

**STRUCTURAL AND OPTICAL STUDIES OF WIDE
BAND-GAP $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$)
SEMICONDUCTORS**

NG SHA SHIONG

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($0 \leq x \leq 1$) SEMICONDUCTORS**

by

NG SHA SHIONG

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	x
LIST OF SYMBOLS	xviii
LIST OF ABBREVIATIONS	xxi
ABSTRAK	xxiii
ABSTRACT	xxv
CHAPTER 1 : INTRODUCTION	1
1.1 Introduction	1
1.2 Research objectives	2
1.3 Originality of the research works	4
1.4 Organization of dissertation	4
CHAPTER 2 : LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Overview on IR active optical phonon modes of wurtzite GaN thin films in the polarized spectra	6
2.3 Overview on the characterization studies of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductor	9
2.3.1 Band gap energy bowing parameter b	9
2.3.2 Brillouin zone (BZ) optical phonon modes	16
2.3.3 Surface phonon polariton (SPP) mode	27
2.4 Remarks	29
CHAPTER 3 : FUNDAMENTAL PROPERTY AND THEORETICAL MODEL	30
3.1 Introduction	30

3.2	Fundamental properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$	30
3.2.1	Crystalline structure of $\text{Al}_x\text{Ga}_{1-x}\text{N}$	32
3.2.2	Band gap energy E_g of $\text{Al}_x\text{Ga}_{1-x}\text{N}$	35
3.2.3	Brillouin zone (BZ) optical phonon modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$	37
3.2.4	Surface phonon polariton (SPP) mode of $\text{Al}_x\text{Ga}_{1-x}\text{N}$	41
3.3	Theoretical Model	43
3.3.1	Lorentzian model	44
3.3.2	Damped single harmonic oscillator model	45
3.3.3	Theoretical model for surface polariton (SP) dispersion curves	46
3.4	Summary	48
 CHAPTER 4 : INSTRUMENTATIONS, MATERIALS AND METHODS		 49
4.1	Introduction	49
4.2	Instrumentations	49
4.2.1	Scanning electron microscope (SEM)	50
4.2.2	Energy dispersive x-ray (EDX)	51
4.2.3	Atomic force microscopy (AFM)	53
4.2.4	X-ray diffraction (XRD)	55
4.2.5	Spectral reflectance technique	58
4.2.6	Ultraviolet-visible (UV-VIS) spectroscopy	61
4.2.7	Photoluminescence (PL) spectroscopy	64
4.2.8	Raman spectroscopy	66
4.2.9	Polarized infrared (IR) reflectance spectroscopy	70
4.2.10	Attenuated total reflection (ATR) IR spectroscopy	73
4.3	Materials	76
4.3.1	GaN thin films grown on various substrates	76
4.3.2	GaN thin films grown on Si substrates at various growth temperatures	77
4.3.3	$\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films grown on sapphire substrate	78
4.4	Methods	79
4.4.1	SEM and EDX measurements	80
4.4.2	AFM measurements	80
4.4.3	XRD measurements	80

4.4.4	Films thickness measurements	81
4.4.5	UV-VIS transmission measurements	82
4.4.6	PL and Raman measurements	82
4.4.7	Polarized IR reflectance and polarized IR ATR measurements	83
4.5	Summary	85
 CHAPTER 5 : CHARACTERIZATION OF GaN THIN FILMS GROWN ON VARIOUS SUBSTRATES		 87
5.1	Introduction	87
5.2	PL characterization	87
5.2.1	PL characterization of GaN/Si	94
5.3	Raman characterization	97
5.4	Polarized IR reflectance characterization	103
5.4.1	Interpretation of the polarized IR reflectance spectra	103
5.4.2	In-depth analysis of the p-polarized GaN reststrahlen band	107
5.4.2.1	Balkanski IR theory for thin films	108
5.4.2.2	Fresnel formulae for the oblique incidence polarized IR reflectivity	109
5.4.2.3	Vector analysis of the polarized IR incident beam.	110
5.4.3	Reststrahlen parameters extraction	113
5.4.4	Comparisons with reported results	115
5.5	Summary	122
 CHAPTER 6 : CHARACTERIZATION OF GaN THIN FILMS GROWN ON Si SUBSTRATE AND AT VARIOUS TEMPERATURES		 125
6.1	Introduction	125
6.2	XRD characterization	125
6.3	Polarized IR reflectance characterization	130
6.4	Summary	133

CHAPTER 7 : STRUCTURAL AND OPTICAL CHARACTERIZATION OF $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) THIN FILMS GROWN ON SAPPHIRE SUBSTRATE 135

7.1	Introduction	135
7.2	Determination of Al composition x	135
7.3	Structural properties of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films	141
7.3.1	The effects of the Al composition, x , on the surface morphology and surface roughness of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films	142
7.3.2	The effects of the Al composition, x , on the lattice constant c and crystalline quality of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films	152
7.4	Optical properties of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films	157
7.4.1	The effects of the Al composition on the band gap energy E_g	157
7.4.2	The effects of the Al composition on the BZ centre optical phonon modes	163
7.4.2.1	Raman measurements	163
7.4.2.2	Polarized IR reflectance measurements	171
7.4.2.3	Composition dependence of the BZ centre optical phonon modes	175
7.4.2.4	Composition dependence of the Raman phonon modes broadening	182
7.4.3	The effects of the Al composition on the SPP mode	186
7.5	Summary	194

CHAPTER 8 : CONCLUSION AND RECOMMENDATION FOR FUTURE STUDIES 198

8.1	Conclusion	198
8.2	Recommendation for future studies	201
8.2.1	To extend the theoretical model for polarized IR reflectance spectra	201
8.2.2	Low temperature PL/Raman measurements	202

8.2.3	Determination of the lattice constant a of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples	202
8.2.4	Home grown III-V nitrides binary and ternary samples	204
8.2.5	In-depth experimental and theoretical studies of the SPP mode of the AlGaN alloys	204
REFERENCES		206
APPENDICES		
APPENDIX 1:	STRUCTURAL AND THERMAL PROPERTIES OF SUBSTRATE MATERIAL FOR NITRIDE GROWTH	221
APPENDIX 2:	RAMAN SPECTRA FOR $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) SAMPLES AND SAPPHIRE SUBSTRATE WITH LORENTZIAN MODEL FITS	222
APPENDIX 3:	THE SECOND DERIVATIVE	228
LIST OF PUBLICATIONS & SEMINARS		230

LIST OF TABLES

		Page
Table 2.1:	Bowing parameter b for energy band gap E_g of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films.	11
Table 2.2:	Optical phonon modes (in unit of cm^{-1}) for wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films.	17
Table 2.3:	An evaluation (based on the literature results) of the behaviour of the BZ centre optical phonon modes of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy over the entire composition range ($0 \leq x \leq 1$).	24
Table 3.1:	Selective material parameters of wurtzite AlN and GaN at 300 K. (Mostly adapted from Levinshtein, Rumyantsev and Shur, 2001 unless stated otherwise.)	32
Table 4.1:	Basic parameters of the GaN films grown on various substrates.	77
Table 4.2:	Basic parameters of the GaN thin films grown at different substrate temperatures.	78
Table 4.3:	Basic parameters for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	79
Table 4.4:	Characterization techniques and the assessed information.	86
Table 5.1:	The near band edge (NBE) luminescence peak λ_{NBE} position and FWHM of GaN thin films grown on various substrates. The derived band gap energy is also shown.	93
Table 5.2:	Optical phonon modes (in cm^{-1}) of GaN thin films grown on various substrates. The full width at half maximum (FWHM) of the phonon modes is given in square parentheses.	97
Table 5.3:	A selective reported Raman active optical phonon modes of $E_2(\text{L})$, $E_2(\text{H})$ and $A_1(\text{LO})$ of wurtzite structure GaN.	101
Table 5.4:	The parameters used in modelling the spectra for GaN epilayer grown on 6H-SiC substrate.	114
Table 5.5:	The reported polarized IR optical phonon frequencies (w_{TO} and w_{LO}) of GaN films in the wurtzite, cubic, and mixed phases.	116
Table 5.6:	The reported IRE, Raman and theoretical results for the BZ centre optical phonon frequencies (in unit of cm^{-1}) of the wurtzite GaN thin films.	121

Table 6.1:	Summary of the XRD results and the reported results for GaN grown on Si substrates by MOCVD techniques.	129
Table 6.2:	Summary of the comparison of IR and the XRD results.	133
Table 7.1:	EDX results and the calculated alloy composition for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	136
Table 7.2:	XRD results for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	140
Table 7.3:	EDX results and the calculated alloy composition for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	141
Table 7.4:	Surface roughness of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films measured by AFM over an area of $20 \mu\text{m} \times 20 \mu\text{m}$.	150
Table 7.5:	The growth mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) layers evaluated from the SEM and AFM measurements.	152
Table 7.6:	The diffraction peak positions of (002) plane, FWHM and lattice constant of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films derived from XRD symmetric RC.	154
Table 7.7:	The absorption edges and the derived band gap energies of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	159
Table 7.8:	Optical phonon modes (in cm^{-1}) of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films obtained from the Raman and polarized IR reflectance measurements.	169
Table 7.9:	The parameters used to calculate the $\varepsilon(\text{A}_x\text{B}_{1-x}\text{C})_{\parallel, \perp}$ and to model the SP dispersion curves for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films.	189
Table 7.10:	The experimental and the theoretical SPP modes for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. The discrepancies, ΔSPP , between the experimental and the theoretical SPP mode are also shown.	192
Table 7.11:	Summary of the characterization results of structural and optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films grown on sapphire substrate.	195
A1.1:	Lattice parameters and thermal expansion of a number of prospective substrate material for nitride growth, and their lattice mismatch with GaN (Morkoc, 1998).	221

LIST OF FIGURES

		Page
Fig. 2.1:	Band gap energy of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) versus the deviation from the zero bowing. The symbols represent the experimental data (band gap energies) from published works. (Adapted from Yun et al., 2002.)	15
Fig. 2.2:	Behaviour of the BZ centre phonons in wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ as a function of alloy composition with the phonon propagation direction perpendicular to the C -axis. The vertical axis represents the density of states (DOS) for the BZ centre phonons. (Adapted from Grille, Schnittler and Bechstedt, 2000.)	22
Fig. 2.3:	Composition dependence of the BZ centre optical phonons in wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$. (Adapted from Davydov et al., 2002.)	23
Fig. 2.4:	Experimental and calculated composition dependences of the BZ centre optical phonons line broadening for wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$. The dots are the experimental data. The solid, dashed and dash-dotted lines represent the theoretical fits. (Adapted from Davydov et al., 2002.)	26
Fig. 3.1:	The crystalline structure of GaN and AlN. (Adapted from Qian et al., 2004.)	33
Fig. 3.2:	Variations of the lattice constants of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ as a function of alloy composition x . The solid line represents the linear interpolation.	34
Fig. 3.3:	Schematic band structure for wurtzite GaN and AlN. (Adapted from Levinshtein, Rumyantsev and Shur, 2001.)	35
Fig. 3.4:	Graphical illustration of the composition dependence of band gap energy of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$). The solid line represents the linear interpolation. The dashed and dash-dot-dot lines represent the non-linear interpolation with a positive and negative bowing value b , respectively.	37
Fig. 3.5:	First Brillouin zone (BZ) of wurtzite structure (Suzuki, Uenoyama and Yanase, 1995).	38
Fig. 3.6:	Schematic representation of the atomic displacement of the BZ optical phonon modes. (Adapted from Harima, 2002.)	38

