Growth and characterization of AlGa_N/Ga_N HEMT heterostructures on 100-mm Si (111) by MBE

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Growth and characterization of AlGaN/GaN HEMT heterostructures on 100-mm Si (111) by MBE

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University in partial fulfillment of the requirement for
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2013

***To my late grandfather
Dr. Manoharlal Agrawal***

Ideal of the lily

Train yourselves in the ideal of the lily, which blossoms in the mud and has to keep itself engaged in the struggle for existence day in and day out, parrying, bracing and fighting the shocks of muddy water and the force of storms and squalls and various other vicissitudes of fortune; and yet it does not forget the moon above. It keeps its love for the moon constantly alive. It seems but a most ordinary flower: there is nothing extraordinary about it. Yet, this most ordinary little flower has a romantic tie with the great moon. It has focused all its desires on the moon. Similarly, perhaps you are an ordinary creature – perhaps you have to pass your days in the ups and downs of worldly existence – yet do not forget that Supreme One. Keep all your desires inclined towards Him. Always keep yourself merged in His thought. Go deep into the mood of that Infinite Love. By this your worldly activities will not be hampered in any way.

--Shrii Shrii Anandamurtiiji

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Abbreviations

2D	Two-dimensional
3D	Three-dimensional
2DEG	Two-dimensional electron gas
AFM	Atomic force microscopy
BEP	Beam equivalent pressure
BFM	Beam flux monitor
CBED	Convergent beam electron diffraction
CCD	Charge-coupled device
CL	Cathodoluminescence
CRT	Cathode-ray tube
DMS	Desorption mass spectroscopy
FIB	Focused ion beam
FWHM	Full width at half maximum
FE-SEM	Field emission scanning electron microscopy
HEMT	High electron mobility transistor
HNPS	High nitrogen pressure solution
HR-TEM	High resolution transmission electron microscopy
HR-XRD	High resolution X-ray diffraction
HVPE	Hydride vapor phase epitaxy
LED	Light emitting diode
MBE	Molecular beam epitaxy
MME	Metal modulated epitaxy
MOCVD	Metal organic chemical vapor deposition
PA-MBE	Plasma assisted molecular beam epitaxy
QMS	Quadruple mass spectrometer
RF	Radio frequency
RGA	Residual gas analyzer
RHEED	Reflection high energy electron diffraction
RMS	Root mean square
SEI	Secondary electron image
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectroscopy
TEC	Thermal expansion coefficient
TEM	Transmission electron microscopy

Abstract

III-nitride semiconductors have received significant research attention and undergone immense development due to their widely found applications in microelectronic and optoelectronic devices. Among them, GaN based materials promise great potential for high frequency, high power, and high temperature applications because of their excellent material properties such as wide band-gap, high break down field, high saturation velocity, and high electron mobility, mechanical and thermal stability. However, due to the unavailability of native substrates, GaN based materials are grown heteroepitaxially on foreign substrates such as SiC, sapphire and Si. Of these potential substrates, Si is a more preferred option on account of favorable factors such as low cost, large size and easy availability. Besides, Si is an excellent choice for microelectronics integration of GaN with its matured technology. However, the large lattice mismatch of $\sim 17\%$ and the thermal expansion coefficient (TEC) mismatch of $\sim 54\%$ are the major challenges in GaN growth on this substrate. In fact, thick GaN layers are needed to yield a device quality layer, which is particularly challenging to achieve on large diameter Si substrates due to high wafer bowing and cracking of the layers. This dissertation focuses on the growth optimization and characterization of AlGaN/GaN heterostructures on 100-mm Si (111) substrates for high electron mobility transistor (HEMT) applications using plasma assisted molecular beam epitaxy (PA-MBE) and ammonia MBE techniques.

In order to achieve AlGaN/GaN HEMTs on Si with good two-dimensional electron gas (2DEG) properties, the III/V ratio has been optimized to obtain smooth surface morphology, good crystalline quality and strain-free AlN and GaN layers in the intermediate growth regime by PA-MBE. The effect of III/V ratio on the polarity of AlN and GaN layers in the metal-rich growth regime has also been studied. Al metal flux is found to play a major role in controlling the polarity of AlN layers and hence, determining the polarity of the subsequent GaN layers, which in turn is essential for the development of the conventional Ga polar AlGaN/GaN HEMTs grown on Si (111). Due to the narrow growth window of PA-MBE, a bilayer based technique using in-situ reflection high energy electron diffraction (RHEED) is employed in order to obtain reproducible material properties of the GaN layers. A smooth surface morphology having a root mean square (RMS) roughness of ~ 1.0 nm is obtained for $5 \times 5 \mu\text{m}^2$ scan area. The screw dislocation density obtained is $4 \times 10^9 \text{ cm}^{-2}$ while the edge dislocation density ranges from 1.5 to $2.0 \times 10^{11} \text{ cm}^{-2}$. In addition, nearly relaxed and crack-free GaN layers with thicknesses up to $1.5 \mu\text{m}$ are obtained with a small

residual tensile strain of 0.02%. Further, AlGaIn/GaN HEMT heterostructures have been optimized to obtain the highest 2DEG mobility and sheet carrier density of 1100 cm²/V.s and 9×10^{12} cm⁻², respectively.

As mentioned above, the growth by PA-MBE technique provides narrow growth window making the precise control of III/V ratio difficult. Moreover, low cracking efficiency of the nitrogen molecule limits the growth rates to be low in the range of 0.1 to 0.4 $\mu\text{m/hr}$. This dissertation also discusses the growth of AlGaIn/GaN HEMT heterostructures by ammonia MBE, as it offers several advantages such as wider growth window, better uniformity, stable growth conditions and easy cracking of the ammonia molecule to produce active nitrogen for higher growth rates. Another advantage is the fact that metal-polar layers are always obtained in the ammonia rich growth conditions and hence are better suited for the growth of conventional Ga polar AlGaIn/GaN HEMT heterostructures. Unlike PA-MBE, the use of stress mitigating layers is necessary for the growth of thick GaN layers on Si by ammonia MBE. To address this, an in-depth study has been done on the growth of GaN layers using AlGaIn/AlN and AlN/GaN as stress mitigating layers on Si (111).

The structural properties of GaN grown on AlGaIn/AlN stress mitigating layers are assessed as a function of AlN thickness and AlGaIn growth temperature. GaN grown on thicker AlN shows reduced dislocation density and lesser tensile strain. Three-dimensional (3D) growth regime is observed for GaN grown at lower AlGaIn growth temperature while higher AlGaIn growth temperature results in two-dimensional (2D) growth mode. The origin of tensile strain in the GaN layers is also determined by comparing the experimentally and theoretically obtained strain values. The average plastic relaxation due to the dislocation looping and the tensile strain generated due to the grain coalescence are found to be the major factors influencing the strain states of GaN grown on AlGaIn/AlN stress mitigating layers. The growth of GaN layers using AlGaIn/AlN stress mitigating layers is found to have resulted in either 3D surface morphology or high threading dislocation density, both of which are detrimental for the 2DEG properties in AlGaIn/GaN HEMT heterostructures.

On the other hand, GaN grown using AlN/GaN as stress mitigating layers exhibit 2D growth mode and reduced threading dislocation density. The bending and looping of dislocations at the two subsequent AlN/GaN interfaces have been found to be the reason for the annihilation of the dislocations. In addition, high lattice mismatch induced compressive strain at the second AlN/GaN interface and the slow relaxation

process of the subsequently grown thick GaN layers are found to be effective in obtaining crack-free GaN. GaN layers are further improved by increasing the growth rate resulting in smoother surface morphology and compressively strained GaN layers. Crack-free buffer layers with thicknesses up to 1.7 μm were obtained with screw and edge dislocation density of 1.6×10^9 and $4.6 \times 10^{10} \text{ cm}^{-2}$, respectively. Subsequently, AlGaIn/GaN HEMT heterostructures using AlIn/GaN stress mitigating layers have been optimized to exhibit the highest 2DEG mobility and sheet carrier density values of $1350 \text{ cm}^2/\text{V.s}$ and $1.2 \times 10^{13} \text{ cm}^{-2}$, respectively.

1. Introduction

1.1 III-Nitrides

Silicon as a base for electronic devices is dominating the semiconductor industry due to its material properties and matured technology. III-arsenide and phosphide related materials and their alloys have also been developed for microelectronic and optoelectronic applications. However, these materials have limitations in areas which require devices operating at high temperature, high frequency and high power for electronic applications and wavelengths in green to ultra-violet regions for optoelectronic applications [1].

Fig. 1.1 shows the band gaps and the corresponding lattice constants of various popular semiconductors. The compound semiconductors such as AlN and GaN of III-nitrides and SiC with wider band gaps than those of Si, arsenides and phosphides are of interest as they allow operation at high temperatures and high breakdown fields [2]. On the other hand, the smaller lattice constants lead to stronger binding energy, and consequently higher chemical stability. The higher binding energy also leads to higher thermal conductivity and higher saturation drift velocity.

Fig. 1.1 The lattice constant versus band gap of various popular semiconductors.

Table 1.1 lists the physical properties of various semiconductors for the purpose of comparison. Even though GaAs and InP materials have high electron mobilities, they have disadvantages such as poor breakdown fields and thermal conductivity. Thus, GaAs or InP based devices remain unsuitable for high power applications. SiC

devices have high saturation drift velocity, breakdown fields and excellent thermal conductivity but SiC technology suffers from unavailability of large sized substrates, high material cost and complex processing. SiC also lacks heterojunction technology due to which the mobility of SiC based devices is significantly low. Moreover, SiC is an indirect band gap material which makes it unsuitable for optoelectronic applications.

Table 1.1 The physical properties of various semiconductors for comparison [3-5].

Material Properties	Si	GaAs	InP	6H-SiC	AlN	GaN	InN
Band gap (eV)	1.11	1.42	1.35	3.00	6.20	3.40	0.65
Electron mobility ($\text{cm}^2/\text{V.s}$)	1350	8500	5400	370	1100	900	4400
Relative dielectric constant	11.8	12.8	12.5	9.7	8.7	9.0	15.3
Breakdown electric field (MV/cm)	0.3	0.4	0.5	2.4	11.7	3.3	1.2
Saturated drift velocity ($\times 10^7$ cm/s)	1.0	2.0	1.0	2.0	1.8	2.5	4.2
Thermal conductivity (W/cm.K)	1.5	0.5	0.7	4.5	2.5	1.3	0.8

In III-nitrides, the breakdown field of GaN is about 10 times higher than those of Si and GaAs. The thermal conductivity of GaN is also higher than that of GaAs while comparable to that of Si. GaN has excellent transport properties with high saturated drift velocity of 2.5×10^7 cm/s at room temperature. AlN with the widest band gap in III-nitrides has been reported to have high surface acoustic wave velocity which makes it suitable to operate in the GHz range [6]. It also exhibits an interesting combination of high thermal conductivity and electrical insulation. Thus, AlN finds applications as a ceramic substrate for integrated circuits or as a heat sink in power electronics and also in solid state lighting technology [7]. Among III-nitrides, InN has the highest mobility of $4400 \text{ cm}^2/\text{V.s}$ at room temperature, which makes it an excellent semiconductor to fabricate electronic devices for extremely high speed applications [8]. III-nitrides and their alloys exhibit a broad range of band gaps from 0.65 eV for InN to 6.2eV for AlN. This enables flexible tailoring of the band gaps for wide optoelectronic applications.

III-nitrides also form heterostructures with its alloys such as GaN with AlGaN exhibiting an exciting development of 2DEG at the interface of the heterostructure for HEMT application. The development of GaN with AlInN lattice matched material system offers higher current densities, low access resistances and ultra-scaling of

HEMTs for high frequency and high power applications [9-13]. AlInN/AlN/GaN HEMTs fabricated using dielectric free passivation [11] and regrown ohmic contacts [12] have exhibited a high current gain cut-off frequency of 370 GHz [13]. Moreover, quaternary alloy barrier GaN based HEMTs such as AlInGaN/AlN/GaN display low sheet resistances [14] which would enable lower on resistances for switching devices. Ultrathin all-binary AlN/GaN HEMTs have also been realized for very low sheet resistances and high performances [15, 16].

In addition, heterostructures such as GaN with InGaN form quantum wells and quantum dots for efficient light emitting diode (LED) and laser diode operations [17-20]. InGaN with varying band gap provides almost a perfect fit for the solar spectrum allowing the design of multi-junction solar cells for photovoltaic applications [21]. The wider band gap over arsenides and phosphides utilizes higher energy photons for better conversion efficiency.

The growth of various semiconductors such as GaAs and InP has been performed on their respective bulk substrates in order to obtain device quality layers with dislocation density below 10^6 cm^{-2} . However, III-nitride based devices grown on Si substrates have demonstrated excellent performances for both electronics and optoelectronics applications in spite of the fact that the dislocation density in the layers is of the order 10^{10} cm^{-2} [22]. In contrast to the other semiconductors, the electrical and optical properties of the III-nitrides do not degrade even in the presence of high dislocation density. Thus, one of the major advantages of III-nitrides over other semiconductors is that they can be grown on Si substrates, which allow them to be integrated with the existing Si technology. Si based devices can also be fabricated for higher throughput and yield on the economically viable large sized Si wafers.

III-nitrides find wide applications in various domains which require technologies stable at high working temperatures and harsh environments such as automotive industries, rectifiers and converters for aerospace applications, petroleum industries etc. Their ability to operate at high frequencies make them suitable for wireless communication such as fixed wireless, mobile and satellite communication systems.

The high demand and need of high density read/write and optical storage technologies operating at short wavelengths is driving their development in the field of optical devices [1, 3, 23]. Blue and white LEDs, lasers for full color display, indicator lights, traffic signs and signals with a capability of bringing all three colors together

have made III-nitrides a popular material. With such vast applications, III-nitrides are definitely a lucrative choice to achieve any breakthrough in these domains which may not be possible using the existing Si and GaAs based semiconductor materials. Thus, research and development in the field of III-nitrides becomes indispensable.

1.2 Gallium nitride

Among III-nitrides, GaN and its alloys are emerging as promising compound semiconductors because of their unique electronic and optoelectronic properties. Owing to the potential of GaN based devices for a wide variety of applications, extensive research and developmental work has been carried out on their growth and processing. A better understanding about their properties will aid in developing appropriate growth and reliable process technologies for the fabrication of GaN based devices and circuits.

1.2.1 Crystal structure

III-nitrides exhibit two types of crystal structures, namely wurtzite (also known as hexagonal or α) and zinc blende (also known as cubic or β) structures. Under ambient conditions, wurtzite is a thermodynamically more stable structure than zinc blende for III-nitrides. A typical structure of wurtzite GaN is shown in Fig. 1.2. The main difference between the wurtzite and the zinc blende structures is the stacking sequence. The stacking sequence for the zinc blende structure is AaBbCc.... while that for wurtzite is AaBbAa.... The wurtzite structure has a hexagonal unit cell consisting of four atoms (space group $P6_3mc$) and thus two lattice constants, c and a . Ideally, wurtzite lattice constant relation is $c/a = \sqrt{8/3} = 1.633$ and internal parameter, $u = 3/8 = 0.375$. However, the ionicity of the III-nitrides lets the pair of anion and cation atoms to interact due to the electrostatic force between them. These electrostatic interactions make wurtzite structure more stable than the zinc blende structure and the c/a value to be smaller than the ideal value of 1.633 while u to be larger than 0.375.

Fig. 1.2 A stick and ball representation of a typical structure of wurtzite GaN.

Wurtzite GaN crystal can be cut into desired orientations for various device applications. Table 1.2 shows a list of polar, non-polar and semi-polar planes of wurtzite GaN.

Table 1.2 Various important crystal planes of wurtzite GaN along with their miller indices and polarity.

Plane	Index	Polarity
c	(0001)	polar
a	(11 $\bar{2}$ 0)	non-polar
m	(10 $\bar{1}$ 0)	non-polar
r	(1 $\bar{1}$ 02)	semi-polar

GaN was conventionally grown along c-plane to utilize the associated polarization for electronic applications. However, polarization induced fields have been found to limit optical device performances due to which fabrication of optical devices on non-polar and semi-polar GaN has garnered more attention [24]. More details on the polarization effects of GaN will be discussed in Section 1.2.3.

1.2.2 Physical and chemical properties

Some of the physical properties of GaN have been already discussed and listed in Table 1.1 (on page 2) for the purpose of comparison with various semiconductors. Other important properties are listed in Table 1.3. Unlike silicon, GaN has a high melting point which makes the bulk growth of GaN from the melt difficult. Moreover, it requires high nitrogen overpressures, an additional challenge in the bulk growth of GaN.

GaN is a highly stable compound exhibiting significant hardness. Its chemical stability along with the hardness due to its high binding energy of 2.22 eV makes it an attractive material for devices operating under hostile environments. Conversely, it also makes the semiconductor processing challenging. The traditional wet etching is not used in the device fabrication of GaN and its alloys as they remain insoluble in acids and bases. However, they do undergo etching in alkalis which is used to identify defects and determine the polarities. Various dry etching processes are, thus, promising possibilities for the technology development of GaN based devices.

Table 1.3 The physical properties of bulk GaN [25, 26].

Properties	Values
Lattice constant (Å)	a = 3.189, c = 5.185
Molecular weight (gmol ⁻¹)	83.7267
Density (g.cm ⁻³)	6.11
Melting point (°C)	2500
Linear expansion coefficients (×10 ⁻⁶) (K ⁻¹)	a: 5.59, c: 3.17
Refractive index	2.85
Young's modulus (GPa)	150
Optical phonon energy (meV)	91.8
Binding energy (eV)	2.22
Electron effective mass	0.22m ₀
Hole effective mass	1.0m ₀
Electron mobility (300K) (cm ² V ⁻¹ s ⁻¹)	~ 1000
Hole mobility (300K) (cm ² V ⁻¹ s ⁻¹)	<200

1.2.3 Electrical properties

GaN has been observed to be unintentionally n-type. Even in the strict grown conditions, the electron concentration is found to be $\sim 10^{16} \text{ cm}^{-3}$. It is attributed by Perlin et al. [27] to the nitrogen vacancies as dominant native defects which act as donors. They are of the opinion that N vacancies require low energy than Ga interstitial. Thus, it results in a difficult p-type doping situation which forms highly compensating or insulating GaN without the p-type conduction. Elements such as Cd, Zn, Be and Mg have been used as a p-type dopant in GaN. Among them, Mg has been established as a potential acceptor for the growth of p-type GaN as other elements either produced highly resistive GaN or too low hole concentration. However, the growth of GaN done in hydrogen environment requires post-growth Mg activation as hydrogen passivates Mg atoms and is thus removed by subsequent thermal annealing treatment [28] making GaN p-type conducting.

One of the fundamental characteristics of III-nitrides which differentiate it from the other well developed semiconductors, such as Si and GaAs, is the polarization effects. This feature is shown to influence carrier distributions, electric fields, and consequently a wide range of optical and electronic properties of nitride materials and devices [29]. The two types of polarization effects; spontaneous and piezoelectric polarization found in III-nitrides are discussed below.

(a) Spontaneous polarization

III-nitrides bonding constitutes N atom which is the smallest and most electronegative element in the group V. Moreover, the wurtzite III-nitride are non-centrosymmetric along the [0001] direction. The ionicity of the N atom leads to the displacement of the electron cloud towards one atom and the lack of inversion symmetry leads to a net positive charge at one face of the crystal and net negative charge at the other face. Thus, a strong macroscopic polarization along the [0001] direction exists and the crystal is “naturally” distorted. This polarization effect is known as spontaneous polarization since it is a non-vanishing effect in III-nitrides and occurs in their equilibrium lattice at zero strain. GaN exhibits highly pronounced polarization due to the lack of inversion symmetry with the surfaces having either a Ga-polarity with a designation of [0001] or an N-polarity with a designation of $[000\bar{1}]$. A stick and ball representation of Ga-polar and N-polar GaN wurtzite structure is depicted in Fig. 1.3 (a) and (b), respectively. As can be seen, the polarization depends on the arrangement of atoms along the c direction [0001]. When the bonds are from Ga (cation) to N (anion) atoms, the polarity is termed as Ga-polar marking the [0001]

direction while if the bonding is in the reverse direction, the polarity of GaN crystal is called as N-polarity along $[000\bar{1}]$ direction. The distinction between these two directions is essential in nitrides because of the implications of the polarity on the polarization charge [30].

Fig. 1.3 A stick and ball representation of (a) Ga-polar and (b) N-polar GaN.

(b) Piezoelectric polarization:

When III-nitrides are subjected to an external strain, the distortion in the crystal is reflected in the polarization effect. Thus, this polarization is called strain induced or piezoelectric polarization. The piezoelectric effect is due to two reasons:

- (i) Lattice mismatch strain (misfit)
- (ii) Thermal strain (TEC difference between the substrate and the epitaxial layers)

The piezoelectric constant of III-nitrides is about 5-20 times larger compared to the arsenides. The importance of the piezoelectric polarization effect is utilized in pseudomorphic AlGaIn/GaN based HEMT heterostructures. The polarization induced fields significantly influence the distribution of charge carriers and has also been found to impact the performance of InGaIn/GaN based optoelectronic devices [31, 32]. Highly insulating buffers have also been achieved by exploiting the high polarization fields in III-nitrides without any external doping [33].

1.3 Formation of 2DEG

The polarization effects play a major role in determining the electrical properties of the heterojunction devices, such as AlGaIn/GaN HEMTs. As shown in Fig. 1.4, the polarization charges exist at the (hetero)interfaces of such devices and lead to the generation of polarization induced charge carriers.

Fig. 1.4 The schematic diagram of AlGaIn/GaN heterostructure showing the polarization charges and the 2DEG formation.

The band diagram of a typical AlGaIn/GaN heterostructure is shown in Fig. 1.5. An undoped AlGaIn barrier layer with a wider band gap lies on top of GaN material which results in a high electron concentration formed in the quantum well at the AlGaIn/GaN interface.

Fig. 1.5 The band diagram of AlGaIn/GaN heterostructure showing the quantum well and the 2DEG formation.

The electron “gas” is free to move in two dimensions of the quantum well while tightly confined in the third and is called as 2DEG. A 2DEG formation is possible only if the Fermi level passes through the quantum well and the AlGaIn/GaN band offset (ΔE_c) is sufficiently high. The charges due to both spontaneous and piezoelectric polarization can induce 2DEG (Fig. 1.4) with a sheet carrier density in the order of 10^{13} cm^{-2} at the AlGaIn/GaN interface without any doping. Thus, it becomes interesting to study the

role of these polarization effects in inducing 2DEG at the interface in the absence of any doping.

The non-ideality of the crystal structure increases from GaN to AlN due to the structural differences. Considering the growth of AlGaIn/GaN HEMT along the c-axis, the spontaneous polarization (P_{SP}) of GaN is -0.029 Cm^{-2} while that for AlGaIn barrier layer with Al mole fraction of x is given by:

$$P_{SP}(x) = (-0.052x - 0.029) \text{Cm}^{-2} \quad \text{Eq. 1.1}$$

In AlGaIn/GaN HEMT heterostructures, AlGaIn has less relaxed lattice constant than GaN. Since the underlying GaN layer is nominally relaxed and the AlGaIn layer is under an equibiaxial tensile strain, there will be an additional lattice mismatch induced piezoelectric polarization (P_{PE}) in the AlGaIn barrier layer. The piezoelectric polarization is given by:

$$P_{PE}(x) = e_{33}\varepsilon_z + e_{31}(\varepsilon_x + \varepsilon_y) \quad \text{Eq. 1.2}$$

where, e_{33} and e_{31} are the piezoelectric coefficients, $\varepsilon_z = (c_{meas} - c_0)/c_0$ is the out-of-plane strain (along c axis) while $\varepsilon_x = \varepsilon_y = (a_{meas} - a_0)/a_0$ is the in-plane strain, assumed to be isotropic.

The out-of-plane and the in-plane strains are related using:

$$\varepsilon_z = -(2C_{13}/C_{33})\varepsilon_x \quad \text{Eq. 1.3}$$

where, c_{meas} and a_{meas} are the measured lattice parameters, c_0 and a_0 are the relaxed lattice constants, and C_{13} and C_{33} are the components of the elastic stiffness tensor.

Thus, combining Eq. 1.2 and Eq. 1.3, the piezoelectric polarization can be represented as:

$$P_{PE} = (2a_{meas} - a_0)/a_0(e_{31} - e_{33}(C_{13}/C_{33})) \quad \text{Eq. 1.4}$$

Table 1.4 lists the physical constants for the AlN, GaN and InN. As can be seen from the table, the spontaneous polarization of III-nitrides is negative. Moreover, e_{31} is negative while e_{33} , C_{13} and C_{33} are positive. This indicates that the term within brackets of Eq. 1.4 will always be negative. Thus, piezoelectric polarization will be negative for epilayers under tensile strain and positive for epilayers under compressive strain. As shown in Fig. 1.6 (a) and (b), the spontaneous and piezoelectric polarizations are parallel to each other in the same direction for the layers under tensile strain while anti-parallel for the layers under compressive strain, respectively.

Table 1.4 List of physical constants for AlN, GaN and InN.

Constants	AlN	GaN	InN
P_{PE} (Cm ⁻²)	-0.081	-0.029	-0.032
e_{33} (Cm ⁻²)	1.46	0.73	0.97
e_{31} (Cm ⁻²)	-0.6	-0.49	-0.57
C_{13} (GPa)	108	103	92
C_{33} (GPa)	373	405	224
a_0 (Å)	3.112	3.189	3.540

The piezoelectric polarization for AlGaIn barrier layer with x Al mole fraction is calculated by following the linear interpolations of the physical properties between AlN and GaN [34].

Lattice constant:

$$a_0(x) = (-0.077x + 3.189)10^{-10}\text{m} \quad \text{Eq. 1.5}$$

Elastic constants:

$$C_{13}(x) = (5x + 103) \text{ GPa} \quad \text{Eq. 1.6}$$

$$C_{33}(x) = (-32x + 405) \text{ GPa} \quad \text{Eq. 1.7}$$

Piezoelectric constants:

$$e_{31}(x) = (-0.11x - 0.49) \text{ Cm}^{-2} \quad \text{Eq. 1.8}$$

$$e_{33}(x) = (0.73x + 0.73) \text{ Cm}^{-2} \quad \text{Eq. 1.9}$$

As the Al mole fraction x in the AlGaN barrier layer increases, the lattice constant given in Eq. 1.5 decreases. Thus, the piezoelectric polarization will also increase with the increasing Al mole fraction. The polarization induces a sheet carrier density given by:

$$\begin{aligned}\sigma_{POL} &= P(\text{bottom}) - P(\text{top}) \\ &= \{P_{SP}(\text{bottom}) + P_{PE}(\text{bottom})\} - \{P_{SP}(\text{top}) + P_{PE}(\text{top})\}\end{aligned}\quad \text{Eq. 1.10}$$

The piezoelectric polarization of GaN is zero if it is fully relaxed. Thus, equation 1.10 can be rewritten as:

$$\begin{aligned}\sigma_{POL} &= P(\text{bottom}) - P(\text{top}) \\ &= P_{SP}(\text{bottom}) - \{P_{SP}(\text{top}) + P_{PE}(\text{top})\}\end{aligned}\quad \text{Eq. 1.11}$$

Fig. 1.6 The directions of spontaneous and piezoelectric polarization in tensile and compressively strained layers.

As shown in Fig. 1.7, the polarization induced sheet carrier density is positive and increases with the increasing Al content. Thus, electrons will compensate the positive sheet of charges and form a 2DEG with concentration n_s given as:

$$n_s(x) = +\sigma(x)/e - (\epsilon_0 \epsilon(x)/de^2) (e\phi_b(x) + E_F(x) - \Delta E_C(x)) \quad \text{Eq. 1.12}$$

where, ε is the relative dielectric constant of AlGaIn, d is the barrier layer thickness, $e\phi_b$ is the Schottky-barrier of a gate contact and E_F is the Fermi level with respect to GaN conduction band energy. For AlGaIn barrier layer with x Al mole fraction,

AlGaIn relative dielectric constant:

$$\varepsilon(x) = -0.5x + 9.5 \quad \text{Eq. 1.13}$$

Schottky barrier height:

$$e\phi_b(x) = (1.3x + 0.84)\text{eV} \quad \text{Eq. 1.14}$$

Fig. 1.7 Polarization induced sheet charge density at the AlGaIn/GaN interface as a function of the Al content.

Ibbetson et al. [35] have shown that donor like surface states are the source of 2DEG at the AlGaIn/GaN interface. The donor like states are neutral when filled while positive when empty. As shown in Fig. 1.8, if the surface state donor level (E_D) below the conduction band edge is sufficiently deep that it lies below E_F then there will not be any 2DEG. However, $(E_F - E_D)$ reduces with increasing barrier layer thickness. Eventually, E_D approaches E_F at a critical thickness d_{CR} and the electron transfer occur from the surface to the empty states in the conduction band of the interface. Thus, more electrons are transferred with the increasing barrier layer thickness to form 2DEG at the AlGaIn/GaN interface while positive charges are left behind on the surface.

Fig. 1.8 The band diagram of AlGaIn/GaN heterostructure showing the surface donor state (E_D) below the Fermi level (E_F).

The critical thickness d_{CR} is given as:

$$d_{CR} = (E_D - \Delta E_C) \varepsilon / q \sigma_{POL} \quad \text{Eq. 1.15}$$

The 2DEG sheet carrier density as a function of barrier thickness is given as:

$$n_s = \sigma_{POL} (1 - d_{CR}/d) \quad \text{Eq. 1.16}$$

Thus, combining Eq. 1.12 and Eq. 1.16, the 2DEG sheet carrier density can be rewritten as:

$$n_s(x) = +\sigma_{POL}(x) (1 - d_{CR}/d) / e - (\varepsilon_0 \varepsilon(x) / d e^2) (e \phi_b(x) + E_F(x) - \Delta E_C(x)) \quad \text{Eq. 1.17}$$

The source of the surface donors has been widely investigated and many reports have been made on its cause. The surface donors could be intrinsic (ex. dangling bonds) or extrinsic due to nitrogen vacancies and residual impurities.

1.4 Growth of AlGaIn/GaN HEMT heterostructure: Challenges

The ability of AlGaIn/GaN HEMTs to achieve 2DEG without intentional doping due to the strong polarization effect and surface states makes it a promising candidate for high voltage, high power and high frequency applications. However, due to the unavailability of native substrates at low cost, GaN based heterostructures are grown epitaxially on foreign substrates such as sapphire, SiC and Si. Among them, Si has attracted a lot of attention because of its low cost, easy availability in large wafer sizes (up to 12 in. diameter) and the potential integration of GaN based devices with matured Si technology. However, high lattice mismatch of ~ 17% and high thermal

mismatch of $\sim 54\%$ are the major challenges for GaN growth on Si. The former generates high density of threading dislocations which has been found to scatter the electrons at the AlGaIn/GaN interface thereby reducing 2DEG mobility and also causes current leakage in HEMT devices [36]. The high thermal mismatch between GaN and Si leads to tensile strain in GaN during post growth cooling which particularly exacerbates on large diameter wafers causing high wafer bowing and cracking of the epilayers [37, 38]. Moreover, the variations in the interface roughness or Al content may further influence the characteristics of the 2DEG.

