractometer to evaluate the crystal quality. SIMS analysis

was employed to probe the impurities in N-polar GaN films. PL was measured with the excitation laser wavelength of 266 nm at room temperature to characterize the optical properties of GaN. TEM analysis was performed on a JEOL 2010F by Dr. Xiaojun Weng to determine the polarity of GaN film grown on C-face SiC substrates and examine microstructures of N-polar GaN film grown with indium surfactant.

6.2.2 In-situ Stress Measurements

Figure 6.3 shows the stress-thickness data of 1.9 μ m thick N-polar GaN films grown on vicinal C-face SiC substrates at 950 °C with indium surfactant and Si doping by MOCVD. All samples show similar initial incremental stress of -1.5 ± 0.1 GPa up to ~



Figure 6.3. Stress-thickness versus film thickness in N-polar GaN epilayers grown on vicinal C-face SiC substrates at 950 °C by MOCVD. Indium surfactant (TMIn = 4.5 μ mol/min) and Si doping (SiH₄ = 9.2 nmol/min) do not result in stress change which was observed in Ga-polar GaN films.

100 nm. This compressive stress value is higher than the -0.9 GPa of Ga-polar GaN films studied in chapter 4. In general, the initial stress is greatly affected by surface diffusivity of Ga and N adatoms. When growth temperature increases and V/III source input ratio decreases, the initial incremental stress is lowered. Thus, the higher compressive stress implies that surface migration of adatoms on the N-polar GaN surface might be relatively limited, as compared to Ga-polar GaN films grown under the identical condition. From the control experiment on the Ga-polar GaN film, the growth rate of 0.45 nm/s in N-polar GaN film turned out to be slower than 0.49 nm/s of Ga-polar GaN film. Thus, in addition to possible limited surface diffusion, the effective V/III ratio on the N-polar GaN surface could be relatively higher, which increase the initial compressive stress.

As the reference N-polar GaN films grow, compressive incremental stress relaxes and changes to tensile incremental stress beyond about 900 nm while the film is still under compression, as seen in Fig. 6.3. When indium surfactant is employed during growth, no significant stress change is observed in comparison to the reference. Also, when Si doping is accompanied with the indium surfactant, film stress becomes slightly more tensile with respect to the reference, but the change is very small. In chapter 4, Gapolar GaN films grown on Si-face SiC showed that the compressive stress was relaxed by indium and Si doping through V-defect formation [Fig. 4.1 and 4.14]. Hence, we may speculate that V-defects do not form on the N-polar GaN films, as predicted by firstprinciples calculations. This will be discussed later along with AFM measurements.

Fig. 6.4 presents reflectivity data of Ga-polar and N-polar GaN films grown under the same growth conditions, obtained from MOSS. As described in section 4.2.2, the reflectivity data can represent each growth stage, i.e., nucleation, coalescence, and 2D



Figure 6.4. Reflectivity variations of Ga-polar and N-polar GaN films grown on SiC substrates at 950 °C. The reflectivity was measured by MOSS integrated onto the MOCVD system.

growth. In Ga-polar GaN, when GaN nucleates on the AlN buffer layer, the intensity of reflected light decreases corresponding to islanding of GaN nuclei because of light scattering arising from the increased aspect ratio of GaN islands. When these islands combine to form a continuous film during coalescence, the reflectivity recovers towards the saturation associated with step-flow growth, thus indicating 3D to 2D transition in growth modes. On the other hand, the N-polar GaN film does not show the initial reduction of reflectivity. The oscillation rather starts with full amplitude, suggesting that the size of each GaN nuclei is small and the density of GaN islands is high. This observation implies that quasi-2D growth starts from the initial nucleation stage in the case of N-polar GaN without an islanding stage. Similar observation on the quasi-2D growth was reported in the N-polar GaN growth on sapphire substrates.¹⁵⁸ Thus, a high density of GaN nuclei is expected to increase tilt and twist of N-polar GaN films, which

in turn may increase TD density. HRXRD rocking curve measurements will be conducted to examine the crystallinity of N-polar GaN epilayers.

6.2.3 Surface Morphology

AFM measurements were carried out to investigate the surface morphology change of N-polar GaN films due to the presence of indium and Si doping. Figure 6.5(a) - (c) shows AFM images of N-polar GaN films over $2 \times 2 \mu m^2$ area when indium surfactant and Si doping were used during GaN growth. N-polar GaN films usually have rough surface morphology, as compared to Ga-polar GaN films. In chapter 4, the reference Ga-polar GaN film exhibited RMS surface roughness of 0.5 nm in $2 \times 2 \ \mu m^2$ area, and the surface becomes smoother with indium, decreasing the roughness down to 0.15 nm. In Fig. 6.5(a), the reference N-polar GaN film shows rough surface morphology over 2 \times 2 μ m² area, showing an RMS roughness of 6.2 nm. However, the surface morphology of the N-polar GaN film is dramatically improved by indium surfactant, resulting in RMS roughness of 0.5 nm, as seen in Fig. 6.5(b). Thus, the effect of indium surfactant seems to be much greater on the N-face GaN film. Although RMS roughness of 0.5 nm is not comparable to 0.15 nm of Ga-polar GaN, the roughness less than 1 nm seems to be excellent and comparable to the other studies of N-polar GaN films reported in the literature.^{36,159-161} When Si doping was simultaneously done with indium surfactant, surface morphology remained similar, resulting in 0.5 nm roughness in Fig. 6.5(c). Thus, even though Si has been reported to act as an anti-surfactant, a SiH₄ flow



Figure 6.5. AFM images of N-polar GaN eplilayers grown on vicinal C-face SiC substrates when indium surfactant (TMIn = 4.5 μ mol/min) and Si doping (SiH₄ = 9.2 nmol/min) were introduced during GaN growths. AFM images of (a), (b), and (c) were obtained over 2 × 2 μ m², and AFM images of (d), (e), and (f) were obtained over 20 × 20 μ m². The white arrow indicates the misorientation direction of C-face SiC substrates towards <1120 > from the c-axis.

rate up to 9.2 nmol/min was not detrimental to the surface of N-polar GaN films in the presence of indium.

In order to find possible V-defect formation observed in Ga-polar GaN films and examine the surface morphology at the macroscopic scale, AFM measurements were done on $20 \times 20 \text{ }\mu\text{m}^2$ area, as presented in Fig. 6.5(d) – (f). The surface of reference Npolar GaN film shows triangular features which consist of (1010) and (0001) planes, resulting in a rough surface [Fig. 6.5(d)]. The tips of the triangular features are aligned along the $<11\overline{2}0>$ direction. Thus, these anisotropic steps along a particular direction are believed to arise from the misorientation of the C-face SiC substrate, which was miscut towards the $<11\overline{2}0>$ direction by 3.57 degree from the c-axis. Similar triangular features have been reported in homoepitaxy of N-polar GaN grown on vicinal bulk GaN substrates misoriented towards $<11\overline{2}0>$ by 4 degree at 1040 °C using MOCVD.⁴⁶ The formation mechanism of these anisotropic hillocks seems to correlate with two types of step edges in the bilayer stacking sequence of wurzite GaN, as schematically illustrated in Fig. 6.6.^{46,162} Type A step has two dangling bonds in contrast to one bond of type B step edge [Fig. 6.6(a)], which lead to faster lateral growth rate of type A step. Thus, lateral growth of type A step is limited due to slower growth rate of type B step, as shown in Fig. 6.6(b). When steps propagates along the $[01\overline{10}]$ and $[10\overline{10}]$ directions, a pinning may occur at a certain point, giving rise to the anisotropic triangular hillock towards $<11\overline{20}>$. The source of possible pinning is not clear. However, it seems to be related to limited surface diffusion of Ga and N adatoms since these triangular features disappear when indium surfactant was used during N-polar GaN growth. As seen in Fig. 6.5(e), the



Figure 6.6. (a) Plan view of configurations of type A and type B step edges. Type A step edge has two dangling bonds, as compared to one dangling bond of type B step edge, which may give rise to faster lateral growth rate of type A step. (b) Schematic illustration of triangular hillock formation due to misorientation-induced steps towards $<11\overline{20}>$. Lateral growths of type A steps are limited by slower type B steps. When pinning occurs between laterally propagating steps between [0110] and [1010] directions, anisotropic triangular steps may form towards [1120]. [Refs. J. J. Schermer, J. Cryst. Growth **240**, 14 (2002), and M. H. Xie, S. M. Seutter, W. K. Zhu, L. X. Zheng, H. Wu, and S. Y. Tong, Phys. Rev. Lett. **82**, 2749 (1999), and A. R. A. Zauner, E. Aret, W. J. P. van Enckevort, J. L. Weyher, S. Porowski, and J. J. Schermer, J. Cryst. Growth **240**, 14 (2002).]

surface becomes much smoother under the In-rich condition, suggesting that the enhanced surface diffusivity by indium overcomes pinning and the slow growth rate of the type B step. The RMS surface roughness dramatically decreases from 18.1 nm down to 3.5 nm in $20 \times 20 \ \mu\text{m}^2$ AFM images, confirming that the presence of indium surfactant

leads to the enhanced 2D growth of N-polar GaN film. As observed in $2 \times 2 \ \mu m^2$ AFM images, Si doping did not change surface roughness, as shown in Fig. 6.5(f).

In addition to the improved surface morphology of N-polar GaN films by indium surfactant, Figure 6.5(e) and (f) do not show any V-defect with indium and Si doping, as predicted by theoretical first-principle calculations. Thus, this result supports that stress relaxation mechanisms such as V-defect did not play a role, as evidenced in the stress evolution of N-polar GaN films monitored by MOSS [Fig. 6.3]. Also, V-defect free N-polar GaN films grown with indium and Si doping implies that high indium composition InGaN films can be grown without V-defects along the N-polar growth direction unlike Ga-polar GaN films. As a result, without using expensive high quality bulk GaN substrates, heteroepitaxy of N-polar GaN films on lattice-mismatched substrates can potentially provide the base material for V-defect free InGaN films.