Fig. 3.7:	Schematic diagram of (a) “one-mode”, (b) “two-mode” and (c) “mixed-mode” behaviours of the optical phonon in a mixed crystal of type $A_xB_{1-x}C$ ($0 \leq x \leq 1$). The circle and square symbols represent the TO and LO phonon mode, respectively. The close and open symbols indicate the included and excluded data point, respectively. (Adapted from Yang, 1991.)	40
Fig. 3.8:	Schematic diagram of the relationship between the (a) dielectric constant $\epsilon(\omega)$, (b) dispersion of bulk polariton (BP) and (c) dispersion of surface phonon polariton (SPP). The shaded area between the frequencies of transverse-optic (TO) and longitudinal-optic (LO) represents the forbidden band for the BP. ω_s denote the frequency of the surface excitation. Brewster modes (BM) are dispersion of electromagnetic surface waves at the regions where the real part of the dielectric constant, $\epsilon_1 > 0$ and the imaginary part of the dielectric constant, $\epsilon_2 \neq 0$. (Adapted from Otto, 1976.)	42
Fig. 4.1:	Schematic of the interaction of an electron beam with the sample and the signals generated (Philips, 2005).	50
Fig. 4.2:	Schematic diagram of a scanning electron microscope (Young and Kalin, 1986).	52
Fig. 4.3:	Schematic diagram of the emission of a characteristic x-ray (Jun, 2002).	53
Fig. 4.4:	Schematic diagram of the operation of an AFM. (Adapted and redrawn from Schroder, 1998.)	54
Fig. 4.5:	Diffraction of x-rays by parallel atomic planes in a crystalline material (Callister, 1997).	56
Fig. 4.6:	Basic features of a typical XRD experiment (Moeck, 2004).	57
Fig. 4.7:	Example of reflectance spectrum with oscillations obtained through spectral reflectance technique. (Adapted form Filmetrics, 1999.)	59
Fig. 4.8:	Filmetrics F20 setup configuration for the film thickness measurement (Filmetrics, 1999).	60
Fig. 4.9:	Schematic diagram of fundamental absorption or interband absorption. Pairs of electron-hole are created after the absorption of photons energy ($E = h\nu_{in}$). The ΔE and E_g represent the energy difference between two electronic states and the band gap energy, respectively. (Adapted and redrawn from Lovell, Avery and Vernon, 1976.)	62

Fig. 4.10:	Optical system of a double-beam UV-VIS spectrophotometer. (Adapted and re-drawn from Hitachi, 1985.)	63
Fig. 4.11:	Typical UV-VIS transmission spectrum. The band gap energy of the samples is determined from the intersection of linear interpolation of the steeply declining transmission profile and the x -axis.	64
Fig. 4.12:	(a-d) Radiative recombination processes: (a) band to band; (b) donor to valence band; (c) conduction band to acceptor; (d) donor to acceptor; (e) Non-radiative recombination via an intermediate state. The E_d , E_a and E_i indicate the donor, acceptor and intermediate states, respectively. [Adapted and redrawn from Gfroerer (2000) and Smith (1981).]	65
Fig. 4.13:	Typical experimental setup for PL measurements (Gfroerer, 2000).	66
Fig. 4.14:	Schematic diagrams of Rayleigh scattering, Stokes Raman scattering, and anti-Stokes Raman scattering (Kaiser Optical Systems, Inc., 2001). The ν_i and ν_f represent the initial and final states, respectively.	67
Fig. 4.15:	(a) Conventional and (b) modern sampling geometries for Raman spectroscopy (McCreery, 2000).	68
Fig. 4.16:	Schematic configuration of polarized specular IR reflection measurement.	71
Fig. 4.17:	Schematic representation of the types of specular reflection experiments.	72
Fig. 4.18:	Schematic representation of the IR reflectance experiment. (Adapted from Ng et al., 2005.)	74
Fig. 4.19:	Graphical representation of total internal reflection with a single reflection internal reflecting element (IRE). [Adapted and redrawn from PIKE Technologies (2005) and Gremlich (2002).]	76
Fig. 4.20:	Schematic diagram of (a) an ATR with germanium (Ge) single reflection plate (MIRacle, PIKE Technologies), and (b) ATR experiment.	84
Fig. 5.1:	Room temperature PL spectra of GaN thin films grown on various substrates. The scales of the vertical axis of the spectra of the samples G2 to G4 have been magnified by factor of about 2, 8 and 53, respectively.	88
Fig. 5.2:	Near band edge (NBE) luminescence spectra of GaN thin films grown on various substrates and the Lorentzian fitting.	90

Fig. 5.3:	Room temperature PL spectrum and the Lorentzian function fitting of GaN epilayer on AlN buffer layer grown on Si substrate.	95
Fig. 5.4:	Schematic recombination models to explain the appearance of the blue, yellow, red and near infrared emission bands in GaN epilayer on AlN buffer layer grown on Si substrate. [Adapted from Kaufmann et al. (1999) and Tansley and Egan (1992).]	96
Fig. 5.5:	Room temperature Raman spectra of GaN thin films grown on different substrates measured with 514.5 nm argon ion laser excitation source in the $z(x, \text{unpolarized})\bar{z}$ scattering configuration. The scales of the vertical axis of the spectra of the GaN thin film grown on 6H-SiC, GaAs and Si substrate have been magnified by factors of about 12, 23 and 17, respectively. The peaks with labels correspond to the Raman active optical phonon modes of GaN while the others (without labels) are due to the vibrational modes of the underlying layers.	98
Fig. 5.6:	SEM images of GaN thin film grown on GaAs substrate (sample G3) measured at magnifications of (a) 2000 \times and (b) 25,000 \times .	99
Fig. 5.7:	SEM images of GaN thin film grown on Al ₂ O ₃ , 6H-SiC and Si substrates measured at magnifications of (a) 10,000 \times and (b) 25,000 \times .	100
Fig. 5.8:	Room temperature IR reflectivity spectra of GaN/6H-SiC measured with (a) s- and (b) p-polarization radiation at an angle of incidence of 16°. The solid line and the dashed line represent the experimental and theoretical reflectivity spectra, respectively. The enlargement in (b) shows the dip corresponding to the LO of the 6H-SiC substrate.	105
Fig. 5.9:	Room temperature micro-Raman spectra of GaN/6H-SiC measured at (a) the surface of the GaN thin film and (b) the surface of the 6H-SiC substrate. The Raman scattering experiments are carried out in the $z(x, \text{unpolarized})\bar{z}$ scattering configuration. The A ₁ (LO) or LO of the GaN is observed at 733.55 cm ⁻¹ ; while the A ₁ (LO) or LO of the 6H-SiC are clearly observed at 967.18 cm ⁻¹ and 967.23 cm ⁻¹ .	106
Fig. 5.10:	Polarized IR reflectance spectra of the GaN thin films grown on (a) GaAs substrate (Ng et al., 2002) and (b) Si substrate with AlN buffer layer (Ng et al., 2004). The solid line and the dashed line indicate the experimental and theoretical reflectivity spectra, respectively. For both cases, high reflectivity features at 560 cm ⁻¹ are clearly visible in both polarized spectra.	108

Fig. 5.11:	Polarized IR reflectance spectra for GaN/6H-SiC taken at different angles of incidence: (a) 15°; (b) 30°; (c) 45°; (d) 60°; (e) 75°. The solid line and the dashed line indicate the experimental and theoretical reflectivity spectra, respectively.	111
Fig. 5.12:	Beam geometry of the p-polarized IR reflectance measurement and the resolution of the electric field vector E in the components of x and z -axes.	113
Fig. 5.13:	p-polarized IR ATR spectra of GaN/6H-SiC measured with an ATR Ge prism. The measurements are made at a resolution of 2 cm ⁻¹ and have been repeated for 3 times. The number of scans is 128. The surface phonon mode of GaN is observed at 706 cm ⁻¹ . The dip at about 915 cm ⁻¹ most probably arises from the absorption of the surface phonon mode of 6H-SiC.	117
Fig. 6.1:	XRD spectra of GaN on Si(111) grown at 1000°C.	126
Fig. 6.2:	XRD spectra of GaN on Si(100) grown at (a) 600°C, (b) 200°C and (c) 170°C. (Taken from Hassan et al., 1999.)	127
Fig. 6.3:	Schematic representation of the correlations between the growth temperature and the crystallinity of GaN films grown by MOCVD technique.	130
Fig. 6.4:	IR reflectance spectra of GaN/Si films at various growth temperatures for (a) s- and (b) p-polarization.	131
Fig. 7.1:	XRD spectra of the Al _x Ga _{1-x} N (0 ≤ x ≤ 1) samples taken from the (002) diffraction plane and measured by the 2θ-ω scan mode. The scales of the vertical axis for Al _x Ga _{1-x} N (0 < x ≤ 1) samples have been adjusted to magnify these low intensity XRD spectra. The double-peak feature is due to the diffraction from K _{α1} and K _{α2} lines of the x-ray.	138
Fig. 7.2:	Surface morphologies of Al _x Ga _{1-x} N (0 ≤ x ≤ 1) thin films grown on sapphire substrate measured by SEM at magnifications of (a) 10,000x and (b) 25,000x.	143
Fig. 7.3:	The 2-dimensional (2-D) and 3-dimensional (3-D) AFM topography of the Al _x Ga _{1-x} N (0 ≤ x ≤ 1) thin films grown on sapphire substrate measured with non-contact mode AFM for a scan area of 20 μm x 20 μm.	147
Fig. 7.4:	AFM RMS surface roughness (with a scan size of 20 μm × 20 μm) as a function of Al composition for Al _x Ga _{1-x} N (0 ≤ x ≤ 1) thin films grown on sapphire substrate. The solid line represents the non-linear interpolation of the RMS data (excluding the data for S7).	150