Therefore, AlGaIn/GaN growths on Si substrate have been optimized extensively using both metal organic chemical vapor deposition (MOCVD) and MBE techniques. MOCVD can produce GaN layers with high growth rates. However, MBE offers several advantages such as in-situ diagnostic techniques, atomically sharp and good quality interfaces, carbon free growth environment and a capability of low temperature growths. GaN based HEMT heterostructures have been demonstrated on 50-mm SiC using PA-MBE and ammonia MBE [39-41] and 50-mm Si by ammonia MBE [42]. However, AlGaIn/GaN HEMT heterostructures on 100-mm Si (111) using MBE growth technique have not been reported. Thus, the primary goal of this dissertation is the development of AlGaIn/GaN HEMT heterostructures on 100-mm Si (111) by PA-MBE and ammonia MBE growth techniques.

1.5 Objectives

The following objectives have been set to achieve the goal of the development of AlGaIn/GaN HEMT heterostructures on 100-mm Si (111) by PA-MBE and ammonia MBE growth techniques.

PA-MBE:

1. Study the effect of III/V ratio on the surface morphology, structural and electrical properties of AlN and GaN layers on Si (111) and growth optimization to achieve layers with smooth surface morphology, low dislocation density and low residual tensile strain.
2. Study the effect of III/V ratio on the polarity of AlN and GaN layers.
3. Study the growth kinetics of GaN using in-situ RHEED.
4. Optimization of the growth parameters to obtain high quality and reproducible AlGaIn/GaN HEMT heterostructures.

Ammonia MBE:

1. Study the cracking behavior of ammonia to understand the growth mechanism of AlN and GaN layers.
2. Optimization of growth parameters such as growth rate and substrate temperature to obtain AlN and GaN layers with smooth surface morphology, low dislocation density and low residual tensile strain.
3. Study the effect of different stress mitigating layers on the surface morphology and structural properties of GaN layers.
4. Optimization of the growth parameters to obtain high quality and reproducible AlGaIn/GaN HEMT heterostructures.

1.6 Organization of dissertation

This dissertation focuses on the growth and characterization of AlGaIn/GaN HEMT heterostructures on 100-mm Si (111).

Chapter 2 gives a research background on the growth of AlGaIn/GaN HEMT heterostructures. A brief description on the bulk growth methods of GaN is followed by a section on the foreign substrates such as sapphire, SiC and Si (111) used for the heteroepitaxial growth of GaN. Various growth techniques for the growth of AlGaIn/GaN HEMTs on foreign substrates are primarily discussed in this chapter.

Chapter 3 describes the growth technique and the characterization techniques used for the development of AlGaIn/GaN HEMT heterostructures on 100-mm Si (111) substrate.

Chapter 4 discusses the growth of AlGaIn/GaN HEMT heterostructures by PA-MBE technique. The III/V ratio is optimized to obtain AlN and GaN layers with smooth surface morphology, good crystalline quality and low residual tensile strain. In-situ RHEED is employed to obtain reproducible GaN material properties. AlGaIn barrier layer is optimized and AlGaIn/GaN HEMT is demonstrated with good 2DEG properties.

In Chapter 5, the growth of AlN and GaN layers performed using ammonia MBE technique is discussed. The growth rate and growth temperature are optimized for AlN and GaN layers. AlGaIn/AlN and AlN/GaN stress mitigating layers are investigated to alleviate the thermal mismatch induced tensile strain and obtain crack-

free GaN with smooth surface morphology and good crystalline quality. The material properties of GaN layers such as dislocation density, surface morphology and strain states using both AlGaN/AlN and AlN/GaN stress mitigating layers are compared in order to determine the suitable stress mitigating layers for the growth of AlGaN/GaN HEMT heterostructures on 100-mm Si (111).

Chapter 6 discusses the improvement in the surface morphology, dislocation density and strain states of the GaN layers. The effect of growth rate of the GaN layer in AlN/GaN stress mitigating layers on the subsequently grown thick GaN is investigated. This is followed by the optimization of the AlGaN barrier layer for the growth of AlGaN/GaN HEMT heterostructures with good 2DEG properties.

Chapter 7 gives the conclusions of this dissertation and an outlook for prospective future work.

2. Growth of AlGaIn/GaN HEMT heterostructure: Status

2.1 Bulk growth of gallium nitride

The fabrication of devices based on semiconductors such as silicon, SiC, GaAs and InP are realized on their respective bulk substrates. Bulk substrate is generally the best choice for epitaxy and obtaining good device performance. However, in the case of GaN, the traditional bulk growth to obtain large sized crystal or ingot is difficult as it requires very high nitrogen overpressures of 14000 atm and high temperatures of 2500 °C [43, 44]. Nonetheless, the need for improving the performance of GaN based devices by fabricating them on native substrates has led to recent advances in the research of growing GaN bulk crystals. In the past decade, many methods to achieve high quality, scalable and cost-effective GaN crystals have been developed.

Among several methods of GaN bulk growth, ammonothermal growth technique [45] is a promising candidate to achieve low cost wafers, due to its excellent scalability as it offers multiple seeded growth in a single run [46]. It is a solvothermal process in which the polycrystalline nitrides or feedstock are made soluble in supercritical ammonia under high pressure. The dissolved material is transported to the seed crystals for re-crystallization. The transport of the material is done from high to low temperature zones. In general, ammonothermal growth technique is associated with low growth rate capacity, but the recent technological developments have achieved greater than 40 $\mu\text{m/hr}$ GaN growth rate with diameters up to 2 in. and thicknesses up to 3 mm in various orientations such as c-plane, semi-polar and non-polar planes [47]. Significant efforts are still being made to overcome issues such as metal (mineral) contamination of GaN due to the corrosion of autoclave, oxygen impurity due to the moisture absorption of ammonia [48], unintentional high background carrier density in the order of 10^{18} cm^{-3} [49] and relatively smaller size of GaN crystals.

The growth of GaN crystals from the solution of nitrogen in liquid gallium under high nitrogen pressures has also been performed. These growths, known as high nitrogen pressure solution (HNPS) growth, are performed in ~ 20 kbar and temperatures of ~ 1750 °C [50]. The biggest advantage of a HNPS grown GaN crystal is that it is almost dislocation free $\sim 10^2 \text{ cm}^{-2}$ [51]. GaN crystal growth performed without the use of any seed result in anisotropic growth leading to hexagonal platelet formation. The crystals could be grown in a more stable way using the platelets as the seed for the

growth. Seeded growth using GaN/sapphire template by MOCVD technique has been performed as well. The dislocation density reduced from 10^9 cm^{-2} in the GaN template to 10^7 cm^{-2} in the HNPS grown GaN [52]. Being one of the “truly” bulk growth techniques, HNPS has its own shortcomings. Firstly, combating oxygen contamination is necessary since it leads to the formation of parasitic gallium oxide. Secondly, the apparatus supporting such high temperatures and pressures are very limited and expensive. Thus, scaling of the GaN crystals requires infrastructure expansion together with controlled growth parameters over large areas of growth.

Another alternate growth approach using solution of sodium was suggested by Yamane et al. [53] in 1998. The GaN crystal using this method could be grown at a relatively low nitrogen pressure of < 50 atm and a moderate temperature range of 500 to 900 °C using a very simple set up. There are basically two processes of obtaining bulk growth of GaN from sodium flux. One of the processes utilizes the growth of bulk GaN crystal on a seed grown by vapor phase method and the other process uses the seed GaN crystal obtained by spontaneous nucleation [54]. Kawamura et al. [55] used the liquid phase epitaxy technique in a sodium flux for the growth of GaN using MOCVD grown GaN as a homsubstrate. Growth rates of up to 20 $\mu\text{m/hr}$ were obtained with a boule thickness of 3 mm. GaN crystals have been obtained using the process of spontaneous nucleation by doping carbon in the solution and thereby preventing undesired nucleation other than the seed. So far, the growth of GaN bulk crystals by sodium flux method is limited by the slow growth rate of a few microns per hour. Moreover, the diffusion of nitrogen through the Ga melt makes it difficult to obtain homogenous growth over large areas.

Hydride vapor phase epitaxy (HVPE) is found to be one of the practical methods to obtain thick GaN layers [56, 57]. The high growth rates of HVPE have established it as a quasi-bulk technique. Thick films can be grown on the sapphire substrate which can be removed using techniques such as substrate polishing, laser induced thermal decomposition, void assisted method or facet controlled epitaxial growth [58-60]. The subsequently obtained GaN can be used as a free standing substrate or as a seed for the growth of bulk GaN by other methods [61]. However, the major challenge in bulk growth by HVPE is the significant bowing of GaN upon separation from the substrate and the limited boule length. The strong bowing of the wafer is a limitation in the device fabrication process and causes inhomogeneties in the temperature profile when used as a substrate for the subsequent epitaxial growth. The surface degradation is found to occur for boules grown for longer lengths [62].

Among all the growth techniques discussed, HVPE is the most developed method of bulk GaN growth. Although the GaN bulk obtained using this technique is not “truly” bulk, the thick GaN templates grown using this technique are being used for laser diode production. Other techniques are still in the developmental stage and require substantial improvement to obtain large sized GaN crystals with reduced impurities. The bulk growth, thus, is still lacking in the doping technology and wafer preparation procedures for bigger GaN crystals.

2.2 Substrate issues

Despite the extensive ongoing research on the production of native substrates, they are still available in small sizes only and are extremely expensive. Therefore, III-nitrides are grown heteroepitaxially on foreign substrates such as sapphire, SiC, Si, LiGaO₂ and GaAs. Among them, sapphire, SiC and Si have been widely used to develop GaN technology. A comparative list of properties of these substrates is shown in Table 2.1. Sapphire has a lattice mismatch of 15% which has resulted in a dislocation density of 10^{10} cm^{-2} in the epitaxially grown GaN.

Table 2.1 Comparison of the properties of various substrates used for epitaxial growth of GaN.

Properties	Sapphire	6H-SiC	Si (111)	GaN
Lattice constant, a (Å)	4.785	3.081	3.846	3.189
Lattice mismatch (%)	15	3	17	--
Thermal expansion coefficient (10^{-6}K^{-1})	7.3	4.5	2.6	5.6
Thermal mismatch (%)	-30	20	54	--
Thermal conductivity ($\text{Wcm}^{-1}\text{K}^{-1}$)	0.5	4.5	1.5	1.3
Wafer size (inch)	2 to 8	2 to 6	2 to 12	2
Cost	moderate	high	low	extremely high

The dislocations reduce the carrier mobility and thermal conductivity. The TEC of sapphire is higher than GaN producing biaxial compressive stress in GaN layers upon cool down. Sapphire is semi-insulating material and it can withstand high growth temperatures. However, the thermal conductivity of sapphire is the poorest among all the substrates suggesting that it has the lowest heat dissipating capability. Hence, this reduces its application for high temperature tolerant devices. The oxygen from the

sapphire substrate has been found to diffuse into GaN layer doping it n-type contributing towards its background electron concentration [63].

SiC exhibits better material properties than sapphire such as lower lattice and thermal mismatch and higher thermal conductivity. Thus, GaN layers obtained are of better quality when grown using SiC as a substrate. TEC of SiC is smaller than that of GaN, generating tensile strain in the layers at room temperature. However, the SiC substrates are very expensive and are not easily available in large diameters. Thus, they are mainly used for microelectronic devices such as HEMTs for microwave applications where high thermal conductivity is needed. Alternately, Si is an attractive substrate because it is cheap and easily available in large diameters. It is well known for its reasonably good thermal conductivity which is similar to that of GaN. The matured Si technology also enables its processing and integration for both optoelectronic and microelectronic applications [64]. Si (100) with four fold symmetry is a preferred substrate for this purpose as it is widely used in silicon technology. However, Si (111) is a more commonly used substrate for the growth of III-nitrides due to its six fold symmetry. The four fold symmetry is more suitable for the growth of metastable cubic phase nitrides while the six fold symmetry assists in the growth of thermodynamically stable wurtzite phase.

The growth of GaN on Si (100) substrate shows an epitaxial relationship as GaN [0001] || Si [001] and Ga [11 $\bar{2}$ 0] || Si [110] [65] while GaN on Si (111) is oriented as GaN [0001] || Si [111], Ga [2 $\bar{1}$ $\bar{1}$ 0] || Si [$\bar{1}$ $\bar{1}$ 0] and Ga [01 $\bar{1}$ 0] || Si [2 $\bar{1}$ 1] [66]. With all these acclaimed advantages, Si suffers from a high lattice mismatch of ~ 17% and a thermal mismatch of ~ 54% with GaN. The lattice mismatch causes high dislocation density in GaN but the thermal mismatch is more severe as it leads to the cracking of the epilayers rendering it unsuitable for device fabrication [67]. Nevertheless, the benefit of using Si as a substrate is much more compared to the other substrates. Thus, a rigorous progress has been made towards reducing the dislocation density and compensating the thermal mismatch induced tensile strain in GaN on Si substrate.

Good quality epilayers of GaN have been grown heteroepitaxially on different substrates using various techniques which will be discussed in the next section.

2.3 Growth techniques

The growth of III-nitrides is spread over more than a century. AlN powder was produced from liquid Al and N₂ gas in 1862. This was soon followed by GaN powder [1]. However, the growth rates were limited by the formation of an Al (Ga)N film on the metal source reducing the growth rates by lowering the evaporation of the metals. Good quality crystals could not be grown despite several attempts between the period of 1930 to 1960. The difficulty in obtaining bulk and single crystal GaN has led to the exploration of the heteroepitaxy of III-nitrides. Various growth techniques have been developed since then which will be discussed in the following sections.

2.3.1 Hydride vapor phase epitaxy

Hydride vapor phase epitaxy (HVPE) is one of the early techniques used for GaN growth. This technique gained popularity as it offered high growth rates of ~100 µm/hr and the lack of incorporation of carbon in the layers. The conventional HVPE system uses gallium monochloride (*GaCl*) as the Ga source and ammonia (*NH₃*) as the nitrogen source. *GaCl* is prepared when hydrogen chloride (*HCl*) gas is allowed to pass through a crucible containing metallic Ga. *GaN* is formed according to the following reaction [57]:

Maruska et al. [68] reported on the growth of single crystal GaN using sapphire as a substrate in 1969. They determined that GaN has a direct band gap which proved to be an early breakthrough in the development of GaN based blue LEDs. The undoped GaN was found to be inherently doped with a very high electron concentration of ~ 10¹⁹ cm⁻³ due to the high density of nitrogen vacancies. Ilegems [69] was successful in growing GaN with significantly reduced electron concentrations in the lower order of ~ 10¹⁷ cm⁻³. The usual Si and O n-type dopants in GaN grown by HVPE were found to be from the quartz source in the HVPE reactor. Despite this, GaN with reduced background electron concentration of ~10¹⁶ cm⁻³ have been obtained [70, 71]. One of the first results demonstrating the presence of 2DEG at the AlGaIn/GaN interface grown by HVPE established it as a promising technique for the growth of HEMT heterostructures [72]. The surface showed excellent surface morphology with RMS roughness of ~ 0.2 nm. HVPE grown GaN on sapphire was used as templates for the growth of epilayers by other techniques such as MOCVD and MBE due to its low cost. It helped in the reduction of overall dislocation density as the growth was initiated

directly on HVPE grown GaN template instead of lattice mismatched substrates such as SiC and sapphire. Thus, very high quality AlGaIn/GaN HEMTs with mobilities up to 75000 cm²/V.s at 4K have been achieved [73]. Storm et al. [74] have demonstrated AlGaIn/GaN HEMTs on HVPE templates exhibiting low dislocation density of $\sim 10^7$ cm⁻², RMS roughness of 0.4 nm and room temperature hall mobility of 1920 cm²/V.s with an electron sheet density of 0.9×10^{13} cm⁻². HVPE is the oldest and a matured technology for GaN growth. High background carrier concentration in HVPE grown GaN makes it difficult to be used for high performance device structures. Nevertheless, efforts are being made to exploit its potential to obtain bulk substrates to be used for homoepitaxial growth of GaN.

2.3.2 Metal organic chemical vapor deposition

Metal organic chemical vapor deposition (MOCVD) technique employs the transport of volatile metalorganic compounds as a metal source mixed with hydrides (N_xH_y) as nitrogen source to a heated substrate for the gases to undergo pyrolysis and deposit III-nitride layers on the substrate. The gases chemically react in the following manner:

where, M is the group III atom (Ga, Al, In), R is organic radical (CH_3 or C_2H_5) and E is a group V atom (N).

Trimethylgallium (TMGa) for gallium, trimethylaluminum (TMAI) for aluminum, trimethylindium (TMIn) for indium and ammonia for nitrogen are the typically used precursors. The scope of MOCVD for the growth of nitrides was first demonstrated by Manasevit et al. [75] in 1971. The successful experiments proved that MOCVD is a viable method for further research and experimentation on III-nitrides. Dingle et al. [76] demonstrated optically pumped UV-emission from GaN at 2K around the same time. Early results on sapphire substrate by Khan et al. [77] and Hashimoto et al. [78] were very encouraging, proving the suitability of MOCVD technique for the growth of single crystal GaN on a foreign substrate. Sapphire was a widely chosen substrate for heteroepitaxial growth of GaN as it is capable of sustaining high MOCVD growth temperatures (~ 1000 °C) and exhibits closest crystal geometry as GaN. However, a breakthrough in GaN technology was achieved after persistent efforts by Amano et al. [79] who demonstrated the use of thin AlN layer grown at low temperature as buffer layer for the growth of GaN on sapphire. GaN single crystals with optically flat surfaces, free from cracks and good quality were successfully grown by MOCVD for

the first time [80]. AlN buffer layer was found to reduce the interfacial energy between GaN and sapphire substrate. The fluctuations in the orientation of the nucleation were relatively small and it promoted lateral growth more than the vertical growth of GaN.

Nakamura et al. [81] demonstrated the use of low temperature GaN as a buffer layer instead of AlN. A novel two-flow-MOCVD reactor was constructed and GaN layers were grown with improved electrical properties such as high electron mobility of 600 $\text{cm}^2/\text{V.s}$ and one order lower carrier concentration. Since good quality GaN layers were already achieved using low temperature buffer layer, next step was to dope for p-type conductivity and control the n-type conductivity in GaN. In 1989, Mg was found to be a useful acceptor dopant than Zn [82], irradiated using a beam of electrons known as low energy e-beam irradiation phenomenon. This success story was soon followed by the demonstration of world's first p-n junction blue/UV LED with good current-voltage characteristics [83]. In 1992, an alternative method of Mg activation in GaN was demonstrated by thermal annealing of Mg doped GaN [84]. The growth of GaN under H_2 conditions passivated the acceptors and thus, these ex-situ processes were performed to activate the acceptors by releasing hydrogen. The control of n-type conductivity of GaN was equally important due to the presence of existing donors in as-grown GaN. The n-type doping of GaN was first demonstrated by Si doping using silane (SiH_4) as the precursor. Eventually, blue, blue-green and UV LEDs were developed for commercial use [85].

With the development in the GaN growth on sapphire substrate, the growth of AlGaIn/GaN HEMT heterostructures was also made possible. The first results of 2DEG in an AlGaIn/GaN HEMT were reported by Khan et al. [86, 87]. They observed a room temperature mobility of 834 $\text{cm}^2/\text{V.s}$ which increased monotonically to 2626 $\text{cm}^2/\text{V.s}$ at 77K. The 2DEG carrier concentration was estimated to be $1 \times 10^{11} \text{ cm}^{-2}$. This first ever demonstration of 2DEG in AlGaIn/GaN system led to an immense development in the area of nitrides based electronic devices.

Post the initial demonstrations in 1999, tremendous development of AlGaIn/GaN HEMTs has occurred since then on sapphire, SiC and Si (111) substrates by MOCVD technique. A hall mobility of 10300 $\text{cm}^2/\text{V.s}$ with a sheet carrier density of $6.19 \times 10^{12} \text{ cm}^{-2}$ was measured at 1.5K for AlGaIn/GaN HEMTs on sapphire substrate [88]. An enhancement in the 2DEG mobility of 1770 $\text{cm}^2/\text{V.s}$ was observed by introducing an optimum 1 nm thick AlN interfacial layer compared to 1287 $\text{cm}^2/\text{V.s}$ obtained without the interfacial layer [89]. The insertion of AlN interfacial layer can significantly improve

the 2DEG properties due to the reduction of alloy disorder scattering. A high resistive Fe doped GaN ($>10^8 \Omega$) with dislocation density $\sim 10^8 \text{ cm}^{-2}$ and flat surface morphology was demonstrated which showed high room temperature mobility of $2200 \text{ cm}^2/\text{V.s}$ at sheet carrier density of $7.6 \times 10^{12} \text{ cm}^{-2}$ [90].

SiC was not used for radiofrequency (RF) devices due to the electrical conductivity of the substrate until 1999, when the first semi-insulating SiC was available. It became a commonly used substrate for high power devices due to its high thermal conductivity. Gaska et al. [91] achieved a record high room temperature mobility of $2019 \text{ cm}^2/\text{V.s}$ at a sheet carrier density of $1.3 \times 10^{13} \text{ cm}^{-2}$ for the AlGaIn/GaN HEMT heterostructures on SiC substrate. Moreover, AlGaIn/GaN HEMT heterostructures of high crystal quality and sub-nm surface roughness grown using 1 nm AlN interlayer showed high room temperature mobility of $2215 \text{ cm}^2/\text{V.s}$ with a sheet carrier density of $1 \times 10^{12} \text{ cm}^{-2}$ [92]. Good uniformity, wafer to wafer reproducibility and high material quality was obtained for even larger diameter SiC wafers [93].

AlGaIn/GaN HEMTs on Si have also gathered enormous interest due to the possibility of combining AlGaIn/GaN HEMTs with the existing silicon technology. Selvaraj et al. [94] demonstrated the highest mobility of $1863 \text{ cm}^2/\text{V.s}$ in 2007. GaN layer with $1 \mu\text{m}$ thickness was grown on 4 in. Si (111) wafer with 20 pairs of AlN/GaN superlattice structure and an AlN cap layer. This was followed by the report of record high room temperature mobility of $3215 \text{ cm}^2/\text{V.s}$ [95]. Such high mobility was achieved mainly by reducing the overall dislocation density to as low as 10^{10} cm^{-2} in the $9 \mu\text{m}$ thick GaN buffer layers and introducing the AlN interfacial layer.

2.3.3 Molecular beam epitaxy

Molecular Beam Epitaxy (MBE) growth technique enables the growth of III-nitrides at a lower substrate temperature in an ultra-high vacuum (UHV) system ($\sim 10^{-11}$ Torr) for producing high quality epitaxial layers with monolayer control. MBE remains a method of choice for the growth of multilayer GaN based HEMT heterostructures where abrupt changes in film composition or doping profile are required. Selected elements (Ga, Al etc.) are heated in vacuum furnaces called effusion cells. Nitrogen is not dissociated using the conventional effusion cells but using a radio frequency plasma source to produce active nitrogen in PA-MBE. However, ammonia is used as a nitrogen precursor employing surface pyrolysis or cracking principle in ammonia based MBE. More on the MBE growth technique is given in Chapter 3.

The growths by MOCVD are typically performed at high growth temperatures ($>1000^{\circ}\text{C}$). Common impurities in GaN grown by MOCVD include C [96], Si and O [97]. The advantages of MBE over vapor phase growth techniques for the growth of III-nitrides are discussed below.

- a) One of the main benefits of PA-MBE for the growth of GaN and related alloys is that it offers growths at low temperatures as the generation of active nitrogen species is independent of the growth temperature. This is very critical for In-based semiconductors, such as InN, InGaN and InAlN, since In incorporation is significantly improved at lower temperatures. Lower growth temperatures are also important for increasing the incorporation of Mg for p-type doping of nitride materials. It causes lower diffusion at lower temperatures which improves the quality of abrupt semiconductor interfaces and sharp doping profiles.
- (b) A combination of UHV operation, high thermal velocity of source atoms, and fast source shutters allow a precise control of layer thickness down to the atomic scale in MBE. This is very important for the growth of electronic and optoelectronic structures. Moreover, the interfaces between the layers are smooth and abrupt. The ability to rapidly change film composition at an interface also prevents the accumulation of impurities, which would otherwise lower the interface quality.
- (c) With in-situ diagnostic capabilities, MBE gives a clearer image of the growth mechanisms involved. These measurement techniques include RHEED, residual gas analyzer (RGA), desorption mass spectroscopy (DMS), cathodoluminescence (CL), reflectometry, pyrometry and various optical measurements. These tools can be used during the growth to determine substrate temperature, growth rate, thin film composition and strain states, surface roughness and atomic structure.

Despite the above mentioned advantages, MBE as a viable growth technique for the growth of III-nitrides was lagging behind the performance benchmarks set by MOCVD in the early 90s. However, with the advances in the growth technology, the material properties of MBE grown III-nitrides have become equally competitive. In fact, MBE has played a vital role in extending the knowledge of the growth process as it allows real-time growth monitoring due to its in-situ diagnostic capability.

2.3.3.1 Plasma assisted molecular beam epitaxy

2.3.3.1.1 Activation of nitrogen

In PA-MBE, the reactive nitrogen is supplied to the surface from an RF source. The active nitrogen species are produced by nitrogen plasma. The amount of active nitrogen generated does not depend on the growth temperature permitting flexibility in the choice of the growth temperatures. Thus, this technique allows growths to be performed at low temperatures.

The nitrogen plasma comprises of various species, produced by the activation of the nitrogen molecules, such as atomic nitrogen (N), excited nitrogen molecule (N_2^*) and ionic nitrogen (N^+ , N_2^+) [98]. Considering the lifetimes of the active nitrogen species, the excited nitrogen or metastable molecule has been found to reach the substrate and is therefore considered to be participating in the growth. The nitrogen atoms also have a very long lifetime in the chamber and the nitrogen molecule is formed only when the collision of the two nitrogen atoms interacts with the third body, which usually involves a wall collision. In fact, atomic nitrogen (N) has also been found to be the preferred species in the growth process. Schenk et al. [99] have studied the yield of atomic nitrogen by optical and mass-spectrometry. The atomic optical emission intensities increased linearly with the increasing RF power for a constant nitrogen flow rate. This phenomenon was attributed to the enhanced nitrogen cracking efficiency with the charge generation rate within the plasma. However, the optical intensity decreased with the increasing nitrogen flow for a set RF power. The reduction in the available dissociation energy per molecule with the increasing pressure was suggested to be a possible reason for this behavior. Besides RF power and nitrogen flow, the composition and the amount of the nitrogen plasma were also affected by factors such as wall-temperature of the RF source and the design of holes in the PBN aperture.

2.3.3.1.2 Growth of AlGaIn/GaN HEMT heterostructures

Yoshida et al. [100] were the first to report on the use of AlN buffer layer between GaN and the sapphire substrate for the improvement of the electrical and luminescence properties by MBE. Unlike MOCVD, wherein the cleaning of the sapphire substrate was performed at high temperatures of 1000 °C, the sapphire substrates were conventionally chemically cleaned or thermally cleaned at 800 °C before initiating the growth process by MBE. Many novel methods were also devised

to perform the cleaning at low substrate temperatures. The exposure of the substrate to hydrogen radicals using plasma source was found to be an effective method of low temperature cleaning at 200 °C [101].

The subsequent nitridation of the sapphire substrate caused the N atom to replace the O to form a thin layer of AlN or AlNO. The effect and mechanism of the nitridation temperature was also studied in detail by Namkoong and Losurdo et al. [102, 103]. The AlN layer formed at high temperatures of 700 °C included 30% of NO while those formed at a low temperature of 200 °C showed only 10% of NO. Moreover, the AlN layer grown at high temperatures showed rough and inhomogeneous layer leading to a defective and poor quality GaN layer with inversion domains. On the other hand, the growth at low temperature resulted in smooth and homogenous AlN layer. Thus, high quality GaN layers with smooth surface morphology were eventually obtained.

Besides the use of AlN as the buffer layer for the growth of GaN, low temperature GaN was also used as a buffer layer to obtain good quality GaN [104]. This process was found to produce 2D growth with a lateral growth rate 100 times faster than the vertical growth rate. The GaN layers showed the highest mobility $> 200 \text{ cm}^2/\text{V.s}$ among films grown by MBE. The growth of GaN layers was strongly affected by the III/V flux ratio [105]. The growth performed under Ga-rich conditions led to atomically flat surfaces while rough and faceted surfaces were obtained for growths in N-rich growth conditions. Films with monolayer surface roughness were obtained under optimized nucleation and growth conditions. GaN films grown under Ga-rich conditions on sapphire exhibited very low XRD full width at half maximum (FWHM) of 60 arcsecs.

Heying et al. [106] have also observed variations in the surface morphology and transport properties of GaN as a function of III/V ratio. GaN layers grown in the N-rich conditions were found to be semi insulating and exhibited pitted morphologies. GaN layers grown with higher III/V ratio in the intermediate growth regime showed fewer pits with atomically flat surfaces in between the pits. However, pit-free and completely atomically flat surfaces were obtained in the droplet growth regime. The growths in Ga-rich conditions promoted step flow growth in which the Ga adatom having large surface diffusion length reached the step edges by surface diffusion before the new nucleation occurs. As the substrate temperature increases, the diffusion length of the adatoms also increases but their surface residence time reduces due to enhanced

evaporation. A very high room temperature mobility of $1191 \text{ cm}^2/\text{V.s}$ was obtained for the layers with highest III/V ratio in the intermediate growth regime. However it decreased significantly for the layers grown in the droplet regime. Thus, it was concluded that the optimum properties were obtained in the presence of Ga adlayer without the formation of Ga droplets in the intermediate growth regime.