6.2.4 Crystallinity of N-polar GaN Films

X-ray rocking curve measurements were employed to probe the mosaicity, i.e., tilt and twist of N-polar GaN epilayers. As described in section 4.2.4, TD density can be estimated from FWHMs of $(000\overline{2})$ and $(10\overline{1}0)$ planes. For simplification, FWHM of $(30\overline{32})$ was used here as a figure of merit for $(10\overline{1}0)$ since FWHM of $(10\overline{1}0)$ can be estimated by FWHM of $(30\overline{32})$ times 1.14.¹⁴⁹ Then, TD density was calculated by Eq. 4.4 and 4.5. The measured FWHMs and estimated TD density of N-polar GaN films are summarized in Table 6.1. The reference GaN film has a total TD density of 5.4×10^9 cm⁻² which is higher than the 3.8×10^9 cm⁻² of Ga-polar GaN film grown under identical growth conditions. In the reflectivity data [Fig. 6.4], the N-polar GaN film growth began with a quasi-2D growth mode, which indicates that the density of each GaN nuclei is high at the nucleation stage. Thus, higher TD density in N-polar GaN film seems to be correlated with the characteristic of N-polar GaN modes.

Table 6.1. The measured FWHMs of $(000\overline{2})$ and $(30\overline{32})$ planes, and TD density in N-polar GaN films. FWHM of $(10\overline{1}0)$ was estimated from $(30\overline{32})$.

Sample	FWHM $(000\overline{2})$ $(arcsec)$	FWHM $(30\overline{32})$ $(arcsec)$	FWHM $(10\overline{1}0)$ (arcsec)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)
Reference	494	845	963	4.9×10^{8}	4.9×10^{9}	5.4×10^{9}
TMIn = 4.5 $\mu mol/min$	532	1097	1251	5.7×10^{8}	8.3×10^{9}	8.9×10^{9}
$TMIn = 4.5$ $\mu mol/min$ $+$ $SiH_4 = 9.2$ $nmol/min$	522	1032	1177	5.5×10^{8}	7.3 × 10 ⁹	7.9 × 10 ⁹

When indium surfactant is used, the total TD density increases to 8.9×10^9 cm⁻² due to the increase of edge type TD density. As Si doping is simultaneously included with indium, the total TD density is slightly decreased to 7.9×10^9 cm⁻². The origin for the increase of twist by indium is not clear. Huang *et al.* observed a similar tendency.¹⁶³ Their GaN films grown on sapphire with indium at 750 °C by MBE showed that total TD density increases as the amount of indium increases while screw type TD density

decreases. They speculated that the degradation of crystal quality might be because of the incorporation of indium which may increase strain due to larger size of indium atom. Due to the low growth temperature of 750 °C, indium incorporation may be possible in their growth conditions since they also observed stress change caused by indium surfactant. However, the growth temperature is 950 °C here in MOCVD, which does not allow for indium incorporation due to the high vapor pressure of indium, suggesting that indium doping does not occur. Thus, a possible reason might be correlated to the initial nucleation of GaN films modified by indium, which may result in smaller GaN nuclei that can increase TD density. However, the origin of degradation in crystal quality by indium needs to be further studied.

6.2.5 SIMS Analysis

Due to the polar nature of wurtzite GaN along the c-axis, as shown in Fig. 6.1, N-face GaN has been known to be highly reactive, giving rise to different unintentional auto-doping behaviors of oxygen and carbon in comparison to Ga-polar GaN films.^{160,164-166} Sumiya *et al.* reported that N-polar GaN films grown on sapphire at 1040 °C by MOCVD showed 170 times more O and 17 times more C, as compared to Ga-polar GaN films.¹⁶⁴ Tuomisto *et al.* found that O and C impurity levels were 2×10^{19} cm⁻³ and 2×10^{17} cm⁻³ in N-polar GaN epilayers grown by hydride vapor phase epitaxy, which were 50 times and 4 times higher than those of Ga-polar GaN films, respectively.¹⁶⁵ Fichtenbaum *et al.* observed that unintentional O doping concentration was about 3 ×

10¹⁸ cm⁻³ in their N-polar GaN epilayers grown on on-axis and vicinal sapphire substrates by MOCVD, which was two orders higher than that of Ga-polar GaN films.¹⁶⁰ Therefore, polarity of GaN films has a strong impact on the unintentional O and C incorporations.

In order to characterize impurity levels, possible indium incorporation, and incorporation rates of impurities altered by indium in 1.9 µm thick N-polar GaN films here, SIMS analysis was performed on two samples, the reference and N-polar GaN grown with TMIn = $4.5 \,\mu$ mol/min, at Evans Analytical Group, Inc., as plotted in Fig. 6.7. The most significant feature is O impurity levels in both samples, which are 1.2×10^{19} cm⁻³ and 1.3×10^{19} cm⁻³, respectively. Typically O impurity level is less than about 1.0 $\times 10^{17}$ cm⁻³ in Ga-polar GaN films grown in our MOCVD system. Thus, at least 100 times more oxygen seems to be unintentionally doped into N-polar GaN films, as compared to Ga-polar GaN films. Besides the experimental results observed here and reported in the literature, theoretical investigation utilizing first-principle calculations supports the high incorporation rate of O on the highly reactive N-polar GaN surface.¹⁶⁷ This study found that the oxygen adsorption energy on N-face GaN is more exothermic, which suggests that oxygen incorporation on (0001) of GaN is expected to be much higher than that on (0001) of GaN. Basically, both Ga- and N-polar GaN faces are highly active to the adsorption of oxygen for low coverage of oxygen, i.e., when 0.25 monolayer of oxygen exists. However, as Ga adatoms are added on GaN surface, which is the case of GaN growths in experiments, and as oxygen coverage increases, Ga-polar GaN films become less active towards oxygen whereas the oxygen adsorption energy of N-polar GaN film remains unchanged, leading to markedly different O auto-doping levels corresponding to



Figure 6.7. SIMS results on (a) the reference N-polar GaN and (b) N-polar GaN grown with indium surfactant (TMIn = $4.5 \mu mol/min$). The indium concentration was below the sensitivity of SIMS equipment in both samples.

GaN polarity. Qualitatively, the difference in O incorporation on (0001) and $(000\overline{1})$ planes of GaN can be explained by surface atomic configurations, as illustrated in Fig. 6.8.¹⁶⁷ When one oxygen monolayer covers both surfaces, the energetically most preferred site is the on-top position for Ga-polar GaN and fcc site for N-polar GaN. The bond distance between Ga and O is 1.79 Å in Ga-polar GaN, but the O atoms sit 0.53 Å above the Ga layer in N-polar GaN which provides screening between negatively charged O adatoms. This configuration makes O adsorption stable on the N-face GaN. On the other hand, electrostatic interaction between O adatoms in Ga-polar GaN is repulsive. Therefore, as explained theoretically and as evidenced experimentally in other studies, N-polar GaN films in the current study are believed to show high O impurity levels due to reactive N-polar GaN surface, converting the GaN film to n-type with an electron concentration of about 10^{19} cm⁻³.

Indium content in both samples is below the sensitivity limit of SIMS, as shown in Fig. 6.7. Thus, indium composition is less than 0.01 % in both samples, confirming that indium acted only as a surfactant without isoelectronic doping although the source input ratio of TMIn to TMGa was 0.49. The effect of indium surfactant on unintentional



Figure 6.8. Side view of atomic configurations on (a) Ga-polar GaN and (b) N-polar GaN in hexgagonal wurtzite structure. Both surfaces are covered by one monolayer of oxygen. [Ref. T. K. Zywietz, J. Neugebauer, and M. Scheffler, Appl. Phys. Lett. **74**, 1695 (1999).]

O incorporation appears to be negligible. However, indium seems to reduce C incorporation and enhance Si incorporation in N-polar GaN films, as seen in Fig. 6.7. The reference N-polar GaN shows C concentration of 1.8×10^{18} cm⁻³, but it decreases to 1.1×10^{18} cm⁻³. Si concentration increases from 3.7×10^{16} cm⁻³ to 9.5×10^{16} cm⁻³ when indium was used during N-polar GaN growth. As explained in section 4.4.4, carbon can quench NBE emission in PL and Si can enhance NBE emission as well as YL. Therefore, N-polar GaN film grown with indium surfactant is expected to show improved NBE transitions of carriers in the PL spectra because of reduced carbon and increased Si concentrations, which will be studied in the next section.

6.2.6 Optical Properties of N-polar GaN Films

PL measurements were employed to investigate the optical properties of N-polar GaN epilayers modified by indium surfactant and Si doping, using forth harmonic generated 266 nm from 1064 nm in Nd:YAG laser at room temperature. Figure 6.9 presents PL spectra of N-polar GaN films. The reference GaN film shows NBE emission around 364 nm and YL band around 510 ~ 560 nm with superimposed Fabry-Perot interference corresponding to the film thickness. In section 4.4.4, the reference Ga-polar GaN film grown under the identical growth environment showed zero NBE emission presumably due to carbon impurities and low unintentional doping of Si or O. In contrast, the reference N-polar GaN film here shows much stronger efficiency of NBE emission. This seems to be attributed to high O concentrations that result in a high density of



Figure 6.9. PL spectra of 1.9 μ m thick N-polar GaN films grown on vicinal C-face SiC substrates at 950 °C by MOCVD. Indium surfactant improves NBE emission around 365 nm and suppresses defect-related YL around 500 ~ 570 nm. Si doping further enhances NBE emission.

electron carriers, which contribute to radiative recombination of excitons, because O is another n-type dopant like Si in GaN. Also, strong YL intensity suggests that Ga vacancies were formed by O-related Ga vacancy complexes, giving rise to the defectassisted recombination of carriers. O prefers occupying N site, behaving as a donor. This can lead to formation of stable $V_{Ga} - O_N$ complexes, which act as double deep acceptors, because a positively charged donor (O_N) can induce formation of Ga vacancies (V_{Ga}), and they attract each other. Therefore, YL in the reference N-polar GaN seems to stem from a high density of $V_{Ga} - O_N$ complexes due to high O concentration of 1.2×10^{19} cm⁻³, as analyzed by SIMS in the previous section.