Fig. 7.5:	Symmetric RC XRD spectra of (002) plane for the wurtzite structure $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples. The scale of the vertical axis of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 < x \leq 1$) samples has been magnified in order to reveal these low intensity spectra.	153
Fig. 7.6:	The FWHM of the (002) diffraction RC peak of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films as a function of the Al composition over the entire composition range ($0 \leq x \leq 1$). The solid line is a non-linear interpolation of the FWHM data.	156
Fig. 7.7:	Room temperature UV-VIS transmission spectra of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. Note that the UV-VIS transmission spectra for samples S7 and S11 have been taken at different spectral range.	158
Fig. 7.8:	Band gap energy of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ versus Al composition over the entire composition range ($0 \leq x \leq 1$). The solid line represents the linear interpolation between the band gap energy of GaN ($x = 0$) and AlN ($x = 1$). The dashed line indicates the best fit of the non-linear interpolation (with a bowing parameter $b = 0.87$ eV) of the UV-VIS data.	160
Fig. 7.9:	Room temperature Raman spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples and sapphire substrate measured with $z(x, \bar{z})$ scattering configuration. The scales of the vertical axis of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 < x \leq 1$) samples and sapphire substrate have been adjusted to magnify the features of the optical phonon modes. The allowed Raman optical modes are indicated by the $E_2(\text{L})$, $E_2(\text{H})$ and $A_1(\text{LO})$. The labelled features marked by “*” and “#” correspond to the optical phonon modes of the sapphire substrate.	165
Fig. 7.10 (a):	The enlargement of the Raman spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples in the spectral range of $100 - 300 \text{ cm}^{-1}$. The scale of the vertical axis has been adjusted to magnify the feature of the $E_2(\text{L})$ phonon mode.	166
Fig. 7.10 (b):	The enlargement of the Raman spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples in the spectral range of $500 - 700 \text{ cm}^{-1}$. The scale of the vertical axis has been adjusted to magnify the feature of the $E_2(\text{H})$ phonon mode. The square symbols indicate the GaN-like (■) and AlN-like (□) of the $E_2(\text{H})$ phonon modes. The E_{1g} corresponds to optical phonon mode of the sapphire substrate.	167

Fig. 7.10 (c):	The enlargement of the Raman spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples in the spectral range of $700 - 900 \text{ cm}^{-1}$. The scale of the vertical axis has been adjusted to magnify the feature of the $\text{A}_1(\text{LO})$ phonon mode. The triangle (\blacktriangle) symbols indicate the $\text{A}_1(\text{LO})$ phonon mode. The E_{1g} (marked by "#") is the optical phonon mode of the sapphire substrate.	168
Fig. 7.11 (a):	s-polarization IR reflectance spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples measured at room temperature. Spectrum of sapphire substrate is also shown for comparison. The GaN-like and AlN-like $\text{E}_1(\text{TO})$ optical modes of the of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films are represented by the close (\blacklozenge) and open (\blacklozenge) diamonds, respectively. The labelled features marked by stars (\star) and crosshairs ($+$) are optical phonon modes of the sapphire substrate.	172
Fig. 7.11 (b):	p-polarization IR reflectance spectra of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) samples measured at room temperature. Spectrum of sapphire substrate is also shown for comparison. The $\text{A}_1(\text{LO})$ optical mode of the of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films is indicated by the open triangles (\triangle).	173
Fig. 7.12 (a):	The $\text{E}_2(\text{L})$ optical phonon mode behaviour of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$). The solid line indicates the non-linear interpolation of the GaN-like $\text{E}_2(\text{L})$ data.	176
Fig. 7.12 (b):	The $\text{E}_2(\text{H})$ optical phonon mode behaviour of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$). The solid line and the dashed lines represent the non-linear interpolation of the GaN-like and AlN-like $\text{E}_2(\text{H})$ data, respectively.	176
Fig. 7.12 (c):	The $\text{A}_1(\text{LO})$ optical phonon mode behaviour of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$). The solid line represents the non-linear interpolation of the data.	177
Fig. 7.12 (d):	The $\text{E}_1(\text{TO})$ optical phonon mode behaviour of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$). The solid line and the dashed lines represent the non-linear interpolation of the GaN-like and AlN-like $\text{E}_1(\text{TO})$ data, respectively.	177
Fig. 7.13:	Raman line width of (a) $\text{E}_2(\text{L})$, (b) GaN-like $\text{E}_2(\text{H})$, (c) AlN-like $\text{E}_2(\text{H})$ and (d) $\text{A}_1(\text{LO})$ modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films as a function of the Al composition. The solid lines indicate the non-linear interpolation of the data.	183
Fig. 7.14:	Room temperature p-polarized IR ATR spectra for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films grown on sapphire substrate. The ATR spectrum for sapphire substrate is also shown for comparison. The measurements have been repeated at two different areas on the sample and the average values of these spectra are calculated. The positions of the absorption dips are determined by means of second order derivative method.	187

Fig. 7.15:	The surface polariton (SP) theoretical dispersion curves for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. The vacuum light wave and the light wave in ATR crystal are indicated by dash line and dash-dot-dot line respectively. The intersections of the ATR crystal line and the branches of the SP dispersion curve correspond to the SPP mode.	190
Fig. 7.16:	The SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films as a function of Al composition. The full circles and the triangles are respectively the theoretical and experimental data. The SPP theoretical data for $x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8,$ and 0.9 are also included. The solid line and the dash line are the best fit of the theoretical and experimental data, respectively.	193
Fig. A3.1:	A single absorption band IR spectrum and its second derivative spectrum (Stuart, 1996).	228
Fig. A3.2:	Typical single resonance IR reflectance spectra $R(\omega)$ for (a) an ideal case (phonon damping, $\gamma = 0$) and (b) for non-ideal case ($\gamma \neq 0$). The spectra of the real refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ are also shown (Ng, Hassan and Abu Hassan, 2006).	229

LIST OF SYMBOLS

2θ - ω	2theta-omega scan mode for XRD measurement
\times	Magnification
\perp	Direction perpendicular to C -axis
\parallel	Direction parallel to C -axis
β	Hexagonal wurtzite structure
α	Cubic zinc-blende structure
$\alpha_{a(c)}$	Thermal expansion coefficient perpendicular (parallel) to C -axis
γ	Phonon damping
ϵ_{xx} (ϵ_{yy})	Dielectric tensors perpendicular to C -axis
ϵ_{zz}	Dielectric tensors parallel to C -axis
ϵ_{∞}	High frequency dielectric constant
ϵ_0	Vacuum permittivity
$\epsilon_{\parallel(\perp)}$	Dielectric function parallel (perpendicular)
$\epsilon_{\infty,\parallel(\perp)}$	High-frequency dielectric constant parallel (perpendicular)
$\epsilon_{0,\parallel(\perp)}$	Dielectric constant static parallel (perpendicular)
$\epsilon(\text{AC})_{\parallel,\perp}$	Dielectric constants parallel and perpendicular for AC binary compound.
$\epsilon(\text{BC})_{\parallel,\perp}$	Dielectric constants parallel and perpendicular for BC binary compound.
\mathbf{k}_{\parallel}	Wave vector of the of the incident radiation (or evanescent wave)
\mathbf{k}_{vac}	Wave vector of the vacuum light wave
λ	Wavelength
λ_c	Critical wavelength
λ_{in}	Wavelength of the absorption photon
λ_{Abs}	Absorption edge
θ	Incident/diffraction angle
θ	Internal angle of incidence
θ_c	Critical angle
ν	Poisson ratio
$\nu_{\text{AlN}} (\nu_{\text{GaN}})$	Poisson ratio of AlN (GaN)
ν_i	Initial state
ν_{in}	Frequency of the incident photons
ν_f	Final state
ω	Angular frequency of the SP
ω	Omega scan mode for XRD measurement
ω_0	Frequency of the peak
ω_s	Frequency of the surface excitation
ω_{TO}	TO phonon frequency
ω_{LO}	LO phonon frequency
ω_{Al}	Weight percent of the Al element
$\omega_{\text{E}_1(\text{TO})}$	$E_1(\text{TO})$ phonon frequency
$\omega_{\text{E}_1(\text{LO})}$	$E_1(\text{LO})$ phonon frequency
$\omega_{\text{A}_1(\text{TO})}$	$A_1(\text{TO})$ phonon frequency

$w_{A_1(\text{LO})}$	$A_1(\text{LO})$ phonon frequency
w_{Ga}	Weight percent of the Ga element
w_p	Plasma frequency
Γ_0	BZ centre
Γ_{HM}	Full width at half maximum
ΔE	Difference in energy between two electronic states
ΔSPP	Average discrepancy between the experimental and theoretical SPP values
a	Lattice constant
$a_0^{\text{AlN}} (c_0^{\text{AlN}})$	Lattice constants a (c) of AlN
$a_0^{\text{GaN}} (c_0^{\text{GaN}})$	Lattice constants a (c) of GaN
A_{1g}	Raman active mode of sapphire
$A_1(\text{LO})$	Phonon mode
$A_1(\text{TO})$	Phonon mode
A_{Al}	Atomic weight of the Al
A_{Ga}	Atomic weight of the Ga
b	Band gap energy bowing parameter
B	Phonon mode
c	Lattice constant
c	Velocity/speed of light
C	Crystallographic axis
$C_{13} (C_{33})$	Elastic modulus
d_{hkl}	Interplanar spacing between two consecutive scattering planes
e	Electron
e	Electron charge
\mathbf{E}	Electric field vector
E_{1g}	Raman active mode of sapphire
$E_1(\text{LO})$	Phonon mode
$E_1(\text{TO})$	Phonon mode
$E_2(\text{L})$	Phonon mode
$E_2(\text{H})$	Phonon mode
E_a	Acceptor state
E_d	Donor state
E_g	Band gap energy
E_i	Intermediate state
h	Planck's constant
hkl	Miller indices
I	Intensity
I_0	Intensity at peak w_0
I_s	Integrated intensity of the peak
j	j -th oscillator
$K_{\alpha 1}$	X-ray emission line
$K_{\alpha 2}$	X-ray emission line
m	m -th order
m^*	Effective mass of the electron
m_e	Electron mass
n	Order of reflection
n	Refractive index
n_p	Refractive index of the Ge prism
N	Carrier concentration
\mathbf{q}	Wave-vector

r	Angle of refraction
R	Reflectivity
S	Phonon oscillator strength
t	Film thickness
T	Temperature
x	Al mole fraction / Alloy composition
x_{Al}	Al composition
x_{Ga}	Ga composition

LIST OF ABBREVIATIONS

2-D	2-dimensional
3-D	3-dimensional
arb. units	Arbitrary units
AFM	Atomic force microscopy
ATR	Attenuated total reflection
BL	Blue luminescence
BM	Brewster modes
BP	Bulk polariton
BSE	Backscattered electron
BZ	Brillouin zone
CB	Conduction band
CCD	Charge-coupled-device
CRT	Cathode ray display tube
DOS	Density of states
eV	Electron volt
e-beam	Electron beam
ECR	Electron cyclotron resonance
EDX	Energy dispersive x-ray
EW	Evanescent wave
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
HR	High resolution
IR	Infrared
IRE	IR ellipsometry
IRE	Internal reflecting element
LDs	Laser diodes
LEDs	Light emitting diodes
LO	Longitudinal-optic
LP-MOCVD	Low pressure metalorganic chemical vapour deposition
LPP	LO plasmon-phonon
LST	Lyddane-Sachs-Teller
MBE	Molecular beam epitaxy
MM	Mixed mode behaviour
MOCVD	Metalorganic chemical vapour deposition
NA	Not available
NBE	Near band edge
NIRL	Near infrared luminescence
OM	One-mode behaviour
PA-MOCVD	Plasma-assisted metalorganic chemical vapour deposition
PL	Photoluminescence
RA	Reflection – absorption
RC	Rocking curve
RL	Red luminescence
RMS	Root-mean-squared
SE	Secondary electron
SEM	Scanning electron microscopy
SIS	Surface imaging systems
SP	Surface polaritons
SPP	Surface phonon polariton
TM	Two-mode behaviour

TO	Transverse-optic
UD	Unable to detect
UV	Ultraviolet
UV-VIS	Ultraviolet-visible spectroscopy
VB	Valence band
VIS	Visible
XRD	X-ray diffraction
YL	Yellow/orange-yellow luminescence

KAJIAN CIRI STRUKTUR DAN OPTIK BAGI SEMIKONDUKTOR BERJURANG TENAGA LEBAR $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$)

ABSTRAK

Tujuan projek ini ialah untuk mengkaji ciri struktur dan optik bagi semikonduktor-semikonduktor berjurang tenaga lebar $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) dengan pelbagai peralatan pencirian yang tak bersentuhan dan tak memusnahkan. Ini termasuklah mikroskopi imbasan elektron (SEM), serakan tenaga sinar-x (EDX), mikroskopi daya atomik (AFM) dan pembelauan sinar-x (XRD) untuk pencirian struktur, dan teknik pemantulan spectrum, spektroskopi ultraungu-cahaya nampak (UV-VIS), fotoluminesen (PL), spektroskopi Raman, spektroskopi pantulan inframerah (IR) terkutub dan pantulan penuh inframerah (IR) terkutub yang dilemahkan (ATR) untuk pencirian optik.