In-situ RHEED was employed to distinguish the polarity of GaN as N-polar and Ga-polar [107]. The RHEED patterns of (1×1), (3×3), (6×6) and (6×12) were indicative of N-polar GaN while (2×2), (5×5), (6×4) and (1×1) surface reconstructions were observed for Ga-polar GaN. The polarity assignments were further confirmed by KOH wet etching studies. N-polar films showed a change in the morphology while the GaN surface with Ga-polarity was resistant to the etching and remained unchanged. The mechanism of such polarity selective etching was investigated by Li et al. [108] using optical microscope and X-ray photoelectron spectroscopy (XPS). The surface chemistry for both Ga and N-polar GaN using aqueous KOH solution was studied in detail. It was found that the etching mechanism is due to different surface bonding and is independent of deposition methods and growth conditions. The Ga-polar GaN is chemically inert due to the presence of N terminated surface. Hydroxide ions in KOH solution cannot attack the N terminated surface due to the repulsion between OH^- and three occupied dangling bonds of nitrogen. However, the N-polar GaN is etched because the OH^- are first adsorbed on the sample surface due to the presence of just one dangling bond of nitrogen and subsequently react with the Ga atoms. KOH works as a catalyst and gallium oxide gets dissolved in the KOH solution by the following reaction:

In-situ RHEED was also used very efficiently to overcome the issue of narrow optimum growth window offered by PA-MBE. Burnham et al. [109] proposed metal modulated epitaxy (MME) method to overcome the slight substrate temperature or flux deviations which makes it difficult to maintain the optimum growth conditions and reproducibility. MME method involved the periodic shuttering of the metal (Al, Ga) cells while maintaining a constant nitrogen flux. The growths were performed in excess metal-rich growth conditions that comes to nearly two to four times the fluxes used for non-shuttered growths. The excess metal was consumed by the constant supply of nitrogen flux eliminating the need of growths to be performed at high substrate temperatures. It showed to improve the surface morphology of both AlN and

GaN layers [110]. MBE method was successfully implemented in obtaining Mg doped GaN with very high and repeatable hole concentrations of $1.5 \times 10^{19} \text{ cm}^{-3}$ [111]. This demonstration of achieving high hole concentrations in GaN by PA-MBE without any ex-situ treatments demonstrated the capability of this technique for the development of nitrides based electronic and optical devices.

Several attempts were made to improve the crystal quality of GaN layers by ex-situ and in-situ methods. One of the ex-situ methods, epitaxial lateral overgrowth (ELO) has been proved to be effective in the reduction of dislocations in GaN. However, the need of masking, etching and the risk of growth chamber contamination have generated immense interest in achieving maskless methods of ELO. Cherns et al. [112] demonstrated the ELO of GaN on GaN nano-columns grown on sapphire using AlN buffer layer. Threading dislocations in the range of $10^8 - 10^9 \text{ cm}^{-2}$ was obtained by changing the polarity of the GaN layers from N to Ga-polar. An improvement in the GaN crystalline quality was also achieved by inserting a high temperature interlayer of AlN between GaN layers [113]. The threading dislocation density of $1 \times 10^{10} \text{ cm}^{-2}$ reaching the surface was seven times lower than that without any AlN layer.

With all the initial demonstrations of AlGaIn/GaN HEMT heterostructures grown by MBE on GaN templates, Manfra et al. [114] demonstrated an all MBE grown AlGaIn/GaN HEMTs directly on sapphire substrate using a high temperature AlN nucleation layer. The 7 nm thick nucleation layer was deposited at the same temperature of 800 °C as GaN. Ga-polar AlGaIn/GaN HEMT heterostructure with a 2DEG sheet carrier density of $8.8 \times 10^{12} \text{ cm}^{-2}$ and mobility of $1478 \text{ cm}^2/\text{V.s}$ at room temperature was achieved at an optimized AlGaIn barrier layer thickness and composition of 30 nm and 42%, respectively [115].

High quality AlGaIn/GaN HEMTs have also been demonstrated on SiC substrate by PA-MBE [39, 116]. The cleaning and removal of oxide formed on the SiC surface was accomplished using the process of Ga deposition and desorption prior to the growth [117]. This was followed by the growth of AlN nucleation layer using Al flux close to the Al droplet formation. GaN layers were subsequently grown in N-rich, intermediate and Ga-rich growth conditions. N-rich and intermediate growth regimes exhibited low dislocation density and low residual lattice mismatch strain than Ga-rich growth regime. However, the layers grown in N-rich and intermediate growth conditions suffered from rough surface morphology. A two-step GaN buffer was thus grown for AlGaIn/GaN HEMTs [118] similar to Manfra et al. [119]. The first layer was grown in

the intermediate growth regime followed by the second layer grown in Ga-stable conditions. The GaN grown by this method showed three times lower threading dislocation density of $2 \times 10^{10} \text{ cm}^{-2}$ compared to the one step GaN buffer layers grown in the intermediate growth regime.

The effect of the III/V ratio of the AlN nucleation layer on the buffer leakage of AlGaN/GaN HEMTs was also investigated [120]. Silicon incorporation from the SiC substrate at the AlN/GaN interface was found to be the source of buffer leakage in the case of AlN nucleation layer grown under Al-rich growth conditions. The silicon incorporation reduced by two times for AlN nucleation layer grown in N-rich growth conditions. The silicon incorporation was found to form a thin doped layer at the AlN/GaN interface causing high leakage currents.

Similar to the MME method, a modulated growth technique utilizing in-situ RHEED and line of sight quadrupole mass spectrometer (QMS) was demonstrated for the growth of GaN layers on SiC substrate as well [121]. Excess of Ga resulted in the formation of droplets at cooler areas while Ga desorption occurring in the hotter areas showed highly pitted surface. The temperature and flux non-uniformities leading to significant variation in the structural quality of the GaN layers was controlled by modulating the Ga on the surface during GaN growth. Thus, the Ga flux was modulated by short-period shuttering of the Ga, N or both the sources together. The excess Ga near the cross over to the droplet regime ensured smooth and pit free surface morphologies while low III/V ratio or a growth interruption allowed excess Ga to be consumed for GaN growth thus avoiding droplet build up. A two-step buffer layer with a total thickness of $1.4 \mu\text{m}$ was grown using the “modulated growth” technique. AlGaN/GaN HEMT heterostructures using the improved two-step and nucleation conditions exhibited good 2DEG room temperature mobility of $1400 \text{ cm}^2/\text{V.s}$ with a sheet carrier density of $1 \times 10^{13} \text{ cm}^{-2}$.

As discussed earlier, low temperature GaN has been used as a buffer layer for the growth of GaN epilayers on sapphire and SiC substrate. However, Ga has a poor wetting of the Si surface which hinders the nucleation of GaN and results in poor quality and morphology of the GaN layers on Si substrate. Moreover, GaN grown directly on Si leads to melt back etching of the Si substrate at elevated growth temperatures. It also leads to the formation of amorphous Si_xN_y disrupting GaN epitaxy. The formation of this amorphous layer certainly limits the crystal quality of the subsequent GaN growth although it might not hinder the growth of single crystalline

GaN [122]. Besides these difficulties, one of the biggest impediments in the growth of GaN on Si substrate is the high lattice and thermal mismatch. Hence, several materials have been considered as buffer layers which include AlN [123-125], ZnO [126, 127], HfN [128], SiC [129-131], AlAs [132] and oxidized AlAs (AlO_x) [133], intentionally formed SiN [134, 135] and BP [136].

Among these, using AlN as a buffer layer has been the most encouraging way of achieving good GaN material properties. The preliminary results of mono-crystalline growth of AlN on Si was achieved by ECR assisted MBE [137]. The formation of Si_xN_y was suppressed by opening the Al shutter and depositing a monolayer of Al before opening the nitrogen plasma. The AlN layers with XRD FWHM of 26 arcmin exhibiting spotty RHEED surface reconstruction pattern suggesting quasi-2D growth mode with a rather flat surface was obtained at 900 °C. Calleja et al. [138] performed a systematic study to investigate the effect of III/V ratio and the growth temperature to achieve good quality AlN layers using RF nitrogen plasma. The growth of AlN layer was initiated by Al predeposition for an optimized time of 30 s [139]. There was no change in the growth rate with the variation in the substrate temperature between 780 to 920 °C but it strongly affected the growth mode and the surface roughness. The III/V ratio that saturated the growth rate of AlN was termed as “stoichiometry” and it was found that the crystal quality degraded drastically as the III/V ratio approached N-rich conditions. However, the layers grown above stoichiometry attained good quality with XRD FWHM of 10 arcmin. The AlN layers were found to have relaxed fully within a thickness of only 400 Å. Rough surface morphology was obtained for the layers grown in the N-rich growth conditions while smoother surfaces with RMS roughness of 48 Å were achieved at the stoichiometric conditions and beyond. The surface roughness decreased from 140 to 48 Å when the substrate temperature was increased from 780 to 920 °C. The high substrate temperatures increased the Al adatom mobility and consequently, improved the surface morphology. Thus, AlN layers with good crystalline quality and flat surfaces were realized at III/V ratio close to the stoichiometry with substrate temperatures high enough to avoid Al condensation.

Similar results were obtained by Chuah et al. [140] who obtained best AlN films at high substrate temperatures of 875 °C and III/V ratios close to stoichiometry. The supply of nitrogen and aluminum close to unity resulted in 2D growth with atomically flat surfaces as reported by Schenk et al. [6]. The N-rich growth conditions resulted in

($\sqrt{3}\times\sqrt{3}$) and Al-rich showed (2×6) RHEED patterns. N-rich conditions resulted in 3D morphology while Al-rich resulted in cracks and Al droplets. The effect of Al monolayers on the subsequent GaN layers was also investigated at low and high substrate temperatures of 450 and 640 °C, respectively. At low temperatures, Al thickness below 1 monolayer provided the best and comparable GaN quality while more than 1 monolayer was required at high temperatures [141].

Alternate to the process of Al predeposition for the nucleation of AlN, Karmann et al. [142] tried nucleating AlN layers on the Si substrate by exposing it to nitrogen plasma. The process of intentional nitridation led to disorientation of the AlN crystals exhibiting wider values of XRD FWHM than that obtained without the nitridation step for similar growth parameters and thicknesses. On the contrary, it is interesting to note that the formation of crystalline α -Si₃N₄ intentionally at the AlN and Si (111) interface reduced the lattice mismatch and transformed the stress in the AlN layers from tensile to compressive [143]. The crystalline α -Si₃N₄ formation involved diffusion of nitrogen through the AlN layer and reaction with the Si substrate during the growth of AlN layer. Yasutake et al. [144] demonstrated that Al/Si (111) γ phase is effective in establishing an orientation relationship between AlN and Si. The single crystal AlN was achieved at the growth temperatures as low as 400 °C. However, the growth conditions were optimized at 800 °C to achieve smooth surface roughness of 0.3 nm and resistivity of 2×10^9 Ω .cm for thicknesses up to 100 nm.

The nucleation conditions of the AlN buffer layer was also critical in determining the polarity to be either Al-polar or N-polar [145]. The RHEED reconstruction patterns of (1×1) and (2×6) confirmed the polarity of AlN as Al-polar while (1×1), (1×3), (3×3) and (6×6) as N-polar [146]. The nucleation temperature of about 700 °C resulted N-polar AlN layers with RMS roughness of 0.4 to 0.6 nm. The nucleation temperature ranging from 770 to 800 °C demonstrated Al-polarity with similar roughness. However, temperatures beyond 880 °C showed the existence of both the polarities. High quality N-polar AlN layers with smooth surface morphology have also been demonstrated on Si (111) using Al predeposition at 780 °C [147]. N-polarity of AlN layers was confirmed as the surface showed the presence of triangular shaped pyramids after etching in KOH solution.

Similar to the studies for the optimization of AlN layers, the effect of III/V ratio on the growth of GaN layers was also investigated [139, 148]. The active nitrogen was varied

while keeping the Ga flux and substrate temperatures fixed in one set of experiments. The growth rate increased with the supply of active nitrogen species and saturated at 0.5 $\mu\text{m/hr}$. Surplus Ga could be seen for lower supply of active nitrogen species with only slight excess of Ga near the stoichiometry. In the second set of experiments, the active nitrogen was kept constant while the substrate temperature and Ga flux was varied from N-rich to Ga-rich conditions. The growth rate was found to increase linearly with increasing Ga flux until it reached saturation at all the substrate temperatures. However, the Ga flux required to reach the saturation also increased with the increasing substrate temperatures. This clearly indicated that Ga desorption rate increased at high temperatures. N-rich conditions led to columnar or whisker like morphologies and was related to the reduced Ga adatom diffusion in N-rich growth conditions of GaN. Similar results reported by Yoshizawa et al. [149] showed that the columns (3D growth) exhibited complete relaxation from the lattice and thermal mismatch and were of very high optical quality. However, the layer became more compact (2D growth) as the growth was done at stoichiometry or Ga-rich conditions.

Similar to the studies on sapphire and SiC, a two-step growth method was employed to improve the overall surface morphology and quality of GaN layers [139]. The optimized GaN layers showed surface roughness of 6 nm, XRD FWHM of 8 arcmin, strong PL emission with narrow line-width of 15 meV and (2 $\times$ 2) reconstruction pattern. These results suggest that the GaN layers grown using this approach are of good structural and optical quality. Similar approach has also been demonstrated by Roh et al. [150] using Ga and N flux modulation. An N-rich GaN was grown to suppress the defect propagation followed by Ga-rich GaN to facilitate the lateral growth.

The first AlGaIn/GaN HEMT heterostructure on 100-mm Si (111) by PA-MBE was realized by the growth optimization of two-step low temperature and high temperature AlN layers and GaN buffer layer [151, 152]. GaN buffer layer exhibiting Ga-polarity with a thickness of 1500 nm was grown on AlN in the intermediate growth regime. The AlGaIn barrier layer was optimized for Al content of 29% and the thickness of 25 nm. A high electron mobility of 1100 $\text{cm}^2/\text{V.s}$ was achieved with the sheet carrier density of $9.0 \times 10^{12} \text{ cm}^{-2}$. Soon after that, Hoke et al. [153] also demonstrated 1.7 μm thick GaN films with high structural and electrical properties. A high electron mobility of 1600 $\text{cm}^2/\text{V.s}$ was achieved for similar barrier layer composition and thicknesses. Very recently, Aidam et al. [154] have grown GaN films with thicknesses up to 4.2 μm on Si (111) with a maximum bowing of 10 μm without the use of any stress mitigating

layers. The III/V ratio in the first 100 nm of the GaN buffer layer was found to be important in determining the compressive strain of the overall structure. Carbon doping was employed for n-type charge carrier compensation which resulted in low carrier concentration of $2 \times 10^{13} \text{ cm}^{-2}$. AlGaIn/GaN HEMT heterostructure with a 22 nm thick AlGaIn barrier layer and 22% Al content exhibited the highest room temperature mobility of $1350 \text{ cm}^2/\text{V.s}$ with a sheet carrier density of $7 \times 10^{12} \text{ cm}^{-2}$.

2.3.3.2 Ammonia molecular beam epitaxy

Another MBE growth technique used for the growth of AlGaIn/GaN HEMT heterostructures is ammonia based where the nitrogen is supplied by pyrolysis of ammonia on the substrate surface during the growth. Most of the studies on AlGaIn/GaN HEMTs have been done using PA-MBE while there are few reports from ammonia MBE. PA-MBE utilizes a RF-plasma cracking cell to produce active nitrogen and the nitrogen cracking efficiency of the RF sources is only up to 10 %, depending on the system [155]. Hence, the growth rate by this method is low, in the range of 0.1 to 0.4 $\mu\text{m/hr}$. Growth should be performed under metal-rich conditions by PA-MBE [106, 156], i.e., with a metal adlayer or bilayer conditions which imply that the III/V ratio must be precisely controlled within the narrow growth window. The narrow growth window gets affected by the minor fluctuations in the substrate temperature and material fluxes. Ammonia MBE based GaN growth method offers several advantages over PA-MBE which include, easy cracking of ammonia molecule to produce active nitrogen, higher growth rate, wider growth window, better uniformity, droplet-free surface and lower buffer leakage currents [41, 157, 158]. Ammonia MBE uses nitrogen precursor ammonia with significantly reduced bond strength making it relatively easy to dissociate ammonia and produce active nitrogen. Due to the ease of cracking ammonia, growth rates as high as few $\mu\text{m/hr}$ have been achieved. Due to the wider growth window, the optimized growth parameters are insensitive to the minor fluctuations in the substrate temperature and material fluxes which lead to stable growth and better uniformity. However, the corrosive nature of ammonia gas led to a very few reports from the GaN research community. Recently, ammonia resistive components for MBE system being offered commercially have accelerated the interest in exploring the advantages of ammonia MBE.

2.3.3.2.1 Ammonia cracking efficiency

The ammonia radicals (NH_x) are made available by the pyrolysis of ammonia molecules on the substrate surface. They undergo reaction with the Ga metal from the effusion cell as represented by the following equation.

Eq. 2.4

Evidently, the availability of ammonia radicals is an important governing parameter for GaN growth. As the ammonia radicals are produced by the process of thermal cracking, it becomes important to study the effect of growth temperature and the ammonia flow on the cracking efficiency of ammonia molecules. Mesrine et al. [159] performed a systematic study on the ammonia cracking efficiency as a function of substrate temperature on a pre-deposited Ga on the GaN surface using optical surface reflectivity experiments. The reflected intensity did not show any change for temperatures below 350 °C indicating low decomposition of ammonia at these temperatures. The change in the reflectivity was seen beyond 450 °C suggesting the onset of the nitrogen atom incorporation for GaN growth. The ammonia cracking efficiency increased with increasing substrate temperature and was estimated to be about 4% at 700 °C. The nitrogen incorporation was further investigated by monitoring the growth rate with the incident ammonia flow. The growth rate increased with increasing ammonia flow in the ammonia limited regime (Ga-rich) while it reached saturation beyond 12 sccm of flow in the Ga limited regime (N-rich) at 830 °C. It was found that the nitrogen incorporation reached saturation although the cracking efficiency had increased at temperatures beyond GaN decomposition temperature. This was because the cracked ammonia would be used to compensate for the N evaporating from the decomposing GaN surface. Low III/V ratio was found to be necessary for GaN growth beyond 700 °C to maintain sufficient overpressure to compensate N evaporation due to GaN decomposition. Ammonia cracking efficiency was also studied on different surfaces such as sapphire and SiO₂ and compared with GaN and AlN [160]. The cracking efficiency was determined by measuring the partial pressure of hydrogen using RGA. All the factors such as background hydrogen, hydrogen from RGA cracking of ammonia and that out-gassed from the heater were considered to accurately determine the ammonia cracking efficiency. The ammonia cracking was found to be an order higher on the AlN and GaN surfaces compared to sapphire and SiO₂.

2.3.3.2.2 Growth of AlGaN/GaN HEMT heterostructures

Two distinct growth regimes of GaN in both ammonia limited and Ga limited regimes were identified by Held et al. [161, 162] using in-situ RHEED and DMS tools. The substrate temperature was decreased in order to determine the temperature at which the incident Ga flux exceeds the desorbing flux and Ga adsorbs leading to its

condensation. It was observed that the growth rate of GaN for a given ammonia flow and Ga flux decreased with decreasing substrate temperature and became zero at the condensation temperature of about 750 °C. In other study, the growth rate was found to reach unity with increasing Ga flux beyond which it started to decrease for a fixed ammonia flow. However, the growth rate reached saturation when the ammonia flow was varied for a constant Ga flux. This phenomenon was attributed to the adsorption of the Ga atoms which blocked the active Ga terminated sites. Thus, it could be said that the growth of GaN should be performed beyond the condensation temperature for a given Ga flux but below the decomposition temperature of GaN.

The surface morphology of GaN was also investigated in these two regimes. The ammonia limited (Ga-rich) growth conditions resulted in atomic steps on micro sized islands while Ga limited (ammonia-rich) surfaces demonstrated faceting. Under excess ammonia, the growth proceeded by island nucleation and changed to step flow growth with the increasing substrate temperature. However, relatively smoother surfaces were obtained in excess gallium conditions and no damping oscillations in the RHEED intensity showed that the layers exhibited step flow growth mode [163]. In the Ga limited growth conditions, the Ga adatom diffusion length is small hence the mobility of Ga adatoms on the surface was limited due to the diffusion length and the arriving Ga flux. Availability of more Ga atoms and the decrease in their fluctuations were attributed to flat surfaces observed in Ga-rich growth conditions. However, studies by Veizian et al. [164] showed that the roughness for both the surfaces was comparable and was determined by the presence of screw type dislocations. Moreover, the roughness was independent of the GaN layer thickness in Ga-rich growth conditions. However, it increased with increasing thicknesses in N-rich growth conditions where the kinetic roughening mechanism was involved.

The growth of GaN in Ga-rich conditions resulted in the formation of Ga droplets and residual n-type doping while N-rich growth conditions have resulted in high material quality with low n-type residual doping and residual impurities [157]. GaN layers were grown on sapphire substrate and the effect of III/V ratio was studied on the optical and structural properties. The growth was initiated by the standard process of nitridation to form AlN layer. This was followed by the growth of 25 nm GaN buffer layer at a low temperature of 500 °C. The subsequent GaN layers were grown at 835 °C with variable III/V ratio. The RMS roughness increased with the increasing III/V ratio and best value obtained was 3.6 nm for 5×5 μm^2 scan area. The concentration

of the residual impurities such as Si and C was found to reduce with the decreasing III/V ratio. However, it did not have any influence on the overall crystal quality of the GaN layers. Thus, unlike PA-MBE, growth conditions in the excess of nitrogen were found to be suitable when ammonia is used as a nitrogen source. The increase in the substrate temperature by 100 °C in ammonia MBE compared to PA-MBE was found to assist in improving the optical properties of the GaN layers [165]. Further studies on the effect of growth temperature on the properties of GaN layer showed that GaN decomposition accelerates beyond 800 °C and is independent of III/V ratio in N-rich growth conditions [166]. Desorption of GaN leads to the reduction in the growth rate and increased surface roughening between 850 to 870 °C. GaN layers with 2 µm thickness grown in N-rich conditions on sapphire substrate using AlN buffer layer exhibited excellent crystal quality with XRD FWHM of 210 arcsec [167]. The layers were Si doped and showed high electron mobility of 560 cm²/V.s and carrier density of $\sim 5 \times 10^{13}$ cm⁻³.

Studies by Tang et al. [171, 172] also showed that the growth rate of GaN layers diminishes beyond 880 °C as it undergoes decomposition and desorption of the adsorbed ammonia species. They demonstrated AlGaIn/GaN HEMTs at high temperatures on sapphire [168] as well as SiC substrates [169] with intentional carbon doping. The growth temperature was in a narrow window of 10 to 20 °C coinciding with the onset of the decline in growth rate at around 900 °C. It was found that low growth temperatures led to a rise in the dislocation density while the growth at high temperatures yielded 3D growth, reduced dislocation density of 10⁸ cm⁻² [170] and high electron mobility of 560 cm²/V.s for 2 µm thick GaN. Carbon was doped in the GaN layers to compensate the residual donors and obtain resistivity greater than 10⁶ Ω.cm using methane ion source. AlGaIn/GaN HEMT heterostructures with room temperature mobility of up to 1200 cm²/V.s were obtained. On the other hand, the same group demonstrated the growth of semi-insulating (high resistive) unintentionally doped GaN in the range of 10⁶ – 10⁸ Ω.cm at the lower temperature range of 740 to 780 °C exhibiting 2D growth mode [171]. This growth regime led to super-saturation of the surface with ammonia radicals which led to 2D growth mode and reduced oxygen incorporation. Corrion et al. [41] also studied the effect of the growth temperature and III/V ratio on GaN grown on SiC substrate. 3D or columnar growth was observed at lower growth temperatures and pitted surface morphology at higher temperatures. Similar observations were made as a function of ammonia flow. GaN layers with 2D growth mode (RMS $\sim$ 1 nm), pit-free surfaces, uniform mound

structures and threading dislocation density in the order of $3 \times 10^9 \text{ cm}^{-2}$ were obtained in the optimized growth conditions at moderate growth temperatures of $\sim 770^\circ\text{C}$ and lower III/V ratio with the ammonia beam equivalent pressure (BEP) of 3.1×10^{-4} Torr.

With the extensive ongoing studies on sapphire and SiC, the growth of GaN on Si (111) substrate is a relatively more challenging process due to high lattice and thermal mismatch. To begin with, partial nitridation of the Si surface was found to be unavoidable by background ammonia in the growth chamber [172, 173]. Thus, several groups tried to avoid its formation as it may result in the formation of amorphous Si_xN_y which is undoubtedly not suitable for the epitaxial growth. This was achieved by predeposition of Al on the Si surface before exposing it to the ammonia intentionally [174-176]. This process resulted in the formation of Al-N bond with the Si surface which is already ammonia exposed. Alternately, other groups preferred uniform intentional nitridation of the surface as the nitridation of the Si surface was anyway unavoidable. The SiN formation has been found to completely relax the lattice mismatch between AlN and Si [177]. The studies by Louarn et al. [178] showed that faster nucleation and transition of growth to 2D mode was obtained by exposing the Si surface to ammonia first followed by Al predeposition. However, disordered domains were formed due to the strain induced by atomic size difference between Al and Si (Al-Si γ phase) by depositing Al first on Si surface. The pre exposure of ammonia improved the overall quality of AlN buffer and also the corresponding GaN epilayers.

The high thermal mismatch between GaN and Si makes it difficult to grow thick layers and leads to cracking of the epilayers. Thus, various stress mitigating layers such as AlN/GaN stack interlayer [42], AlGa N interlayer [175] and AlGa N /GaN superlattice structures [174] have been used in order to obtain crack-free GaN on Si. Nikishin et al. [174] performed the growth of GaN layers on 2 and 3 in. Si substrates using AlN as a buffer layer and AlGa N /GaN superlattice as stress mitigating layers. The growth was initiated by predeposition of the Si surface with Al metal which assisted in reducing SiN islands formed due to the nitridation. It was found that the best quality AlN layers with XRD FWHM of 2.9 arcmin were obtained by optimizing the growth conditions. The III/V ratio was optimized such that rapid 3D to 2D transition occurred during the AlN growth. This was followed by introducing a short-period AlGa N /GaN superlattice for controlling the defect propagation from the AlN/Si interface and improving the quality of the subsequent GaN. Crack-free GaN layers with a thickness of 2.2 μm and good crystalline quality exhibiting XRD FWHM of 14 arcsec were

obtained. Zhang et al. [175] also used AlGaN/AlN as the buffer layer for the growth of GaN on 2 in. Si (111) substrate. They studied the effect of $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ layer thicknesses and the Al mole fraction of AlGaN layers on the crack density of GaN layers. It was found that by keeping the Al content between 30 to 60% and an optimum thickness of 120 and 250 nm for AlN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers, respectively, 1 μm thick GaN layers could be grown.

Semond et al. [42] have obtained high quality and crack-free GaN layers with up to 3 μm in thickness on 2 in. Si (111) using AlN/GaN stack. The AlN/GaN stack not only assisted in inducing compressive stress in the subsequent GaN but also filtered the dislocations for improved device performances. The dislocation density of $5 \times 10^9 \text{ cm}^{-2}$ was obtained for the GaN layer which is among the best on Si substrate [173]. The GaN surface showed the presence of mounds whose evolution via screw type dislocation mediated step flow growth was studied in detail [179]. The growth temperature of GaN buffer layer was found to be very critical in determining the stress relaxation and threading dislocation density [173]. The 2DEG and structural properties were correlated with the substrate curvature and the best results were obtained on a compressively strained layer structure. Finally, AlGaN/GaN HEMT heterostructures with Al content of 28% and a barrier layer thickness of 25 nm with a 1 nm AlN spacer layer were grown exhibiting room temperature mobility of $2000 \text{ cm}^2/\text{V.s}$ at a sheet carrier density of $9 \times 10^{12} \text{ cm}^{-2}$.

3. Growth and characterization techniques

3.1 MBE growth

All the epilayers studied in this thesis were grown using a MBE system (Veeco-GEN20MZ) which is configured for the growth of nitrides. It is a compact system for low volume wafer production. It comprises of several modules such as a load lock module, a growth module, a preparation (prep) module, and a storage module. The functional diagram and a picture of the system are illustrated in Fig. 3.1 and Fig. 3.2, respectively.

The substrate is loaded horizontally through the load lock door and is transferred finally to the growth module. The prep module is where the substrates are conditioned by out-gassing before transfer to the growth module for the epitaxial growth. Storage module as the name indicates is simply a location to store platens as needed before or after the growth. The growth module is where the effusion cells are located and the epitaxial growth process is carried out. The module is equipped with several effusion "SUMO" cells for metals such as Al and Ga, Veeco Uni-bulb as a nitrogen plasma source and a low temperature ammonia gas source. The plasma source generates an active nitrogen flux using high frequency RF (13.56 MHz) power source and can be tuned up to 500 W power. The low temperature ammonia source can be kept at a moderate temperature to avoid condensation. A unique feature of this MBE system is that PA-MBE and ammonia MBE growths can be performed in the same chamber and also for the same layer structure growth, if necessary.

Growth of III-nitrides by MBE is a non-equilibrium process where the vaporized and collimated beam of group III elements and the activated nitrogen species are directed towards a suspended heated substrate for the growth. The shutters on the cell orifice can be used to interrupt the molecular beam. Inner chambers are surrounded by cryo-panels that are cooled by liquid nitrogen ($\sim 77\text{K}$) during the growth.

The growth module is also equipped with process monitoring and analysis instruments, including ion vacuum gauges, pyrometer, beam flux monitor (BFM), RGA, RHEED, thin-film reflectivity and wafer curvature measurement tools. RGA is an instrument critical in the analysis of vacuum environment. It identifies residual gases that are present during the epilayer growths. The temperature measurement is assisted by the pyrometer and thermocouples. The pyrometer accurately measures

the surface temperature of the substrate before and during the epitaxy. Thermocouples give a control feedback signal to the temperature controllers for each heated zone. The in-situ reflectivity measurements are used to determine the growth rate, surface roughness and optical constants of the epilayers by monitoring the change in the laser beam intensity with time. The changes in the spacing of the reflected beam spot assists in the determination of the wafer curvature and the corresponding stress in real time.

Item		Item	
1	Effusion cells with shutter mechanism	9	Heated station for substrate outgassing
2	Growth module	10	Prep module
3	Growth module/storage module gate valve	11	Load lock module/prep module gate valve
4	Load lock transfer rod	12	Load lock module
5	Storage module elevator	13	Load lock cassette elevator
6	Storage module	14	Load lock door
7	Growth module transfer rod	15	Venting/roughening manifold
8	Optional prep module/storage module gate valve	16	z-axis manipulator

Fig. 3.1 Functional diagram of the MBE system.

Fig. 3.2 A partial picture of the MBE system.

The RHEED pattern display facilitates in the determination of the growth mechanism, growth parameters and crystal structure. The schematic representation of a typical RHEED set-up is shown in Fig. 3.3. It consists of an electron gun that generates a high energy beam of electrons which obliquely strike the surface of the substrate at grazing angles. The electrons get diffracted from the surface to form regular patterns on the phosphor screen. RHEED is sensitive to surface changes either due to the structural changes or growth kinetics such as adsorption, desorption etc.

The RHEED surface reconstruction patterns have been used for the thermal cleaning process and removal of surface oxides from Si (111) substrates. The appearance of (7×7) surface reconstruction pattern confirms the clean Si surface once the oxide is completely desorbed. The substrate temperature is calibrated by observing the transition of the (7×7) to (1×1) surface reconstruction pattern at 810 °C. RHEED study also assists in monitoring the arrangement of the surface atoms for polarity control and determining the growth modes of the epilayers. Sharp RHEED patterns are obtained for smooth surfaces while a rough surface produces diffused patterns. The variation in the RHEED intensity is analyzed to understand the adsorption and desorption kinetics.

Fig. 3.3 The schematic representation of a typical RHEED set-up.