By introducing indium surfactant (TMIn = $4.5 \mu mol/min$) during GaN growth, the intensity of NBE emission is improved by a factor of 4 and YL intensity decreases by a

factor of 3.8 with respect to the reference N-polar GaN. The ratio of NBE emission to YL (at about 525 nm) is about 0.5 and 7.8 for the reference and N-polar GaN grown with indium, respectively, indicating that indium leads to marked improvement of optical properties of N-polar GaN epilayers. Since the TD density, estimated from x-ray rocking curves, was increased by indium, the enhancement of optical properties seems to be greatly affected by point defects and impurities. From the SIMS results, C concentration was found to be reduced while unintentional Si incorporation was enhanced by indium surfactant. Therefore, the improvement of NBE emission appears to be due to a reduction of C-related complexes and increase of electron concentration arising from Si doping when indium was used during GaN growth. In addition, reduction of YL band intensity is observed. This may correspond to a reduction of native Ga vacancies rather than V_{Ga} – O_N complexes because O concentration remained similar in the presence of indium. Another possibility might be deep donors induced by indium surfactant. In section 4.4.4, the BL band, associated with deep donors, was observed in the Ga-polar GaN film grown with indium. Similarly, indium surfactant here may induce deep donors which can compensate V_{Ga} -related deep acceptors, thus reducing YL intensity. The improvement of NBE emission and reduction of YL band demonstrate that the use of indium surfactant is an effective way to improve the optical properties of N-polar GaN films, although indium can degrade the structural quality by increasing edge type TD density.

In addition to indium surfactant (TMIn = $4.5 \mu mol/min$), intentional Si doping (SiH₄ = 9.2 nmol/min) further improves NBE emission by a factor of 1.6 while YL intensity remains unchanged, as seen in Fig. 6.9. The ratio of NBE emission to YL band is 13.0. As explained, assuming the concentration of non-radiative recombination centers

is independent of doping, the increase of electron concentration enhances the efficiency of carrier recombination, thus improving the efficiency of NBE emission. In section 4.4.4, intentional Si doping amplified both NBE emission and YL of Ga-polar GaN film at the same time. On the other hand, only NBE emission is affected by Si doping here in the N-polar GaN film, which is not clear yet. Si also occupies Ga site, providing electrons and leading to the formation of V_{Ga} – Si_{Ga} complexes, which may enhance YL efficiency. The most probable explanation may be that the formation of V_{Ga} – Si_{Ga} complexes is not driven strongly when N-polar GaN film is heavily doped with O ([O] = 1.3×10^{19} cm⁻³). However, further study is necessary on this point.

6.2.7 TEM Analysis

Cross-sectional TEM analysis was conducted by Dr. Xiaojun Weng to examine microstructure of the N-polar GaN grown with indium, as shown in Fig. 6.10(a). This bright-field TEM image was collected along the $[1\overline{1}00]$ zone axis under multi-beam diffraction condition. Besides the inclined TDs, a high density of stacking mismatch boundaries, a special type of double-positioning boundaries often observed in nitride films grown on miscut SiC substrates, are observed. These boundaries are all inclined by approximately 4 degree with respect to surface normal, which appears to be correlated to the substrate misorientation of 3.57 degree towards $<11\overline{2}0>$. Figure 6.10(b) shows a high-resolution TEM image collected from such a boundary. The stacking mismatch at the boundary seems to be nearly parallel to $[000\overline{2}]$. This observation suggests that the



Figure 6.10. (a) Cross-sectional bright-field TEM image of N-polar GaN film grown with indium surfactant, collected along the $[1\overline{1}00]$ zone axis under multi-beam diffraction condition. A high density of stacking mismatch boundaries appears to be inclined by approximately 4 degree from surface normal. (b) High-resolution TEM image collected from a stacking mismatch boundary. Stacking mismatch at the boundary seems to be nearly parallel to $[000\overline{2}]$. (c) Experimental and JEMS-simulated CBED patterns confirm the N-polarity of GaN film grown on vicinal C-face SiC substrate with indium.

origin of stacking mismatch boundaries comes from the exposed step edges associated with the substrate misorientation.¹⁶⁸ The polarity of GaN film grown with indium surfactant was determined to be N-polar by comparing experimental convergent beam electron diffraction (CBED) patterns with JEMS-simulated CBED patterns, as shown in Fig. 6.10(c). Thus, this result confirms that GaN films grown on the vicinal C-face SiC are N-polar, as expected from the polarity of SiC substrate.

6.2.8 Discussion

The most important observation in the current series of experiments is that Vdefects were not favored in the N-polar GaN films grown in the presence of indium surfactant and Si dopant despite using foreign substrates. Under the same growth environment, indium and Si doping strongly drove V-defects in Ga-polar GaN films grown on Si-face SiC and Si(111), as evidenced in chapter 4 and 5. Therefore, without using expensive high quality bulk GaN substrates, V-defect free N-polar InGaN films even with high indium composition are expected to be achieved on N-polar GaN films. This observation will lead to great interest towards fabrication of green LEDs and LDs utilizing N-polar In GaN/GaN heterostructures without V-defects.

Indium surfactant dramatically improved surface morphology and optical properties of N-polar GaN films grown on vicinal C-face SiC substrates at 950 °C. However, the crystal quality of N-polar GaN film was found to be degraded because edge type TD density was raised by using indium. Although N-polar GaN film grown with indium surfactant showed smooth surface morphology, further study on the structural properties of N-polar GaN films is essential to improve crystal quality by reducing tilt and twist. Additionally, the growth of N-polar GaN films by MOCVD has not been extensively investigated. Thus, as described in the next section, various growth conditions for N-polar GaN films were studied.

6.3 Study of N-polar GaN Growth

For the future N-polar InGaN growths, 1.9 μ m thick N-polar GaN film grown with indium in section 6.2 meets device quality in terms of surface morphology since the RMS surface roughness was 0.5 nm in 2 × 2 μ m² area, and 3.5 nm in 20 × 20 μ m² area. However, TD density increased by introducing indium surfactant during GaN growth. Thus, to improve crystal quality while keep surface morphology smooth, fundamental studies of N-polar GaN growth with varying growth conditions such as growth temperature and buffer layer thickness are essential to realize high quality smooth N-polar films grown on vicinal C-face SiC substrates. Therefore, the effect of growth temperature on the surface morphology and structural properties of 1.1 μ m thick N-polar GaN films were conducted first as described in this section. A two-step process, using low temperature GaN (~ 140 nm) followed by high temperature GaN (~ 960 nm) growth, will be exploited to achieve low TD density with smooth surface morphology. Lastly, the effect of AlN buffer layer thickness on N-polar GaN films will be investigated.

6.3.1 Experimental Details

N-polar GaN epilayers were grown by MOCVD on the same C-face 6H-SiC substrates misoriented towards $<11\overline{2}0 >$ by 3.57 degree from the c-axis used in section 6.2. Source precursors were TMGa, TMAl, and NH₃ for Ga, Al, and N, respectively. H₂

was used to carry these source precursors into the reactor where pressure was maintained at 100 Torr. C-face 6H-SiC wafers were diced into 1×1 cm² pieces and cleaned through a series of sonication in acetone, isopropanol, and DI water, followed by a dip in 10% HF solution and rinse in DI water, before they were loaded onto the rotating susceptor inductively heated by a remote RF generator. AlN buffer layers (~ 90 nm) were initially grown on the SiC substrate at 1100 °C. Molar flow rates of TMAl and NH₃ were 10.3 µmol/min and 89.3 mmol/min (V/III ratio = 8670). In order to observe the effect of growth temperature, 1.1 µm thick N-polar GaN epilayers were grown on the AlN buffer layer as the growth temperature was increased as 950, 1000, 1050, and 1100 °C. TMGa and NH₃ were controlled at 9.2 µmol/min and 35.7 mmol/min (V/III ratio = 3880), respectively. For the two-step process of N-polar GaN films, 140 nm thick N-polar GaN film was initially grown at 950 °C on AlN buffer layer (~ 90 nm at 1100 °C). Then, 960 nm N-polar GaN films were grown at higher growth temperatures from 1000 °C to 1100 °C. For the effect of AlN buffer layer thickness, 1.1 µm thick N-polar GaN film was grown at 1100 °C on a 30 nm AlN buffer layer. Since surface morphology and crystal quality are the main focuses in this section, only AFM and HRXRD rocking curves were employed to investigate surface morphology and evaluate mosaic structures of the Npolar GaN films with changing growth conditions.

6.3.2 Effect of Growth Temperatures

1.1 µm thick N-polar GaN films were grown as a function of growth temperature by MOCVD in order to observe the effect of growth temperature on the surface morphology and structural properties of GaN films. Figure 6.11 presents AFM images of N-polar GaN films over $2 \times 2 \ \mu m^2$ and $20 \times 20 \ \mu m^2$ areas. RMS surface roughness was estimated from each AFM images, as plotted in Fig. 6.12. In general, Ga-polar GaN films usually show that surface morphology becomes smoother by increasing growth temperature due to the enhanced surface migration of Ga and N adatoms. However, in Npolar GaN films here, RMS surface roughness in $2 \times 2 \mu m^2$ AFM images from 6.11(a) to (d) changes as 2.6 nm, 1.1 nm, 1.5 nm, and 1.7 nm when the growth temperature increases from 950 °C to 1100 °C by every 50 °C. The minimum roughness is observed at 1000 °C, but the surface becomes rougher as the temperature increases from 1000 °C. This result seems to originate from the nano-sized triangular hillocks pointing towards the misorientation direction of C-face SiC substrates, as seen in Fig. 6.11(c) and (d). In $20 \times 20 \ \mu\text{m}^2$ AFM images from Fig. 6.11(e) and (f), larger triangular hillocks in the Npolar GaN grown at 950 °C disappear when the growth temperature increases to 1000 °C. However, as the temperature keeps increasing, the surface becomes rougher due to macrosteps which run roughly along $<10\overline{10}>$ direction perpendicular to the misorientation of the substrate, as seen in Fig. 6.11(g) and (h). RMS roughness from $20 \times$ $20 \ \mu\text{m}^2$ AFM images changes as 16.3 nm, 5.3 nm, 12.6 nm, and 16.1 nm as the growth temperature increases as 950 °C, 1000 °C, 1050 °C, and 1100 °C, as shown in Fig. 6.12, indicating that the N-polar GaN grown at 1000 °C has minimum surface roughness at the



Figure 6.11. AFM images of N-polar GaN epilayers grown on vicinal C-face SiC substrates as a function of growth temperature. (a), (b), (c), and (d) on the first column indicate AFM images over $2 \times 2 \ \mu m^2$ area, and (e), (f), (g), and (h) on the second column show images over $20 \times 20 \ \mu m^2$ area. The arrow indicates the misorientation direction of substrate towards $<11\overline{2}0>$ from the c-axis.