Kerja-kerja awal ke atas ciri struktur dan optik bagi filem-filem nipis GaN yang telah ditumbuhkan di atas pelbagai substrat, seperti substrat silikon (Si), batu nilam (Al_2O_3), gallium arsenida (GaAs), dan silikon karbida 6H (6H-SiC) telah dijalankan. Walau bagaimanapun, kajian-kajian ini telah difokuskan kepada pencirian PL dan Raman, kajian mendalam bagi asal-usul puncak berpantulan tinggi di dalam spektrum pantulan IR yang terkutub p, dan kajian XRD dan pantulan IR yang terkutub mengenai penghabluran bagi filem-filem nipis GaN yang ditumbuhkan atas substrat Si pada suhu substrat yang berlainan. Keputusan telah menunjukkan bahawa kualiti hablur yang lebih baik dapat diperolehi jika lapisan GaN ditumbuhkan atas substrat 6H-SiC. Tambahan pula, keputusan telah mendedahkan bahawa asal-usul puncak berpantulan tinggi di dalam spektrum pantulan IR yang terkutub p ialah mod fonon TO_\perp . Satu kolerasi di antara penghabluran dan bentuk jalur reststrahlen IR juga telah diperolehi.

Untuk semikonduktor-semikonduktor $\text{Al}_x\text{Ga}_{1-x}\text{N}$, ketebalan dan komposisi aloi bagi filem-filem nipis $\text{Al}_x\text{Ga}_{1-x}\text{N}$ telah ditentukan terlebih dahulu. Kajian-kajian terperinci ke atas kesan-kesan komposisi aloi, x , terhadap morfologi permukaan, kekasaran

permukaan, pemalar kekisi c dan kualiti hablur telah dijalankan. Tambahan pula, kesan-kesan pengalioian terhadap jurang tenaga asas E_g , mod-mod fonon optik pada pusat Brillouin zon (BZ) dan mod fonon polariton permukaan (SPP) telah disiasat dengan terperinci. Melalui kajian-kajian ini, keputusan-keputusan terhadap kelakuan dan kebersandaran terhadap komposisi bagi ciri-ciri asas struktur dan optik telah diperolehi atau diterbitkan. Bagi mod SPP, kelakuan satu-mod dan satu faktor lengkung ke atas (bagi persamaan kebersandaran terhadap komposisi) telah diperolehi. Adalah penting disebutkan bahawa ini merupakan kali pertama kelakuan dan kebersandaran terhadap komposisi bagi mod SPP aloi $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (begitu juga untuk aloi-aloi terner yang berstruktur wurtzit) diperolehi.

Secara keseluruhan, keputusan-keputusan telah mendedahkan bahawa pengalioian mempunyai satu impak yang besar ke atas ciri-ciri struktur dan optik bahan. Banyak ciri bagi aloi $\text{Al}_x\text{Ga}_{1-x}\text{N}$ telah berubah dengan sepenuhnya dan berkelakuan dengan cara lain berbanding dengan bahan-bahan induk mereka, iaitu GaN ($x = 0$) dan AlN ($x = 1$). Akan tetapi, ciri-ciri bahan bagi aloi-aloi yang terbentuk adalah bergantung kepada komposisi aloi dan secara biasa dapat diwakilkan dengan satu interpolasi secara linear atau tak-linear antara unsur-unsurnya.

STRUCTURAL AND OPTICAL STUDIES OF WIDE BAND-GAP $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) SEMICONDUCTORS

ABSTRACT

The aim of this project is to study the structural and optical properties of wide band gap $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) semiconductors by means of various non-contact and non-destructive characterization tools. These include the scanning electron microscopy (SEM), energy dispersive x-ray (EDX) analysis, atomic force microscopy (AFM) and x-ray diffraction (XRD) for structural characterization, and spectral reflection technique, ultraviolet-visible (UV-VIS), photoluminescence (PL), Raman, polarized infrared (IR) reflectance and polarized IR attenuated total reflection (ATR) spectroscopy for optical characterization.

Initial works on the structural and optical properties of the GaN thin films grown on various substrates, such as silicon (Si), sapphire (Al_2O_3), gallium arsenide (GaAs), and 6H-silicon carbide (6H-SiC) substrates have been carried out. Studies are, however, focused on PL and Raman characterization and in-depth polarized IR reflectance study on the origin of the high reflection peak in the p-polarization spectrum as well as XRD and polarized IR reflectance studies on the crystallinity of GaN thin films. The results showed that a better crystalline quality can be achieved if the GaN layer is grown on 6H-SiC substrate. In addition, the results revealed that the origin of the high reflection peak in the p-polarization IR reflectance spectrum is the TO_\perp phonon mode. A correlation between the crystallinity and the IR reststrahlen band shapes has also been obtained.

For $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductors, the thickness and the alloy composition of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films are first determined. Thorough studies on the influence of the Al composition, x , on the surface morphology, surface roughness, lattice constant c and the crystalline quality are conducted. In addition, alloying effects on the fundamental band gap energy E_g , the Brillouin zone (BZ) centre optical phonon modes and the

surface phonon polariton (SPP) mode are investigated thoroughly. Through these studies, a number of results on the behaviour and composition dependence of the fundamental structural and optical characteristics have been obtained or derived. For the SPP mode, a one-mode (OM) behaviour and an upward bowing factor (for the composition dependence equation) have been obtained. It is important to note that this is the first time the behaviour and the composition dependence of the SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy (as well as the wurtzite structure ternary alloys) are obtained.

Overall, the results revealed that the work of alloying has a great impact on the structural and optical characteristics of the materials. Many properties of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy have been completely changed and behave differently as compared to their parent materials, namely, the GaN ($x = 0$) and the AlN ($x = 1$). However, the material properties of the alloy materials formed are dependent on the alloy composition and typically can be represented by a linear or non-linear interpolation between its constituents.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Owing to the outstanding optical properties such as wide range band-gap energy and high emitting performance, group-III nitride semiconductors such as aluminium nitride (AlN), gallium nitride (GaN), indium nitride (InN) and their alloys have attracted both academic and technological extensive research in recent years. As a consequence, efficient green-blue-ultraviolet light emitting diodes (LEDs), blue-violet laser diodes (LDs) and ultraviolet (UV) detectors as well as high voltage, high temperature and high frequency electronic devices have been successfully realized (Nakamura, 1999; Kung and Razegui, 2000; Asif Khan et al., 1994; Shur et al., 1999).

Group-III nitride ternary alloys, particularly aluminium gallium nitride (AlGaN) have been recognized to have the potential for applications in semiconductor light emitting devices and solar-blind UV detector as well as sensor devices, particularly for operating under harsh environment conditions (Shur et al., 1999; Gotthold and Guo, 2003; Razeghi, 2002; Allerman et al., 2003; Munoz et al., 2001; Mukai et al., 2001). Besides that, it also has the capacity to cover the spectrum from visible (VIS) to deep UV spectral range. These are strongly driven by their superior physical properties such as excellent thermal, mechanical and chemical stability, and unique optical properties such as direct and tuneable band gap energy (ranging from 3.4 to 6.2 eV).

Although great progress has been achieved in the fabrication of AlGaN-based devices, little is known about their fundamental materials properties. As compared to its family, the physical properties of III-V nitrides binary semiconductors have been reviewed in-depth and summarized in many books (Adachi, 2005; Ruterana, Alberecht

and Neugebauer, 2003; Levinshtein, Rumyantsev and Shur, 2001; Pankove and Moustakas, 1999; Morkoc, 1998; Pearton, 1997) as well as technical papers (Reshchikov and Morkoc, 2005; Jain et al., 2000; Pearton et al., 1999; Ambacher, 1998; Mohammad and Morkoc, 1996; Strite, Lin and Morkoc, 1993).

For AlGa_N alloys, many attentions have been paid to the device applications. For the fundamental material properties, most of the works are devoted to the determination of the band gap energy bowing parameter b as well as the behaviour of the optical phonon modes as a function of Al composition. Despite these findings, there is no consensus between the literature results concerning these subjects. This is mainly due to the differences in the sample quality and the narrow range of the alloy compositions that are explored. Apart from that, many basic physical properties still remain unclear or unexplored. For instance, knowledge on the surface phonon polariton (SPP) modes, which is crucial for understanding the behaviour of the coupling effect between the photon and surface phonon, is still rare and has not received sufficient attention. Hence, from both the fundamental physics point-of-view and the potential application of the nitrides semiconductor, there is an absolute need for thorough studies on the fundamental properties of these materials.

In order to contribute to the understanding of the fundamental properties of this advanced material as well as the advancement of knowledge in the condensed matter, the influences of the Al composition on the structural and optical as well as surface properties of this ternary alloy will be investigated.

1.2 Research objectives

In this work, initial investigation is focused on the detailed studies of the structural and optical properties of the GaN thin films. The aims of these studies are to characterize the optical properties of the GaN thin films grown on various substrates

and to perform an in-depth study of the origin of the high reflection peak in the p-polarization infrared (IR) reflectance spectrum. The objective of these studies also includes the investigation of the correlation between the crystalline quality and the variations of IR reststrahlen band of a set of GaN thin films (with a variety of structural or crystalline quality) grown on silicon (Si) substrates at various substrate temperatures.

In general, these preliminary works eventually provides a better understanding on the fundamental properties for the subsequent study of the wide band gap $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) semiconductors, and hence facilitates the characterization research as well as the analyses of the obtained results.