The surface of the samples were characterized in the $[2\bar{1}\bar{1}0]$ and $[01\bar{1}0]$ azimuths using a commercial RHEED (KSA-400) system with the electron beam energy of 15 keV.

3.2 Characterization techniques

The structural characterization of the epilayers were performed using high resolution X-ray diffraction (HR-XRD), micro-Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Elemental analysis was carried out using secondary ion mass spectroscopy (SIMS). Hall effect and mercury probe C-V measurements were used for electrical characterization. These techniques are described briefly in the following sub-sections.

3.2.1 High resolution X-ray diffraction

High resolution X-ray diffraction (HR-XRD) is a versatile and non-destructive technique that assists in determining the detailed information of the crystalline quality, composition and the strain states of the material. Consider a perfect crystal arrangement to diffract monochromatic X-Rays of wavelength λ and the lattice planes spaced at a distance d . The rays after diffraction emerge at twice the “Bragg angle”, θ defined by $\theta = \sin^{-1}(\frac{\lambda}{2d})$ as shown in Fig. 3.4. The diffracted X-rays are detected using a detector with a high angular resolution.

Fig. 3.4 Illustration of the X-Ray incidence and diffraction from the crystal planes placed 'd' distance apart.

Any change in d for an imperfect crystal arrangement due to the strain in the epilayer results in producing a change in θ . Therefore, by measuring the shift in θ in $2\theta - \omega$ scan, one can observe the change in d and hence the strain in the lattice parameter. The out-of-plane lattice parameter is determined using $2\theta - \omega$ scans along the (004) plane of the epilayers. The contraction of the lattice parameter in the growth direction $\varepsilon_{\perp} = (c_{\text{meas}} - c_0)/c_0$ is related to its corresponding dilation $\varepsilon_{\text{II}} = (a_{\text{meas}} - a_0)/a_0$ in the in-plane as:

$$\varepsilon_{\perp} = -(2C_{13}/C_{33})/\varepsilon_{\text{II}} \quad \text{Eq. 3.1}$$

where, c_{meas} and a_{meas} are the measured lattice parameters, c_0 (GaN = 5.185 Å, AlN = 4.980 Å) and a_0 (GaN = 3.189 Å, AlN = 3.110 Å) are the relaxed parameters, and C_{13} and C_{33} are the components of the elastic stiffness tensor [180]. The Vegard's rule is applied to estimate the elastic constants and the relaxed lattice parameters for AlGaIn. By knowing the value of d using $2\theta - \omega$ measurements, the composition of unknown materials can be obtained. The Al composition in the AlGaIn layers were determined from the separation of the peaks obtained in the (004) $2\theta - \omega$ scans.

In addition, HR-XRD technique was also used in determining the crystal quality by measuring the FWHM of the X-ray rocking curve. The threading dislocations cause significant broadening of the X-ray rocking curve when the epitaxial layer thickness is beyond the critical layer thickness. The analysis of rocking curve FWHMs have been used for the quantitative determination of threading dislocation density. The screw and edge dislocations with burger vectors $b = \langle 0001 \rangle$ (c-type) and $b = \frac{1}{3} \langle 11\bar{2}0 \rangle$ (a-type) are related to the values of the lattice tilt and twist, respectively [181]. The tilt angle is measured from the slope of Williamson Hall plot using symmetric rocking

curves along (002), (004) and (006) planes. The rocking curve obtained in the asymmetric reflection of $(30\bar{3}2)$, occurring at $\chi = 70.449^\circ$ for GaN, is used to determine the in-plane twist in the epitaxial layers.

PANalytical X'pert Pro MRD system with a Cu K α 1 radiation source ($\lambda = 1.5406 \text{ \AA}$) and a detector acceptance angle of 0.25° was used for the HR-XRD measurements.

3.2.2 Micro-Raman spectroscopy

Raman spectroscopy involves the observation of inelastic scattering of monochromatic light supplied from a laser. The monochromatic light interacts with various vibrational modes (phonons) of the material resulting in an energy shift. The shift in this energy determines the type of vibrational modes in the material. Once the vibrational modes are identified, Raman spectroscopy can be used to determine the crystalline quality, free carrier concentration and residual stresses in the epitaxial layers as the vibrational modes are affected by these material properties. A typical Raman spectroscope consists of a laser light source of a fixed wavelength, incident normally on the sample through a microscope. The microscope can be used to focus on the area of interest even below the surface and collect the signal from a small volume ($< 1 \text{ }\mu\text{m}$ diameter). Reflected, elastically scattered and inelastically scattered signals are collected by the microscope and are directed on to a pair of notch filters. These filters allow the inelastically scattered light on to the detector and attenuate the reflected and elastically scattered light completely. The grating resolves the received signal and sends it to a sensitive charge-coupled device (CCD).

Group theory predicts that eight set of phonon modes exists for wurtzite structures (C_{6v}^4) and they are $2E_2$, $2A_1$, $2E_1$ and $2B_1$. Among these, two E_2 , one A_1 and one E_1 modes are active and the B_1 modes are silent [182]. In the back scattering $z(xx)\bar{z}$ configuration, with the laser beam incident on the (0001) surface, only E_2 and $A_1(\text{LO})$ phonon modes are allowed. Stress in the epitaxial layer shifts the E_2 phonon mode frequency and is linear with the stress. A list of standard phonon wave numbers for freestanding GaN and AlN are listed in Table 3.1.

Table 3.1 Raman active phonon modes for GaN and AlN.

	$E_2(\text{low})$	$A_1(\text{TO})$	$E_1(\text{TO})$	$E_2(\text{high})$	$A_1(\text{LO})$	$E_1(\text{LO})$
GaN	144	532	559	567.5	734	741
AlN	248	610	670	657	890	912

Hence, the shift in the E_2 mode of the Raman spectrum with respect to these values can be used to determine the stress and strain [183] in the epitaxial layers. The Raman spectrum was obtained using a confocal micro-Raman-WITech alpha300 system equipped with a laser wavelength of 532 nm.

3.2.3 Atomic force microscopy

Atomic force microscopy (AFM) technique is employed for imaging and measuring matter at the nanoscale; in terms of surface roughness, profiling and 3D views. It functions by measuring the forces between a probe and a sample. The force is influenced by the nature of the sample, the distance between the sample and the probe and also the probe geometry and surface contamination.

The basic principle of AFM is that the probe is maintained close to the surface and is maintained through a feedback mechanism as the scan continues. Also, this feedback helps in maintaining the probe at a constant distance from the sample to obtain sample topography [184].

Fig. 3.5 shows the schematic of a typical AFM set-up. It consists of a cantilever with a sharp tip at the end.

Fig. 3.5 A schematic of a typical AFM set-up.

The tip is brought closer to the surface for topographical imaging. The movement of the tip is sensed by a photo-detector. The sample height variation can be determined through a feedback arrangement [185].

An AFM system can operate in the following three modes:

(a) Non-Contact Mode: It works on the principle of van-der Waal attractive force between the oscillating tip and the surface. The tip is excited at its resonant frequency by the piezoelectric transducer where the amplitude of oscillations is a few nanometers ($< 10\text{nm}$). As the tip approaches the sample surface, the attractive force increases leading to a decrease in the resonance frequency. This decrease in the resonance frequency combined with the feedback loop system maintains a constant oscillation amplitude or frequency by adjusting the average tip-to-sample distance. Measuring the tip-to-sample distance at each (x, y) data point allows the scanning software to construct a topographic image of the sample surface.

(b) Tapping Mode/ Intermittent Mode/ Vibration Mode/ AC Mode: Similar to the non-contact mode, the tip oscillates at the resonant frequency excited by the piezoelectric transducer in this mode. However, the tip touches the sample and moves completely away in each oscillation in this mode [184].

(c) Contact Mode: In contact mode, AFM is done with the probe in contact with the sample surface. The resolution of the image is better than the non-contact and tapping modes. However, the attractive force, coupled with the electrostatic force, create substantial frictional forces, which might lead to sample damage. Contact mode is often called the static mode [184].

Shimadzu SPM-9500J2 and Asylum research Cypher-MFP-3D systems were used in tapping mode for the AFM measurements.

3.2.4 Scanning electron microscopy

Scanning electron microscopy (SEM) is an electron beam technique for the observation of materials in micron and sub-micron ranges. It is capable of generating 3D images for analysis of topographic features. It is also useful to measure the thickness of thin films. When used in conjunction with Energy Dispersive X-Ray Spectroscopy (EDX), one can perform an elemental analysis on microscopic sections of the material or contaminants that may be present. SEM is similar to light microscopy except that electrons are used instead of photons. Thus, much larger

magnification is possible since the electron wavelength is much smaller than the photon wavelength and the depth of field is higher.

SEM images the sample surface by scanning it with high energy electron beam. An electron beam of energy incident on the sample surface causes electron emission from the surface over a wide range of energies. The interaction of an electron beam with a solid can lead to the ejection of loosely bound electrons from the conduction band called secondary electrons. Auger electrons are emitted in an intermediate energy range while the back scattered electrons that have undergone large-angle elastic collisions leave the sample with the energy same as the incident electrons. The image in an SEM is produced by detecting secondary electrons. The secondary electrons are collected and their density is amplified and displayed on a CRT (cathode-ray tube). Mapping occurs from a specimen space to CRT space. These can be focused, deflected and accelerated using appropriate potentials. They don't contaminate the sample or the vacuum system.

JSM-7500F field emission-SEM (FE-SEM) system operating at an accelerating voltage of 1 kV was used for the measurements.

3.2.5 Transmission electron microscopy

In transmission electron microscopy (TEM) technique, a beam of electrons is transmitted through a very thin sample to form an image. The incident beam is focused on the sample using a condenser lens system. The electrons interact with the sample and are transmitted to form an image. The image is focused to a point using an objective lens and is magnified by a series of projector lenses on a fluorescent screen. If the sample is illuminated by parallel electron beam then this geometry is termed as selective area electron diffraction (SAED). However, if a convergent beam is incident on the sample, it generates diffraction patterns over several incident angles. This geometry is called as convergent beam electron diffraction (CBED).

There are two basic modes in TEM – bright field and dark field modes. The image obtained using the transmitted beam is a bright field image while the transmitted beam is excluded in the dark field imaging mode. The samples are typically prepared by focused ion beam (FIB) technique using a beam of Ga ions to sputter the material. TEM in this study was performed using a JEOL- 2100F and JEOL-JEM2100 system operated at 200 kV.

3.2.6 Secondary ion mass spectroscopy

Secondary ion mass spectroscopy (SIMS) is an analytical technique used to quantify the composition of a material. The surface of the material is bombarded with a primary beam which ionizes the particles. The mass spectrum of the subsequently ejected secondary ions is analyzed to determine the elemental or molecular composition of the material. The bombardment of the material with oxygen increases the yield of positive ions while cesium beam is used to increase the yield of negative ions. The electron affinity of the oxygen favors electron capture leaving the ejected ions as positively charged. However, the surface electron affinity is decreased using cesium due to which more negative ions are formed. The ion yields cannot be predicted and strongly depends on the element being analyzed and the material matrix. SIMS is quantified using standards with the same element and matrix material as the unknown sample to be analyzed. The standards must be analyzed under the same conditions as the change in beam species, energy or angle changes the ion yield.

SIMS can be performed in two modes namely, static and dynamic mode. Static or time of flight SIMS is a surface sensitive technique for precise elemental and molecular analysis. The material is bombarded with a pulsed ion beam and the lighter ions arrive at the detector first, with sequentially heavier ions following later. Thus, each pulse of primary ions produces a full mass spectrum of the secondary ions. However, the dynamic SIMS is a destructive technique where the ions are collected by the process of material removal using sputtering method. This technique is more suitable for elemental analysis using magnetic sector or quadrupole mass spectrometer. The acquisition time of the depth profile is converted to depth by either physical profilometry measurements or determining the sputtering rate from a standard of known depth or thickness.

The doping concentration in the samples was determined using time of flight-secondary ion mass spectroscopy (TOF-SIMS IV, ION TOF GmbH) by sputtering the surface area of $200\text{ }\mu\text{m}^2$ at 3kV using a focused Cs ion beam.

3.2.7 Hall effect

Hall effect is the presence of a measureable transverse voltage in a thin flat conductor. If an electric current flows through a conductor in a magnetic field, the magnetic field exerts a transverse force on the moving charge carriers which tends to push them to one side of the conductor and produces an electric field perpendicular

to the magnetic field. The Hall effect measurement technique is employed to obtain the resistivity, carrier type, density and mobility.

Applying the basic physical principle of Lorentz force, the Hall Effect can be well understood. Consider a semiconductor sample of Fig. 3.6 with a current I flowing in the right direction, and a magnetic field applied in z direction.

Fig. 3.6 Schematic illustrating Hall effect in a semiconductor.

When the magnetic field is applied perpendicular to the direction of the moving charges, they experience a force, called Lorentz force. The force acts normal to both directions. The formula for Hall voltage (V_H) is given by:

$$V_H = (I \times B) / q \times \eta \times d \quad \text{Eq. 3.2}$$

where, I is the current, B is the magnetic field, d is the sample thickness and q (1.6×10^{-19} C) is the elementary charge. Thus, the density of the charge carries can be determined using Eq. 3.2. The Hall voltage is negative for n-type and positive for p-type semiconductors. The sheet carrier density can be defined as $\eta_s = \eta \times d$.

Van der Pauw technique is widely used technique for the hall measurements. One can accurately measure an arbitrarily shaped sample having a two dimensional geometry and four ohmic contacts at the periphery. For a square geometry, the sheet resistance is denoted by R_S . Knowing the Hall voltage V_H as well as the sheet resistance R_S , the Hall mobility can then be determined using the following equation:

$$\mu = V_H / (R_S \times I_B) = 1 / (q \eta_s \times R_S) \quad \text{Eq. 3.3}$$

If the conducting layer thickness d is known, the bulk resistivity ($\rho = R_s d$) and the bulk carrier density ($\eta = \eta_s/d$) can be determined.

The hall measurements in this study were performed on square shaped samples ($1 \times 1 \text{ cm}^2$) using In metal as ohmic contacts. Bio-rad HL5500 system equipped with a standard sample stage, used for work at ambient and liquid nitrogen temperatures, having both high and low resistivity measurement capabilities was used for the measurements.

3.2.8 Mercury probe based Capacitance-Voltage (C-V) system

Capacitance-Voltage (C-V) measurements are useful for characterization of semiconductors and devices as they provide in-depth analysis of doping profiles. Mercury probe based C-V system is a non-destructive electrical characterization tool for semiconductors and dielectric materials. Mercury probe makes contact to the sample employing the unique dot-ring configuration allowing both front-back and front-front modes on semiconductor materials. It works on the principle of making a simple Schottky contact (dot contact) and ohmic contact (ring contact) with the semiconductor surface. A DC and AC voltage signal with small amplitude and high frequency is applied to the Schottky contact. The DC voltage V produces a space-charge region (SCR) of width W . The differential capacitance (expressed in F/cm^2) is defined by:

$$C = dQ_s/dV \quad \text{Eq. 3.4}$$

where, Q_s is the semiconductor charge.

The small signal ac voltage v will induce a charge increment in SCR:

$$dQ_s = qN(W)dW \quad \text{Eq. 3.5}$$

where, $N(W)$ is the carrier concentration, dW is a slight increase in the SCR width. Substituting Eq. 3.4 and Eq. 3.5 in the equation for parallel plate capacitance, $C = \epsilon/W$, and differentiating with respect to voltage leads to:

$$N(W) = -C^3/q\epsilon \left(\frac{dC}{dV} \right) \quad \text{Eq. 3.6}$$

Or,

$$N(W) = \frac{2}{q\epsilon} \left[\frac{d\left(\frac{1}{C_2}\right)}{dV} \right] \quad \text{Eq. 3.7}$$

Using Eq. 3.7, carrier concentration at a depth of W can be obtained from a C-V curve by calculating the slope of $\frac{1}{C_2}$ versus voltage plot. The depth profile can be used for the characterization of GaN HEMTs to get the position of 2DEG (thickness of the barrier layer) and the back ground carrier concentration in GaN layers.

4. Growth and characterization of AlGaN/GaN HEMT heterostructures on Si (111) by PA-MBE

4.1 Growth of aluminum nitride layers

The growth of GaN on Si (111) substrate leads to the development of large stresses in the GaN layer causing cracks and high density of threading dislocations due to the high thermal mismatch of ~54% and lattice mismatch of ~17% with Si (111), respectively. AlN is widely used as a buffer layer for the growth of GaN on Si since it helps to prevent the formation of amorphous Si_xN_y because the bond formation between Al and N prevails over Si and N [156]. Aluminum also has a good wetting characteristic on Si surface due to which formation of AlN is easier than GaN [186]. GaN grown on Si leads to melt-back etching of the Si substrate at elevated growth temperatures. Thus, AlN buffer layer protects the Si substrate by avoiding the Si out-diffusion and subsequent alloy formation of Ga with Si. Moreover, AlN also helps to reduce the thermal mismatch and lattice mismatch (~2.4 %) between GaN and Si. Hence, the realization of good quality AlN with smooth surfaces is crucial for obtaining high quality GaN layers.

This section discusses the optimization of the growth temperature and III/V ratio to obtain smooth surface morphology, good crystalline quality and low tensile strained AlN layers. AlN layer was grown on high resistive ($> 10,000 \Omega\cdot\text{cm}$) 100-mm Si (111) substrate having a thickness of 525 μm . The Si substrate was thermally cleaned by degassing it at 785 $^\circ\text{C}$ for 60 min. As shown in Fig. 4.1, the in-situ RHEED showed the typical (7 $\times$ 7) surface reconstruction pattern which indicates a clean Si (111) surface.

Fig. 4.1 RHEED reconstruction pattern along the Si $[1\bar{1}0]$ azimuth showing (7 $\times$ 7) on thermally cleaned Si (111) surface.

This was followed by a ramp down to low growth temperature of 550 °C. The Si (111) surface was then nucleated by exposing it concurrently to both active nitrogen and Al flux ranging from 1.15 to 1.9×10^{-7} Torr for 60 sec resulting in the formation of a thin layer of low temperature AlN (LT-AlN). It should be noted that the Al flux of LT-AlN was found to play a critical role in determining the surface morphology of the subsequently grown AlN and GaN layers. More details on its effect will be discussed in Section 4.4.

As shown in Fig. 4.2, streaky (1×2) RHEED reconstruction pattern is obtained for LT-AlN upon cooling down below 300°C substrate temperature. Smith et al. [107] have also observed similar reconstruction pattern for the Ga (metal) polar surface of GaN grown by PA-MBE which suggests that the LT-AlN in our samples is Al (metal) polar.

Fig. 4.2 Streaky (1×2) RHEED reconstruction pattern for LT-AlN along the (a) $[2\bar{1}\bar{1}0]$ and (b) $[01\bar{1}0]$ azimuths.

Subsequently, the substrate temperature was ramped up and the growth temperature of AlN layers was optimized in order to achieve good material properties such as smooth surface morphology, low dislocation density and residual tensile strain as discussed in the following section.

4.1.1 Growth temperature optimization

Table 4.1 lists four samples of AlN (samples A to D) grown over a temperature range of 700 to 860 °C on Si (111). The thickness of the AlN layer, grown using a constant Al flux of 2×10^{-7} Torr, was kept at 120 nm. It should be noted that the RF power was maintained at 300 W with a nitrogen flow of 2 sccm for the growth of all the layers by PA-MBE.

As can be seen, the surface roughness ($2 \times 2 \mu\text{m}^2$ scan area) and the screw dislocation density decrease with the increasing growth temperature. As the growth

temperature is increased, the surface mobility of adatoms increases that aids in the uniform coverage of the AlN surface leading to smooth surface morphology. The growth of sample A performed at the lowest growth temperature of 700 °C showed very high surface roughness indicative of Al condensation on the AlN surface. The high density of Al droplets on the AlN surface accounts for the increased surface roughness of sample A. An increase in the substrate temperature to 860 °C of sample D reduced the surface roughness to 0.5 nm and produced droplet free surface. The screw dislocation density has been found to systematically decrease with the increase in the substrate temperature. This is because the increased surface diffusion or migration of the Al adatoms also assisted in reducing the tilt between the AlN layer and the substrate. Additionally, the lowest residual tensile strain is also obtained for AlN layer grown at 860 °C. Thus, AlN layers with smooth surface morphology, lowest dislocation density and residual tensile strain was obtained at a growth temperature of 860 °C.

Table 4.1 The RMS roughness, dislocation density and residual tensile strain in AlN layers grown at different growth temperatures.

Sample	Growth temperature (°C)	RMS roughness (2×2 μm ²) (nm)	Screw dislocation density (× 10 ¹⁰ cm ⁻²)	Residual tensile strain (%)
A	700	67.6	3.86	0.22
B	760	5.4	2.15	0.27
C	800	2.5	2.10	0.34
D	860	0.5	1.94	0.21

This was followed by the growth of AlN layers at the optimized substrate temperature using various Al fluxes and the thicknesses were kept between 0.08 and 0.5 μm. Fig. 4.3 shows the growth rate of AlN as a function of incident Al flux with constant RF power and nitrogen flow.

The growth rate of AlN increases linearly for lower Al fluxes ($III/V < 1$) corresponding to N-rich growth regime. However, the growth rate saturates as the growth proceeds in the metal-rich growth regime when the Al flux is increased further ($III/V \geq 1$). A typical growth rate of 0.19 μm/hr is obtained in the saturation region. The stoichiometric growth condition ($III/V \approx 1$) corresponds to the transition from linear to saturation region. Furthermore, the metal-rich growth regime can be classified into – intermediate and droplet growth regimes.

Fig. 4.3 The AlN growth rate as a function of Al flux.

The growths performed at very high Al fluxes may eventually lead to the formation of Al droplets termed as droplet growth regime. However, no droplet formation occurs while the Al is in excess of the active nitrogen species in the intermediate growth regime.

4.1.2 Surface morphology

Fig. 4.4 shows the RHEED patterns obtained when the growth temperature of AlN was ramped down below 300°C substrate temperature. Spotty RHEED pattern was obtained for AlN grown in the N-rich growth regime indicative of 3D growth mode while 2D growth was obtained for AlN grown in the metal-rich growth regime. Streaky (2×6) or (1×1) surface reconstructions were observed in the intermediate growth regime indicative of Al-polarity [145]. Since the surface reconstruction depends on the Al coverage, the former occurs for 2-3 monolayers of Al on the surface and the latter is derived from a contracted and rotated surface lattice, when the surface coverage is greater than a few monolayers of Al [146]. Moreover, (3×3) RHEED pattern was obtained in the droplet growth regime corresponding to very high Al fluxes indicative of N-polar AlN [145].

The evolution of the RHEED pattern from spotty to streaky with increasing Al flux indicates that the transition of the growth mode from 3D to 2D depends on the surface wetting by Al flux. Similar observations have been made for the surface of AlN layers using AFM.

Fig. 4.4 RHEED reconstruction patterns along the $[2\bar{1}\bar{1}0]$ (left) and $[01\bar{1}0]$ (right) azimuths. AlN shows (a) spotty pattern in N-rich growth regime, (b) (2×6) and (c) (1×1) in the intermediate growth regime while (d) (3×3) pattern in the droplet growth regime.

Fig. 4.5 shows the AFM images ($1\times 1\ \mu\text{m}^2$ scan area) of the surface of 500 nm thick AlN layers. The AlN layers shown in Fig. 4.5 (a-c) were grown in the N-rich, intermediate and droplet growth regimes at Al fluxes of 5.4×10^{-8} , 2.4×10^{-7} and 5.0×10^{-7} Torr, respectively.

Fig. 4.5 The $1\times 1\ \mu\text{m}^2$ AFM images of the AlN layers grown in (a) N-rich, (b) intermediate and (c) droplet growth regimes at Al fluxes of 5.4×10^{-8} , 2.4×10^{-7} and 5.0×10^{-7} Torr, respectively.

The AFM images obtained for the AlN grown in N-rich growth regime show rough and 3D surface with RMS roughness of 10 nm, while smooth surfaces of AlN grown in the

intermediate and droplet growth regimes exhibit RMS roughness varying between 0.2 to 0.3 nm. Thus, rough surfaces are obtained for AlN grown in the N-rich growth regime developing into smoother surfaces when Al flux reaches stoichiometry and beyond. N-rich (Al limited) growth conditions of AlN lead to higher diffusion barrier for Al adatom diffusion. Thus, non-uniform wetting of the surface leads to 3D growth or highly columnar like morphologies [187] whereas increasing Al fluxes enable higher surface mobility of Al adatoms leading to smoother surfaces. The higher Al flux wets the surface and facilitates faster coalescence of 3D island nucleation followed by 2D lateral growth.

4.1.3 Structural properties

The crystalline quality of 500 nm thick AlN layers as a function of Al flux was determined using HR-XRD technique. The threading dislocation density in AlN as a function of Al flux is shown in Fig. 4.6. The screw and edge type dislocation densities determined in all the samples suggest that the overall quality of AlN improves with the increasing Al flux. A reduction of nearly 50% in the overall threading dislocation density can be seen for AlN layers grown in the droplet growth regime compared to N-rich growth regime.

Fig. 4.6 The screw and edge type dislocation density in AlN as a function of Al flux obtained from HR-XRD.

The residual strain and stress values determined in the AlN layers as a function of Al flux measured using micro-Raman spectroscopy are shown in Fig. 4.7. The residual

tensile strain and stress reduces with increasing Al flux from N-rich to intermediate growth regime. However, it increases for AlN grown in the droplet growth regime.

Fig. 4.7 The residual tensile strain and stress in AlN layers as a function of Al flux.

As discussed in Section 4.1.2, the transition of the growth mode from 3D to 2D depends on the mobility of Al adatoms due to the increased surface wetting in the metal-rich growth regime. The 3D to 2D transition enhances the dislocation bending by climb mechanism at the growth surface which promotes the annihilation of dislocations by looping and corresponding plastic relaxation of epitaxial layers [188] in the metal-rich growth regime. Thus, a 30 % reduction in the threading dislocation density in AlN layers has led to a 75% decrease in the residual tensile strain from N-rich to intermediate growth regime. As observed from the RHEED patterns, the growth of AlN layers in the intermediate and droplet growth regime exhibited Al and N-polarity, respectively. This suggests that polarity inversion has occurred in the AlN layers grown in the droplet growth regime. Thus, the presence of inversion domains may be a probable reason for an increased residual tensile strain and stress in the AlN layers grown in the droplet growth regime. The details on polarity studies can be found in Section 4.3.

4.1.4 Electrical properties

Hall measurements were performed using van der Pauw technique in order to determine the electrical properties of AlN layers as a function of Al flux. Fig. 4.8 shows the sheet resistivity and sheet carrier density variation for various Al flux

values. It should be noted that positive hall coefficient indicative of p-type conduction was obtained for all the samples. A decrease in the sheet resistivity by up to two orders of magnitude together with a three order increase in the sheet carrier density was observed with increasing Al fluxes. It is likely that the p-type conductivity occurs due to the diffusion of Al metal into Si at high substrate temperatures [189].

Fig. 4.8 The sheet resistivity and sheet carrier density as a function of Al flux. The sheet resistivity reduces while sheet carrier (hole) density increases with increasing Al flux.

If the AlN growth is performed in N-rich growth regime, Al does not have an opportunity to react with Si substrate, as all Al atoms arriving at the substrate react with active nitrogen to form AlN and thus no wetting layer of metallic aluminum is available on the Si surface to diffuse. However, the diffusion may increase with increasing Al flux doping Si as p-type and generating holes as charge carriers.

Thus, the study on morphological, structural and electrical properties of AlN layers as a function of Al flux suggests that good quality AlN layer with droplet-free surface and moderate resistivity can be obtained for an Al flux of 2.4×10^{-7} Torr in the intermediate growth regime.

It should be noted that high resistive AlN layers are obtained in the N-rich growth conditions. These growth conditions result in poor quality AlN layers with rough surface morphology. Thus, AlN layer grown in the intermediate growth regime using an Al flux of 2.4×10^{-7} Torr is chosen as an optimized flux value.

4.2 Growth of gallium nitride layers

The AlN buffer layers were grown at the optimized conditions as discussed in Section 4.1. This was followed by the optimization of the growth temperature of GaN in order to obtain good material properties.

4.2.1 Growth temperature optimization

Table 4.2 lists four samples of GaN (samples A to D) grown over the temperature range of 740 to 765 °C on Si (111) using the optimized AlN buffer layer. The thickness of the AlN buffer layer and GaN layer was kept at 120 and 500 nm, respectively. The GaN layers were grown using a constant Ga flux of 8.6×10^{-7} Torr.

As can be seen, the surface roughness ($5 \times 5 \mu\text{m}^2$ scan area) and residual tensile strain increases with increasing substrate temperature. A study by Garcia et al. [148] shows that as the growth temperature increases, Ga is found to desorb with an activation energy of 2.5 eV. The Ga flux is required to be increased with the increasing growth temperature to attain similar growth rates. Thus, it is evident from their study and our results that Ga desorption may be the cause for the increased surface roughness at high growth temperatures. The non-uniform Ga metal coverage of the GaN surface leads to rough surface morphology. The process of desorption at high growth temperatures causes low adatom surface diffusion or kinetically limited growth producing pitted surface morphology. It is also worth to notice that compact GaN layer of sample A grown at 740 °C shows the lowest residual tensile strain. However, no significant difference is observed in the dislocation density of the GaN layers grown at different growth temperatures. Thus, GaN layer with smooth surface morphology and lowest residual tensile strain is obtained at a growth temperature of 740 °C.

Table 4.2 The RMS roughness, dislocation density and residual tensile strain in GaN layers grown at different growth temperatures.

Sample	Growth temperature (°C)	RMS roughness ($5 \times 5 \mu\text{m}^2$) (nm)	Residual tensile strain (%)	Dislocation density ($\times 10^{10} \text{ cm}^{-2}$)	
				Screw	Edge
A	740	0.9	0.037	0.35	12.2
B	750	8.6	0.060	0.36	10.5
C	755	11.3	0.076	0.38	13.7
D	765	12.7	0.085	0.38	12.8

Subsequently, GaN layers were grown at the optimized growth temperature of 740 °C by varying the Ga fluxes. The thickness of AlN buffer layer was kept at 120 nm while the GaN layers were grown with the thicknesses ranging from 0.1 – 0.6 μm . The growth rate of GaN as a function of Ga flux is shown in Fig. 4.9.

Fig. 4.9 GaN growth rate as a function of Ga flux.

As can be observed, the growth rate of GaN layers exhibited similar trend as that for AlN when the Ga flux was varied. The growth rate is found to be linear under N-rich growth regime ($\text{III}/\text{N} < 1$) and it reaches saturation as the Ga flux is increased ($\text{III}/\text{N} \geq 1$). The GaN growth rate reaches saturation while the Ga metal is in excess of the active nitrogen species in the metal-rich growth regime. A growth rate of 0.19 $\mu\text{m/hr}$ is obtained in the saturation region for a constant supply of active nitrogen species.