Figure 6.12. RMS surface roughness of 1.1 μ m thick N-polar GaN films as a function of growth temperature, estimated from AFM images over 2 × 2 μ m² and 20 × 20 μ m² areas.

macroscopic scale. The origin of surface undulations, causing macrosteps at higher growth temperatures than 1000 °C, is not clear, but this trend is consistent with the study reported by Brown *et al.*⁴⁷ They observed that the surface roughness of N-polar GaN films grown on C-face SiC substrates misoriented to $<10\overline{10} >$ by 4 degree increased as the growth temperature was raised up to 1130 °C. Also, they noticed that macrosteps run parallel to $<11\overline{20} >$ which was perpendicular to the misorientation direction of the substrate. Consequently, higher growth temperatures than 1000 °C used here are deleterious to surface morphology of N-polar GaN films, and the N-polar GaN film grown at 1000 °C shows the best result in terms of surface morphology.

X-ray rocking curve measurements (ω - scans) were performed to examine the crystallinity of N-polar GaN films as a function of growth temperature, as presented in

Fig. 6.13. TD densities for all samples, estimated from x-ray rocking curves, are summarized in Table 6.2. As explained, FWHM of (0002) plane in GaN is related to tilt, i.e., screw and mixed TD density, whereas FWHM of ($30\overline{3}2$), which can be a figure of merit for twist, is relevant to all type TD density including edge type TD. Since edge type TD is dominant in GaN films, broadening of ($30\overline{3}2$) peak width in rocking curve usually correlates to increase of edge and mixed type TD density. Thus, for the N-polar GaN films, x-ray rocking curves of ($000\overline{2}$) and ($30\overline{3}\overline{2}$) planes were measured to probe tilt and twist, respectively, as seen in Fig. 6.13(a). When the growth temperature increases from 950 °C, FWHM of ($000\overline{2}$) does not change, indicating that screw type TD density is insensitive to the growth temperature in the N-polar GaN films. For comparison, ω - scans on Ga-polar GaN films grown under the identical growth conditions were done, as



Figure 6.13. FWHMs of (a) (0002) and (3032) planes in x-ray rocking curves (ω - scans) of 1.1 µm thick N-polar GaN films, and (b) FWHMs of (0002) and (3032) planes in ω - scans of 1.0 µm thick Ga-polar GaN films as a function of growth temperature.

plotted in Fig. 6.13(b). Unlike N-polar GaN films, the FWHM of (0002) in Ga-polar GaN films gradually decreases with increasing growth temperature. Therefore, in the N-polar GaN films, tilt seems not to be affected by growth temperature, which means that other process variables such as substrate misorientation and AlN buffer layer thickness may be dominant factors in the generation of screw type TDs.

Table 6.2. FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1 µm thick N-polar GaN films and on (0002) and $(30\overline{32})$ planes in 1.0 µm thick Ga-polar GaN films as a function of growth temperature. FWHM of $(10\overline{10})$ was estimated from FWHM of $(30\overline{32})$ and $(30\overline{32})$ planes. TD density was calculated by Eq. 4.4 and 4.5.

N-polar GaN films	$(000\overline{2})$ FWHM (arcsec)	$(30\overline{32})$ FWHM (arcsec)	(1010) FWHM (arcsec)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)
950 °C	512	790	901	5.3×10^{8}	4.3×10^{9}	4.8×10^{9}
1000 °C	503	898	1024	5.1×10^{8}	5.6×10^{9}	6.1×10^{9}
1050 °C	487	704	803	4.8×10^{8}	3.4×10^{9}	3.9×10^{9}
1100 °C	505	766	873	5.1×10^{8}	4.0×10^{9}	4.6×10^{9}
Ga-polar GaN films	(0002) FWHM (arcsec)	(3032) FWHM (arcsec)	(1010) FWHM (arcsec)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)
Ga-polar GaN films 950 °C	(0002) FWHM (arcsec) 270	(3032) FWHM (arcsec) 989	(1010) FWHM (arcsec) 1128	Screw TD density (cm ⁻²) 1.5×10^8	Edge TD density (cm ⁻²) 6.7×10^9	Total TD density (cm ⁻²) 6.9×10^9
Ga-polar GaN films 950 °C 1000 °C	(0002) FWHM (arcsec) 270 259	(3032) FWHM (arcsec) 989 619	(1010) FWHM (arcsec) 1128 706	Screw TD density (cm ⁻²) 1.5×10^8 1.3×10^8	Edge TD density (cm ⁻²) 6.7×10^9 2.6×10^9	Total TD density (cm ⁻²) 6.9×10^9 2.8×10^9
Ga-polar GaN films 950 °C 1000 °C 1050 °C	(0002) FWHM (arcsec) 270 259 212	(3032) FWHM (arcsec) 989 619 382	(1010) FWHM (arcsec) 1128 706 436	Screw TD density (cm ⁻²) 1.5×10^{8} 1.3×10^{8} 9.0×10^{7}	Edge TD density (cm ⁻²) 6.7×10^9 2.6×10^9 1.0×10^9	Total TD density (cm ⁻²) 6.9×10^9 2.8×10^9 1.1×10^9

Growth temperature has a significant impact on edge type TD density in Ga-polar GaN epilayers, as seen in the FWHMs of $(30\overline{3}2)$ of Ga-polar GaN films [Fig. 6.13(b)]. As the growth temperature increases from 950 °C up to 1050 °C, twist dramatically decreases, and then slightly increases at 1100 °C. In contrast, FWHMs of $(30\overline{32})$ in N-polar GaN films [Fig. 6.13(a)] show no clear tendency as a function of growth

temperature. In contrast to Ga-polar GaN films, the N-polar GaN film grown at 1000 °C shows higher twist than the film grown at 950 °C, which is not well understood. Since N-polar GaN film grown at 1000 °C showed the minimum surface roughness in the given series of growths, reduction of triangular hillocks appears to be correlated to an increase of twist in the N-polar GaN film grown at 1000 °C. A similar result was observed in section 6.2. When indium surfactant reduced the triangular hillock surface defects and lead to the smooth surface morphology of N-polar GaN film grown at 950 °C, edge type TD density increased. However, the correlation of twist with triangular hillocks needs to be studied furthermore.

Although N-polar GaN films show higher screw and edge TD density with respect to Ga-polar GaN, both Ga- and N-polar GaN films grown at 1050 °C provides the lowest total TD density, and edge type TD density slightly increases beyond 1050 °C in common. Therefore, to achieve high quality of N-polar GaN film, 1050 °C seems to be the optimum growth temperature. However, in AFM measurements [Fig. 6.11 and 6.12], the N-polar GaN film at 1050 °C showed a rough surface due to macrosteps running parallel to $<10\overline{10}>$, resulting in RMS roughness of 12.6 nm in $20 \times 20 \ \mu\text{m}^2$ AFM image. Brown *et al.* reported that a two-step process using 250 nm thick LT GaN layer grown at 975 °C improved crystal quality and kept a smooth surface of their N-polar GaN films grown at 1080 °C. Thus, from the current results here, a similar approach can be made utilizing low and high growth temperatures to achieve high crystallinity with smooth surface morphology, which is investigated in the next section.

6.3.3 Two-step Process

In the previous section 6.3.2, the lowest surface roughness was obtained at the growth temperature of 1000 °C, but the film showed the highest TD density. For crystal quality, 1050 °C was found to be optimum although surface roughness was as high as 12.6 nm. Thus, in this section, a two-step process for N-polar GaN films, utilizing low temperature (LT) GaN nucleation layer followed by high temperature (HT) GaN, is investigated. For smooth surface morphology, initial LT N-polar GaN layer (~ 140 nm) was grown first at 950 °C, and then HT N-polar GaN growths (~ 960 nm) were done between 1000 °C and 1100 °C for reduction of TD density. Since N-polar GaN film grown at 1000 °C followed by 960 nm GaN grown at 1050 °C, was also conducted. However, surface roughness was higher than the case of LT GaN grown at 950 °C. Thus, 950 °C was selected for the initial LT N-polar GaN growth.

Figure 6.14 shows AFM images of two-step processed 1.1 μ m thick N-polar GaN films with increasing growth temperature of HT GaN films. The corresponding RMS surface roughness is shown in Fig. 6.15. In all samples, initial 140 nm thick LT GaN layer was grown at 950 °C. Surface morphology of HT N-polar GaN grown at 1000 °C in Fig. 6.14(a) and (d) shows combined characteristics with two samples grown at 950 °C and 1000 °C in previous section, i.e., reduced triangular features and intermediate RMS roughness values in both 2 × 2 μ m² and 20 × 20 μ m² AFM images. The most significant improvement in surface morphology by the two-step process was observed in the N-polar GaN films grown at 1050 °C and 1100 °C. RMS roughness of the two-step processed N-

polar GaN at 1050 °C is 4.5 nm over $20 \times 20 \ \mu\text{m}^2$ area, which was reduced from 12.6 nm in the case of the one step process. Similarly, the roughness of 16.1 nm for the GaN grown at 1100 °C was decreased to 4.9 nm by the two-step process. The formation of



Figure 6.14. AFM images of two-step processed 1.1 μ m thick N-polar GaN epilayers grown on vicinal C-face SiC substrates as a function of growth temperature of HT GaN films. In all samples, initial 140 nm thick LT GaN layers were grown at 950 °C. (a), (b), and (c) indicate AFM images over 2 × 2 μ m² area, and (d), (e), and (f) show images over 20 × 20 μ m² area. The white arrow indicates the misorientation direction of substrate towards <1120 > from the c-axis.