Thorough studies on structural and optical characteristics of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) semiconductors have been carried out by means of various non-contact and non-destructive characterization tools. These include the scanning electron microscopy (SEM), energy dispersive x-ray (EDX) analysis, atomic force microscopy (AFM), x-ray diffraction (XRD), spectral reflectance technique, ultraviolet-visible (UV-VIS) spectroscopy, photoluminescence (PL) spectroscopy, Raman spectroscopy and polarized IR reflectance spectroscopy as well as polarized IR attenuated total reflection (ATR) spectroscopy. The main research objectives are to investigate the effects of the alloys composition, x , on the surface morphology, the surface roughness, the lattice constant c , and the crystalline quality of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. Besides that, the research objectives also included investigations of the alloying effects on the fundamental band gap energy E_g , the behaviour of the Brillouin zone (BZ) centre optical phonon modes, particularly the $E_2(\text{L})$, $E_1(\text{TO})$, $E_2(\text{H})$ and $A_1(\text{LO})$, and the behaviour of the SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. Determinations of the composition dependence equation of these characteristics in the entire Al composition range are carried out in parallel with the above characterization studies.

1.3 Originality of the research works

The main originality of this research work lies in the experimental and theoretical studies of the influences of the alloy composition, x , on the SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films. Through this research study, the composition dependence and the behaviour of the SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) thin films are reported for the first time.

Apart from that, the alloying effects on the surface morphology and the surface roughness, the lattice constant c and the crystallite quality, the fundamental band gap energy E_g , and the behaviour of the BZ optical phonon modes of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films have been investigated thoroughly over the entire Al composition range ($0 \leq x \leq 1$). Through this sequential study, many previously reported experimental results have been confirmed or verified. Moreover, some new findings, mainly the composition dependence equation for the optical phonon modes, have been derived.

On the other hand, the results of this research project have also led to new explanations of the origin of the optical phonon modes that can be obtained through the oblique incident polarized IR measurements on the wurtzite nitrides. In addition, an alternative technique to determine the crystallinity of the deposited films based on the IR reflectance measurements has also been proposed.

1.4 Organization of dissertation

Generally, the content of this dissertation is organized as follows.

In Chapter 2, early studies on the structural and optical properties of the AlGaIn semiconductor are reviewed. However, emphasis will be placed on the band gap energy bowing parameter b , the behaviour of the BZ optical phonon modes and the

SPP mode. Apart from that, an overview of the assignment of the IR optical phonon modes will be presented in this chapter.

Chapter 3 is devoted to the fundamental properties of the GaN and the AlN as well as the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductors. Theoretical models used to fit/generate the PL, the Raman, the polarized IR reflectance and the SPP spectra of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductors are also included.

In Chapter 4, the general principles underlying the operation of the characterization tools and the experimental details for each characterization work are discussed. These include the samples details, experimental set-up and the operating conditions as well as the resolution.

In Chapter 5, the results and discussion for the PL and Raman characterization of the GaN thin films grown on various substrates, namely, sapphire (Al_2O_3), 6H-silicon carbide (6H-SiC), gallium arsenide (GaAs) and Si are presented. In-depth polarized IR reflectance analyses, with emphasis on the GaN thin film grown on 6H-SiC substrate, are also given.

Chapter 6 discusses the results of the XRD and polarized IR reflectance characterization of a set of GaN thin films grown on Si substrate at various substrate temperatures.

Chapter 7 contains the structural and optical studies of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) semiconductors. The results and discussion is mainly devoted to the influence of alloying on the structural and optical properties of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductors.

Finally, in Chapter 8, conclusions on the characterization results covered in this dissertation and recommendations for future research are given.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the overview of the IR active optical phonon modes of wurtzite GaN thin films in the polarized spectra will be discussed briefly. Next, the present status of the characterization studies of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductor will be reviewed. Emphasis will be placed on the band gap energy bowing parameter b , the behaviour of the BZ optical phonon modes, and the SPP mode of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ semiconductor. In the final section of this chapter, a concluding remark of these literature reviews is presented.

2.2 Overview on IR active optical phonon modes of wurtzite GaN thin films in the polarized spectra

Up to now, a number of studies on the optical properties of the GaN in the IR region have been carried out by measuring the reflectivity of the thin films for radiation at normal or oblique incidence (Perlin et al., 1995; Perlin et al., 1996; MacMillan et al., 1996; Yu et al., 1998; Iller et al., 1999; Hou et al., 1999; Deguchi et al., 1999; Li et al., 1999; Frayssinet et al., 2000; Hou et al., 2000; Feng, Yang and Hou, 2001; Feng et al., 2002; Zhang et al., 2001). Since wurtzite structure GaN is a uniaxial crystal, two sets of phonon parameters are required to describe the dielectric function, namely, one set to model ε_{\perp} and another set to model ε_{\parallel} (Barker and Ilegems, 1973). As a result, these experimental data provided fairly little information as compared to polarized

measurements. According to Dumelow et al. (1993), the materials parameters can be determined more accurately if the reflectance measurements are performed by means of the oblique incidence polarized light. This is owing to purely transverse-optic (TO) and longitudinal-optic (LO) phonon modes can be observed for phonons propagating in the direction perpendicular (\perp) and parallel (\parallel) to the crystal axis, C , respectively; hence, more strongly marked features can be obtained. Consequently, more informative and accurate results can be obtained through the polarized measurements.

To date, detailed investigations of the polarized IR reflectance on GaN have been reported by Barker and Ilegems (1973), Manchon et al. (1970), Sobotta et al. (1992), Hao et al. (1999), Wetzel et al. (1996), Mirjalili et al. (1996, 1998) and Yu, Rowell and Lockwood (2004) research groups. Besides that, there are numerous polarized IR ellipsometry (IRE) measurements on GaN thin films, however, the interpretation of the spectra and the ways to extract the lattice vibrational parameters are different as compared to typical polarized IR reflectance analysis. Thus, it will not be discussed here.

The early investigation of the GaN thin films (most probably of poor quality) by Barker and Ilegems (1973) and Manchon et al. (1970) resulted in the determination of the optical parameters with large uncertainty. Sobotta et al. (1992) measured GaN samples with crystallographic C -axis along the plane of the layers. Consequently, they were able to determine the optical parameters from the reflectivity spectra exactly for the polarizations perpendicular ($E \perp C$) and parallel ($E \parallel C$) to the C -axis. (It is important to note here that, the results obtained both in this study and in all the IR studies quoted here are different from Sobotta et al. (1992) because the GaN samples with the C -axis oriented along the growth direction have been used.) Hao et al. (1999) had studied on the polarized transmission and reflection measurements of bulk GaN, but their analyses were mainly on the determinations of absorption coefficient and refractive index. Wetzel et al. (1996) studied the polarized IR reflection of heterostructures of GaN and AlGaIn thin films with AlN buffer layers. However, their studies were mainly

focused on the LO phonon modes of the GaN and AlN. Polarized IR measurements of GaN films with various structures, which were deposited on various substrates, were reported by Mirjalili et al. (1996, 1998). However, as commented by Huo et al. (1999), the simulated spectra do not exactly fit the experiment well enough. For Yu, Rowell and Lockwood (2004), a study was done on the polarized IR reflection of GaN epilayer grown on sapphire substrate at three different angles of incidence (18° , 45° and 75°). Their studies were mainly focused on the fitting of numerical first differential reflectance by using a factorized model of dielectric constant and more attention was paid to the sapphire. For GaN thin films on sapphire, they were unable to observe and fix the $A_1(\text{TO})$ phonon mode (as quoted by the authors); hence, an $A_1(\text{TO})$ mode with a large uncertainty was obtained.

Commonly, all these polarized IR studies are able to determine a set of TO (\perp and \parallel) and LO (\perp and \parallel) phonon modes for both $E \perp C$ and $E \parallel C$. Principally, the TO_\perp and the LO_\parallel are first obtained from the best fits of the theoretical model to the experimental curve, then Lyddane-Sachs-Teller (LST) relation (Lyddane, Sachs and Teller, 1941) is applied to calculate the corresponding LO_\perp and TO_\parallel . Up to now, good agreement has been obtained between these reported results and there are no doubts about the reported results. However, it seems that the fundamental principle of the IR phonon coupling has not been taken into consideration. It is well known for typical IR measurements that the wave-vector (q) of the radiation may be taken as zero ($q = 0$). This is often referred to as the “long-wavelength limit” or “zone-centre” approximation (Houghton and Smith, 1966; Moller and Rothschild, 1971). Consequently, the optical phonon modes that can be detected are those coming from the BZ centre only, namely, the TO_\perp and the LO_\parallel ; while the BZ edge modes of LO_\perp and TO_\parallel are forbidden. Note that the condition $q = 0$ holds also for Raman scattering (Moller and Rothschild, 1971). As a result, there is a need to look into the details of the interpretation of the polarized IR reflectance spectra and the use of the LST equation for determinations of the LO_\perp

and the TO_{\parallel} phonon modes. Furthermore, through the in-depth studies, it is found that the origin of the transverse-optic (TO_{\parallel}) phonon mode in the p-polarized spectrum thus far is inappropriate. Based on Balkanski IR theory for thin films (Balkanski, 1972), Fresnel formulae for the oblique incidence polarized IR reflectivity, and vector analysis of the polarized IR incident beam, it can clearly confirm that this mode actually has the same origin as the TO mode in s-polarized spectrum and can be attributed to the TO_{\perp} optical phonon mode. A detailed discussion will be given in Chapter 5.

2.3 Overview on the characterization studies of $Al_xGa_{1-x}N$ semiconductor

As mentioned in Chapter 1, much of the works on the AlGaN alloys are devoted to the device applications. For the fundamental material properties, although there are a number of studies, it is found that there is no consensus among the literature results concerning the band gap energy bowing parameter b and the behaviour of the BZ optical phonon modes. For SPP mode of the $Al_xGa_{1-x}N$ semiconductor, the research in this field is still rare and has not received sufficient attention. This is even true for the case in GaN ($x = 0$) and AlN ($x = 1$). Therefore, in this section, a brief review of the above issues will be given. For simplicity, the discussion will be presented separately.

2.3.1 Band gap energy bowing parameter b

As mentioned in Chapter 1, a unique characteristic of AlGaN ternary alloy is its tuneable band gap energy, namely, ranging from 3.4 to 6.2 eV. Since a precise knowledge of the dependence of the band gap on the material composition is crucial

for band gap engineering in order to realize device applications; many studies on AlGa_xN have been devoted to the determination of band gap energy bowing parameter b . Note that the bowing parameter b represents the deviation from a linear interpolation between the two forming binary semiconductors. Detailed description of the bowing parameter b will be given in Chapter 3.

Up to now, a number of investigations (experimental or theoretical) have been carried out to determine the values of the bowing parameter of Al_xGa_{1-x}N alloy. An overview of these studies is summarized in Table 2.1. In spite of huge efforts, a consensus concerning the bowing parameter value is not yet reached owing to the results obtained by different researchers are quite diverging, as shown in Fig. 2.1. Nevertheless, the bowing parameter values reported are in the range of -0.8 to +1.56 eV, as evident from Table 2.1.

In order to explain the uncertainties of these bowing parameter values, many explanations have been proposed. It is supposed that the uncertainties are stemming from the uncertainties and peculiarities of the various techniques used to grow and to measure the band gap energy as well as to determine the alloy composition of the Al_xGa_{1-x}N alloys (Ozgun et al., 2001; Ochalski et al., 1999; Teofilov et al., 2002). In other words, the derivations of b seem to be technique-dependent.