4.2.2 Surface morphology

The RHEED patterns obtained for GaN grown in N-rich and metal-rich growth regimes are shown in Fig. 4.10 (a) and (b), respectively. The surface reconstruction patterns were obtained when the growth temperature of GaN was ramped down below 300 °C. Spotty RHEED patterns were obtained for GaN grown in the N-rich growth regime indicative of 3D island growth mode. In the intermediate growth regime with a Ga flux between 4.5 to 9.5×10^{-7} Torr, (2×2) reconstructed GaN surface was observed suggestive of Ga-polarity [107]. However, extremely dark RHEED patterns were obtained for GaN grown at a very high Ga flux of 1.16×10^{-6} Torr due to the accumulation of excess Ga in the form of droplets in the droplet growth regime.

Fig. 4.10 RHEED reconstruction patterns along the $[2\bar{1}\bar{1}0]$ (left) and $[01\bar{1}0]$ (right) azimuths. GaN shows (a) spotty and (b) (2×2) patterns in the N-rich and intermediate growth regimes.

Fig. 4.11 (a) and (b) shows the $3\times 3\ \mu\text{m}^2$ AFM images of the typical surface morphology of GaN layers in the N-rich and intermediate growth regime, respectively. The AFM images show rough and 3D surface with large pit density for GaN grown in N-rich growth regime with RMS roughness of 21.5 nm. The GaN surface shows 2D growth with increasing Ga flux in the intermediate growth regime.

Fig. 4.11 The $3\times 3\ \mu\text{m}^2$ AFM images of the GaN layers grown in the (a) N-rich and (b) intermediate growth regimes.

As the Ga flux increases, a smooth and nearly pit-free surface is obtained with atomically flat terraces and RMS roughness of 0.9 nm. The increase in the Ga flux has been found to increase the Ga adatom diffusion on the surface thereby reducing the surface pit density [190].

4.2.3 Structural properties

The dislocation density in 500 nm thick GaN with increasing Ga flux is shown in Fig. 4.12. The overall crystal quality is found to improve with the increasing Ga flux from N-rich to intermediate growth regime. However, a sudden degradation in the crystal quality is observed for GaN grown with a very high Ga flux in the droplet growth regime. The dislocations in GaN might be primarily due to two sources. Firstly, a high density of dislocations is generated at the highly mismatched AlN/Si interface. The dislocations which manage to propagate all the way in AlN up to GaN/AlN interface is one of the sources of dislocations in GaN. Secondly, some lattice mismatch induced dislocations are also generated at the GaN/AlN interface itself.

Fig. 4.12 The screw and edge type dislocation density in GaN as a function of Ga flux obtained from HR-XRD.

Assuming that the dislocations from the two sources is the same, the 3D columnar type growth in the N-rich growth regime may cause columnar grain coalescence leading to the degradation of the overall crystal quality. However, both screw and edge type dislocation density reduces with the increasing Ga flux as GaN layers exhibit 2D growth mode in the intermediate growth regime. Almost similar overall

dislocation density is obtained for all the GaN layers grown in the intermediate growth regime. It can be seen that the overall dislocation density increased again in the droplet growth regime. The poor surface below the droplets has been found to degrade the bulk properties of GaN grown in the droplet growth regime [191]. Highly non-stoichiometric conditions of the droplet growth regime might have led to the stacking faults resulting in poor quality GaN layers. Thus, “modulated growth” have been proposed to obtain conditions which results in atomically smooth surfaces and the absence of pitting, but with no droplet formation [121]. In our studied set of samples, the layers grown in the intermediate growth regime have been found to exhibit droplet-free and smooth surfaces with good crystalline quality.

The residual strain and stress in GaN layers was measured as a function of Ga flux. The layers were found to be nearly relaxed in all the growth regimes with residual tensile strain values ranging between 0.05 to 0.02% for GaN layers grown in N-rich and metal-rich growth regimes, respectively. The slightly higher residual tensile strain in the GaN layers grown in N-rich growth regime may be generated due to columnar grain coalescence.

4.2.4 Electrical properties

Hall measurements were performed using van der Pauw technique in order to determine the electrical properties of GaN layers as a function of Ga flux. Fig. 4.13 shows the sheet resistivity and sheet carrier density of GaN layers for various Ga flux values.

Fig. 4.13 The sheet resistivity and sheet carrier density as a function of Ga flux. The dotted line separates p and n-type conductivities in GaN layers.

The GaN layers grown under N-rich and intermediate growth regimes show p-type while n-type conductivity is seen in the droplet growth regime. A sudden drop in the sheet resistance can be observed at the transition of the growth regime from intermediate to droplet regime.

Since it is difficult to obtain unintentionally doped p-type GaN, the p-type conductivity observed for GaN layers grown in the N-rich and intermediate growth regimes is believed to be due to Al diffusion in Si substrate forming a conducting p doped Si layer as Al is a shallow acceptor in Si. The n-type conductivity for GaN layers grown in the metal or droplet growth regime and the sudden drop in the resistance could be due to the electrical conduction through the excess metal on GaN surface.

Slightly high resistive GaN layers were obtained using Ga flux of 7.6×10^{-7} Torr and below. However, they exhibited high surface roughness which is detrimental for the performance of AlGaIn/GaN HEMTs. GaN layers grown in the intermediate growth regime using a Ga flux of 8.6×10^{-7} Torr showed smooth surface morphology, droplet-free surface and moderate resistivity value. The growths performed in this regime also showed good crystalline quality and relaxed GaN layers as observed for up to 1.5 μm thickness in HR-XRD and micro-Raman measurements, respectively.

4.3 Effect of III/V ratio on the polarity of AlN and GaN layers grown in the metal-rich growth regime

Extensive studies made in this work on the growth of GaN in the N-rich growth regime showed layers with spotty RHEED pattern and rough columnar morphologies. However, excess Ga on the GaN surface in the metal-rich growth regime produced streaky RHEED patterns with smooth 2D growth morphologies and improved crystalline quality. Since both the rough surface morphology and the poor quality are undesirable for device epilayers, GaN layers grown in the metal-rich growth regime have been successfully utilized in the development of both Ga-polar and N-polar HEMTs for their unique advantages [116, 153, 192]. In addition, we have also demonstrated Ga-polar AlGaIn/GaN HEMTs grown in the metal-rich growth regime [151, 152] as discussed in Section 4.6. In AlGaIn/GaN HEMT heterostructure, the presence of 2DEG and the device performance are governed by the spontaneous and piezoelectric polarization properties of (Al)GaN. Hence, the determination of polarity of GaN material becomes an important study.

Polarity selection and inversion in GaN has been showed using Al insertion layers and AlN intermediate layers [193, 194]. However, the polarity study of AlN on Si (111) and its influence on the polarity of subsequent GaN has been investigated to a lesser extent than GaN on Si (111) by PA-MBE [147]. Since AlN is widely used as a buffer layer for the growth of GaN on Si (111), investigation on the polarity of AlN becomes necessary. In this study, a simpler approach for a good polarity control of AlN and its subsequent effect on GaN grown using Si (111) by PA-MBE technique is demonstrated by varying the III/V ratio in the metal-rich growth regime.

Fig. 4.3 (on page 58) and Fig. 4.9 (on page 64) show the growth rates of AlN and GaN, respectively. As discussed in Sections 4.1 and 4.2 and shown in Fig. 4.4 (on page 59) and Fig. 4.10 (on page 65), AlN and GaN layers grown in N-rich growth regime exhibited spotty RHEED patterns while metal-polar layers were obtained in the intermediate growth regime. However, N-polar AlN was attained in the droplet growth regime and very dark or nearly no RHEED pattern could be observed for GaN grown in the droplet growth regime. Thus, all the samples were then etched in aqueous KOH solution to confirm the polarities of these layers. The KOH etching characteristics of AlN and GaN layers are different for N-polar and metal-polar (Al,Ga) surfaces. The N-polar layers get etched quickly and show the presence of hexagonal hillocks or pyramidal features on the surface while metal-polar layers remain intact with the formation of only defect related hexagonal etch pits on the surface [195]. The mechanism of this selective etching of N-polar layers can be explained by the atomic configuration and the reaction formula given by Dongsheng et al. [108]. The single dangling bond of the nitrogen atom on the surface of N-polar layers allows the hydroxide ions (OH^-) to react with the metal atoms. It is presumed that AlN and GaN form their respective hydroxides which dissolve in KOH solution leading to the etching of N-polar layers.

Thus, the samples were cut into several pieces of approximately 1 cm^2 area and then etched in 2 to 6M aqueous solution of KOH in deionized water, maintained at $60\text{ }^\circ\text{C}$ for polarity determination. The solution was magnetically stirred, and the etching was performed as a function of time. AlN and GaN layers grown under intermediate growth conditions exhibited similar etching characteristics. These samples remained inert even after 30 min. of etching in the KOH aqueous solution indicative of metal-polarity which is in confirmation with the observed RHEED patterns. However, unlike GaN, hexagonal etch pits were formed on the surface of AlN grown in the intermediate growth regime which appeared in various sizes (not shown). Fig. 4.14 (a)

and (b) show the cross-sectional secondary electron image (SEI) micrographs of AlN and GaN layers grown in the droplet growth regime, respectively. Triangular shaped pyramidal features limited by $(11\bar{2}1)$ plane were observed for AlN indicative of N-polarity [147]. However, no evident change was observed for GaN even when the sample was dipped in KOH aqueous solution for up to 30 min. Hence, AlN exhibited N-polarity while Ga-polar GaN is obtained in the droplet growth regime. It can thus be deduced that polarity inversion might have occurred in AlN from Al-polar to N-polar whereas no inversion is seen for Ga-polar GaN layers.

Fig. 4.14 SEM image obtained after KOH etching at 60 °C. Pyramidal features are developed in (a) N-polar AlN while no change is observed in (b) Ga-polar GaN grown in the droplet growth regime.

An explanation has been proposed for the occurrence of inversion in AlN and is schematically illustrated in Fig. 4.15. As can be seen, LT-AlN terminates with Al-polarity, though subsequent growth of AlN in the droplet growth regime results in N-polarity. In the droplet growth regime, it can be expected that excess Al accumulates on the surface due to insufficient supply of active nitrogen species or highly Al-rich growth conditions of AlN. The observed inversion in the polarity of AlN may perhaps be due to the saturation of the underlying growth surface with the excess Al metal. This might enable the formation of Al-Al bonding (encircled in Fig. 4.15) causing a disruption in the stacking sequence and the subsequent growth of N-polar AlN. On the contrary, no inversion is observed in GaN grown in the droplet growth regime.

A possible reason for the GaN-polarity selection is schematically shown in Fig. 4.16. The type of bonding occurring at the position marked with the arrows is expected to determine the subsequent polarity of GaN grown on Al-polar AlN. Three possible bonding configurations comprising of Al-N, Al-Al or Al-Ga and the corresponding polarities are depicted in case I, II and III, respectively in Fig. 4.16. While case I type of bonding results in Ga-polar GaN, N-polar GaN is obtained for case II and case III type of bonding. Hence, metal-metal bonding (Al-Al or Al-Ga) is necessary for the inversion to occur resulting in N-polar GaN on Al-polar AlN. The growth of AlN in the

intermediate growth regime inhibits the possibility of excess Al metal on the surface of AlN. Consequently, the formation of Al-Al bonding of case II and the subsequent polarity inversion of GaN to N-polarity may not be a possibility. Furthermore, since the bonding energy between Al-N is higher than that between Al-Ga, the polarity of GaN grown on Al-polar AlN will depend on the availability of Ga and N species arriving at the surface of AlN. Al-N bonding becomes more probable than Al-Ga bonding if sufficient active N species are reaching the surface of AlN and Ga metal flux is not abundant enough to completely mask the AlN surface.

Fig. 4.15 The schematic model to illustrate the inversion of Al-polar to N-polar AlN and the formation of Al-Al bonding (encircled).

Thus, even though the growth of GaN is performed in the droplet growth regime, Al-N bonding of case I may prevail over the Al-Ga bonding of case III resulting in Ga-polar GaN. Hence, it can be suggested that N-polar GaN may be obtained by facilitating the formation of Al-Al bonding through the insertion of Al metal layers on the surface of Al-polar AlN.

A separate study was performed on the influence of AlN-polarity on the polarity of GaN layers. Two GaN/AlN samples numbered 1 and 2 were grown with GaN in the intermediate growth regime. The GaN layers of sample 1 and 2 were grown on AlN grown in the intermediate and the droplet growth regimes, respectively. AlN of sample 1 exhibited Al-polarity with a (2×6) RHEED surface reconstruction pattern whereas N-polar AlN was obtained for sample 2 that showed a (3×3) RHEED pattern as shown in Fig. 4.4 (b) and (d) (on page 59), respectively.

Fig. 4.16 GaN-polarity selections in droplet growth regime on Al-polar AlN. Al-N, Al-Al and Al-Ga bonding marked by arrows determine the polarity selection in Case I, II and III, respectively. Case I illustrates GaN with Ga-polarity while Case II and III show N-polarity.

It was observed that GaN layers grown under intermediate growth regime on both Al-polar and N-polar AlN remained inert to KOH etching indicating Ga-polarity of GaN. Thus, it can be inferred that polarity inversion might have happened in sample 2 leading to Ga-polar GaN grown on N-polar AlN. To further confirm the polarity of GaN on the underlying N-polar AlN layer of sample 2, CBED patterns were obtained along $[10\bar{1}0]$ zone axis. TEM was performed using a focused probe of 1 nm and a condenser aperture of 10 μm . Patterns have been simulated at thicknesses from 50 to 200 nm obtained by blochwave calculation embedded in the JEMS software for direct comparison with the experimental patterns [196].

The bright field cross-sectional TEM image of GaN/AlN layers of sample 2 can be seen in Fig. 4.17 (a). The experimental CBED $[10\bar{1}0]$ pattern and the simulated diffraction pattern corresponding to a thickness of 83 nm for GaN layer are shown in Fig. 4.17 (b) and (c), respectively. The identical comparison of the experimental and simulated patterns confirms that GaN has grown with Ga-polarity on N-polar AlN. It should be noted that the CBED $[10\bar{1}0]$ patterns were also obtained for N-polar AlN. Unlike GaN, the asymmetry for (0002) and (000 $\bar{2}$) discs was found to be weak and indistinct in order to confirm the polarity of AlN as N-polar by CBED technique. The observed dissimilarity is due to the fact that the difference between the atomic number of Al and N is much smaller than that between Ga and N [197]. However, the (3 $\times$ 3) RHEED reconstruction pattern observed on the surface of AlN and the triangular pyramidal structures observed after KOH etching have confirmed the polarity of AlN grown in the droplet growth regime as N-polar.

Fig. 4.17 (a) Bright field cross-sectional TEM image of sample 2 recorded with diffraction vector $g = [11\bar{2}0]$. (b) Experimentally obtained CBED $[1\bar{1}00]$ pattern is compared with (c) simulated pattern for 83 nm thick GaN layer.

This observation suggests that the polarity might have inverted from N-polar AlN to Ga-polar GaN. The high resolution TEM (HR-TEM) image of one such location where the inversion occurs at the GaN/AlN interface of sample 2 is shown in Fig. 4.18 (a). The atomic arrangement illustrating the growth of Ga-polar GaN on N-polar AlN is overlaid as an inset in Fig. 4.18 (a) and is schematically illustrated in Fig. 4.18 (b). The HR-TEM images have been post-processed using a Weiner filter for the noise reduction [198]. The orientation of the sample is in the $[1\bar{2}10]$ zone axis and the inversion domain boundary (IDB) marked with the dotted line in the inset is along the (0001) plane. It should be noted that the arrangement of the atoms is slightly distorted at certain locations of the interface which might be due to the dislocations at the lattice mismatched GaN/AlN interface. As can be seen, Al-Al bonding indicated by an arrow at the GaN/AlN interface is favorable in the presence of excess Al metal on the surface of N-polar AlN grown in the droplet growth regime. Thus, it is interesting to note that Al-Al bonding at the GaN/AlN interface is the cause for the conversion of the polarity of N-polar AlN to Ga-polar GaN.

Fig. 4.18 (a) HR-TEM image of the GaN/AlN interface of sample 2 in the $[1\bar{2}10]$ zone axis. The arrangement of Ga (large white circles), Al (small white circles) and N (black circles) atoms is shown as overlay in the inset. The image has been Weiner filtered to reduce the noise. The Al-Al bonding is indicated with an arrow and the IDB along (0001) plane is marked with the dotted line. (b) A schematic model illustrating the polarity inversion structure of Ga-polar GaN grown on N-polar AlN. The metal bonding (Al-Al) at the GaN/AlN interface is encircled.

Hence, it can be concluded that the polarities of the layers determined through KOH etching studies are in agreement with the observed RHEED patterns. The growth of both AlN and GaN layers in the intermediate growth regime resulted in metal-polarity. While the polarity of AlN obtained was N-polar, Ga-polar GaN was achieved in the droplet growth regime. Thus, a polarity inversion was observed for AlN from Al-polar to N-polar in the droplet growth regime. Furthermore, the studies also illustrated that polarity inversion occurred at the GaN/AlN interface enabling the growth of Ga-polar GaN on N-polar AlN. Hence, Ga-polar GaN could be obtained on Si (111) using both Al and N-polar AlN buffer layer by PA-MBE. The formation of Al-Al bonding was found to be the reason for the observed inversions in AlN and GaN layers. Thus, it is suggested that Al metal flux played a major role in controlling the polarity of AlN and hence determining the polarity of the subsequent GaN layers, which is essential for the development of conventional Ga-polar AlGaN/GaN based HEMTs grown on Si (111) by PA-MBE.

4.4 Study on the “comets” and micro-crystals

Both AlN and GaN layers obtained in the intermediate growth regime showed 2D growth modes with smooth surfaces and good structural properties. As discussed, smooth surface morphology is essential to obtain good 2DEG properties for the HEMT applications. Poor AlGaIn/GaN interface decreases the mobility significantly due to the increase in the interface roughness scattering [199]. Thus, the effect of the Al flux during the growth of LT-AlN on the surface morphology of subsequent AlN and GaN layers is investigated in this study.

Fig. 4.19 (a) and (b) show the optical microscope images of LT-AlN grown with Al flux of 1.9×10^{-7} and 1.15×10^{-7} Torr, respectively. LT-AlN grown with higher Al flux of 1.9×10^{-7} Torr shows the presence of some distinct features on the surface while featureless surface is obtained for the LT-AlN grown at a lower Al flux of 1.15×10^{-7} Torr. Thus, it is likely that the excess Al metal in the LT-AlN plays an important role in the development of these features on the surface.

Fig. 4.19 The optical microscope images of the LT-AlN surface grown with Al flux of (a) 1.9×10^{-7} and (b) 1.15×10^{-7} Torr.

The features were further investigated using AFM technique for their surface morphology and shape. Fig. 4.20 shows the $5 \times 5 \mu\text{m}^2$ AFM image of a typical feature that appears on the surface of LT-AlN grown with higher Al flux of 1.9×10^{-7} Torr. As can be seen, the feature derives its name as “comet” since it is found to exhibit a “comet” like shape.

Fig. 4.20 A typical AFM image ($5 \times 5 \mu\text{m}^2$) of the “comet” like feature that appears on the surface of LT-AlN grown with higher Al flux of 1.9×10^{-7} Torr.

The growth of LT-AlN was followed by the growth of AlN and GaN layers to investigate the effect of these comets on the surface morphology of the subsequently grown layers. AlN and GaN layers were grown with a thickness of 120 and 500 nm, respectively at optimized fluxes in the intermediate growth regime. Fig. 4.21 (a) and (b) show the optical microscope images of the AlN surface and the subsequently grown GaN surface.

Fig. 4.21 The optical microscope images of (a) AlN surface and subsequent (b) GaN surface grown on the LT-AlN (Al flux of 1.9×10^{-7} Torr), respectively.

As can be seen, the comets which appeared on the surface of LT-AlN can also be seen on the surface of AlN. Additionally, micro-crystal type structures can be seen emerging on the GaN surface.

FE-SEM technique was used to further investigate the comet type morphology and the micro-crystals appearing on the AlN and GaN surfaces. FE-SEM experiments were carried out at INA, Kassel University, Germany in this study. Fig. 4.22 (a) and (b) show the FE-SEM images of the comet type morphology and the micro-crystals, respectively. Fig. 4.22 (c) shows the magnified image of a typical comet while Fig. 4.22 (d) shows the image of the comet associated with micro-crystals.

Fig. 4.22 FE-SEM images of (a) comet type morphology and (b) micro-crystals, respectively. The magnified image of a (c) typical comet and (d) the comet associated with micro-crystals.

As can be seen in Fig. 4.22 (b), comets are found to be associated with the micro-crystals. It is interesting to note that although micro-crystals exist at the comet site but not every comet is associated with a micro-crystal. Moreover, the density of micro-crystals on the GaN surface was found to increase with the increasing Ga flux from intermediate growth regime ($\sim 8.6 \times 10^{-7}$ Torr) to droplet growth regime ($\sim 1.15 \times 10^{-6}$ Torr), as shown in Fig. 4.23. This increase of micro-crystal density with increasing Ga flux shows that Ga flux aids in the formation of the micro-crystals on the comet sites.

Al-Si interdiffusion undergoing eutectic transformation has been found to result in etch pits on Si [200]. The formation of Al-Si eutectic alloy is probable at the LT-AlN and Si substrate interface if the growth temperature is close to the eutectic temperature and sufficient amount of Al metal is available for the eutectic alloy to form. The dissolution of underlying Si from the substrate into the Al and subsequent penetration of Al into Si

may occur at the growth temperature of LT-AlN. The Al-Si interdiffusion is found to result in the formation of the etch pits [200]. Thus, the etch pits may appear in the form of comets on the LT-AlN surface which lead to similar pit or comet formation on the surface of subsequent AlN as well. As can be seen in Fig. 4.22 (c), the comet seems to exhibit diverse faces because of the etching and possible exposure of some other planes of Si substrate. Moreover, smaller unfilled pits distributed throughout the surface can also be seen which can be attributed to the non-uniform substrate etching.

Fig. 4.23 The optical microscope images of GaN surface with increasing Ga flux. The micro-crystal density increases with increasing Ga flux from (a) 8.6×10^{-7} to (b) 1.15×10^{-6} Torr, respectively.

Fig. 4.22 (d) shows that the comets are associated with micro-crystals when GaN is grown in the intermediate growth regime. The diverse faces of the comets may aid in the formation of various potential nucleation sites for the micro-crystalline GaN growth. The growth rate of micro-crystalline GaN may vary depending on the nucleation site leading to the formation of the micro-crystals with different heights. Many small-sized micro-crystals may also have assembled together to form a bigger cluster of micro-crystals and some are still in the course of developing.

Moreover, the increase in the density of the micro-crystals with the increasing Ga flux in Fig. 4.23 may be because the availability of higher Ga flux may provide favorable conditions for more of such GaN nucleation to occur. Hence, the density of micro-crystals increases with the increasing Ga flux as they nucleate on more number of comets and their respective faces. Conclusively, in order to obtain GaN layers with smooth surfaces and good crystalline quality, it is necessary to grow LT-AlN at the optimized Al flux and the subsequent AlN and GaN layers in the intermediate growth regime.

4.5 Bilayer controlled growth of GaN layers

As discussed in Section 4.2, nearly relaxed GaN layers with smooth surface morphology and good crystalline quality are obtained in the intermediate growth regime. Thus, it is important to perform the growth of GaN in the optimized growth window of this regime. However, the growths are required to be performed for longer durations as the growth rate is limited by the active nitrogen species supplied by the nitrogen plasma. Thus, the narrow growth window for the GaN layer in PA-MBE technique is found to be affected by the fluctuation in Ga fluxes during the longer growth times. Consequently, poor reproducibility results are obtained for the GaN layers and the subsequent AlGaIn/GaN HEMT heterostructures.

Several studies have established the presence of Ga bilayer on the GaN surface in the metal-rich growth conditions [201-203]. This Ga bilayer has been demonstrated to be energetically favorable under metal-rich growth conditions constituting of a bottom Ga monolayer (ML) and a laterally contracted ML on the top [204]. The bilayer can be maintained on the surface throughout the growth by establishing an equilibrium between the amount of incoming Ga flux on the GaN surface and that desorbed away from the surface. In this section, we have utilized the desorption time for the Ga bilayer from the corresponding RHEED intensities in order to obtain controlled and reproducible AlGaIn/GaN HEMT heterostructures.

The Ga desorption kinetics was studied on the smooth and droplet-free surface of 500 nm thick GaN layer grown on 120 nm thick AlN buffer layer. Both AlN and GaN layers were grown at the optimized growth conditions as discussed in Section 4.1 and 4.2, respectively. Fig. 4.24 shows the variation in the RHEED intensity of the specular beam during Ga desorption process on GaN surface. The Ga shutter is opened for 20 sec with a constant Ga flux of 6.7×10^{-7} Torr and then closed. Since the Ga supply is ceased, Ga desorbs and the oscillatory transients can be seen during the desorption which emerges as a function of substrate temperature. As can be seen, Ga desorption rate increases with increasing substrate temperature from 698 to 728 °C.

The initial Ga layer wets the surface while the next is laterally contracted with reduced Ga-Ga spacing which is predicted to be closer to bulk Ga [204]. The excess Ga may also get accumulated on top of this bilayer. Thus, the excess Ga and the contracted layer of Ga get desorbed first followed by the Ga layer which is wetting the surface.

The time delay for the oscillation to appear is due to the reduced desorption rate for the GaN surface as the substrate temperature is reduced.

Fig. 4.24 RHEED intensity of the specular beam as a function of time for GaN at different substrate temperatures (T_s). The Ga flux was maintained at 6.7×10^{-7} Torr.

The physical mechanism involved in the Ga desorption process is illustrated in Fig. 4.25. The bilayer desorption time (t) is plotted against the substrate temperature (T_s) in Fig. 4.26. The activation energy (E_A) for the bilayer desorption is calculated to be 3.7 eV similar to that obtained by Zheng et al. [205].

Fig. 4.25 The physical mechanism involved in the Ga desorption process.

The “growth window” was established by determining the region where the surface coverage is the same despite the fluctuations in the Ga flux at a substrate

temperature of 690 °C. The growth temperature of 690 °C was chosen for this study instead of the GaN growth temperature of 740 °C as discussed in Section 4.2. This is due to the reduced desorption rate for the GaN surface at lower substrate temperature. The longer desorption times at lower substrate temperature allows to obtain the bilayer oscillatory transients even at very low Ga fluxes.

Fig. 4.26 The bilayer desorption time (t) is plotted against the substrate temperature (T_s).

Fig. 4.27 shows the plot of the desorption time for the bilayer as a function of Ga flux at the substrate temperature of 690 °C. The plot is further divided into regions 1, 2 and 3 such that the desorption time of the bilayer increases with increasing Ga flux for regions 1 and 3, while it remains fairly constant irrespective of the change in Ga flux for region 2. The desorption time is zero for the growth of GaN in N-rich growth conditions. However, the desorption time or in other words, the surface coverage increased with increasing Ga flux for the growth of GaN in metal-rich growth conditions in region 1. The surface coverage remains stable in the form of a Ga bilayer in region 2 irrespective of the Ga flux. However, more Ga gets accumulated in the form of droplets on top of the Ga bilayer and consequently the desorption time increases with increasing Ga flux.

As observed in Fig. 4.27, the growth of GaN layers can be performed in Ga stable conditions of region 2, wherein the desorption time or the recovery time (the time required for the recovery of RHEED intensity) of the Ga bilayer is fairly constant.

Fig. 4.27 Ga desorption time for different Ga fluxes at $T_s = 690^\circ\text{C}$. The desorption time increases with increasing Ga fluxes in regions 1 and 3 while it remains fairly constant in region 2.

Fig. 4.28 shows the typical bilayer oscillatory transients occurring in regions 2 and 3 during GaN growth at a substrate temperature of 740°C . Region 1 could not be clearly identified due to the rapid desorption of the Ga bilayer at low Ga fluxes.

Fig. 4.28 RHEED intensity of the specular beam as a function of desorption time during GaN growth at the substrate temperature (T_s) 740°C . The typical bilayer oscillatory transient is shown in regions 2 and 3.

The desorption time was monitored at equal intervals of time by closing the Ga and RF Plasma shutters and allowing the excess Ga to desorb. The Ga flux was adjusted correspondingly to obtain high quality layer in Ga stable conditions of region 2.

The typical growth procedure for obtaining GaN layers using Ga bilayer involves 3D growth of GaN layers for the first 60 min (~ 200 nm) followed by the transition to the 2D growth mode. Fig. 4.29 shows the desorption time transient for Ga on the surface and the corresponding RHEED patterns in 3D and 2D growth modes of GaN. The Ga bilayer was thus maintained for the growth of 1 μm thick GaN in Ga stable growth conditions by adjusting the Ga flux where the slightly excess Ga formed a steady-state layer of Ga adatoms on the surface without the formation of Ga droplets. A RHEED pattern of (2 $\times$ 2) reconstruction was observed after cooling the sample below 300 $^{\circ}\text{C}$ substrate temperature indicative of Ga-polarity and smooth surface morphology.

Fig. 4.29 The desorption time transient observed in the 3D and 2D growth modes of GaN. The corresponding RHEED patterns are shown as an inset.

Thus, the growth of GaN layers controlled using the bilayer technique produced smooth surface morphology with RMS roughness varying between 1.3 to 1.7 nm for $5 \times 5 \mu\text{m}^2$ scan area. The screw dislocation density was obtained to be $4 \times 10^9 \text{ cm}^{-2}$ while the edge dislocation density ranged from 1.5 to $2.0 \times 10^{11} \text{ cm}^{-2}$. Moreover, nearly relaxed and crack-free 1 μm thick GaN layers were obtained with a small residual tensile strain of 0.02%. This ascertained that the grown GaN had good and reproducible material properties.

4.6 AlGaN/GaN HEMT

A schematic diagram of the typical AlGaN/GaN HEMT heterostructure on Si (111) substrate is shown in Fig. 4.30. The AlN layers were grown with 120 nm thickness at an optimized Al flux of 2.4×10^{-7} Torr. Subsequently, 0.5-1.5 μm thick GaN was grown using the bilayer technique followed by AlGaN barrier layer and 2 nm GaN cap layer. As investigated by Ambacher et al. [34], Al content $> 40\%$ may cause structural defects due to the highly mismatched AlGaN/GaN interface. This along with the interface roughness may cause scattering of the electrons leading to mobility degradation. Moreover, Al content $< 15\%$ results in poor carrier confinement due to reduced conduction band offset between AlGaN/GaN. Thus, the barrier layer was grown with Al content within the range of 15 to 40% and different thicknesses to obtain high quality HEMTs. The Al content in the barrier layer for a typical HEMT heterostructure is obtained at five different locations using HR-XRD symmetric (004) ω -2 θ scan as shown in Fig. 4.31. The measured data is fitted against the simulated data to estimate the Al content based on the separation of the peaks. The coordinates of the locations on the wafer and the respective Al content along with the FWHM values of GaN (004) peak are compiled in the adjoining table. The standard deviation of 0.39 in the Al content and 8.25 in the FWHM values indicated good uniformity across the 100-mm wafer.