Figure 6.15. RMS surface roughness of 1.1 μ m thick N-polar GaN films grown by two-step process as a function of growth temperature of HT GaN films, estimated from AFM images over 2 × 2 μ m² and 20 × 20 μ m² areas.

macrosteps, which caused a rough surface in N-polar GaN films grown at 1050 °C and 1100 °C as reported in section 6.3.2, seem to be hindered by inserting an initial LT GaN layer, as seen in Fig. 6.14(e) and (f), thus reducing surface roughness dramatically. Since the N-polar GaN grown at 1100 °C with LT GaN layer shows the minimum value of 0.7 nm in $2 \times 2 \mu m^2$ area with reduced small-sized triangular hillocks, the combination of LT GaN at 950 °C and HT GaN at 1100 °C appears to be optimum in the two-step process for the surface morphology.

In order to examine the crystallinity of N-polar GaN films grown by the two-step process, x-ray rocking curve measurements were performed on the $(000\overline{2})$ and $(30\overline{32})$ planes, and the FWHMs of these planes are shown in Fig. 6.16. The two-step process appears to reduce screw TD density, as compared to the one step process, since the FWHMs of $(000\overline{2})$ in all samples are approximately ~ 437 arcsec which is reduced from

~ 512 arcsec observed in the one step process. FWHMs of (0002) in all samples do not change significantly with HT GaN growth temperature, which is consistent with the Npolar GaN films whose screw type TD density was insensitive to growth temperatures in section 6.3.2. In the case of $(30\overline{32}) \ \omega$ - scans, N-polar GaN grown at 1000 °C by the twostep process shows the lowest edge TD density. However, this film exhibited the highest surface roughness of 10.0 nm in AFM measurements. In addition, the N-polar GaN grown at HT GaN temperature of 1050 °C shows the highest edge TD density, as seen in Fig. 6.16. As a result, the N-polar GaN grown at 1100 °C by two-step process seems to be optimum in the given growth conditions if FWHM of $(30\overline{32})$ and surface roughness are taken into account at the same time. TD density of all samples utilizing the two-step process is summarized in Table 6.3.

Table **6.3.** FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1 µm thick N-polar GaN films grown by two-step process as a function of HT GaN growth temperature. 140 nm thick LT GaN was grown first at 950 °C prior to HT GaN growths. FWHM of $(10\overline{10})$ was estimated from FWHM of $(30\overline{32})$ plane. TD density was calculated by Eq. 4.4 and 4.5.

HT GaN growth temperature	$(000\overline{2})$ FWHM (arcsec)	$(30\overline{3}\overline{2})$ FWHM (arcsec)	(1010) FWHM (arcsec)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)
1000 °C	413	668	762	3.4×10^{8}	3.1×10^{9}	3.4×10^{9}
1050 °C	437	839	957	3.8×10^{8}	4.9×10^{9}	5.2×10^{9}
1100 °C	421	740	844	3.6×10^{8}	3.8×10^{9}	4.1×10^{9}



Figure 6.16. FWHMs of $(000\overline{2})$ and $(30\overline{32})$ planes in x-ray rocking curves (ω - scans) in 1.1 µm thick N-polar GaN films grown by two-step process as a function of HT GaN growth temperature.

6.3.4 Effect of N-polar AlN Buffer Layer Thickness

In the current thesis research, an AlN buffer layer of ~ 90 nm has been used for all GaN films regardless of polarity and growth conditions for the purpose of comparison. In order to observe the effect of AlN buffer layer thickness on N-polar GaN films, an N-polar AlN buffer layer of ~ 30 nm was grown at 1100 °C on vicinal C-face SiC substrate under the identical growth conditions used for 90 nm AlN film.

Figure 6.17 shows AFM image over $2 \times 2 \ \mu m^2$ area in 30 nm and 90 nm AlN buffer layers. 30 nm thick AlN film shows high density of nano-sized hillocks, suggesting that a high density of N-polar AlN nuclei forms on the SiC substrate. The size of the hillocks becomes larger in 90 nm thick AlN by coalescence between nano-sized AlN nuclei, resulting in a rough surface although hillock density becomes lower. RMS



Figure 6.17. AFM images of (a) 30 nm and (b) 90 nm thick N-polar AlN buffer layers grown on vicinal C-face SiC substrates over $2 \times 2 \ \mu m^2$ area. The RMS surface roughness was 1.0 nm and 3.6 nm for 30 nm and 90 nm AlN films, respectively.

surface roughness increases from 1.0 nm to 3.6 nm, i.e., by a factor of 3.6, as the AlN grows from 30 nm to 90 nm.

1.1 µm thick N-polar GaN film was then grown at 1100 °C on 30 nm AlN film to compare with the N-polar GaN film grown on 90 nm AlN buffer layer in section 6.3.2. Figure 6.18 presents AFM images of N-polar GaN grown on 30 nm AlN buffer film over $2 \times 2 \mu m^2$ and $20 \times 20 \mu m^2$ areas. The small triangular hillocks, which were observed in the N-polar GaN grown on 90 nm AlN in Fig. 6.11(d), seem to be reduced by using a thinner AlN layer, as seen in $2 \times 2 \mu m^2$ AFM image [Fig. 6.18(a)]. RMS surface roughness is 1.5 nm, which is similar with 1.7 nm in N-polar GaN grown on 90 nm AlN buffer layer. However, RMS surface roughness of 19.4 nm in $20 \times 20 \mu m^2$ AFM image, as seen in Fig. 6.18(b), implies that the use of a thinner AlN buffer layer developed rougher macrosteps since N-polar GaN grown on 90 nm AlN buffer layers showed 16.1 nm in Fig. 6.11(h). Thus, although a 30 nm AlN buffer layer exhibited a much smaller surface roughness than 90 nm AlN by a factor of 3.6, N-polar GaN film grown on a smoother 30 nm AlN film indicates a rougher surface at the macroscopic scale.

X-ray rocking curve measurements were performed to characterize the crystallinity of N-polar GaN film grown on 30 nm thick AlN. FWHMs of $(000\overline{2})$ and $(30\overline{32})$ planes and estimated TD density are summarized in Table. 6.4. FWHM of $(000\overline{2})$ in the N-polar GaN grown on 30 nm AlN shows 469 arcsec, which indicates slightly lower tilt, as compared to N-polar GaN grown on 90 nm AlN. FWHM of $(30\overline{32})$ is 612 arcsec, which is the lowest value among all N-polar GaN films reported in this chapter. Therefore, the use of a thinner AlN buffer layer appears to reduce edge type TD density substantially. This result strongly suggests that larger size hillocks of 90 nm thick AlN in Fig. 6.17(b) increases the twist of N-polar GaN film whereas tilt is not significantly degraded by these hillocks. Thus, although 30 nm AlN buffer layer



Figure 6.18. AFM images of 1.1 μ m N-polar GaN film grown at 1100 °C on 30 nm thick AlN buffer layer over (a) 2 × 2 μ m² area and (b) 20 × 20 μ m² area. The white arrow indicates the misorientation direction of vicinal C-face SiC substrate.

increased the surface roughness of the N-polar GaN film, a combination of thinner AlN buffer layer with two-step process may result in improved surface smoothness as well as enhanced crystal quality. This will be studied in the future.

Table 6.4. FWHMs of x-ray rocking curves on $(000\overline{2})$ and $(30\overline{32})$ planes in 1.1 µm thick N-polar GaN films grown at 1100 °C on 30 nm and 90 nm thick AlN buffer layers. FWHM of $(10\overline{10})$ was estimated from FWHM of $(30\overline{32})$. TD density was calculated by Eq. 4.4 and 4.5.

Samples	$(000\overline{2})$ FWHM (arcsec)	$(30\overline{32})$ FWHM (arcsec)	$(10\overline{1}0)$ FWHM (arcsec)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)
N-polar GaN on 30 nm AlN	469	612	698	4.4×10^{8}	2.6×10^{9}	3.0×10^{9}
N-polar GaN on 90 nm AlN	505	766	873	5.1×10^{8}	4.0×10^{9}	4.6×10^{9}

6.4 Conclusions

In chapter 4 and 5, indium surfactant and Si doping gave rise to V-defect formation in heteroepitaxial growth of GaN epilayers on foreign substrates such as SiC and Si(111) while the improved 2D growth was observed due to the kinetically enhanced surface diffusion of Ga and N adatoms at the same time. Without using high quality bulk GaN substrates, V-defect formation could not be hindered in heteroepitaxially grown Gapolar GaN films in the presence of indium and Si dopants. Thus, in this chapter, N-polar GaN films were grown at 950 °C on vicinal C-face SiC substrates miscut towards $<11\overline{20} >$ by 3.57 degree using indium surfactant (TMIn = 4.5 µmol/min) and intentional Si doping (SiH₄ = 9.2 nmol/min) since a theoretical study utilizing first-principle
calculations predicted that V-defects are not energetically favored along N-polar growth direction. AFM measurements on 1.9 µm thick N-polar GaN films revealed that V-defects did not form on the N-face GaN in the presence of indium surfactant and Si dopant despite using foreign SiC substrate. From this result, we may expect that V-defect free N-polar InGaN films with high indium composition can be grown on N-polar GaN films without using extremely expensive bulk GaN substrates. Therefore, stable green LDs with long lifetime, which has been challenging along the Ga-polar direction, may be realized utilizing N-polar InGaN/GaN heterostructures without V-defects.