In addition, it is found that the derivations of b seem to be also growth dependent, which is a consequence of variations in growth conditions. Correlation between the measured band gaps and the methods used for epitaxial growth of the AlGa_xN has been investigated by Lee et al. (1999). They have found that directly nucleated or buffer growths of AlGa_xN initiated on sapphire at temperatures $T > 800^{\circ}\text{C}$ usually lead to stronger apparent bowing ($b > 1.3$ eV); while growths initiated using low-temperature buffers on sapphire, followed by high-temperature, lead to weaker bowing ($b < +1.3$ eV).

Table 2.1: Bowing parameter b for energy band gap E_g of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films.

Type of study	Composition measurement	Al content, x	Thickness (μm)	Growth technique	E_g measurement	Strain state	Bowing parameter, b (eV)	Reference
Experimental	IMS, RBS and XRD	$0 \leq x \leq 1$	$\sim 0.15, \sim 0.8$	MBE	LT PR	Strained	1.0	Yun et al., 2002
	XRD	$0.4 < x < 1$	$0.66 - 0.82$	PA-MBE	Optical trans.	Strained	0.75	Fedler et al., 2002
	XRD	$0 \leq x \leq 1$	$0.65 - 2.0$	RF-PE-MBE	LT PR and CL	NA	0.91 ± 0.14	Teofilov et al., 2002
	EPMA and XRD	$0 \leq x \leq 1$	$0.2 - 1.1$	GS-MBE	PR	NA	1.56	Holtz et al., 2001
	XRD	$0 \leq x \leq 1$	$0.5 - 2.0$	MBE	Opt. ABS	NA	1.08	Ozgur et al., 2001
	XRD and EDS	$0 \leq x \leq 1$	$0.25 - 5$	MOCVD	UV-VIS trans.	Relaxed	1.38	Katz et al., 2001
	NA	$0 \leq x \leq 0.66$	$0.4 - 1.5$	GS-MBE	CL	NA	1.5	Nikishin et al., 2000
	RBS	$0 \leq x \leq 1$	$0.1 - 1.0$	MOCVD	Opt. ABS	NA	1.33	Shan et al., 1999
	XRD and RBS	$0 \leq x \leq 0.45$	~ 1.0	MOCVD	PL	Strained	0.69	Lee et al., 1999
						Unstrained	0.62^a	
	NA	$0 \leq x \leq 0.76$	$0.35 - 0.65$	MOVPE	PL	NA	0.7	Meyer et al., 1999
	RHEED and XRD	$0 \leq x \leq 0.20$	NA	MOVPE	PR	NA	0	Ochalski et al., 1999

Table 2.1: (Continued).

Type of study	Composition measurement	Al content, x	Thickness (μm)	Growth technique	E_g measurement	Strain state	Bowing parameter, b (eV)	Reference
Experimental	XRD	$0 < x < 0.22$	$0.35 - 0.65$	MOVPE	PL	Strained	0.6	Steude et al., 1998
	NA	$0 \leq x \leq 1$	NA	ECR-MBE	SXA	NA	0	Duda et al., 1998
	XRD and ERDA	$0 \leq x \leq 1$	~ 1.0	PI-MBE	Opt. ABS	Strained	1.3	Angerer et al., 1997, Brunner et al., 1997
	XRD	$0 < x < 0.25$	$0.35 - 0.65$	MOVPE	ES	Strained	0.25	Takeuchi et al., 1997
	ERDA	$0 \leq x \leq 1$	$1.0 - 1.50$	MBE	UV-VIS trans.	Strained	1.3	Stutzmann et al., 1997
	XRD	$0 \leq x \leq 0.48$	$0.02 - 0.36$	LP-MOCVD	UV-VIS trans. and PDS	Strained	1.48	Ambacher et al., 1997
	EDS and XRD	$0 \leq x < 0.40$	$0.8 - 1.8$	LP-MOCVD	Opt. ABS	Relaxed	0	Wickenden et al., 1994
	EPMA and XRD	$0 \leq x \leq 0.40$	FM	MOVPE	Opt. ABS	NA	1.0	Koide et al., 1987
	XMA	$0 \leq x \leq 0.24$	FM	MOVPE	LT PL	NA	0.98	Khan et al., 1986
	EPMA	$0 \leq x \leq 1$	NA	MBE	Opt. Trans. and CL	NA	-0.8 ± 0.3	Yoshida, Misawa and Gonda, 1982

Table 2.1: (Continued).

Type of study	Composition measurement	Al content, x	Thickness (μm)	Growth technique	E_g measurement	Strain state	Bowing parameter, b (eV)	Reference	
Theoretical	Simulation (FPC)	$0 \leq x \leq 1$	-	-	Simulation	Relaxed	0.341 [#] 0.351 [*]	Liou et al., 2005	
	Simulation (EPP)	$0 \leq x \leq 1$	-	-	Simulation	Strained	0.44	Voznyy and Deibuk, 2004	
	Simulation (FP-LAPW)	$0 \leq x \leq 1$	-	-	Simulation	Relaxed	0.71	Drirdi et al., 2003	
	Simulation	$0 \leq x \leq 1$	-	-	Simulation	Relaxed	0.353	Kuo and Lin, 2002	
	VCA	$0 \leq x \leq 1$	-	-	Simulation	NA	-0.08	Goano et al., 2000	
	Simulation (FPLOC)	$0 \leq x \leq 1$	-	-	Simulation	Relaxed	0.56	Fritsch et al., 1999	
	LMTO	$0 \leq x \leq 1$	-	-	Simulation	NA	0.34	Schiffgaarde, Sher and Chen, 1997	
	Theoretical and experimental	XRD and LMPP	$0 \leq x \leq 1$	0.5 – 2.0	PD	ABS	Strained	0.609	Deibuk, Voznyy and Sletov, 2000

Table 2.1: (Continued).

NA – Information not available	MBE – Molecular beam epitaxy	#Obtained through numerical simulation for the nonlinear lattice constant
FM – Few microns.	GS-MBE – Gas-source MBE	
FPC – First principle calculation	PI-MBE – Plasma induced MBE	*Obtained through numerical simulation for the linear lattice constant
FP-LAPW – Full-potential linear augmented plane-wave calculations	PA-MBE – Plasma assisted MBE	
RBS – Rutherford backscattering spectroscopy	RF-PE-MBE – Radio frequency plasma enhanced MBE	
EPP – Empirical pseudopotential	ECR-MBE – Electron cyclotron resonance assisted MBE	^a intrinsic bowing of the unstrained AlGaIn which
VCA – Virtual crystal approximation approach	PD – Pyrolytic deposition	estimated by averaging fitted bowing parameters from
IMS – Ion mass spectroscopy	MOCVD – Metalorganic chemical vapour deposition	different measurements made on the AlGaIn layers.
LMPP – Local model pseudopotential	LP-MOCVD – Low pressure metalorganic chemical vapour deposition	
LMTO – Linear muffin-tin orbital	MOVPE – Metalorganic vapour phase epitaxy	
EDS – Energy dispersion spectroscopy		
UV-VIS trans. – UV-VIS transmission		
PDS – Photothermal deflection spectroscopy		
Opt. trans. – Optical transmittance		
LT PR. – Low temperature Photoreflectance		
LT PL – Low temperature photoluminescence		
PL – Photoluminescence		
EPM – Electron probe microanalysis		
ERDA – Elastic recoil detection analysis		
XMA – X-ray micro analyses		
SXA – Soft X-ray absorption		
RHEED – Reflection high-energy electron diffraction		
PR – Photoreflectance		
CL – Cathodoluminescence		
Opt. Abs – Optical absorption measurement		

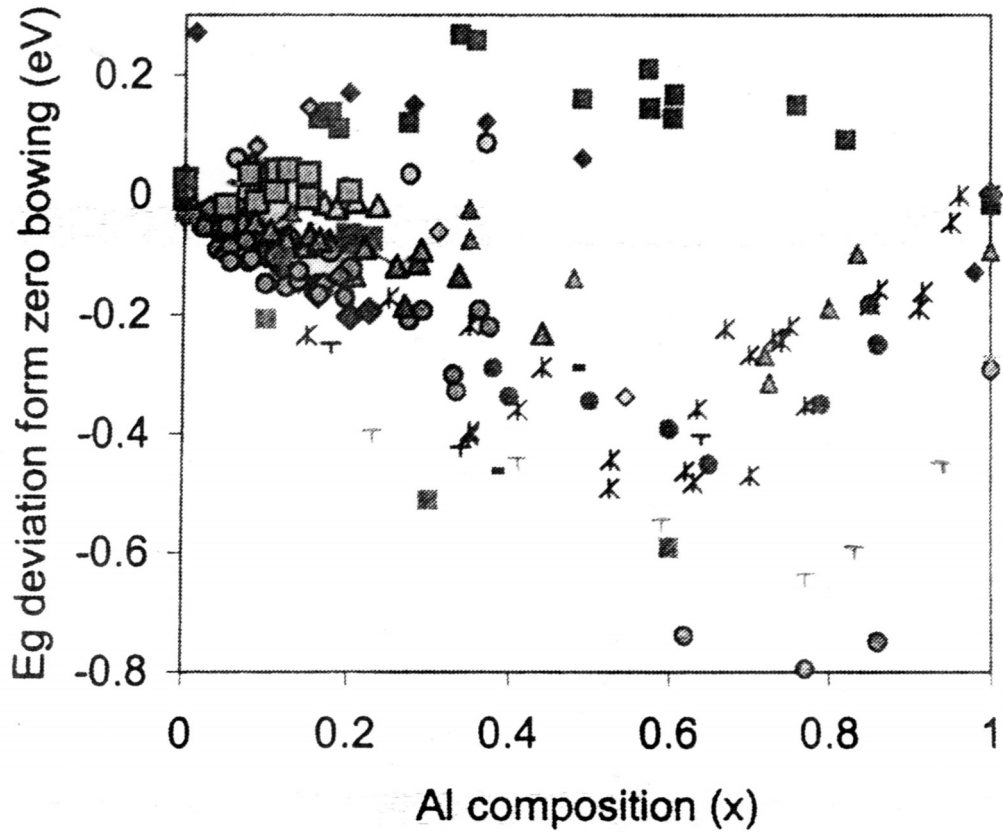


Fig. 2.1: Band gap energy of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) versus the deviation from the zero bowing. The symbols represent the experimental data (band gap energies) from published works. (Adapted from Yun et al., 2002.)

Besides that the dispersion of bowing parameters reported by various researchers is mostly emanating from the quality (e.g., strain, uniformity of the alloy composition, defects, etc.) of the AlGa_N samples (Shan et al., 1999; Katz et al., 2001; Yun et al., 2002). For instance, Vurgaftman, Meyer and Ram-Mohan (2001) have presented a brief review on the variation of band gap bowing parameter for AlGa_N thin films due to the strain.

Other factors that cause the uncertainties in the determination of the b value are the range of alloy compositions explored being narrow ($x < 0.5$), structural effect, i.e., the composition-induced disorder in the bond lengths (Ferhat, Furthmuller and Bechstedt, 2002), compositional inhomogeneities (Steude et al., 1999), concentration

of free carriers (Brunner et al., 1997), non-uniformity in the energy band gap (Koide et al., 1987) and uncertainty for band gap energy of its constituent binary materials (Dridi, Bouhafs and Ruterana, 2003). Again, despite these factors, the essential factor that affects the accuracy of bowing parameter value is still not yet definitely concluded.