Fig. 4.30 The schematic diagram of a typical AlGaN/GaN HEMT heterostructure on Si (111) grown by PA-MBE.

A systematic study has been performed to investigate the effect of Al content in the barrier layer and its thickness on the 2DEG properties of AlGaN/GaN HEMT heterostructures. Moreover, the effect of GaN layer thickness is also studied on the

structural properties of AlGaN/GaN HEMT heterostructures and the corresponding 2DEG properties.

Fig. 4.31 The measured and simulated symmetric (004) ω -2 θ scan at five different locations for AlGaN/GaN HEMT heterostructure obtained using HR-XRD. The co-ordinates of the locations and the respective Al content along with the FWHM values of GaN (004) peak are compiled in the adjoining table.

Samples H1, H2 and H3 were grown with AlGaN barrier layer having different Al contents and barrier layer thicknesses on a constant 1 μm thick GaN layer. For samples H4, H5 and H6, the thickness of GaN layer was varied while the AlGaN barrier layer was grown with the optimized Al content and thickness. The structural and electrical properties of the HEMT samples H1-H3 are listed in Table 4.3. The screw and edge type dislocation density of $3.9 \times 10^9 \text{ cm}^{-2}$ and $1.6 \times 10^{11} \text{ cm}^{-2}$, respectively is obtained for all the GaN layers of the HEMT heterostructures.

Table 4.3 The structural and electrical properties of AlGaN/GaN HEMT heterostructures grown with different barrier layer thicknesses and Al content.

Sample	Dislocation density ($\times 10^{10} \text{ cm}^{-2}$)		Sheet carrier density ($\times 10^{13} \text{ cm}^{-2}$)	Mobility ($\text{cm}^2/\text{V.s}$)	Barrier layer thickness (nm)	Al content (%)
	Screw	Edge				
H1	0.40	17	1.9	570	28	31
H2	0.39	16	1.2	863	25	31
H3	0.39	16	1.0	970	25	29

The mobility and sheet carrier density of the 2DEG ranges between 570 to 970 $\text{cm}^2/\text{V.s}$, and 1.0 to $1.9 \times 10^{13} \text{ cm}^{-2}$, respectively. The lowest mobility is obtained for the sample H1 with the highest Al content of 31% and AlGaIn barrier layer thickness of 28 nm. However, higher mobilities and reduced sheet carrier density are obtained for sample H2 when the barrier layer thickness is reduced to 25 nm for the same Al content. The mobility further improves for sample H3 by maintaining the barrier layer thickness at 25 nm while reducing the Al content to 29%. The poor mobility of sample H1 can be attributed to the increased carrier scattering due to the higher sheet carrier density. The presence of the carriers too close to the AlGaIn/GaN interface may also result in alloy scattering or interface roughness scattering and hence degrade the mobility. The enhanced carrier density at higher barrier layer thickness and Al content could be due to the combined effect of surface states and polarization as a source of electrons [35]. Hence, moderate sheet carrier densities and improved mobilities were obtained by reducing the barrier layer thickness for sample H2. In order to further increase the mobility, reducing the barrier layer thickness would appear to be a logical means, however, reducing the barrier layer thickness further may result in the depletion of the surface states leading to lower sheet carrier density and reduced mobility. Hence, controlling the 2DEG carrier density by reducing the Al content in the barrier layer would be a feasible choice. Thus, Al content was reduced from 31 to 29% in sample H3 resulting in the highest mobility of $970 \text{ cm}^2/\text{V.s}$.

Table 4.4 lists the structural and electrical properties of HEMT samples namely H4, H5 and H6 with different GaN layer thicknesses. For all the samples, the barrier layer grown was 25 nm thick with the Al content of 29%. Fig. 4.32 shows that the FWHM of the rocking curves (002) of samples H4 to H6 reduces with the increasing GaN layer thickness. As shown in Table 4.4, the screw dislocation density reduces from 15.7 to $3.0 \times 10^9 \text{ cm}^{-2}$ while the edge dislocation density reduces from 7.0 to $1.1 \times 10^{11} \text{ cm}^{-2}$ as the GaN layer thickness increases from 0.47 to $1.5 \mu\text{m}$, respectively.

Table 4.4 The structural and the electrical properties of AlGaIn/GaN HEMT heterostructures grown with different GaN layer thicknesses.

Sample	GaN layer thickness (μm)	Dislocation density ($\times 10^{10} \text{ cm}^{-2}$)		Sheet carrier density ($\times 10^{13} \text{ cm}^{-2}$)	Mobility ($\text{cm}^2/\text{V.s}$)
		Screw	Edge		
H4	0.47	1.57	70	1.7	262
H5	1.00	0.40	16	1.0	950
H6	1.50	0.30	11	0.9	1100

The pure screw dislocations are likely to annihilate if they are able to glide and undergo cross-slip between $\{1\bar{1}00\}$ slip planes [206] with the increasing buffer layer thickness. However, as per the model by Mathis et al. [207], pure screw dislocations are not involved in the reactions and the decrease in the dislocation density is driven by the reaction of the mixed type threading dislocations. The inclined line direction of these dislocations makes them travel laterally with the increasing buffer layer thickness causing the overall reduction in the dislocation density. Moreover, they also showed that the dislocations do not undergo significant reduction for the GaN layers with pure edge dislocations. The reduction in the dislocation density with increasing thickness in these GaN layers was found to be primarily driven by the reactions between pure edge and mixed dislocations. Thus, decrease in both the screw and edge type dislocations indicate the presence of mixed character of dislocations in the GaN layers of samples H4-H6.

Fig. 4.32 The rocking curves of GaN (002) plane with different thicknesses.

The mobility clearly increases with the increasing GaN layer thickness which could be due to the reduced dislocation density in thicker GaN layer. The dislocations have been found to reduce the electron mobility as they are considered to be scattering centers for electrons moving in the 2DEG [36]. The dangling bonds along the edge dislocation line act as an electron acceptor and gets occupied by the electrons from the channel. The dislocations acquire negative charge and scatters the electrons to reduce the 2DEG mobility.

The highest room temperature mobility and the sheet carrier density of $1100 \text{ cm}^2/\text{V.s}$ and $9 \times 10^{12} \text{ cm}^{-2}$, respectively is achieved for sample H6. Thus, the optimized

AlGaN/GaN HEMT heterostructure consists of $\text{Al}_{0.29}\text{Ga}_{0.71}\text{N}$ barrier layer with 25 nm thickness and 1.5 μm thick GaN buffer layer. Fig. 4.33 (a) shows the image of AlGaN/GaN HEMT heterostructure grown epitaxially on 100-mm Si (111) substrate. As shown in Fig. 4.33 (b), the wafer bow of 44 μm corresponding to a wafer curvature of 0.05 m^{-1} was measured ex-situ at room temperature using a laser based system operating at a wavelength of 670 nm. The average tensile stress in the GaN layer is estimated to be 0.33 GPa using Stoney's equation. The corresponding stress thickness product obtained is $4.95 \times 10^{-7} \text{ GPa.m}$.

Fig. 4.33 (a) AlGaN/GaN HEMT heterostructure on 100-mm Si (111) substrate and (b) wafer bow of 44 μm measured ex-situ at room temperature.

Fig. 4.34 (a) shows crack-free surface of the optimized AlGaN/GaN HEMT heterostructure obtained using optical microscope. The typical $2 \times 2 \mu\text{m}^2$ amplitude AFM image of the surface exhibiting smooth surface morphology and low RMS roughness of 0.7 nm is shown in Fig. 4.34 (b). The surface shows the presence of small “mound” type morphology formed as a result of kinetically roughened step flow growth [179].

Fig. 4.34 (a) Optical microscope image and (b) a typical $2 \times 2 \mu\text{m}^2$ amplitude AFM image of the optimized AlGaN/GaN HEMT heterostructure.

The residual tensile strain in the GaN layers of the AlGaIn/GaN HEMT heterostructure was measured using micro-Raman spectroscopy. Fig. 4.35 shows that the E_2 peak of GaN is slightly red shifted with respect to the standard E_2 peak of free standing GaN (567 cm^{-1}), indicative of small tensile strain in the GaN layers. The shift in the E_2 peak of 1.6 cm^{-1} corresponds to a residual tensile stress of 0.37 GPa and a strain of 0.07%. The residual tensile stress agrees well with that obtained using the bow measurements of Fig. 4.33 (b).

Fig. 4.35 E_2 phonon peak of the Raman spectra acquired from the GaN layers. The vertical line indicates the E_2 position (567 cm^{-1}) of free standing GaN.

SIMS analysis was performed to understand the Si diffusion from the substrate into the layers of the AlGaIn/GaN HEMT heterostructure. Fig. 4.36 shows the SIMS depth profile of nitrogen (N), aluminum (Al), gallium (Ga) and silicon (Si) in the layer structure. The profile shows slow exponential decay of Al diffusion in the Si substrate and Si diffusion in AlN. The sudden decline in the Si counts at the GaN/AlN interface indicates that there is no Si incorporation in the GaN layers. Although the Al-Si interdiffusion is observed at the AlN/Si interface, the GaN layers remain almost free of Si.

Fig. 4.36 SIMS depth profile of N, Al, Si and Ga in AlGaIn/GaN HEMT heterostructure.

In order to confirm the presence of 2DEG at the AlGaIn/GaN interface, temperature dependent hall measurements were done by varying the temperature from 90 to 400K. Fig. 4.37 shows the mobility and the sheet carrier density as a function of temperature. The mobility is found to be temperature dependent and increased to $2330 \text{ cm}^2/\text{V.s}$ which is almost double the RT mobility of $1100 \text{ cm}^2/\text{V.s}$. This behaviour could be due to the reduced polar optical phonon-electron scattering at lower temperatures. On the other hand, the sheet carrier density remains relatively constant throughout the range of 90 to 400K. This insensitivity of the sheet carrier density to the temperature confirms the presence of 2DEG near the interface of AlGaIn/GaN heterostructure.

Fig. 4.37 The temperature dependence of sheet carrier density and mobility of AlGaIn/GaN HEMT heterostructure.

Mercury probe C-V measurements were performed to determine the 2DEG confinement and background carrier concentration. As shown in Fig. 4.38 (a), the capacitance appears to be fairly high and constant with increasing reverse bias voltage suggesting presence of the 2DEG at the AlGaIn/GaN interface. This is followed by a decrease of the capacitance indicating confinement of the 2DEG and attaining a pinch off at a reverse bias voltage of 5.5 V. Fig. 4.38 (b) shows the carrier density profile of the HEMT heterostructure which demonstrates high carrier density at the interface between the AlGaIn barrier and GaN channel and a background carrier density ($\sim 10^{16} \text{ cm}^{-3}$) in the GaN layer. However, an increase in the carrier density near the AlN/Si interface is observed which might be due to Al and Si interdiffusion.

Fig. 4.38 (a) Mercury probe C-V measurements and (b) carrier density profile of AlGaIn/GaN HEMT heterostructure.

The buffer leakage current measurements of the AlGaIn/GaN HEMT heterostructures were conducted using a gap of 5 μm between the two ohmic contacts and maintaining a width of 50 μm. The buffer leakage current of 1 mA/mm was determined at 20 V with the I_{ON}/I_{OFF} ratio of 4×10^{12} . The 1.5 μm gate length devices were also fabricated to study the performance of the AlGaIn/GaN HEMT heterostructure [152]. The devices exhibited the maximum drain current density of 530 mA/mm at $V_g = +1$ V and the peak extrinsic transconductance of 156 mS/mm at $V_d = 5$ V. The threshold voltage of the device is 3.7 V.

4.7 Summary

The AlN and GaN layers were optimized for the growth of AlGaN/GaN HEMT heterostructures on Si (111) by PA-MBE. AlN layers were grown on Si (111) followed by GaN layers at an optimized substrate temperature of 860 and 740 °C, respectively. The III/V ratio was also optimized by growing the AlN and GaN layers as a function of metal fluxes at a constant RF power of 300 W and nitrogen flow of 2 sccm. Streaky RHEED pattern, droplet-free and smooth surface morphology with sub-nm RMS roughness, good crystalline quality and nearly strain free AlN and GaN layers were obtained in the intermediate growth regime.

The polarity of AlN and GaN layers was studied by varying the III/V ratio in the metal-rich growth regime. The growth of both AlN and GaN layers in the intermediate growth regime resulted in metal-polarity. While the polarity of AlN obtained was N-polar, Ga-polar GaN was achieved in the droplet growth regime. The studies also illustrated that polarity inversion occurred at the GaN/AlN interface enabling the growth of Ga-polar GaN on N-polar AlN. The formation of Al-Al bonding was found to be the reason for the observed inversions in AlN and GaN layers.

A separate study was done to investigate the effect of the Al flux of LT-AlN on the surface morphology of subsequent AlN and GaN layers. LT-AlN grown with higher Al flux showed the presence of “comet” type features on the surface. The comets were found to be associated with micro-crystals on the GaN surface. Al-Si interdiffusion undergoing eutectic transformation in the presence of excess Al metal was found to be the reason for the comets and micro-crystals in the AlN and GaN layers. Reducing the Al flux of LT-AlN resulted in the improved and comet-free surface morphology.

Ga bilayer based technique was implemented using in-situ RHEED to overcome the Ga flux fluctuations during the longer growth periods and obtain reproducible material properties. The desorption time of the bilayer was monitored using the corresponding RHEED intensities and was kept within the established “growth window” by adjusting the Ga flux during the entire GaN growth. The growths of GaN layer controlled using bilayer technique resulted in good and reproducible material properties.

AlGaN/GaN HEMT heterostructures were grown using the optimized AlN and GaN layers. The Al content and thickness of AlGaN barrier layer were also optimized to obtain good 2DEG mobility of 1100 cm²/V.s and corresponding sheet carrier density

of $9.0 \times 10^{12} \text{ cm}^{-2}$. AlGaIn/GaN HEMT with 1.5 μm gate length exhibiting good device characteristics were fabricated using the grown structure. Hence, crack-free 1.5 μm thick GaN layers with reproducible material properties have been optimized and AlGaIn/GaN HEMT heterostructure with good 2DEG properties have been demonstrated on 100-mm Si (111) substrate by PA-MBE.

5. AlN and GaN layers grown on Si (111) by ammonia MBE

One of the main advantages of PA-MBE is that it offers the possibility of low temperature growth as the generation of active nitrogen species is independent of the growth temperature. Thus, this technique allows GaN growths to be done at low substrate temperatures which aids in alleviating the degree of thermal mismatch induced tensile strain in GaN on Si. However, PA-MBE provides narrow growth window, and hence the precise control of optimum III/V ratio becomes difficult. The strong bond energy of the nitrogen molecules (N-N bond energy 9.5 eV) makes it difficult to break them in the formation of GaN. The low cracking efficiency of the nitrogen molecule limited the growth rates to be small (0.19 $\mu\text{m/hr}$).

Alternately, our MBE system equipped with both a nitrogen RF plasma source and an ammonia source allowed us to explore the growth of AlGaIn/GaN HEMT heterostructures by ammonia MBE. Wider growth window of ammonia MBE allows a good control over the III/V ratio to obtain good crystalline quality. The growths using ammonia MBE are conducted in N-rich conditions which have been found to result in improved uniformity due to droplet-free surfaces, stable growth conditions and lower buffer leakage currents [41, 157, 158]. Ammonia has a significantly reduced bond strength which makes it relatively easy to dissociate and produce active nitrogen. Thus, the higher cracking efficiency of ammonia assists in obtaining higher growth rates. Moreover, metal-polar layers are always obtained in the ammonia rich growth conditions and hence suitable for the growth of conventional Ga-polar AlGaIn/GaN HEMT heterostructures. The following sections discuss the optimization of the growth parameters for the growth of AlN and GaN layers by ammonia MBE.

5.1 Ammonia cracking efficiency

In ammonia MBE, the active nitrogen species for the growth are supplied by the pyrolysis or thermal “cracking” of ammonia molecules. Hence, it is important to study the cracking behavior of ammonia molecules in order to understand the growth mechanism of nitrides by ammonia MBE. Thus, studies have been conducted similar to Tang et al. [171] to obtain the thermal cracking efficiency of the supplied ammonia. The ammonia injector was kept at a temperature of 100 °C and the ammonia molecules were thermally cracked upon their incidence on the Si (111) surface. The cracking efficiency is determined by measuring the partial pressure of hydrogen using a RGA employed in the growth chamber of the MBE system. The hydrogen signal

obtained due to the cracking of ammonia on the surface is taken to be proportional to the ammonia cracking efficiency.

Fig. 5.1 (a) shows the ammonia cracking efficiency as a function of the substrate temperature at various ammonia flows. The ammonia cracking efficiency increases with the increasing substrate temperature for a particular ammonia flow. This trend can be attributed to the fact that more of ammonia molecules dissociate to produce NH_x species with increasing substrate temperature. However, it is evident that the rate of ammonia cracking increases significantly beyond 700 °C. This phenomenon can be explained based on the enhanced availability of adsorption sites for NH_x radicals with increasing substrate temperature [171]. As the substrate temperature increases beyond 700 °C, the NH_x radical thermally activates, recombines and desorbs from the surface as N_2 and H_2 molecule. Thus, ammonia is said to be self-cracking at such temperatures via $NH_x + NH_x \rightarrow N_2 + H_2$. This phenomenon leads to the availability of increased adsorption sites thereby causing increased ammonia cracking.

The ammonia cracking efficiency as a function of ammonia flow at various substrate temperatures is shown in Fig. 5.1 (b). The ammonia cracking efficiency increases with the increasing ammonia flow as the availability of ammonia increases and hence the cracking. However, it reaches saturation when the flow is increased beyond 250 sccm (BEP of 2.8×10^{-4} Torr) due to the saturation of the available adsorption sites by the sufficient amount of NH_x radicals on the Si (111) surface. The analysis of Fig. 5.1 (a) and (b) illustrates that the cracking of ammonia is found to be more sensitive to the substrate temperature than the ammonia flow.

Similar to the studies on Si (111) surface for the growth of AlN layers, ammonia cracking efficiency was determined on AlN surface for the growth of GaN layers. Fig. 5.2 (a) shows the ammonia cracking efficiency on the AlN surface as a function of substrate temperature at various ammonia flows. As discussed for the Si (111) surface, the cracking efficiency of ammonia increases for AlN surface also with increasing substrate temperatures for a set of ammonia flows. Fig. 5.2 (b) shows cracking efficiency as a function of ammonia flow at various substrate temperatures. Evidently, the cracking of ammonia enhances with the increasing ammonia flow and reaches saturation approximately beyond the ammonia flow of 250 sccm. It is

interesting to note that the ammonia cracking efficiency for both Si (111) and AlN surface show similar trends.

Fig. 5.1 Ammonia cracking efficiency on Si (111) surface as a function of (a) substrate temperature at various ammonia flows and (b) ammonia flow at various substrate temperatures.

Fig. 5.2 Ammonia cracking efficiency on AlN surface as a function of (a) substrate temperature at various ammonia flows and (b) ammonia flow at various substrate temperatures.

In order to understand the effect of Ga flux on the ammonia cracking efficiency during the growth of GaN, the cracking efficiency was monitored with and without supplying Ga flux as a function of substrate temperature. As shown in Fig. 5.3, the partial pressure of the desorbed hydrogen increases with increasing substrate temperature at a constant ammonia flow of 280 sccm (BEP of 3.1×10^{-4} Torr) with and without the

supply of Ga flux of 2×10^{-7} Torr. However, the hydrogen desorption and hence the cracking efficiency is higher when Ga is supplied.

Fig. 5.3 The ammonia cracking efficiency as a function of substrate temperature with and without supplying Ga flux. The ammonia flow and Ga flux were kept constant at 280 sccm and 2×10^{-7} Torr, respectively.

This phenomenon can be explained based on the replenishment of the available NH_x radical adsorption sites on the growing GaN surface. As the Ga atoms are supplied onto the GaN surface, they readily react with the existing adsorbed NH_x radicals and results in GaN lattice incorporation via $Ga + NH_x \rightarrow GaN + H_2$. The reaction leads to the growth of GaN and release of hydrogen. This process of GaN formation increases the availability of adsorption sites since the sites blocked by the adsorbed NH_x radicals become available again. Consequently, the hydrogen partial pressure or the ammonia cracking efficiency increased with the supply of Ga flux for all the substrate temperatures studied.

5.2 Growth optimization of aluminum nitride layers

5.2.1 Nitridation and Al predeposition

The importance of AlN as a buffer layer for the growth of GaN on Si (111) has been discussed in Section 4.1. However, in contrast to PA-MBE, the unintentional nitridation of Si (111) substrate is unavoidable in ammonia MBE technique due to the

possible residual background ammonia in the growth chamber. As reported by Nikishin et al. [172], partial nitridation can be controlled but cannot be eliminated completely. Thus, the nucleation process was initiated by intentionally nitriding the thermally cleaned Si (111) substrate with the ammonia first at 660 °C , since, the unintentional partial nitridation of the surface is unavoidable [178]. As shown in Fig. 5.4 (a), this resulted in an incomplete (8×8) RHEED surface reconstruction pattern which is a signature corresponding to the presence of nitrogen adatoms on top of the mono-crystalline silicon nitride (β -Si₃N₄) [208]. Thus, this process ensured that the silicon nitride obtained was crystalline instead of amorphous form. The process of nitridation was followed by the pre-deposition of a few monolayers of Al on the nitrided surface, which led to the reaction of Al atoms with the nitrided surface to initiate AlN nucleation.

Fig. 5.4 RHEED reconstruction patterns obtained during the AlN nucleation on Si (111) along $[2\bar{1}\bar{1}0]$ azimuths. (a) Incomplete (8×8) is obtained after the nitridation of the Si (111) surface and (b) (1×1) of AlN exists after Al predeposition together with (1×1) from Si (111).

This was confirmed by the observation of (1×1) RHEED doublet pattern corresponding to both Si (111) and AlN as shown in Fig. 5.4 (b). AlN layer was then grown using optimized growth parameters determined by varying the growth rate and substrate temperatures as discussed in the following sections. It should be noted that a fixed ammonia flow of 280 sccm was kept for the growth optimization of the AlN

layer since the cracking efficiency of ammonia on Si (111) surface reached saturation around this flow.

5.2.2 Effect of growth rate

AlN layers with 100 nm thickness were grown on Si (111) substrate at a high substrate temperature of 920 °C. The growth rate of AlN layers was optimized to obtain good crystal quality and smooth surface morphology which is essential for achieving GaN layers with good structural and morphological properties. Table 5.1 lists three samples A, B and C grown with different Al fluxes corresponding to the AlN growth rate of 0.08, 0.1 and 0.13 $\mu\text{m/hr}$, respectively. As can be seen, the screw dislocation density of AlN decreases and the surface roughness of $5 \times 5 \mu\text{m}^2$ scan area improve with the increasing growth rate.

Table 5.1 The screw dislocation density and surface roughness of AlN layers grown with different growth rates.

Sample	Al flux $\times 10^{-8}$ (Torr)	Growth rate ($\mu\text{m/hr}$)	Screw dislocation density ($\times 10^{10} \text{ cm}^{-2}$)	RMS roughness (nm)
A	1.2	0.08	12.9	1.35
B	1.5	0.10	4.6	1.26
C	1.9	0.13	3.1	1.05

The fast transition of the growth mode from 3D to 2D is critical in obtaining good quality AlN layers [172]. Fig. 5.5 (a), (b) and (c) show the RHEED patterns of samples A, B and C obtained in $[2\bar{1}\bar{1}0]$ azimuth after 7 nm of AlN growth. The spotty pattern for sample A indicates the presence of 3D islands after 7 nm of growth of AlN layer with the lowest Al flux.

Fig. 5.5 RHEED pattern for 7 nm thick AlN layers grown with different growth rates of (a) 0.08 $\mu\text{m/hr}$ – sample A, (b) 0.1 $\mu\text{m/hr}$ – sample B and (c) 0.13 $\mu\text{m/hr}$ – sample C.

The RHEED pattern for sample B shows connecting spots signifying a transition to 2D growth. Sample C grown with the highest Al flux shows the most rapid transition of

growth mode from 3D island nucleation to 2D mode. Moreover, (2×2) RHEED surface reconstruction pattern was obtained upon cool down below 300°C indicative of Al polarity. Thus, Al flux played an important role in determining the transition of the AlN growth mode from 3D to 2D. The faster transition from 3D to 2D growth mode is found to improve the crystal quality and the surface roughness of the AlN layers.

5.2.3 Effect of substrate temperature

Another set of samples were grown to study the effect of different substrate temperatures on the crystal quality and surface roughness of the AlN layers. AlN layers of samples D, E and F were grown at substrate temperatures of 920, 905 and 890 °C, respectively using the optimized growth rate of 0.13 µm/hr and a thickness of 100 nm.

As shown in Table 5.2, the RMS roughness of 5×5 µm² scan area of AlN increases as the substrate temperature is reduced. The increased surface roughness of the AlN surface can be explained based on the understanding that the surface diffusion reduces at low substrate temperatures. The reduced surface diffusion or low surface migration mobility of Al adatoms leads to rough surfaces. The increase in the Al adatom mobility at higher growth temperature aids in the uniform coverage of the AlN surface leading to smoother surface morphology. Moreover, the screw dislocation density of all the AlN layers also reduced with the increasing substrate temperature. The growth of AlN layers at an optimized substrate temperature of 920 °C was found to be necessary to obtain uniformly covered and smooth AlN surface. Thus, AlN layers with lowest dislocation density and smooth surface morphology was obtained using a growth rate of 0.13 µm/hr at a growth temperature of 920 °C.

Table 5.2 The screw dislocation density and surface roughness of the AlN layers grown at different substrate temperatures.

Sample	Substrate temperature (°C)	Screw dislocation density (×10 ¹⁰ cm ⁻²)	RMS roughness (nm)
D	920	3.1	0.55
E	905	3.2	0.65
F	890	3.4	1.03

5.3 Growth of gallium nitride layers

GaN layers were grown on 100 nm thick AlN layers that were grown at an optimized growth rate and substrate temperature of 0.13 $\mu\text{m/hr}$ and 920 $^{\circ}\text{C}$, respectively. It has been reported that the growth of GaN beyond 820 $^{\circ}\text{C}$ leads to 3D growth mode due to its thermal decomposition [171] while the growths done at lower temperatures lead to poor crystalline quality. Hence, a substrate temperature of 800 $^{\circ}\text{C}$ has been chosen to obtain GaN growth in 2D mode with good crystalline quality. Lower III/V ratio has been found to result in improved structural properties and reduced background concentrations to obtain highly resistive GaN layers [157, 209]. Thus, the growth rate of GaN was kept low at 0.22 $\mu\text{m/hr}$ with 280 sccm of ammonia flow in order to maintain high NH_3 overpressure and low III/V ratio. Similar to the growth of AlN layers, a fixed ammonia flow of 280 sccm was used for the optimization of the GaN layers since the cracking efficiency of ammonia on AlN surface saturated around this value. Fig. 5.6 shows the RHEED pattern after the growth of 1 μm thick GaN. As shown, streaky (2 $\times$ 2) RHEED surface reconstruction is obtained upon cooling down below 300 $^{\circ}\text{C}$ substrate temperature indicative of Ga-polarity.

Fig. 5.6 Streaky (2 $\times$ 2) RHEED reconstruction pattern is obtained on cool down below 300 $^{\circ}\text{C}$ indicative of Ga-polarity along the (a) $[2\bar{1}\bar{1}0]$ and (b) $[01\bar{1}0]$ azimuths.

The optical microscope image in Fig. 5.7 (a) shows that the layers have cracked heavily indicating high tensile nature of GaN. The localized residual tensile strain convincingly away from the cracks was determined in the GaN layers using micro-Raman spectroscopy. Fig. 5.7 (b) shows that the E_2 peak of GaN is largely red shifted with respect to the standard E_2 peak of free standing GaN (567cm^{-1}), confirming the high tensile strain in GaN layers. The shift in the E_2 peak of 2.0 cm^{-1} corresponds to a high residual tensile stress of 0.475 GPa and a strain of 0.12%. The dense cracking possibly relaxed the overall tensile strain in the GaN layers. Consequently, the actual residual tensile strain value in GaN before it cracked was likely to be more than the values measured at the room temperature. It should be noted that crack-free GaN

layers were obtained for thicknesses < 500 nm grown under the same growth conditions.

Thus, stress mitigating layers are necessary to obtain thick and crack-free GaN on Si substrate by ammonia MBE. The stress mitigating layers are designed to induce compressive stress in GaN thereby balancing the thermal mismatch induced tensile stress generated upon cooling down to room temperature. More details regarding this will be discussed in Section 5.4.

Fig. 5.7 (a) Microscope image of $1\text{ }\mu\text{m}$ thick GaN layers and (b) E_2 peak of the Raman spectra from a region convincingly away from the cracked GaN layers with the vertical line indicating E_2 position (567 cm^{-1}) for free standing GaN.

5.4 Stress mitigating layers

It is beneficial to grow thick GaN layers in order to achieve improved material properties and subsequent device performances [210]. However, it has been found that unlike PA-MBE, the growth of thick GaN layers (> 500 nm) on 100-mm Si (111) is a challenge in ammonia MBE due to the cracking of the epilayers. It may be due to the dissimilarity in the growth mechanism and the growth temperatures employed in the two different techniques.

In the case of PA-MBE, GaN layers with III/V ratio close to Ga-rich growth conditions have been found to exhibit higher compressive strain compared to those grown under N-rich growth conditions [154]. The metal-rich growth conditions may assist in the early relaxation of GaN such that negligible relaxation occurs in the subsequent growth leading to compressively strained GaN. However, the N-rich growth conditions of ammonia MBE may cause slow compressive stress relaxation throughout the GaN

growth leading to the development of tensile strain and subsequent cracking of the epilayers upon cool down. Furthermore, the lower growth temperature of PA-MBE has shown to produce higher residual compressive strain in the GaN layers [211]. The thermal mismatch between GaN and Si reduces due to the smaller temperature change during cool down. Typically, the layers can be grown at about 100 °C lower using PA-MBE [153] compared to ammonia MBE. Thus, it becomes necessary to introduce stress mitigating layers to alleviate the thermal mismatch induced tensile strain and obtain crack-free GaN by ammonia MBE.

The choice of stress mitigating layers for GaN growth on Si should yield efficient tensile strain compensation, smooth surface morphology and lower dislocation density such that GaN material properties become suitable for HEMT applications. In order to achieve these goals, many groups have reported various stress mitigating structures such as LT-AlN [212], AlGaIn/AlN [175], superlattice [174] and AlN/GaN stack [42]. Among various types of stress mitigating layers studied so far, AlGaIn/AlN and AlN/GaN have been widely used as stress mitigating layers for GaN growth on 50-mm Si (111) substrate. Hence, the growth mechanism and the material properties of AlGaIn/AlN and AlN/GaN stress mitigating layers and the subsequently grown GaN layers on 100-mm Si (111) have been thoroughly investigated and compared in the following sections.