Besides V-defect free N-polar GaN films, indium surfactant dramatically improved the surface morphology and optical properties of N-polar GaN films. The reference N-polar GaN film in the AFM images over $20 \times 20 \ \mu\text{m}^2$ area showed interlaced triangular hillocks associated with limited lateral growth rate of type B step edge along $<10\overline{10}>$, thus pointing towards $<11\overline{20}>$ where the C-face SiC substrate was misorientated. Due to these triangular features, the RMS surface roughness was as high as 18.1 nm over $20 \times 20 \ \mu\text{m}^2$ area. The triangular hillocks on the reference GaN disappeared in the presence of indium because the area between triangular hillocks was flattened by the enhanced step-flow growth along $<10\overline{10}>$ due to indium, thus markedly reducing surface roughness down to 3.5 nm and 0.5 nm in $20 \times 20 \ \mu\text{m}^2$ and $2 \times 2 \ \mu\text{m}^2$ areas, respectively. Additional Si doping combined with indium surfactant did not degrade the surface morphology of N-polar GaN films. X-ray rocking curve measurements showed that the TD density increased by using an indium surfactant. SIMS analysis revealed that N-polar GaN films were unintentionally doped with oxygen at the level of 1.2×10^{19} cm⁻³. This result originated from the atomic configuration of the highly reactive N-face GaN, which provides screening between negatively charged O atoms. Indium surfactant reduced C concentration from 1.8×10^{18} cm⁻³ to 1.1×10^{18} cm⁻³ while it increased the Si concentration from 3.7×10^{16} cm⁻³ to 9.5×10^{16} cm⁻³. In PL measurements, these impurities played an important role in amplifying NBE emission by a factor of 4 and decreasing Ga-vacancy related YL by a factor of 3.8. This demonstrates that the indium surfactant improved the optical properties of N-polar GaN films by reducing non-radiative recombination centers associated with carbon and increasing electron carriers that can contribute to radiative recombination of excitons in NBE emission.

Although the use of indium surfactant lead to a smooth surface morphology with enhanced optical properties in N-polar GaN films, indium increased the edge type TD density. For the future N-polar InGaN growths on GaN, further study of the structural properties of N-polar GaN films is highly desirable to improve crystal quality by reducing tilt and twist. Thus, the effect of growth temperature on the surface morphology and structural properties of 1.1 μ m thick N-polar GaN films were studied first. When the growth temperature was changed from 950 °C to 1100 °C, the N-polar GaN film grown at 1000 °C showed the lowest surface roughness of 1.1 nm and 5.3 nm in 2 × 2 μ m² and 20 × 20 μ m² AFM images whereas this GaN film exhibited the highest TD density of 6.1 × 10⁹ cm⁻² in a given series of N-polar GaN films. Since the N-polar GaN grown at 1050 °C showed the lowest TD density, a two-step process utilizing 140 nm thick initial LT GaN grown at 950 °C and 960 nm thick HT GaN was performed as a function of HT GaN growth temperature between 1000 °C and 1100 °C. AFM and x-ray rocking curves indicated that HT GaN temperature of 1100 °C using LT GaN layer is the optimum growth condition since this N-polar GaN film showed a low surface roughness of 4.9 nm in 20 × 20 μ m² AFM image with reduced TD density. Lastly, the effect of N-polar AlN buffer layer thickness was investigated using 30 nm AlN, as compared to 90 nm AlN buffer layer which has been used in the current thesis study. AFM measurements indicated that 30 nm thick AlN film has a lower surface roughness of 1.0 nm in 2 × 2 μ m² area, as compared to 3.6 nm in 90 nm AlN film. However, the surface morphology of N-polar GaN film grown at 1100 °C on 30 nm AlN became rougher than N-polar GaN grown on 90 nm AlN. In the meantime, x-ray rocking curve measurements demonstrated that the use of thinner buffer layer substantially reduced edge type TD density which seems to correlate to the nano-sized hillocks of N-polar AlN films. From these results, a combination of thinner AlN buffer layer with two-step process for N-polar GaN film is expected to provide improved crystallinity as well as smoother surface morphology, which will be investigated in the future.

Chapter 7

Thesis Summary and Future Work

7.1 Thesis Summary

The effect of indium surfactant on the GaN films grown on various substrates such as Si-face SiC, bulk GaN, Si(111), and C-face SiC substrates by MOCVD was studied in this thesis research to investigate the stress relaxation mechanism, structural, and optical properties of GaN films which were modified by indium surfactant that can alter the surface energy and kinetics of the growing GaN films.

In chapter 4, the effect of indium surfactant on GaN films grown on SiC was investigated first. In the 1.8 μ m thick Ga-polar GaN films grown on lattice-mismatched Si-face SiC substrates using indium surfactant at 950 °C, inverted hexagonal pyramid surface defects, so-called V-defects which consist of six (1011) planes, formed at the TDs on the GaN surface, which gave rise to the relaxation of compressive misfit stress elastically. At the same time, enhanced 2D growth was observed due to the improved surface migration of Ga and N adatoms promoted by the indium surfactant, which can be contradictory to the formation of V-defects because the improved step-flow growth may remove any surface defect. In order to explain the driving force for V-defect formation under In-rich conditions, a nucleation and growth model was developed, taking into account strain, surface, and dislocation energies modified by indium surfactant. This model suggested that V-defect formation can be energetically favored under In-rich conditions because V-defects can overcome the energy barrier beyond the critical size of V-defect when indium reduces the surface energy of $(10\overline{1}1)$ plane. Since these Ga-polar GaN films were unintentionally doped with Si, the effect of intentional Si doping was studied by introducing SiH₄ combined with indium surfactant. It turned out that Si was another important factor that can induce V-defect formation. It was speculated that Si may be incorporated preferentially at the TD cores, acting as masks to locally hinder GaN growth by forming Si – N bonds. This behavior may give rise to the initiation of V-defects which makes V-defects grow beyond the critical radius easily. Thus, the use of indium surfactant and Si doping was the most favorable growth condition for V-defect formation in GaN films grown on the Si-face SiC substrates.

The nucleation and growth model predicted that V-defects may not form in homoepitaxy since the energy barrier approaches infinity for V-defect formation due to zero misfit stress. When indium surfactant and Si doping were introduced simultaneously during the homoepitaxy, V-defects did not form in the 1.8 µm thick Ga-polar GaN films grown on bulk GaN substrates which had very low TD density. Thus, the nucleation and growth model appeared to well describe the behavior of V-defects in the case of homoepitaxy. The use of indium surfactant on GaN films grown on Si(111) substrates revealed that additional tensile stress was added with respect to the reference GaN, thus detrimental to the GaN films because tensile stress is typically relaxed by cracking during cooling from growth temperature to room temperature. The growth stress of GaN films on Si(111) started from compressive stress, but it changed to tension. The generation of tensile stress induced by indium appeared correlated with reduction of V-defects that were generated under the initial compressive stress. Although the misfit stress of GaN films on Si(111) was lower than that of GaN on SiC, high density of V-defects were generated under the compressive stress. Therefore, high density of TD, which serves as nucleation sites for V-defects, was believed to strongly drive the V-defect formation under In-rich conditions.

From the results on Ga-polar GaN films grown on Si-face SiC, bulk GaN, and Si(111) substrates, it was concluded that V-defects cannot be avoided in the heteroepitaxially grown Ga-polar GaN films without using high quality bulk GaN substrates when indium surfactant and Si doping were used during GaN growth. Therefore, N-polar GaN films, which have the opposite polarity, were investigated because theoretical study based on first-principles calculations predicted that V-defects are not energetically preferred along the N-polar growth direction. Since the polarity of the SiC substrate determines the polarity of the GaN, N-polar GaN films were grown on vicinal C-face SiC substrates. When indium surfactant and Si doping were used during GaN growth, V-defects did not form in 1.9 µm thick N-polar GaN film grown at 950 °C, as predicted by theory. This result suggests that V-defect free N-polar InGaN films also can be obtained on the N-polar GaN films, which may allow for the fabrication of stable green LDs utilizing high indium composition N-polar InGaN films that have been challenging to grow along the metal-polar direction.

Further studies of N-polar GaN films with varying growth conditions such as growth temperature, two-step process, and AlN buffer layer thickness, were performed for the future N-polar InGaN growths. When the growth temperature was varied from 950 °C to 1100 °C, the N-polar GaN film grown at 1000 °C showed the lowest surface

roughness whereas this GaN film showed the highest TD density in the given series of Npolar GaN films. Since the N-polar GaN grown at 1050 °C showed the lowest TD density, a two-step process using 140 nm thick initial LT GaN grown at 950 °C and 960 nm thick HT GaN was conducted with increasing HT GaN growth temperature from 1000 °C to 1100 °C. AFM and ω - scans in HRXRD indicated that the HT GaN grown at 1100 °C using LT GaN layer was the optimum growth condition because this N-polar GaN film showed a low surface roughness of 4.9 nm in $20 \times 20 \ \mu\text{m}^2$ AFM image with reduced TD density. The effect of a thinner N-polar AlN buffer layer (~ 30 nm) on the Npolar GaN was investigated, as compared to a 90 nm AlN buffer layer which has been used in the current thesis research. AFM measurements indicated that the surface morphology of N-polar GaN film grown at 1100 °C on 30 nm AlN was rougher than the N-polar GaN grown on 90 nm AlN although the 30 nm thick AlN film has a lower surface roughness of 1.0 nm in 2 \times 2 μ m² area in comparison to 3.6 nm in the 90 nm AlN film. However, x-ray rocking curve measurements showed that the use of thinner buffer layer substantially reduced edge type TD density which correlates with the nano-sized hillocks of N-polar AlN films. Consequently, a combination of thinner AlN buffer layer with the two-step process for N-polar GaN film is expected to provide improved crystal quality as well as smoother surface morphology, which will be investigated in the future.

7.2 Future Work

As described in chapter 6, the substrates used for N-polar GaN growth by MOCVD were C-face SiC wafers misoriented towards $<11\overline{20}$ > by 3.57 degree from the c-axis of SiC to suppress the hexagonal hillocks originating from the inversion domains that have Ga-polarity. N-polar GaN growth on another misorientation direction such as $<10\overline{10}>$ has been also reported in heteroepitaxy as well as homoepitaxy.^{36,45,47} Zauner et al. observed that the formation of hexagonal hillocks can be also suppressed by misorientation of bulk GaN substrates towards < 1010 > by 4 degree in the homoepitaxy of N-polar GaN.⁴⁵ By using 4H-SiC substrates miscut to $<10\overline{10}>$ by 4 degree, Brown et al. reported that two-step processed N-polar GaN film showed a surface roughness of 3.8 nm in 20 \times 20 μ m² AFM image,⁴⁷ which is lower than 4.9 nm of N-polar GaN films grown by the two-step process as reported in section 6.3.3 and is comparable to 3.5 nm in the N-polar GaN film grown with indium surfactant in section 6.2. Keller et al. grew Npolar GaN films on sapphire substrates by increasing the misorientation angle up to 4 degree towards both $<11\overline{20}>$ (a-plane) and $<10\overline{10}>$ (m-plane).³⁶ They found that the N-polar GaN films grown on sapphire miscut by 4 degree to $<11\overline{2}0>$ (equivalent to <1010> in the SiC because GaN film rotates on sapphire by 30 degree) showed the lower surface roughness than the case of sapphire miscut towards <1010> (equivalent to $<11\overline{20}>$ of the SiC) by 4 degree. Therefore, the N-polar GaN growth utilizing C-face SiC substrates misoriented to $<10\overline{10}>$ may provide better surface morphology, as compared to the N-polar GaN films studied in chapter 6.