To summarize, it is difficult to determine an absolute bowing value which is growth- and technique-dependent. Nevertheless, through a systematic study and the utilization of various independent methods in the determination of the composition and the energy band gap of the alloys, more reliable bowing parameter with wide consensus can be attained.

2.3.2 Brillouin zone (BZ) optical phonon modes

There have been many experimental and theoretical studies on the BZ optical phonon modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films. Basically, the behaviour and the composition dependence of the optical modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy are subjects of considerable theoretical and experimental research interest because it reflects the lattice vibration properties, disorder in atomic arrangements, electronic properties, carrier concentration, strain and atomic composition as well as homogeneity of the alloy (Harima, 2002). In some cases, behaviour of the Raman line width, particular the line width of the $E_2(\text{H})$ peak, of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ is of interest because such an investigation provides insight into the alloy microstructure (Bergman et al., 1997). An overview of literature results on the BZ optical phonon modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films is shown in Table 2.2.

Table 2.2: Optical phonon modes (in unit of cm^{-1}) for wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin films.

Method	Growth technique	Substrate (BL)	Thickness (μm)	Composition range	Phonon mode	Behaviour	Interpolation/Remark	Reference
Raman (RT and 100 K)	MBE	Sapphire (GaN)	0.5 ($0 < x < 0.5$)	$0 \leq x \leq 1$	$A_1(\text{LO})$ $E_1(\text{LO})$	OM OM	$A_1(\text{LO}) = 734 + 228x - 75x^2$ $E_1(\text{LO}) = 742 + 235x - 65x^2$	Davydov et al., 2002
	MOCVD	Sapphire ($\text{Al}_x\text{Ga}_{1-x}\text{N}$)	2.0 – 4.0	$0 < x < 0.5$	$E_2(\text{H})$	TM	GaN-like $A_1(\text{TO})$:	
	HVPE	Si (111) (No BL)	1.0 – 4.0	$0.5 < x < 1$	$E_1(\text{TO})$	TM	$A_1(\text{TO}) = 531.8 + 62.6x + 1.9x^2$	
$0.5 < x < 1$				$A_1(\text{TO})$	TM	GaN-like $E_2(\text{L})$:		
				$0.8 < x < 1$	$E_2(\text{L})$	TM	$E_2(\text{L}) = 142.8 + 29x + 14.5x^2$	
Raman	PA-MBE	Sapphire (15 nm GaN)	0.66 – 0.82	$0.4 < x < 1$	$A_1(\text{LO})$	OM	NA.	Fedler et al., 2002
					$A_1(\text{TO})$	TM		
					$E_1(\text{LO})$	TM		
					$E_2(\text{H})$	TM		
Raman	AMT ^a	-	-	$0 \leq x \leq 1$	$A_1(\text{LO})$	OM	$A_1(\text{LO}) = 729.1 + 349.6x - 186.9x^2$	Cao, et al., 2001
					$E_2(\text{H})$	TM		
Raman and FTIR	GS-MBE	Si(111)	0.2 – 1.1 (40 – 60 nm AlN)	$0 \leq x \leq 1$	$A_1(\text{LO})$	OM	NA.	Holtz et al., 2001
					$E_1(\text{LO})$	OM		
					$E_2(\text{H})$	TM		
					$A_1(\text{TO})$	TM		
					$E_1(\text{TO})$	TM		
Raman (RT and 100 K)	MBE	Sapphire (GaN)	0.5 ($0 < x < 0.5$)	$0 < x < 1$	$A_1(\text{TO})$	TM	GaN-like $A_1(\text{TO})$: $A_1(\text{TO}) = 532.5 + 58x + 55x^2$	Klochikhin et al., 2000
	MOCVD	Sapphire ($\text{Al}_x\text{Ga}_{1-x}\text{N}$)	2.0 – 4.0 ($0 < x < 0.5$)					
	HVPE	Si (111) (No BL)	1.0 – 4.0					
$0.5 < x < 1$								

Table 2.2: (Continued).

Method	Growth technique	Substrate (BL)	Thickness (μm)	Composition range	Phonon mode	Behaviour	Interpolation/Remark	Reference
IRES	MOVPE	Sapphire (AlN)	0.2 – 0.8	$0 \leq x \leq 1$	GaN-like	OM	NA.	Schubert et al., 1999
					$E_1(\text{TO})$			
					AlN-like	OM		
					$E_1(\text{TO})$	OM		
Raman	OMVPE	Sapphire (AlN)	~2.0	$0 \leq x \leq 0.84$	$A_1(\text{TO})$	OM	NA.	Demangeot et al., 1998b
					$A_1(\text{LO})$	OM		
					$E_1(\text{TO})$	OM		
					$E_2(\text{H})$	OM:		
						TM:		
FTIR	OMVPE	6H-SiC (80 nm AlN)	0.15 – 0.60	$0 \leq x \leq 1$	$E_1(\text{TO})$	TM	NA.	Wisniewskie et al., 1998
					$A_1(\text{LO})$	OM		
Raman	MOCVD	Sapphire (0.5 μm GaN)	~1.5	0, 0.07, 0.15 and 1.0	$A_1(\text{TO})$	OM	For $0 \leq x \leq 1$ $w(\text{Al}_x\text{Ga}_{1-x}\text{N}) \approx (1 + 0.220x)w(\text{GaN})$	Liu et al., 1998
					$A_1(\text{LO})$			
					$E_1(\text{TO})$			
					$E_1(\text{LO})$			
					$E_2(\text{H})$			
	-	Unable to detect any AlN-like $E_2(\text{H})$ mode in the composition range of study.						
Raman (RT)	MOVPE	Sapphire (AlN)	~2.0	$0 \leq x \leq 0.84$	$A_1(\text{LO})$ and $A_1(\text{TO})$	OM (Valid for $x > 0.05$)	NA.	Demangeot et al., 1997b
					E_2	TM		

Table 2.2: (Continued).

Method	Growth technique	Substrate (BL)	Thickness (μm)	Composition range	Phonon mode	Behaviour	Interpolation/Remark	Reference
Raman (300 K and 10 K)	OMCVD	6H-SiC (1000 Å AlN)	~2.0	$0 < x < 1$	$E_2(\text{H})$	OM	$\text{Al}_x\text{Ga}_{1-x}\text{N}$ of composition $x = 0, 0.06, 0.12, 0.22, 0.77$ and 1 are used.	Bergman et al., 1997
Raman	PE-MBE	Sapphire	~1.0	$0 \leq x \leq 1$	$A_1(\text{LO})$ $E_2(\text{H})$ $A_1(\text{TO})$	OM TM -	$A_1(\text{LO}) = 736.5 + 268.3x - 125.1x^2$ NA. Could not be clearly established	Cros et al., 1997b
Raman	PE-MBE MOCVD	Sapphire	0.5 – 1.0	$0 \leq x \leq 1$ $0 \leq x \leq 0.5$	$A_1(\text{LO})$ $A_1(\text{TO})$ $E_2(\text{H})$	OM OM TM	NA.	Cros et al., 1997a
Raman	MBE	Sapphire (No BL)	1.0 – 1.50	$0 \leq x \leq 1$	$A_1(\text{LO})$ $E_2(\text{H})$ $A_1(\text{TO})$	OM TM OM	NA.	Stutzmann et al., 1997
Raman	MOCVD	Sapphire (AlN)	Thick bulk-like layer	$0 \leq x \leq 0.15$	$A_1(\text{LO})$ $E_2(\text{H})$	OM -	NA. The peak become broader and no detectable frequency shift are observed.	Behr et al., 1997
FTIR	MOVPE	Sapphire (35 nm AlN)	1.0 – 1.2	0, 0.08, and 0.15	$A_1(\text{LO})$	OM	For $x \leq 0.08$	Wetzel et al., 1996
Raman	MOVPE	Sapphire (50 nm AlN)	2.0 – 12.0	$0 < x < 0.15$	$A_1(\text{TO})$ $E_1(\text{TO})$ $E_2(\text{H})$ $E_1(\text{LO})$	OM	NA.	Hayashi et al., 1991

Table 2.2 (Continued).

Method	Growth technique	Substrate (BL)	Thickness (μm)	Composition range	Phonon mode	Behaviour	Interpolation/Remark	Reference
Theoretical (MREI and RIM)	-	-	-	$0 \leq x \leq 1$	$E_1(\text{LO})$ and $A_1(\text{LO})$	OM	-	Grille, Schmittler and Bechstedt, 2000
	-	-	-		$E_1(\text{TO})$	TM	-	
	-	-	-		E_2 and $A_1(\text{TO})$	OM	-	
Theoretical (MREI) and experimental (Raman)				$0 \leq x \leq 1$	$A_1(\text{TO})$ and $A_1(\text{LO})$	OM		Liu, Bursill and Praver, 2001
					$E_1(\text{TO})$ and $E_1(\text{LO})$	OM		
					$E_2(\text{H})$	OM: TM:	Theoretical results. Experimental results.	

BL – Buffer layer.

RT – Room temperature

MOVPE – Metalorganic vapour phase epitaxy

MBE – Molecular beam epitaxy

MOCVD – Metalorganic chemical vapour deposition

HVPE – Hydride vapour phase epitaxy

OMCVD – Organometallic chemical vapour deposition

PE-MBE – Plasma-enhanced MBE

FTIR – Fourier transform infrared spectroscopy

GS-MBE – Gas-source MBE

PA-MBE – Plasma-assisted MBE

IRES – Infrared ellipsometry spectroscopy

MREI – Modified random-element isodisplacement

RIM – Rigid-iron model

OM – One mode behaviour

TM – Two modes behaviour

NA – Not available.

^aNanocrystalline solids with an average size of 40 nm are formed

In general, most of the studies are performed by using Raman methods. This is because Raman spectroscopy is a direct technique for the observation of optical phonons as compared to the IR and IRE spectroscopy. Unlike the Raman approaches, a fitting procedure is normally needed to extract the phonon frequencies from the IR and IRE spectra. The work of extraction may become complicated if the reststrahlen band (IR absorption band) of the concerning layer is superimposed with that from the underlying layer. Nevertheless, in some aspect, the IR or IRE spectroscopy is preferred than the Raman scattering. For instance, they are sensitive to the IR-active lattice vibration modes as compared to Raman scattering measurement.

There have been several reports/reviews on the behaviour and the composition dependence as well as the line width of the optical modes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy (Harima, 2002; Haboeck et al., 2003; Kuball, 2001; Wetzal and Akasaki, 1999). However, only a brief description is given because most of the attention is paid to its constituent materials, namely, the GaN and AlN. A comprehensive Raman scattering and theoretical study has been reported by Davydov et al. (2002) and Grille, Schnittler and Bechstedt (2000), respectively. Therefore, the following discussion mainly refers to the results given in the cited literature.