5.4.1 AlGaIn/AlN stress mitigating layers

AlGaIn/AlN as stress mitigating layers have been introduced in between GaN and Si (111) substrate to overcome the thermal mismatch induced tensile strain and prevent cracking of the epilayers. Zhang et al. [175] have observed a decrease in the crack density of GaN with increasing AlN thickness using AlGaIn/AlN stress mitigating layers on 50-mm Si (111) substrate. Moreover, growth temperature is a well-known growth controlling parameter which may also determine the structural properties of GaN. Thus, a systematic study was conducted on the influence of AlN thickness and AlGaIn growth temperature on the quality and strain of subsequently grown GaN. The schematic diagram of the layer structure investigated is shown in Fig. 5.8. Samples A, B and C were grown with different AlN thicknesses of 50, 100 and 200 nm, respectively at 920 °C followed by AlGaIn at 840 °C. Samples D, E and F were grown with AlGaIn at different growth temperatures of 840, 820 and 800 °C, respectively. For all the samples (A to F), the growth temperature of the top GaN layer was 800 °C, and the thickness of GaN and AlGaIn was kept at 500 and 400 nm, respectively. The mole

fraction of Al in the AlGaN layer was kept at an intermediate value of 0.45 to mitigate the lattice mismatch between AlN and GaN layers.

Fig. 5.8 The schematic diagram of GaN on Al_{0.45}Ga_{0.55}N/AlN stress mitigating layers grown on Si (111) substrate.

5.4.1.1 *Effect of AlN thickness*

While samples A and B were found to have cracked, crack-free GaN was achieved for sample C. Residual tensile strain for the cracked layers was most likely released locally along the cracked regions of samples A and B [213]. Thus, the localized residual tensile strain was probed by micro-Raman spectroscopy. The residual tensile strain values determined in the layers of samples A, B and C are listed in Table 5.3. As can be seen in Fig. 5.9, the residual tensile strain in GaN reduces with the increasing thickness of AlN for samples A to C.

This indicates that thinner AlN induces lesser amount of compressive strain in GaN. It should be noted that unreliable residual strain values are obtained by HR-XRD technique in GaN of samples A and B due to the fact that the X-ray beam probes (~ 6 mm in width) both the cracked as well as the crack-free regions.

Fig. 5.9 The in-plane strain in GaN reduces with increasing AlN thickness for samples A – 50 nm, B – 100 nm and C – 200 nm.

The threading dislocation density in GaN as a function of AlN thickness for samples A, B and C is shown in Fig. 5.10. The screw and edge type dislocation densities determined in all the samples suggest that the overall quality of GaN improves with the increasing thickness of AlN. A reduction of nearly 30% in the overall threading dislocation density can be seen.

Fig. 5.10 The screw and edge type dislocation density in GaN as a function of AlN thickness. The dislocation density in GaN reduces with increasing AlN thickness for samples A – 50 nm, B – 100 nm and C – 200 nm.

Table 5.3 Summary of the structural parameters of investigated samples A to F obtained by HR-XRD and micro – Raman spectroscopy.

Sample	HR-XRD						Micro-Raman spectroscopy			
	GaN		Al _{0.45} Ga _{0.55} N		AlN		GaN		AlN	
	a (Å)	$\epsilon_{ }$ (%)	a (Å)	$\epsilon_{ }$ (%)	a (Å)	$\epsilon_{ }$ (%)	E ₂ (cm ⁻¹)	$\epsilon_{ }$ (%)	E ₂ (cm ⁻¹)	$\epsilon_{ }$ (%)
A	Cracked						564.00	0.20	639.61	1.09
B							564.24	0.17	646.45	0.87
C & D	3.1939	0.155	3.1657	0.342	3.1244	0.398	564.49	0.15	648.63	0.52
E	3.1917	0.087	3.1621	0.229	3.1249	0.415	565.32	0.08	649.08	0.49
F	3.1903	0.042	3.1581	0.102	3.1220	0.322	565.54	0.06	649.06	0.49

The residual tensile strain in GaN of samples A, B and C may depend on the strain states of AlN grown with different thicknesses. AlN with its smaller in-plane lattice constant ($a_{\text{AlN}} = 3.110 \text{ \AA}$) grows tensile strained on Si ($a_{\text{Si}} = 3.846 \text{ \AA}$). Since, AlN of samples A, B and C was grown under the same growth conditions, similar tensile strain relaxation must have occurred in AlN due to the misfit region generated at AlN/Si interface. The AlN/Si interface exhibits a 5:4 coincidence lattice and a misfit of 19% between AlN and Si (111) is then reduced to 1.3% [214]. The subsequent relaxation of the lattice mismatch induced tensile strain is likely to be released by either further misfit dislocation generation [215] or cracking of the layer [216] with increasing AlN thickness. Thus, it is expected that the thicker AlN grows much more relaxed compared to the thinner AlN. Consequently, sample C with the thicker AlN of 200 nm should be in a much more relaxed state than samples A and B. As summarized in Table 5.3, the lesser tensile strain in AlN of sample C compared to samples A and B indicate that the relaxed AlN of sample C is more effective in inducing compressive strain on AlGaIn due to the lattice-mismatch between AlGaIn and AlN. Thus, GaN grown with thicker AlN of sample C is less strained than that grown on the thinner AlN of samples A and B.

The process of cracking not only assists in tensile strain relaxation but it also allows the dislocations to nucleate from the edge of the cracks [216]. It is interesting to note that the means of tensile stress relaxation in AlN lead to the generation of additional dislocations with increasing thickness. Cross-sectional TEM images were analyzed to understand the evolution of dislocations in the layer structure of samples A, B and C as shown in Fig. 5.11 (a), (b) and (c), respectively. It can be observed that the dislocations in AlGaIn and GaN layers of sample A are more than in sample B. However, a significant reduction in the number of dislocations can be seen in the layers of sample C. Some of these dislocations have inclined with respect to [0001] growth direction.

The threading dislocations may interact with the misfit ones to form loops and cause subsequent annihilation in the AlN layer. It can be noticed in Fig. 5.12 that the dislocations with burger vectors of opposite directions have reacted to form closed loops in AlN of sample C (~ up to the initial 100 to 120 nm thickness of AlN) as encircled and indicated by black arrows. Thus, the dislocations in AlN of sample C might have undergone fusion and annihilation leading to their significant reduction. Furthermore, 100 nm AlN of sample B might have also assisted in the process of dislocation annihilation. But, as can be seen in Fig. 5.11 (b), this thickness is

insufficient in aiding significant termination of dislocations leading to higher dislocation density in the AlGaIn and GaN layers of sample B. The AlN of sample A with the smallest thickness of 50 nm seems to have offered the least effective dislocation filtering process which has facilitated their propagation all the way into AlGaIn and GaN layers. Another reason for the observed trend in the strain of GaN of samples A, B and C in Fig. 5.9 is the interactions and looping of these dislocations [217], which occur most evidently in the GaN of sample A and reduces with the increasing AlN thickness as in the case of samples B and C.

Fig. 5.11 Bright-field cross-sectional TEM images of GaN/AlGaIn/AlN/Si layer structure grown with different AlN thickness (a) sample A – 50 nm (b) sample B – 100 nm and (c) sample C – 200 nm, along $[11\bar{2}0]$ zone axis.

Although the process of tensile stress relaxation in AlN might have generated additional dislocations but their interaction seen in the cross-sectional TEM images demonstrate a reduction in the dislocation density with the increasing thickness of AlN grown under nominally identical conditions. The rate at which the dislocations have annihilated seems to have surpassed its rate of generation. It should be noted that the influence of AlN thickness above 200 nm may not play a significant role in determining the quality and the strain state of the subsequently grown GaN since the major dislocation looping and strain relaxation occurs in the initial 100 to 120 nm of thick AlN.

Fig. 5.12 Bright field cross-sectional TEM image of sample C showing the dislocation bending in AlN at ~ 80 nm marked by white arrows. The region showing dislocation looping at ~ 100 to 120 nm of AlN is encircled and indicated by black arrows.

Moreover, as shown in Table 5.4, comparable strains were also observed for 200 nm and 500 nm thick AlN grown on Si (111) which indicated that AlN had reached saturation in strain relaxation for 200 nm thickness.

Table 5.4 The E_2 peak and strain in AlN grown on Si (111) determined by micro-Raman spectroscopy.

AlN thickness (nm)	E_2 peak (cm^{-1})	Residual tensile strain (%)
200	649.0	0.660
500	649.6	0.695

The diffusion of Si from the substrate into the GaN has been observed to occur at high growth temperatures (above 750 °C) [189]. This has also been found to be a potential reason for the cracking of GaN because of the generation of strong tensile stress with the increase in Si doping [218]. In order to understand the diffusion and incorporation of Si into the layer structure of samples A, B and C, SIMS analysis was done. Fig. 5.13 shows the SIMS depth profile of Si in the layer structure of samples A, B and C. The Si concentration determined in GaN is found to reduce with the increasing thickness of AlN as shown in the inset of Fig. 5.13. It can be noted that the Si profile in AlN does not follow an error function. However, the concentration of Si in

AlN is linear as a function of depth, which clearly indicates that Si diffusion from the substrate is not a lattice diffusion but pipe diffusion [219]. The pipe diffusion is generally associated with the regions around the threading dislocations. They provide high mobility routes for the migration of atoms relative to the lattice diffusion. Thus, the increased amount of Si diffusion can be attributed to the higher threading dislocations in the structure of sample A. It should be noted that there is a change in the slope of Si depth profile at around ~ 80 nm of AlN thickness for samples B and C. However, no such trend is observed in sample A. As marked by the white arrows in Fig. 5.12, this can be the result of the interaction of the closely aligned dislocations in 80 nm of AlN. Moreover, it is interesting to observe that the change in the slope of Si depth profile is followed by a sudden reduction in the Si concentration in AlN of sample C. However, this behavior is not observed in AlN of sample B.

Fig. 5.13 SIMS depth profile of Si in GaN/AlGaN/AlN for samples A, B and C with AlN thickness of 50, 100 and 200 nm, respectively. The inset shows the Si concentration in GaN of all the samples.

As can be seen in Fig. 5.12, this may be due to the dislocation looping at 100 to 120 nm of AlN of sample C which is not occurring in the insufficiently thick AlN of sample B. Thus, the thicker AlN of sample C caused substantial reduction in the propagation of dislocations due to which Si diffusion was ceased significantly in AlN before being transported to the upper AlGaN and GaN layers. Conversely, AlN of sample A and B was not thick enough to suppress the dislocations enabling continuous diffusion of Si from the substrate.

5.4.1.2 Effect of AlGaIn growth temperature

Sample C grown with 200 nm thick AlN showed relatively lesser tensile strain, lower dislocation density and reduced Si diffusion from the Si substrate. Therefore, samples D, E and F were grown with the same AlN thickness of 200 nm. It should be noted that samples C and D are the same but named differently for the purpose of separate analysis. During the growth, AlN and AlGaIn layers showed streaky RHEED patterns for all the samples. Fig. 5.14 (a), (b) and (c) show the AFM images of the GaN surface and the corresponding RHEED patterns upon cooling down below 300 °C for samples D, E and F, respectively. Fig. 5.14 (a) and (b) demonstrate RMS roughness of 3.3 and 3.9 nm, and the corresponding (2×2) streaky RHEED patterns of GaN signifying 2D growth for samples D and E, respectively. Fig. 5.14 (c), however, shows heavily pitted and rough surface morphology with an RMS roughness of 25 nm and a spotty RHEED pattern of GaN for sample F suggestive of 3D growth mode.

Fig. 5.14 The 2×2 μm² AFM images of the GaN surface for samples D, E and F and the corresponding RHEED surface reconstruction patterns along [2 $\bar{1}$ 10] azimuth. 2D surface morphology is obtained for (a) sample D and (b) sample E, respectively, with streaky (2×2) patterns. (c) sample F shows 3D surface morphology with a spotty RHEED pattern.

The residual tensile strain values determined in the layers of samples D, E and F are listed in Table 5.3. As can be seen, the strain determination by micro-Raman spectroscopy and HR-XRD are in accordance with each other. The decrease in the in-plane strain in GaN with the decrease in the AlGaIn growth temperature for samples D to F is illustrated in Fig. 5.15. Sample D was found to be highly strained with a residual tensile strain of 0.15% while sample F showed low residual tensile strain value of 0.04%. Similarly, a reduction in the overall dislocation density in GaN was also observed by decreasing the AlGaIn growth temperature from samples D to F. As shown in Fig. 5.16, the GaN quality of sample D that was grown at a higher

growth temperature of 840 °C deteriorated considerably with the increase in both the screw and the edge type dislocations compared to sample F.

Fig. 5.15 GaN in-plane strain reduces with decreasing AlGaIn growth temperature for samples D – 840 °C, E – 820 °C and F – 800 °C.

Fig. 5.16 The screw and edge type dislocation density in GaN as a function of AlGaIn growth temperature. The dislocation density in GaN reduces with decreasing AlGaIn growth temperature for samples D – 840 °C, E – 820 °C and F – 800 °C.

GaN of Sample F with the AlGaIn layer grown at a lower temperature of 800 °C produced 3D growth mode associated with lower dislocation density but rough surface morphology. It was also reported that unintentionally doped GaN grown in the 3D growth regime exhibited n-type conductivity [171]. These attributes make the 3D growth mode inappropriate to realize good quality GaN, and hence, it is rarely applied for high frequency applications. Thus, from this analysis, it is apparent that higher growth temperature of AlGaIn resulted in highly strained and poor quality GaN. This result is unexpected since highly strained layers are usually coupled with reduced defect density [173, 220].

Sample D that was grown at a relatively higher temperature compared to sample E showed higher residual tensile strain. The tensile strain generated due to the thermal mismatch between GaN and Si may not be the reason for the higher residual tensile strain in sample D as the difference in the growth temperatures is only 20 °C. Thus, an alternate reason could be a peculiar mechanism which may play a role in the increased compressive strain relaxation during the growth of GaN in sample D than in E. The cross-sectional TEM images were investigated to rationalize this behavior in samples D and E as shown in Fig. 5.17 (a) and (b), respectively. It can be seen that numerous dislocations are generated at the AlGaIn/AlN interface of sample D compared to a fewer ones at the transition of AlN to AlGaIn in sample E. Most of these dislocations in sample D have bent and formed loops due to their high density and close proximity to one another as indicated by the arrows in Fig. 5.17 (a).

The growth of AlGaIn at higher growth temperature might have favored the generation of numerous dislocations [173]. The lattice mismatch induced compressive stress in AlGaIn grown on AlN enabled excessive looping of the dislocations and faster relaxation [173, 221]. Thus, the faster relaxation rate in sample D at the AlGaIn/AlN interface have reduced further looping of these dislocations due to diminished residual compressive strain with the increasing thickness of AlGaIn [217]. This effect could have guided the dislocations to propagate all the way to GaN. Furthermore, the substantial relaxation in AlGaIn was incapable of stimulating the growth of compressively strained GaN. Thus, the higher AlGaIn growth temperature of sample D has led to the generation of highly strained GaN with excessive dislocations.

Fig. 5.17 Bright-field, cross-sectional TEM images of GaN/AlGaN/AlN/Si grown with different AlGaN growth temperatures (a) sample D – 840 °C (b) sample E – 820 °C and (c) sample F – 800 °C, along $[11\bar{2}0]$ zone axis. The dislocation looping and bending is marked by arrows.

As shown in Fig. 5.17 (c), insignificant dislocation looping is observed at the AlGaN/AlN interface of sample F compared to samples D and E. Consequently, the dislocations can be seen propagating throughout the AlGaN layer of sample F. This shows that the lower AlGaN growth temperature of sample F does not assist in the dislocation generation and subsequent looping. Thus, the AlGaN is expected to exhibit a slower rate of compressive strain relaxation owing to which successive GaN grows compressively strained. Alternately, considerable dislocation looping and bending are observed in the GaN of sample F as indicated by the arrows in Fig. 5.17 (c). This effect might be due to the higher compressive stress in GaN induced by AlGaN or the 3D-growth regime of GaN which is generally associated with lower defect density [171].

The growth of GaN layers on AlGaN/AlN stress mitigating layers is initiated via Volmer-Weber growth mechanism followed by layer by layer growth mode. GaN of samples D and E continued to grow layer by layer, however, sample F is found to have transformed to 3D growth mode. Thus, the evolution of RHEED patterns was analyzed to understand the 3D growth of GaN of sample F. Fig. 5.18 (a) and (b) show

the evolution of the RHEED pattern as the growth progresses from 50 to 300 nm of GaN of sample F, respectively. The RHEED pattern with connecting spots was observed for the initial 50 nm of GaN growth. However, the RHEED pattern became completely spotty with the increasing GaN thickness at approximately 300 nm signifying complete transformation of GaN to 3D growth mode.

The high lattice mismatch induced compressive stress in GaN of sample F might have led to the intensive annihilation and fusion of dislocations. As shown by the white arrows in Fig. 5.17 (c), the abrupt annihilation of dislocations at around ~ 170 nm thickness of GaN is likely to relax the compressive strain locally in the regions where the annihilation occurred. The localized compressive strain relaxation or in other words, the non-uniform distribution of strain in GaN may perhaps be the cause for the 3D growth of GaN.

Fig. 5.18 RHEED surface reconstructions along $[2\bar{1}\bar{1}0]$ azimuth as the growth progresses for (a) 50 and (b) 300 nm thick GaN of sample F, respectively.

Si-diffusion from the substrate has been observed via pipe diffusion mechanism assisted by threading dislocations as shown in Fig. 5.13 (on page 112). In order to understand a similar behavior, SIMS analysis was done on samples D, E and F. Fig. 5.19 shows the SIMS depth profile of Si in the layer structure of samples D, E and F. As can be seen in the inset of Fig. 5.19, the Si concentration in GaN of sample E is higher than sample F while sample D shows the least amount of Si concentration.

Fig. 5.19 SIMS depth profile of Si in GaN/AlGaIn/AlN for samples D, E and F grown at AlGaIn growth temperatures of 840, 820 and 800 °C, respectively. The inset shows the Si concentration in GaN of all the samples.

Similar to the interpretation of Fig. 5.13, the profile of Si in AlN is linear with depth indicating the pipe diffusion effect for all the samples. The profile of Si in AlN of sample F shows higher Si concentration than samples D and E due to distinctive 3D growth mode of GaN. The higher looping of dislocations in GaN of sample F did not allow the Si in AlN to diffuse any further which led to the increased Si concentration in sample F. However, as the AlN in these samples was grown using the same conditions, one can assume comparable dislocation density and behavior for all the samples at the end of AlN. Thus, the reduced diffusion of Si in sample D can be attributed to the markedly high dislocation looping observed at the AlGaIn/AlN interface. The termination of the dislocations in the early stage of growth in sample D is likely to have effectively blocked the Si diffusion into the subsequent layers. However, the insignificant dislocation looping observed in sample E might explain for the high Si concentration in GaN. Furthermore, the dislocation looping observed in GaN of sample F, under 3D growth regime, could have eventually reduced the Si diffusion by means of the pipe diffusion.

It was observed that the dislocation bending and looping at the AlGaIn/AlN interface was found to have significant influence on the dislocation density and strain in GaN. However, besides dislocation looping, the dissimilar growth modes, coalescence of grains [222] and the diffusion of Si from the substrate at high growth temperatures [189] leading to the doping of GaN with Si [218, 223, 224] may still determine the strain states in GaN. Thus, in order to decouple these factors and determine the origin

of tensile strain in GaN, the bending and looping of the dislocations was investigated using the cross-sectional TEM images of sample D, E and F as shown in Fig. 5.20.

The average plastic relaxation ($\bar{\epsilon}$) in GaN caused due to the dislocation looping and bending near the GaN/AlGaIn interface was quantified using the following equation [20]:

$$\bar{\epsilon} = \frac{1}{4} b \rho_{TD} h \tan \alpha \quad \text{Eq. 5.1}$$

where, b is the magnitude of the burger vector, ρ_{TD} is the threading dislocation density, h is the layer thickness of dislocation looping and α is the inclination angle. The outlined regions in Fig. 5.20 depict the typical locations where dislocations are found to have looped and the corresponding dislocation inclination angle from the surface normal of all the samples. The layer thickness ' h ', measured from the cross-sectional TEM images, is the estimated average thickness of GaN wherein the dislocation looping occurs. Furthermore, the dislocation inclination angle ' α ' is calculated considering the geometrical projection of the dislocation along $[1\bar{1}00]$ which is the typical inclination direction. The residual tensile strain values considering the average plastic relaxation and the corresponding ' h ' and ' α ' values for GaN of samples D, E and F are listed in Table 5.5. These values indicate that the decrease in AlGaIn growth temperature from samples D to F has resulted in reduced tensile strain in GaN.

Fig. 5.20 Bright-field, cross-sectional TEM images of GaN/AlGaN/AlN/Si (a) sample D, (b) sample E and (c) sample F grown with different AlGaN growth temperatures. The outlined regions depict the typical location of dislocation looping and the corresponding dislocation inclination angle.

The dislocations are typically looped at nearly half the inclination angle through larger thicknesses despite higher dislocation density in GaN of sample D compared to sample E. Thus, it is evident that the lattice mismatch induced compressive stress increased from sample D-E for GaN grown in 2D growth mode.

Table 5.5 Average plastic relaxation in GaN of samples D, E and F calculated using values obtained from HR-XRD and TEM.

Sample	AlGaN growth temperature (°C)	Parameters for average plastic relaxation			Residual tensile strain using average plastic relaxation
		Edge dislocation density $\times 10^{11} \text{ (cm}^{-2}\text{)}$	h (nm)	α (°)	
D	840	2.00	133	26.2	0.14
E	820	1.65	81	45.6	0.08
F	800	0.90	177	40.6	-0.01*

* (-) sign indicates compressive strain.

Furthermore, the dislocations were found to have inclined through larger thicknesses due to the lowest dislocation density in GaN of sample F grown in 3D growth mode. However, the bending and looping of dislocations with a larger inclination angle

signifies greater lattice mismatch induced compressive stress at GaN/AlGaN interface of sample F.

The residual tensile strain obtained by calculating the average plastic strain relaxation in GaN using Eq. 5.1 (on page 119) is in good agreement with the strain measured using both micro-Raman spectroscopy and HR-XRD techniques for samples D and F as shown in Fig. 5.21. However, these values exhibit a slight deviation for GaN of sample F. Hence, it is apparent that the compressive strain relaxation in GaN is caused by the formation of closed loops as a result of the lateral migration of edge type dislocations in samples D and E.

Fig. 5.21 The residual tensile strain in GaN of samples D to F determined by HR-XRD, micro-Raman and average plastic strain relaxation.

Moreover, the linear profile of Si in AlN (Fig. 5.19 on page 118) affirms that the Si diffusion into the layers is pipe diffusion type and not lattice diffusion. Thus, Si diffusion from the substrate may not be the potential cause for the origin of tensile strain in GaN. The higher value of measured residual tensile strain in GaN of sample F than that calculated using the average plastic strain relaxation can be attributed to the additional tensile strain generated due to the grain coalescence in 3D growth mode [222]. The 3D growth of GaN exhibits columnar grain type morphology and the elimination of the boundaries formed by these grains generates additional stress during the GaN growth of sample F. Thus, the compressive strain relaxation in GaN grown in 2D growth mode was mainly due to the dislocation looping and the grain

coalescence was found to be an additional factor for the origin of tensile strain in 3D grown GaN.

GaN grown in 3D growth mode produced compressively strained layers compared to GaN in 2D growth mode. Thus, the objective of compressively strained layers with low dislocation density on Si (111) using AlGaN/AlN stress mitigating layers was achieved for GaN grown in 3D growth mode. However, 3D growth of GaN exhibiting columnar type morphology is undesirable for HEMT applications as it causes scattering of the electrons at the AlGaN/GaN interface leading to mobility degradation. On the other hand, the GaN layers which showed smooth surface morphology suffered from high residual tensile strain and poor crystal quality. Hence, a different type of stress mitigating layers using AlN/GaN layers is investigated to obtain a suitable combination of these properties.

5.4.2 AlN/GaN stress mitigating layers

AlN/GaN as stress mitigating layers have been used for the growth of GaN to compensate the thermal mismatch induced compressive strain upon cool down. The schematic diagram of the layer structure investigated is shown in Fig. 5.22.

Fig. 5.22 The schematic diagram of GaN on AlN/GaN stress mitigating layers grown on Si (111) substrate.

The AlN layer (50 nm) was grown at the optimized conditions as discussed in Section 5.2 on a thermally cleaned Si (111) substrate. Subsequently, GaN (250 nm)/AlN (250 nm) stress mitigating layers were followed by the growth of a thick GaN layer (500

nm). The AlN and GaN layers were grown at a substrate temperature of 920 and 800 °C, respectively. The growth rates of AlN and GaN layers were kept at 0.13 and 0.22 µm/hr, respectively. The ammonia flow was kept at 280 sccm for both AlN and GaN layers based on the cracking studies as discussed in Section 5.1. Streaky RHEED pattern showing (2×2) surface reconstruction is obtained after cooling down below 300 °C suggestive of Ga-polarity as shown in Fig. 5.23.

Fig. 5.23 RHEED reconstruction patterns along the $[2\bar{1}10]$ azimuth of GaN exhibiting (2×2) pattern upon cooling down below 300 °C indicative of Ga-polarity.

Table 5.6 lists the dislocation density and strain in all the layers of the structure shown in Fig. 5.22. The 1st AlN layer shows the highest overall dislocation density which is undoubtedly due to the large amount of dislocations generated at the highly lattice mismatched AlN/Si interface. The growth of 1st GaN layer on the 1st AlN layer shows a significant amount of reduction in the overall dislocation density signifying that considerable amount of dislocation filtering occurs at the 1st AlN/GaN interface. The dislocations propagating from the AlN/Si interface and newer dislocations generated at the AlN/GaN interface undergoes extensive looping and bending leading to the compressive stress relaxation [217] in the 1st GaN layer. Considering that a maximum of 0.23% of tensile strain is generated due to the thermal mismatch between GaN and Si, the residual tensile strain of 0.15% for the 1st GaN layer at the room temperature indicates substantial compressive stress relaxation of the 1st GaN layer at the growth temperature. The 1st GaN layer tends to develop cracks in a situation where the growth is continued to an extent that the layer is completely relaxed.

Table 5.6 The threading dislocation density and strain in all the layers of the structure shown in Fig. 5.22.

Layers	HR-XRD		Micro-Raman spectroscopy	
	Dislocation density ($\times 10^{10} \text{ cm}^{-2}$)		E_2 (cm^{-1})	$\epsilon_{ }$ (%)
	Screw	Edge		
1 st AlN	4.6	*	*	*
1 st GaN	1.0	9.0	564.60	0.15
2 nd AlN	1.2	7.0	649.06	0.50
2 nd GaN	0.4	6.6	567.20	-0.08**

* weak signal for the measurements due to thin layer

**(-) sign indicates compressive strain.

Thus, sufficiently thick 2nd AlN layer is grown on top of the 1st GaN layer followed by the growth of 2nd GaN layer. The 2nd AlN layer induces adequate amount of compressive stress in the 2nd GaN layer such that it compensates for the tensile strain generated during the cool down. As can be seen, a residual compressive strain of -0.08% is observed in the 2nd GaN layer. Moreover, significant overall dislocation density reduction is also observed in the 2nd GaN layer. The high lattice mismatch induced compressive strain at the 2nd AlN/GaN interface and slow relaxation process of 2nd GaN layer owing to the low dislocation density is effective in obtaining compressively strained GaN layer.

Fig. 5.24 shows the optical microscope images of the surface of 2nd GaN layer. As can be seen, crack-free GaN layers have been obtained. However, a dense network of “buried cracks” was also seen along the crystallographic directions by focusing the microscope into the underlying layers. The formation of these buried cracks was anticipated to be at the 1st AlN/GaN interface. The mechanism of growth of 2nd AlN on the 1st GaN layer leading to the formation of buried cracks has been studied in detail [225]. The AlN layers grow under lattice mismatch induced tensile strain on the GaN layers. The strain in the AlN layers relaxes by the formation of micro-cracks as the process of relaxation by misfit dislocations is unfavorable. The cracking of the AlN layers occurs at the interface and gets eventually filled up by the overgrowth to obtain smoother surfaces [216]. In fact, the formation of buried cracks has been found to

relax the AlN layers thereby mitigating the tensile strain generated during the cool down of GaN layers.

Fig. 5.24 The optical microscope image of the crack-free surface of 2nd GaN layer.

Fig. 5.25 shows the 5×5 μm² AFM image of the 2nd GaN layer. The typical mound type surface morphology is obtained for the GaN layers by ammonia MBE [42]. As can be seen, the mounds are found to be associated with surface pits and correspond to the RMS roughness of 7.2 nm. The evolution of mounds in GaN layer grown by ammonia MBE has been studied in detail by Vezian et al.[179]. They have attributed the growth of mounds as a screw type dislocation mediated step flow growth explained by Burton, Cabrera and Frank (BCF) mechanism [226].

Fig. 5.25 AFM image of 5×5 μm² scan area of the GaN surface exhibiting mound type surface morphology.

The surface morphology of GaN layers grown using AlN/GaN stress mitigating layers is found to be different to that obtained using AlGaIn/AlN stress mitigating layers. The comparison of the material properties of GaN layers such as dislocation density,

surface morphology and strain states using both AlGa_N/AlN and AlN/GaN stress mitigating layers would further assist in determining the suitable stress mitigating layers for the growth of GaN based HEMT heterostructures on Si (111) using ammonia MBE.

5.4.3 Comparison of AlGa_N/AlN and AlN/GaN stress mitigating layers

Table 5.7 lists the RMS roughness of 5×5 μm² scan area, dislocation density and residual tensile strain in GaN layers grown using AlGa_N/AlN and AlN/GaN stress mitigating layers. GaN (500 nm)/AlN (50 nm) structure grown without any stress mitigating layers has been used as a reference for the comparison.

Table 5.7 The RMS roughness, dislocation density and strain in GaN layers.

Stress mitigating layer	RMS roughness (5×5 μm ²) (nm)	HR-XRD		Micro-Raman spectroscopy	
		Dislocation density (×10 ¹⁰ cm ⁻²)		E ₂ (cm ⁻¹)	Residual tensile strain (%)
		Screw	Edge		
None	4.8	0.37	3.9	563.82	0.21
AlGa _N /AlN	3.9	0.37	16.5	565.32	0.08
AlN/GaN	7.3	0.4	6.6	567.2	-0.08*

*(-) indicates compressive strain

GaN layer grown without any stress mitigating layer shows an overall good crystalline quality. The screw dislocation density is comparable to that obtained for GaN grown using stress mitigating layers, while the lowest edge dislocation density of 3.9×10¹⁰ cm⁻² is achieved. However, it exhibits 3D growth with rough surface morphology and high residual tensile strain. The surface roughness has reduced for the GaN layers grown using AlGa_N/AlN stress mitigating layers, but they are found to be of poor crystalline quality with very high edge dislocation density. Comparatively, GaN grown on AlN/GaN stress mitigating layers show reasonably good surface morphology and crystalline quality with compressive strain.