As reported in section 6.3.4, a thinner AIN buffer layer of 30 nm resulted in the reduction of edge type TD density in N-polar GaN film, as compared to a 90 nm AlN, whereas it increased the surface roughness of GaN. Therefore, a two-step process, which reduced the surface roughness of N-polar GaN films by introducing the LT GaN nucleation layer followed by HT GaN, may improve the surface morphology of N-polar GaN films grown on the thin AlN buffer layer. Besides the thickness of AlN film, various growth conditions for the AIN buffer layers should be exploited since the study of Npolar AIN buffer layer has not been done extensively. Keller et al. reported that the polarity of the AIN buffer layer grown using very low V/III ratio of 250 turned out to be Al-polar, subsequently leading to the Ga-polar GaN films grown on this AlN layer, although C-face SiC substrates were used.¹⁶⁹ Therefore, high V/III ratio of 14062 or even higher ratio has been reported for the AlN buffer layer growth on vicinal C-face SiC substrates in order to maintain the N-polarity of AlN and GaN.^{39,47,169} However, the effect of high V/III ratio in N-polar AlN buffer layer on the structural properties of N-polar GaN films have not been investigated in a systematic way. Furthermore, the influence of N-polar AlN film grown with high V/III ratio on the film stress of N-polar GaN has not been reported yet. Thus, a systematic approach to AlN buffer layer growth conditions should be performed to optimize the structural and optical properties of subsequent Npolar GaN films.

In addition to the AlN buffer layers, the growth conditions for N-polar GaN films need to be further investigated in terms of growth temperature and V/III ratio. In chapter 6, the maximum growth temperature and V/III ratio used for the N-polar GaN films were 1100 °C and 3880, respectively. However, a few studies of N-polar GaN epilayers used

higher growth temperature than 1170 °C and very low V/III ratio of 188.^{36,39} Although TD density was raised with increasing growth temperature from 1000 °C in the one step process as reported in section 6.3.2, a two-step process at higher temperature than 1100 ^oC with LT GaN layer may possibly provide the better crystallinity as well as surface morphology due to the enhanced surface mobility of adatoms. Similarly, the lower V/III ratio than 3880 would result in smoother surface morphology since N-rich growth conditions typically reduce the surface diffusion length of Ga adatoms.¹⁷⁰ In addition, the effects of thickness, growth temperature, and V/III ratio of LT GaN layers on the main HT GaN epilayers are also of great interest since the LT GaN layer proved to have a strong influence on the surface morphology and crystallinity of the following main HT GaN films in the two-step process used in section 6.3.3. Since the unintentional O incorporation rate was very high ([O] = 1.2×10^{19} cm⁻³), which converted the N-polar GaN films to highly conductive n-type materials, as evidenced by SIMS analysis in section 6.2.5, systematic studies of the unintentional incorporation of impurities are necessary to control electrical properties of N-polar GaN epilayers. Fichtenbaum et al. reported that the O concentration in N-polar GaN films grown on sapphire by MOCVD decreased when the V/III ratio increased from 672 to 2690, the reactor pressure increased from 100 Torr to 300 Torr, and the substrate misorientation increased from 0 to 5 degree towards $<11\overline{2}0>$ of sapphire, which is equivalent to $<10\overline{1}0>$ of SiC.¹⁶⁰ They speculated that higher V/III ratio and reactor pressure may provide more active N adatoms and the incorporation rate of O may be limited by N because O adatoms, occupying N sites, may compete with N adatoms. Thus, exploring growth conditions for N-polar GaN films

seems critical for the realization of N-polar lighting emitting devices with controllable impurity levels.

Once the growth parameters for N-polar GaN films are optimized, N-polar InGaN film growth on the N-face GaN will be investigated to achieve V-defect free high quality InGaN epilayers for the application of green LDs. In our MOCVD system, metal-polar InGaN and InN films can be grown below 830 °C and 560 °C, respectively, due to the thermal instability arising from the high vapor pressure of indium.^{108,171} Therefore, InN and its alloys with GaN are typically grown using N₂ carrier gas at much higher reactor pressure up to ~ 650 Torr, as compared to 100 Torr for GaN in MOCVD, to suppress the film decomposition. It has been reported that N-polar InN can be grown by MBE at 600 °C which is higher temperature than 500 °C for In-polar InN.¹⁷² This implies that sticking probability of indium on N-face GaN is higher in comparison to Ga-polar direction at a given temperature, which may provide the better crystal quality because of higher growth temperature. Similarly, Keller et al. reported that N-polar InGaN / GaN multiple quantum wells grown on sapphire by MOCVD possessed higher indium composition of ~ 0.24 in contrast to ~ 0.15 in metal-polar inGaN at the same TMIn flow rate of 7.1 μ mol/min and growth temperature of $890 \sim 920$ °C.¹⁷³ However, they observed that the N-polar InGaN showed poorer crystal quality, especially higher twist, and less efficiency in PL when it is compared to the metal-polar InGaN that has the same indium composition. From these studies in the literature, N-polar InGaN films seem to have an advantage for high indium composition in common, but optimizing growth parameters for the N-polar InGaN films needs to be done to realize highly efficient green light emitting devices. Therefore, future works on the N-polar InGaN films will be initiated with the optimized N-polar GaN

templates grown on two different vicinal C-face SiC substrates misoriented towards both $< 11\overline{20} >$ and $< 10\overline{10} >$ by 3.57 and 4 degree, respectively. Using *in-situ* and *ex-situ* stress measurements and characterization techniques such as HRXRD, AFM, Raman scattering spectroscopy, SIMS, TEM, and PL which can probe surface morphology, structural, electrical, and optical properties of N-polar InGaN films will provide information for realization of the high quality N-polar InGaN epilayers grown by MOCVD.

Appendix

Estimation of Threading Dislocation Density by X-ray Rocking Curves

Thin films typically have mosaic structures. In polycrystalline thin films, highly misoriented grains lead to formation of grain boundaries. Even in single crystalline thin films such as epitaxially grown GaN that does not have grain boundaries, they are composed of sub-grains slightly misoriented each other, giving rise to mosaic structures which can be characterized by tilt, twist, and sub-grain size.⁶⁴ The tilt and twist represent misorientation of mosaic sub-grains out-of-plane and in-plane, respectively. In group III-nitrides, microstructures are generally regarded as columnar structures which have very low angle distributions, i.e., tilt with respect to the growth direction of c-axis and twist of each column's rotation about the c-axis, as shown in Fig. A.1.¹⁷⁴ In order to



Figure A.1. Microstructures of group III-nitrides are typically represented by columnar structures with a very low angle distribution. (a) Tilt and (b) twist of columnar structures are schematically illustrated with respect to growth direction of the c-axis of GaN films. [Ref. B. Gil, *Group III Nitride Semiconductor Compounds: Physics and Applications* (Oxford University Press Inc., New York, NY, 1998).]

accommodate the misorientations between these columns, threading dislocations (TDs) are generated, propagating towards film surface.⁸⁹ Therefore, the tilt and twist are related to screw (b = [0001]) and edge ($b = 1/3 < 11\overline{20} >$) TDs, respectively, as shown in Fig. A.2.⁶⁴ Since the tilt and twist correlates to the low angle misorientations between subgrains, x-ray rocking curves (ω - scans) that measure angle distributions of mosaic columns can characterize TD density in group III-nitrides. Thus, FWHMs of (0002) and (1010) rocking curves reflect screw and edge TD densities, respectively. X-ray rocking curve measurement of (0002) plane is simple and straightforward. However, ω - scan of (1010) plane cannot be directly obtained in normal four-circle diffractometer since this measurement requires grazing incidence angle x-ray diffraction (GIXRD). Thus, a couple of models to estimate the twist, i.e., FWHM of (1010) from a series of skew symmetric ω scans with increasing inclination angle χ of diffracting planes have been developed.^{118,119,121} In this section, three models developed by Srikant et al., Sun et al., and Lee et al. are used to estimate TD density of GaN films grown on SiC substrates. From these models, the estimated TD densities were compared with the TD density obtained from plan-view TEM. The most accurate model turned out to be Srikant's model in the case of GaN grown on SiC in the current thesis study.

By considering crystallites rotations, Srikant *et al.* developed a model to estimate twist of thin films.¹¹⁸ According to rigid body rotations theory, FWHMs (*W*) of two distributions, i.e., tilt and twist of crystallites vary as a function of inclination angle (Γ_0) from surface normal, which is given by



Figure A.2. Misorientations of sub-grains leads to (a) tilt (screw TD) and (b) twist (edge TD). [Ref. M. A. Moram and M. E. Vickers, Rep. Prog. Phys. 72, 036502 (2009).]