For wurtzite structures of GaN and AlN, there are six BZ centre optical phonon modes which are IR or Raman active, or active under both investigations, namely, $A_1(\text{TO})$, $A_1(\text{LO})$, $E_1(\text{TO})$, $E_1(\text{LO})$, $E_2(\text{L})$ and $E_2(\text{H})$. Like its parent, wurtzite structure AlGaN also consists of these sets of BZ centre optical phonon modes, however, the situation is more complicated. In some aspect (depends on the alloy composition), these optical phonons may exhibit either a “one-mode” (OM), a “two-mode” (TM) or a “mixed-mode” (MM) behaviour. Note that detail descriptions of the behaviour of these modes will be given in Chapter 3.

A general picture of the behaviour of some BZ centre optical phonon modes as a function of alloy composition has been obtained through the theoretical study by Grille, Schnittler and Bechstedt (2000), as shown in Fig. 2.2. The composition

dependence of the phonon frequencies of all the six BZ centre optical phonon modes of wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ obtained through the Raman scattering study by Davydov et al. (2002) is shown in Fig. 2.3. It is important to note here that Fig. 2.2 and Fig. 2.3 given here are used for reference purposes only, because there may be some discrepancies between these results.

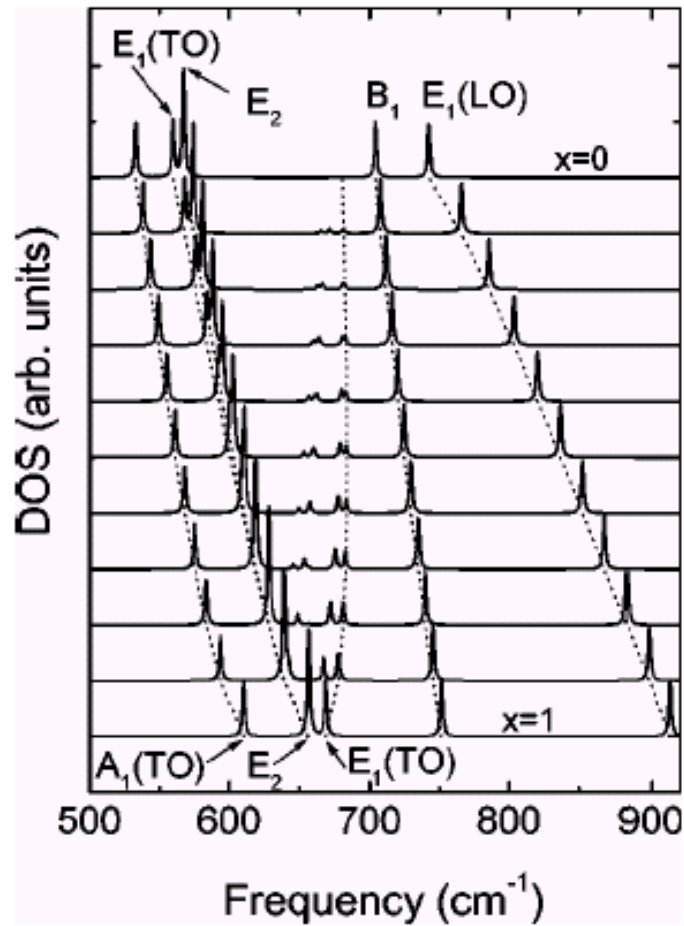


Fig. 2.2: Behaviour of the BZ centre phonons in wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ as a function of alloy composition with the phonon propagation direction perpendicular to the C -axis. The vertical axis represents the density of states (DOS) for the BZ centre phonons. (Adapted from Grille, Schnittler and Bechstedt, 2000.)

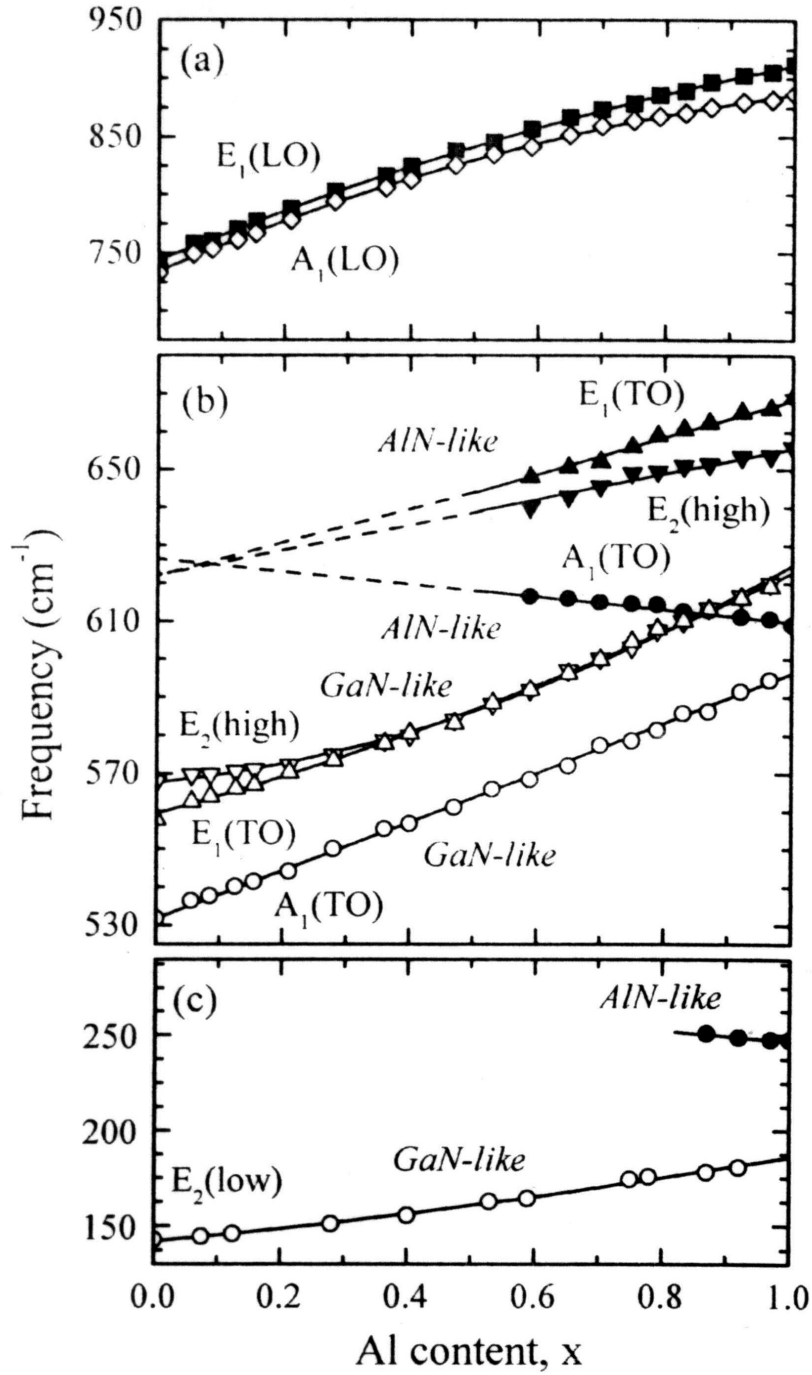


Fig. 2.3: Composition dependence of the BZ centre optical phonons in wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$. (Adapted from Davydov et al., 2002.)

Based on the literature results in Table 2.2 the behaviour of the BZ centre optical phonon modes of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys is evaluated and summarized in Table 2.3.

Table 2.3: An evaluation (based on the literature results) of the behaviour of the BZ centre optical phonon modes of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy over the entire composition range ($0 \leq x \leq 1$).

Phonon mode	Behaviour	Remark
$A_1(\text{TO})$	OM	<ul style="list-style-type: none"> ➤ No consensus is reached concerning the behaviour of this mode. ➤ This conclusion is made after considering the theoretical results.
$A_1(\text{LO})$	OM	➤ A consensus is reached in all the reported results.
$E_1(\text{TO})$	TM	➤ A broad consensus is reached.
$E_1(\text{LO})$	OM	➤ A broad consensus is reached.
$E_2(\text{L})$	TM	➤ There is only one reported result on this mode.
$E_2(\text{H})$	TM	➤ A broad consensus is reached.

OM – One-mode behaviour.
 TM – Two-mode behaviour.

For $A_1(\text{LO})$ mode, all the reported results reveal a OM behaviour. In contrast, the behaviour of the $A_1(\text{TO})$ mode still remains a controversial issue and is a subject of ongoing debate in the literature. This is because both OM and TM have been observed and no consensus is attained among the reported results. An explanation of this issue has not yet been reported. Note that the conclusion, of OM behaviour, is made after taking into account the theoretical results.

A broad consensus is reached between the literature results on the behaviour of the $E_1(\text{LO})$ and $E_1(\text{TO})$ modes, where OM and TM behaviour are, respectively, concluded. Last but not least, a TM behaviour for both $E_2(\text{L})$ and $E_2(\text{H})$ modes is deduced. It is interesting to point-out here that there is only one paper that reported the behaviour of the $E_2(\text{L})$ mode.

On the subject of the composition dependence equation of the optical phonon modes, it can be concluded from Table 2.2 that less attention is paid on this subject. Moreover, it is found that there are no consensuses between the reported results on the derived composition dependence equations.

Another subject of interest on the Raman scattering results of AlGa_N alloy is the behaviour of the Raman peak line width. An earlier Raman analysis on the $E_2(\text{H})$ mode

of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ by Bergman et al. (1997) revealed that the Raman line shape exhibit a significant asymmetric broadening for $x > 0.6$. This Raman line broadening is then attributed to the activation of phonons wave vector $q \geq 0$ arising from the disordered state of the alloys. In addition, they found that the maximum line broadening of the $E_2(\text{H})$ mode at composition $x \approx 0.5$ is an indicator for the disorder state. Cros et al. (1997b), however, observed a maximum line broadening at $x \approx 0.8$. This discrepancy arises most probably due to the difference in the samples quality.

Recently, the composition dependence of the Raman lines [$A_1(\text{TO})$, $A_1(\text{LO})$, $E_1(\text{TO})$, $E_1(\text{LO})$ and $E_2(\text{H})$] broadening has been investigated theoretically and experimentally by Davydov et al. (2002) and the results are shown in Fig. 2.4. They found that all the lines exhibit an asymmetry broadening with respect to the point $x = 0.5$, however, the asymmetric broadening pattern for the $A_1(\text{LO})$ and $E_1(\text{LO})$ modes is skewed to the left, while that for the $A_1(\text{TO})$ and $E_1(\text{TO})$ modes is skewed to the right. The line width of the $E_2(\text{H})$ mode has a less asymmetrical composition dependence. The alloy composition at which these lines exhibit a maximum line width are different, namely, at $x \approx 0.65$ to 0.7 for $A_1(\text{TO})$ and $E_1(\text{TO})$, $x \approx 0.35$ for $A_1(\text{LO})$ and $E_1(\text{LO})$, and $x \approx 0.75$ for $E_2(\text{H})$. However, no explanation is given on these phenomena. Hence, there is a need for more research on these phenomena.

From the brief review above, one can conclude that the behaviour and composition dependence as well as the line width of the BZ optical phonon modes (except the $A_1(\text{LO})$ mode) of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ is still unclear. More work is needed to address these issues.