$$W_0^{tilt}[\Gamma_0] = \cos^{-1}[\cos^2(\Gamma_0)\cos(W_v) + \sin^2(\Gamma_0)], \qquad (A.1)$$

$$W_0^{twist}[\Gamma_0] = \cos^{-1}[\sin^2(\Gamma_0)\cos(W_r) + \cos^2(\Gamma_0)], \qquad (A.2)$$

where W_y and W_z are the FWHM of (0002) and (1010) rocking curves, i.e., tilt and twist. If tilt and twist are independent, then the combination of tilt and twist is the convolution of two distributions. However, depending upon dislocation geometry, introduction of tilt may also result in twist. Thus, in the case of interdependent distributions of tilt and twist, effective FWHM (*W*) needs to be defined by introduction of a new parameter *m*:

$$W_{eff}^{iilt}[\Gamma_0] = W_0^{iilt}[\Gamma_0] \exp\left(-m \frac{W_0^{twist}[\Gamma_0]}{W_0^{twist}[90]}\right),\tag{A.3}$$

$$W_{eff}^{twist}[\Gamma_0] = W_0^{twist}[\Gamma_0] \exp\left(-m \frac{W_0^{tilt}[\Gamma_0]}{W_0^{tilt}[0]}\right),\tag{A.4}$$

where *m* is an interdependence parameter, and $W_0^{tilt}[\Gamma_0]$ and $W_0^{twist}[\Gamma_0]$ are given in Eq. (A.1) and (A.2). In analyzing rocking curves, Pseudo-Voigt function defined by four parameters such as maximum intensity, peak position, FWHM (*W*), and Lorentzian character (*f*) is typically used to fit experimental data since this function generally shows better results as compared to Gaussian or Lorentzian functions. However, unlike Gaussian or Lorentzian distributions, no analytical expression exists for the convolution of two Pseudo-Voigt functions. Thus, the numerical convolution of two Pseudo-Voigt distributions is required to determine *W*, which is given by

$$W = \{ (W_{eff}^{tilt}[\Gamma_0])^n + (W_{eff}^{twist}[\Gamma_0])^n \}^{1/n},$$
(A.5)

where $W_{eff}^{tilt}[\Gamma_0]$ and $W_{eff}^{twist}[\Gamma_0]$ are given in Eq. (A.3) and (A.4), and *n* is a constant between 1 and 2, which can be expressed by

$$n = 1 + (1 - f)^2$$
, (A.6)

where *f* is the fraction of Lorentzian content of distribution. Therefore, by measuring a series of rocking curves as a function of inclination angle and using Eq. (A.5) with two fitting parameters, i.e., W_0^{twist} [90] and *m*, twist of thin films can be estimated.

Sun *et al.* made a purely geometrical approach to estimate twist.¹¹⁹ They developed a model using one fitting parameter instead of two parameters. FWHMs of effective tilt and twist as a function of inclination angle (ϕ) are given by

$$\Delta \theta_{\pm} = \arccos[\cos\varphi\cos\varphi' + \cos(\alpha'\pm\alpha)\sin\varphi\sin\varphi'], \qquad (A.7)$$

where \pm indicates effective tilt and twist, φ is inclination angle, and α is twist. φ' is given by

$$\varphi' = \arccos[\cos t' \cos \varphi], \tag{A.8}$$

where t' is apparent tilt. t' is a function of φ given by

$$t' = \arccos[1 - \cos^2 \varphi(1 - \cos t)], \qquad (A.9)$$

where *t* is tilt. α ' in Eq. (A.7) is given by

$$\alpha' = \arccos\left[\frac{\cos t' \sin \varphi}{\sin \varphi'}\right]. \tag{A.10}$$

The total change in the FWHM of ω -scans is the convolution of effective tilt and twist, which is given by

$$\Delta \theta = \sqrt{f \Delta \theta_{-}^{2} + (1 - f) \Delta \theta_{+}^{2}} , \qquad (A.11)$$

where f and (1-f) are the weight for the respective azimuthal orientation and have values between 0 and 1. Sun *et al.* found that f is close to 0.5, thus α (twist) becomes the only fitting parameter in Eq. (A.11).

Lee *et al.* developed a reciprocal-space model considering coherence length, tilt, and twist of epilayers which contributes to peak broadening in ω - scans.¹²¹ The measured FWHMs (Γ_{hkl}) of rocking curves on reflecting planes (*hkl*) are given by

$$\Gamma_{hkl}^{n} = (\Gamma_{y} \cos \chi)^{n} + (\Gamma_{z} \sin \chi)^{n} + (2\pi/L)^{n}/K_{hkl}^{n}, \qquad (A.12)$$

where Γ_y is tilt, Γ_z is twist, χ is the inclination angle, *L* is coherence length, *K*_{hkl} is the magnitude of scattering vector in reciprocal space, *n*=1 is for a Lorentzian distribution, *n*=2 is for a Gaussian distribution, and 1<*n*<2 is for a pseudo-Voigt function. Since the contribution of coherence length to peak broadening is negligible, the final term in Eg. (A.12) may be omitted by setting *L*=∞. Thus, Eq. (A.12) can be simplified, assuming that Gaussian distribution is optimal for peak profile of rocking curves:

$$\Gamma_{hkl} = \sqrt{(\Gamma_y \cos \chi)^2 + (\Gamma_z \sin \chi)^2} . \tag{A.13}$$

This model provides much simpler manner as compared to two models developed by Srikant *et al.* and Sun *et al.* and utilizes only one fitting parameter. Besides three models introduced in this section, Heinke *et al.* suggested that FWHM of($30\overline{3}2$) in ω - scan can be used as a figure of merit (FOM) for the twist.¹⁴⁹ For a variety of their GaN epilayers, they found that the twist was about 1.14 ± 0.04 times the FWHM of ($30\overline{3}2$). Thus, this relationship will be also evaluated in the current section.

In order to compare three models developed by Srikant *et al.*, Sun *et al.*, and Lee *et al.*, a series of x-ray rocking curve measurements on (0002), (1015), (1013), (1012), (2023), (1011), and (3032) planes were performed with three GaN samples (sample A, B, and C) using a four-circle x-ray diffractometer (Philips X'Pert MRD). The source x-ray was Cu K_{α 1} radiation (λ = 1.5406 Å). For high resolution XRD measurements, a hybrid monochromator composed of a multilayer x-ray mirror and 2-crystal Ge(220) 4-bounce monochromator was configured in the incident beam optics. The detector was set as receiving slit mode (open detector). Figure A.3 shows two typical x-ray rocking curves



Figure A.3. XRD rocking curves (square data points) and Voigt fit (red solid lines) of (a) (0002) and (b) $(30\overline{3}2)$ planes in GaN film.

of (0002) and ($30\overline{3}2$) planes of sample A and the fit lines with pseudo-Voigt function. Similarly, other rocking curves were fit with pseudo-Voigt function and the results are summarized in Table A.1. From the average *f* values, *n* in Eq. (A.5) is determined to be 1.22. Thus, by using Eq. (A.5), (A.11), and (A.13) from three models, the twist of sample A can be estimated to be 0.239°, 0.195°, and 0.174°, as shown in Fig. A.4. By using the FWHM of($30\overline{3}2$) as a FOM, the twist is estimated as 0.228°. Therefore, Srikant's model provides the highest twist value which is also similar with the estimated twist from Heinke's method.

Diffraction plane	Inclination angle (degree)	FWHM (degree)	Lorentzian content f	
(0002)	0	0.103	0.48	
(1015)	20.58	0.113	0.55	
(1012)	43.19	0.127	0.53	
(2023)	51.38	0.143	0.54	
(1011)	61.96	0.144	0.52	
(3032)	70.45	0.200	0.57	

Table A.1. FWHMs and Lorentzian content factors of x-ray rocking curves on (0002), $(10\overline{1}5)$, $(10\overline{1}2)$, $(20\overline{2}3)$, $(10\overline{1}1)$, and $(30\overline{3}2)$ planes in sample A.

Once twist is estimated, threading dislocation density can be calculated by the classical model. For randomly distributed TDs in a thin film without grain boundaries, screw and edge type TDs densities are related by the following equations:^{64,122,123}



Figure A.4. FWHMs of (0002), $(10\overline{1}5)$, $(10\overline{1}3)$, $(10\overline{1}2)$, $(20\overline{2}3)$, $(10\overline{1}1)$, and $(30\overline{3}2)$ ω - scans as a function of inclination angle and the fit lines of three models. Twist can be obtained at the inclination angle of 90°.

$$\rho_{screw} = \frac{\Gamma_{tilt}^2}{4.36b_{screw}^2},\tag{A.14}$$

$$\rho_{edge} = \frac{\Gamma_{twist}^2}{4.36b_{edge}^2},\tag{A.15}$$

where Γ_{tilt} and Γ_{twist} are the FWHMs of the (0002) and (1010) ω - scans, and b_{screw} (5.1850 Å) and b_{edge} (3.1888 Å) are the Burgers vectors along [0001] and $1/3 < 11\overline{2}0 >$, respectively. The calculated TD densities in sample A, B, and C are summarized and compared to TD densities obtained from plan-view TEM in Table A.2. In all samples, Sun's model and Lee's model tend to underestimate TD density whereas Srikant's model and Heinke's FOM show relatively good agreement with TEM results. Therefore, among the extrapolation techniques to obtain the twist, Srikant's model turns out to be the most accurate. For fast and simple estimation of TD density, only (0002) and ($30\overline{3}2$) ω - scans can be done using Heinke's method to estimate the twist.

Sample	Model	Tilt (deg)	Twist (deg)	Screw TD density (cm ⁻²)	Edge TD density (cm ⁻²)	Total TD density (cm ⁻²)	Total TD density by TEM (cm ⁻²)	$ ho_{ m XRD}/ ho_{ m TEM}$
Α	Srikant et al.	0.103	0.239	2.75×10^{8}	3.94×10^{9}	4.21×10^{9}	3.72×10^{9}	1.13
	Sun et al.		0.195		2.61×10^{9}	2.88×10^{9}		0.78
	Lee et al.		0.174		2.07×10^{9}	2.35×10^{9}		0.63
	Heinke et al.		0.228		3.58×10^{9}	3.85×10^{9}		1.04
В	Srikant et al.	0.084	0.239	1.84×10^{8}	3.92×10^{9}	4.11×10^{9}	3.92×10^9	1.05
	Sun et al.		0.192		2.54×10^{9}	2.73×10^{9}		0.70
	Lee et al.		0.179		2.19×10^{9}	2.38×10^{9}		0.61
	Heinke et al.		0.230		3.63×10^{9}	3.81×10^{9}		0.97
С	Srikant et al.	0.053	0.131	7.24×10^{7}	1.19×10^{9}	1.26×10^{9}	1.58×10^{9}	0.80
	Sun et al.		0.115		9.04×10^{8}	9.76×10^{8}		0.62
	Lee et al.		0.114		9.00×10^{8}	9.73×10^{8}		0.62
	Heinke et al.		0.137		1.28×10^{9}	1.36×10^{9}		0.86

Table A.2. Estimated twist and TD densities of sample A, B, and C obtained from x-ray rocking curves and plan-view TEM.

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