The dislocation density in GaN grown directly on AlN layer is mainly due to two sources. A high density of dislocations is generated at the highly mismatched AlN/Si interface. The dislocations which manage to propagate all the way in AlN up to AlN/GaN interface are one of the sources of dislocations in GaN. Secondly, some lattice mismatch induced dislocations are also generated at the AlN/GaN interface itself. Conclusively, AlN/GaN interface suffers from high density of threading

dislocations contributed from these two sources. These numerous dislocations undergo looping leading to their annihilation and subsequent plastic relaxation of the compressively strained GaN layers. Consequently, GaN layers grown without any stress mitigating layers produce good crystalline quality but high residual tensile strain.

Thus, it is important to reduce the threading dislocation density and the resulting plastic relaxation in order to obtain good compression in the GaN layers. In AlGaN/AlN stress mitigating layers, AlGaN as an intermediate layer is introduced in between AlN and GaN layers to reduce the threading dislocations generated due to AlN/GaN lattice mismatch. AlGaN is therefore used to alleviate the compressive stress relaxation in GaN caused due to the bending and looping of the dislocations at the AlN/GaN interface. However, the usage of AlGaN/AlN as stress mitigating layers in our studies has led to high overall threading dislocation density and subsequent compressive stress relaxation in GaN layers.

On the other hand, GaN layer grown using AlN/GaN stress mitigating layers showed an overall reduced dislocation density and higher compression due to the activity of dislocations at the two AlN/GaN interfaces. As observed, the 1st AlN/GaN interface assists in the filtering of dislocations by dislocation bending and looping. This mechanism reduces the dislocation density significantly but relaxes the lattice mismatch induced compressive stress in GaN. In order to regenerate the compressive stress in the GaN layers, a thick 2nd AlN layer has been grown on top of the 1st GaN layer. As listed in Table 5.6, about 90% of the screw type dislocations propagating from the AlN/Si interface have undergone decay at the end of the growth of 1st GaN layer. This observation suggests that numerous dislocations have annihilated in the 1st GaN layer itself due to the intense dislocation activity occurring at the 1st AlN/GaN interface. Thus, the dislocations reaching the 2nd AlN/GaN interface are relatively lesser. The decreased dislocation density at this interface reduces the dislocation activity as well. Hence, the 2nd GaN layer undergoes gradual relaxation with increasing thickness. The residual compressive strain in the 2nd GaN layer is sufficient enough to compensate for the thermal mismatch induced tensile strain generated during the post-growth cooling such that crack-free GaN is obtained. Hence, compressively strained GaN layers with good crystalline quality are obtained using AlN/GaN stress mitigating layers compared to AlGaN/AlN stress mitigating layers in our study.

5.5 Summary

The growth of AlN and GaN layers was optimized on Si (111) by ammonia MBE. The ammonia cracking efficiency was determined as a function of substrate temperature and ammonia flow in order to understand the growth mechanism of AlN and GaN layers. The cracking of ammonia is found to be more sensitive to the substrate temperature than the ammonia flow. The growth of AlN and GaN layers was done using 280 sccm of ammonia flow with growth rates of 0.13 and 0.22 $\mu\text{m/hr}$, respectively. The optimized growth temperature for AlN and GaN layers was 920 and 800 $^{\circ}\text{C}$, respectively.

AlGaIn/AlN and AlN/GaN stress mitigating layers were investigated to alleviate the thermal mismatch induced tensile strain and obtain crack-free GaN with smooth surface morphology and good crystalline quality. The structural properties of GaN grown on AlGaIn/AlN stress mitigating layers were studied as a function of AlN thickness and AlGaIn growth temperature. Thicker AlN facilitated higher annihilation of the dislocations and reduced the tensile strain in the GaN layer grown successively. 3D growth regime was observed for GaN grown at lower AlGaIn growth temperature while higher AlGaIn growth temperature resulted in 2D growth mode. The GaN layers grown in 2D growth mode showed poorer crystalline quality and higher residual tensile strains than 3D grown GaN. The origin of tensile strain in the GaN layers was further determined by comparing the measured and the theoretically obtained strain values. The compressive strain relaxation in GaN grown in 2D growth mode was mainly due to the dislocation looping while grain coalescence was found to be an additional factor for the origin of tensile strain in 3D grown GaN. Thus, GaN layers with either 3D surface morphology or poor crystalline quality and high residual tensile strain were obtained using AlGaIn/AlN stress mitigating layers.

Furthermore, the structural properties of GaN grown on AlN/GaN stress mitigating layers were also investigated. The annihilation of the numerous dislocations at the AlN/GaN interface led to the lattice mismatch induced compressive stress relaxation of the 1st GaN. However, the subsequent growth of thick AlN aided in further dislocation filtering and inducing adequate amount of compressive stress in the 2nd GaN layer such that it compensates for the tensile strain generated during the cool down. Thus, compressively strained GaN layers with good crystalline quality were obtained using AlN/GaN stress mitigating layers. Consequently, AlN/GaN stress

mitigating layers are found to be a relatively better choice for the development of GaN based HEMT heterostructures on Si (111) using ammonia MBE.

6. AlGaN/GaN HEMT heterostructures grown on Si (111) by ammonia MBE

6.1 Improvement of gallium nitride layers

6.1.1 Effect of growth rate

The AlN/GaN stress mitigating layers have resulted in good quality and compressively strained GaN layers on Si (111) substrate as discussed in Chapter 5. However, the surface morphology shows the presence of pits with high RMS roughness. Thus, it becomes necessary to optimize the growth conditions in order to improve the surface morphology of the GaN layers for enhanced HEMT performances.

The recovery of GaN growth from 3D mode to 2D lateral growth has been reported to improve by increasing the growth rate of the nucleation layer in MOCVD technique [227]. The theoretical results of Zyweitz et al. [228] suggests that increased Ga adatom diffusion in the Ga-rich growth conditions of GaN grown by PA-MBE reduces the surface pit density. Thus, a systematic study has been attempted to investigate the effect of growth rate on the material properties of GaN grown by ammonia MBE.

The growth rate of GaN is limited by the Ga flux in the N-rich growth conditions of ammonia MBE. GaN layers of samples A, B and C were grown with 500 nm thickness and increasing growth rates of 0.22, 0.34 and 0.45 $\mu\text{m/hr}$, respectively by effectively increasing the Ga flux. The ammonia flow was also increased and was kept at 280, 560 and 1000 sccm for samples A, B and C, respectively. The simultaneous increase in the ammonia flow with increasing growth rates was done to maintain low III/V ratio which has been found to result in high quality GaN material with reduced impurity incorporation and background electron concentrations [157]. AlN layer with a thickness of 50 nm was grown at the optimized conditions for all the samples as discussed in Section 5.2 of Chapter 5. Fig. 6.1 (a), (b) and (c) show the RHEED patterns of samples A, B and C for 50 nm of the GaN layer growth, respectively. Sample A exhibited spotty RHEED pattern while streaky pattern with connecting spots was observed for sample B and completely streaky pattern was observed for sample C. Fig. 6.1 (d), (e) and (f) show the RHEED patterns obtained after the growth of 500 nm thick GaN layers of samples A, B and C, respectively. The RHEED pattern of sample A remained almost spotty throughout the growth, whereas RHEED patterns of samples B and C evolved to streaky pattern as the growth progressed. This phenomenon suggests that the transition of the RHEED from 3D to 2D is faster with

increasing growth rate. Thus, the evolution from initial 3D island nucleation to the 2D lateral growth is found to be more rapid with the increasing growth rate.

Fig. 6.1 RHEED reconstruction patterns along the $[2\bar{1}\bar{1}0]$ azimuth after (a-c) 50 nm and (d-f) 500 nm of GaN growth for samples A, B and C respectively. GaN layers have been grown at different growth rates of 0.22, 0.34 and 0.45 $\mu\text{m/hr}$ for samples A, B and C, respectively.

Fig. 6.2 (a), (b), and (c) shows $5 \times 5 \mu\text{m}^2$ AFM images of GaN layers of samples A, B and C, respectively. Sample A shows 3D columnar growth with a high RMS roughness of 4.5 nm. Sample B and C show 2D mound type morphology and smoother surfaces with RMS roughness of 2.2 and 1.4 nm, respectively. The average lateral mound size for sample B is 1 μm , slightly higher than the mound size of 0.7 μm for sample C. Moreover, higher pit density is found in sample B than in sample C.

Fig. 6.2 The $5 \times 5 \mu\text{m}^2$ AFM images of the GaN layers grown with different growth rates of (a) 0.22 $\mu\text{m/hr}$ - sample A, (b) 0.34 $\mu\text{m/hr}$ - sample B and (c) 0.45 $\mu\text{m/hr}$ - sample C.

Table 6.1 lists the RMS roughness, residual tensile strain and dislocation density in GaN layers of samples A, B and C. As shown, the RMS roughness of the $5 \times 5 \mu\text{m}^2$ scan area of GaN layers reduces with the increasing growth rate. All the samples show a systematic decrease in the residual tensile strain while an increase in the

overall threading dislocation density with the increasing GaN growth rate. Thus, it can be understood that sample C with the highest threading dislocation density exhibited the maximum compressive strain during growth. This behavior can be explained based on the mechanism of dislocation looping and the corresponding plastic relaxation in the GaN layers.

Table 6.1 The RMS roughness, residual tensile strain and dislocation density in GaN of samples A, B and C grown with different growth rates.

Sample	Growth rate ($\mu\text{m/hr}$)	RMS roughness (nm)	Residual tensile strain (%)	Dislocation density $\times 10^{10} (\text{cm}^{-2})$	
				Screw	Edge
A	0.22	4.8	0.21	0.37	3.9
B	0.34	2.2	0.18	0.55	9.5
C	0.45	1.4	0.12	0.74	19.3

Sample A grown with the lowest growth rate might have the least surface wetting due to the low Ga flux used. Consequently, the higher diffusion barrier for Ga adatoms might have resulted in reduced surface diffusion and subsequent 3D growth. The surface diffusion of Ga adatoms is increased by increasing the Ga flux or the growth rate for the GaN layers of samples B and C. The increase in the Ga flux causes faster transition of the GaN layers from 3D island nucleation to 2D lateral growth. This explains the evolution of smoother surface morphology when the growth rate is increased. Thus, the surface diffusion is found to be limited by the Ga flux for the growth of GaN layers in ammonia rich conditions. While Volmer-Weber growth mechanism is observed for the GaN layers of sample A, GaN growth of samples B and C proceed via screw type dislocation mediated step flow growth phenomenon in the presence of sufficient Ga diffusion, and hence leads to the formation of mounds. However, it is interesting to note that higher pit density is observed on the surface of sample B compared to sample C even though sample C shows an increased screw dislocation density. This behavior defies our common understanding that the pits on the GaN surface are believed to be originated from open core screw type dislocations, which are formed to minimize the surface potential [229]. Since, sample C is grown with high Ga flux or surface diffusion, it is likely that Ga adatom overcomes the barrier created around the open core dislocation and allows the GaN growth to continue without the formation of pits on the surface [230]. Thus, sample C grown with higher growth rate shows lesser pit density than sample B.

Surface diffusion also enhances the dislocation bending by climb mechanism at the growth surface [173]. The bending and looping of the dislocations lead to their annihilation and subsequent plastic relaxation of the GaN layers. The increase in the surface diffusion increases the stress relaxation through looping mechanism leading to a smaller misfit region. The early relaxation of the GaN layers grown with higher growth rate inhibits further dislocation looping leading to an increased dislocation density. Consequently, the GaN layers exhibit lower residual tensile strain and higher dislocation density with increasing growth rates. Furthermore, the increased GaN growth rate has resulted in nearly pit-free surface morphology with reduced RMS roughness.

The effect of the high growth rate of GaN layer in the AlN/GaN stress mitigating layers was investigated on the 500 nm thick 2nd GaN layer. It should be noted that while the growth rate of the 1st GaN was kept high at 0.60 $\mu\text{m/hr}$, the 2nd GaN layer is grown with a lower growth rate of 0.22 $\mu\text{m/hr}$ for the purpose of comparison. It was observed that the buried crack density in the AlN layers reduced with increasing growth rates of 1st GaN layer from 0.22 to 0.6 $\mu\text{m/hr}$. The lower buried crack density can be attributed to the reduced lattice mismatch induced tensile strain at the 1st GaN and 2nd AlN interface. The residual tensile strain in the GaN layers has been found to reduce with increasing growth rate. It can thus be said that the GaN layers grown using higher growth rate exhibit larger compressive strain at the growth temperature. As a result, the subsequent AlN layers are subjected to lesser lattice mismatch induced tensile strain from the bottom GaN layers. Thus, the reduced lattice mismatch between the compressively strained GaN layers grown at the higher growth rate of 0.6 $\mu\text{m/hr}$ lead to lesser buried crack density compared to the GaN layers grown at a lower growth rate of 0.22 $\mu\text{m/hr}$.

Furthermore, AFM was used to investigate the effect of the growth rate of 1st GaN on the surface morphology of the 2nd GaN layer. Fig. 6.3 (a) and (b) shows the $5 \times 5 \mu\text{m}^2$ AFM images of the 2nd GaN layer grown using 1st GaN layer with low and high growth rate, respectively. Fig. 6.3 (c) and (d) show the corresponding images obtained in the amplitude mode. An improved surface morphology with reduced pit density is obtained for the 2nd GaN layer grown on the 1st GaN layer with higher growth rate. In addition, the RMS roughness has reduced significantly from 7.2 to 2.0 nm when the 1st GaN growth rate is increased from 0.22 to 0.60 $\mu\text{m/hr}$, respectively.

Fig. 6.3 AFM images of $5 \times 5 \mu\text{m}^2$ scan area of 2nd GaN grown using 1st GaN layer with (a) low growth rate and (b) high growth rate. (c) and (d) are the corresponding images obtained in the amplitude mode.

Micro-Raman measurements were done to investigate the effect of growth rate on the strain states of GaN layers. As shown in Fig. 6.4, the E_2 phonon peak of the GaN layers grown with improved surface morphology is relatively more blue shifted corresponding to a higher compressive strain of -0.24% compared to the GaN layers exhibiting poor surface morphology. Ex-situ bow measurement results obtained at room temperature on these two wafers are shown in Fig. 6.5. The layer structure with improved GaN showed a wafer bow of $26 \mu\text{m}$ and a corresponding radius of curvature of 0.021 m^{-1} while the GaN layers with poor surface morphology demonstrated higher wafer bowing of $41 \mu\text{m}$ with a radius of curvature of 0.067 m^{-1} . It can be said that in addition to the improvement of the surface morphology, the high growth rate has also assisted in building higher compressive stress in the GaN layers.

Fig. 6.4 Raman shift in E₂ phonon peak of GaN grown with high and low growth rates. The vertical line indicates the E₂ position (567 cm⁻¹) of free standing GaN.

The crystalline quality of the GaN layers was also compared in order to determine the effect of the growth rate on the overall dislocation density. The screw and edge dislocation density in GaN layers grown using high growth rate was estimated to be 5.7×10^9 and $5.14 \times 10^{10} \text{ cm}^{-2}$, respectively while GaN grown using the low growth rate showed screw and edge dislocation density of 4×10^9 and $6.6 \times 10^{10} \text{ cm}^{-2}$.

Fig. 6.5 Ex-situ wafer bow measurements at room temperature using a laser based system.

While the screw dislocation density has increased, the edge dislocations have reduced with increasing GaN growth rate. Hence, a slight improvement in the overall

dislocation density is observed along with improved surface morphology and higher compressive stress in the GaN layers. The higher residual compressive stress in the GaN layers provided an allowance to increase the thickness of the 2nd GaN layer in order to further reduce the overall dislocation density. The thickness of 2nd GaN layer was increased up to 1.2 μm which makes the total buffer layer thickness to be 1.7 μm including the AlN (250 nm)/GaN (250 nm) stress mitigating layers.

Fig. 6.6 shows FWHM of the rocking curve of GaN (002) peak as a function of buffer layer thickness. The inset shows the corresponding rocking curves of GaN (002) plane. The FWHM decreases with increasing buffer layer thickness signifying an improvement in the crystalline quality with increasing buffer layer thickness.

Fig. 6.6 HR-XRD measured FWHM of the GaN (002) rocking curve as a function of buffer layer thickness. Inset shows the rocking curves of GaN (002) plane.

Fig. 6.7 shows the screw and edge dislocation density in the 2nd GaN layer as a function of increasing buffer layer thickness. Both the screw and edge dislocation density reduces as the buffer layer thickness is increased. A reduction of around 16% in the overall dislocation density is observed when the buffer layer thickness is increased from 0.9 to 1.7 μm . As discussed in Section 4.6 of Chapter 4, the decrease in both the screw and edge type dislocations indicates the presence of mixed character of dislocations in the GaN layers investigated in this study. The interaction of edge and mixed type dislocations is likely to be the reason for a decrease in the overall dislocation density with increasing buffer layer thickness. The following section describes the demonstration of AlGaN/GaN HEMT heterostructures using this improved buffer layer.

Fig. 6.7 The screw and edge dislocation density of GaN decreases with the increasing buffer layer thickness.

6.2 AlGaN/GaN HEMT

The schematic diagram of a typical AlGaN/GaN HEMT heterostructure with AlN/GaN stress mitigating layers is shown in Fig. 6.8.

Fig. 6.8 The schematic diagram of a typical AlGaN/GaN HEMT heterostructure on Si (111) grown by ammonia MBE.

The structure consists of 50 nm thick AlN layer, AlN/GaN stress mitigating layers of 250 nm thickness each followed by 1.2 μm thick GaN layer. The Al content in the AlGaN barrier layer and its thickness was varied to obtain an optimum combination for good 2DEG properties. The thickness of the GaN cap layer is about 2 nm. The 1st and 2nd AlN layers were grown at a growth rate of 0.13 $\mu\text{m/hr}$ while the 1st and 2nd GaN layers were grown using a growth rate of 0.60 and 0.22 $\mu\text{m/hr}$, respectively. High ammonia overpressures were used during the growth by keeping the ammonia flow of

680 and 1000 sccm for the growth of AlN and GaN layers, respectively. Streaky RHEED pattern was observed during the growth of all the layers and (2×2) RHEED surface reconstruction pattern was obtained after cooling down below 300 °C suggestive of Ga-polarity as shown in Fig. 6.9.

Fig. 6.9 Streaky (2×2) RHEED surface reconstruction patterns upon cooling down below 300 °C along $[2\bar{1}\bar{1}0]$ and $[01\bar{1}0]$ azimuths for AlGaN/GaN HEMT heterostructure.

The Al content in the barrier layer was obtained using HR-XRD symmetric (004) ω -2 θ scan as shown in Fig. 6.10 for a typical HEMT heterostructure. The measured data is fitted against the simulated data to estimate the Al content based on the separation of the peaks.

Fig. 6.10 The measured and simulated symmetric (004) ω -2 θ scan for a typical AlGaN/GaN HEMT heterostructure obtained using HR-XRD.

Room temperature hall measurements were performed systematically to study the effect of Al content and thickness of the barrier layer on the 2DEG properties of AlGaN/GaN HEMT heterostructures. The samples namely B1, B2 and B3 have been grown with different thicknesses of 23, 24 and 26 nm, respectively with a fixed Al

content of 29%. Another set of samples consisting of samples C1, C2 and C3 have been grown with a fixed barrier layer thickness of 28 nm but a variable Al content of 23, 24.5 and 27.5%, respectively.

Fig. 6.11 shows the plot of mobility versus sheet carrier density for the AlGaIn/GaN HEMT heterostructures. The dashed lines are given as guide to the eye only.

Fig. 6.11 The mobility versus sheet carrier density for the AlGaIn/GaN HEMT heterostructures. Samples B1, B2 and B3 are grown with barrier layer thickness of 23, 24 and 26 nm, respectively at an Al content of 29%. Samples C1, C2 and C3 are grown with Al content of 23, 24.5 and 27.5%, respectively with a barrier layer thickness of 28 nm. The encircled samples are all grown with the barrier layer thickness of 25 nm and Al content of 31%.

The mobility improves with the increasing sheet carrier density as the barrier layer thickness is increased from 23 to 26 nm for samples B1 to B3. The sheet carrier density increases by 16% when the barrier layer thickness is increased from 23 to 24 nm while it increases by 20% with a further increase to 26 nm. Thus, the enhanced sheet carrier density with the increasing barrier layer thickness could be due to the nearing of the surface donor states towards the Fermi level. Similar trend is also observed for samples C1 to C3. However, the rise in the sheet carrier density in this case is due to the increase in the Al content at a fixed barrier layer thickness of 28 nm. The sheet carrier density has improved by 60% when the Al content is increased from 23 to 27.5%. The increase in the Al content increases the polarization induced

sheet carrier density and hence the mobility. The 2DEG properties were further tuned by increasing the Al content to 31% while decreasing the barrier layer thickness to 25 nm in order to maximize the product of the mobility and the sheet carrier density. At lower sheet carrier density, impurity and piezoacoustic scattering reduces the mobility while very high sheet carrier density results in the degradation of the mobility because of the small average distance between the 2DEG and the interface [34]. The encircled set of samples have been grown with a barrier layer thickness of 25 nm and Al content of 31%. The highest mobility achieved is $1350 \text{ cm}^2/\text{V.s}$ with a sheet carrier density of $1.1 \times 10^{13} \text{ cm}^{-2}$. The standard deviation of 3.6% in the mobility values and 2.6% in the sheet carrier density values indicated reasonably good reproducibility from run to run.

Fig. 6.12 (a) shows the image of AlGaIn/GaN HEMT heterostructure grown epitaxially on 100-mm Si (111) substrate. A typical wafer bow of $\sim 40 \text{ }\mu\text{m}$ corresponding to a wafer curvature of 0.03 m^{-1} was measured ex-situ at room temperature as shown in Fig. 6.12 (b).

Fig. 6.12 (a) AlGaIn/GaN HEMT heterostructure on 100-mm Si (111) substrate and (b) wafer bow of $\sim 40 \text{ }\mu\text{m}$ measured ex-situ at room temperature.

A $5 \times 5 \text{ }\mu\text{m}^2$ AFM image of the optimized AlGaIn/GaN HEMT heterostructure obtained in amplitude mode is shown in Fig. 6.13 (a). The typical mound type morphology can be seen having a homogenous size distribution of the mounds with a lateral size of about $1 \text{ }\mu\text{m}$. The surface exhibits an RMS roughness of 3.8 nm and a peak-valley height Δz of 15 nm. A closer look at the typical mound in Fig. 6.13 (b) shows the terrace-step morphology with each mound exhibiting six facets. The formation of these terraces indicates step flow growth mode while the six facets of the mound illustrates an almost regular hexagonal geometry. The propagation of the screw dislocations can also be seen forming depressions upon reaching the surface.

Fig. 6.13 (a) 5x5 μm^2 AFM image of the optimized AlGaIn/GaN HEMT heterostructure obtained in amplitude mode and (b) the typical mound showing terrace-step morphology and six facets of an almost regular hexagonal geometry.

Cross-sectional TEM was also done to understand the dislocation propagation in the AlGaIn/GaN HEMT heterostructure. As discussed in Section 5.4.2, Fig. 6.14 shows that the activity of the dislocations occurs markedly at the two AlN/GaN interfaces.

Fig. 6.14 Bright field, cross-sectional TEM image of AlGaIn/GaN HEMT heterostructure along the $[11\bar{2}0]$ zone axis.

The 1st AlN layer and subsequently grown GaN layer shows high density of dislocations. However, numerous dislocations have annihilated at the 1st AlN/GaN interface. Further, dislocation looping and termination can be seen in about 200 nm

thick initial region of the 2nd GaN layer at the 2nd AlN/GaN interface. The dislocations reaching the GaN surface with a screw component of burger vector lead to the formation of the surface depressions as seen in the AFM image of Fig. 6.13 (b). The inset shows a sharp GaN and AlGa_N barrier layer interface with the AlGa_N barrier layer thickness of 25 nm for the optimized AlGa_N/GaN HEMT heterostructure.

The temperature dependent hall measurements were done to obtain the resistivity, mobility and sheet carrier density from 90 to 400K. Fig. 6.15 shows that the sheet carrier density remains constant irrespective of the operating temperature while the mobility increases more than three times from 1350 cm²/V.s at room temperature to 4290 cm²/V.s at 90K. These results confirm the presence of 2DEG at the AlGa_N/GaN interface.

Fig. 6.15 The temperature dependence of mobility and sheet carrier density of AlGa_N/GaN HEMT heterostructure.

The 2DEG confinement was confirmed by mercury-probe C-V measurements. Moreover, the background concentration of the GaN layer was also determined from the corresponding depth profile. As shown in Fig. 6.16 (a), the capacitance is constant for up to a reverse bias voltage of 5.2 V indicating the presence of 2DEG. The 2DEG carrier density depletes with a sudden drop of capacitance attaining a pinch off at a reverse bias voltage of 6.5 V. This sudden drop of the capacitance indicates carrier confinement of the 2DEG at the AlGa_N/GaN interface.

Fig. 6.16 (a) Mercury probe C-V measurements and (b) carrier density profile of AlGaIn/GaN HEMT heterostructure.

As shown in Fig. 6.16 (b), differentiating the C-V profile gives the carrier density vs depth profile. A very high carrier density is measured after 26 nm of depletion width. This indicates the presence of 2DEG charge at 26 nm from the surface, which nearly matches with the thickness of AlGaIn barrier layer obtained by cross-sectional TEM. The charge carriers deplete throughout 1 μm GaN resulting in a background carrier concentration to be $\sim 10^{15} \text{ cm}^{-3}$.

Fig. 6.17 shows the uniformity of the sheet resistance across the wafer using a contactless method. The average sheet resistance is 368 Ω/sq. with a variation of 7.3% and a standard deviation of 2%. Thus, a growth process has been established

to obtain uniform 2DEG properties of AlGaIn/GaN HEMT heterostructures grown on 100-mm Si (111).

Fig. 6.17 Sheet resistance mapping of a 100-mm AlGaIn/GaN HEMT heterostructure which was measured by a contactless method. The average sheet resistance is 368 Ω/sq . with a variation of 7.3% and a standard deviation of 2%.

The buffer leakage current measurements of the AlGaIn/GaN HEMT heterostructures were conducted using a gap of 5 μm between the two ohmic contacts and maintaining a width of 50 μm . The buffer leakage current of 2.6×10^{-4} mA/mm was determined at 20 V with the $I_{\text{ON}}/I_{\text{OFF}}$ ratio of 7.3×10^6 . This indicates that the undoped GaN buffer has good insulating properties. The 0.3 μm T-gate length devices were also fabricated to study the performance of the AlGaIn/GaN HEMT heterostructure [231]. The dimensions of the fabricated devices were $W_g = (2 \times 142 \mu\text{m})$ and $L_g = 0.3 \mu\text{m}$. The devices exhibited a maximum drain current density, I_{Dmax} of 768 mA/mm at $V_g = +1$ V and a maximum extrinsic transconductance, g_{mmax} of 190 mS/mm at $V_D = 6$ V with good pinch-off characteristics. The device threshold voltage was -4.53 V.

6.3 Summary

A systematic study was undertaken to improve the surface morphology of GaN layers grown on 50 nm thick AlN layer by increasing the GaN growth rate. The evolution of GaN from the initial 3D island nucleation to the 2D lateral growth was rapid when the growth rate was increased. Volmer-Weber growth mechanism was observed for GaN layers grown at lower growth rates while the growth proceeded via screw type

dislocation mediated step flow growth for higher growth rates. GaN layers with improved surface morphology, lower residual tensile strain and high dislocation density was observed at higher growth rates. The process of early relaxation of the GaN layers due to increased Ga diffusion at higher growth rates was found to be a likely reason for the lower residual tensile strain and high dislocation density.

The effect of high growth rate of GaN layer in the AlN/GaN stress mitigating layers was investigated on the 500 nm thick 2nd GaN layer. The buried crack density in the 2nd AlN layer was reduced by increasing the growth rate of the 1st GaN layer. An improved surface morphology with reduced pit density and RMS roughness is obtained for the 2nd GaN layer grown with the 1st GaN layer at a higher growth rate. In addition to the improvement of the surface morphology, the high growth rate also assisted in building higher compressive stress in the GaN layers with slight improvement in the overall crystalline quality. A reduction of around 16% in the overall dislocation density was observed with the increase of the buffer layer thickness from 0.9 to 1.7 μm .

The AlGaN/GaN HEMT heterostructures were grown with 1.7 μm thick buffer layer and the effect of Al content and thickness of AlGaN barrier layer on the 2DEG properties was studied. The sheet carrier density and the mobility of 2DEG increased with increasing the Al content and the thickness of the AlGaN barrier layer. The highest mobility of 1350 $\text{cm}^2/\text{V.s}$ was achieved with a sheet carrier density of $1.2 \times 10^{13} \text{ cm}^{-2}$ for the optimized AlGaN/GaN HEMT heterostructure. The standard deviation of 3.6% in the mobility values and 2.6% in the sheet carrier density values indicated good reproducibility of AlGaN/GaN HEMT heterostructures from run to run. The average sheet resistance of 368 $\Omega/\text{sq.}$ with a variation of 7.3% and a standard deviation of 2% indicated good uniformity across the 100-mm wafer. HEMT devices with 0.3 μm gate length exhibiting good device characteristics and low buffer leakage current were fabricated on the grown structure. Thus, ammonia MBE technique is shown to be a viable method of growing high-quality and reproducible AlGaN/GaN HEMT heterostructures with good uniformity on 100-mm Si (111) substrates.

7. Conclusions and Future work

7.1 Conclusions

The growth of AlGaIn/GaN HEMT heterostructures has been performed on 100-mm Si (111) by PA-MBE and ammonia MBE techniques. A set of systematic studies has been attempted to optimize the growth parameters in order to obtain good 2DEG properties.

7.1.1 Growth of AlGaIn/GaN HEMT heterostructure on Si (111) by PA-MBE.

1. The optimization of III/V ratio for the growth of AlN and GaN layers was conducted by varying the metal flux at a constant RF power of 300 W and nitrogen flow of 2 sccm. The growth of AlN and GaN layers was done at a substrate temperature of 860 and 740 °C, respectively. Smooth surface morphology, good crystalline quality and low residual tensile strains were obtained for the layers grown in the intermediate growth regime at a growth rate of 0.19 $\mu\text{m/hr}$.
2. The effect of III/V ratio on the polarity of AlN and GaN layers grown on Si was investigated. The growth of both AlN and GaN layers in the intermediate growth regime resulted in metal-polarity. While the polarity of AlN obtained was N-polar, Ga-polar GaN was achieved in the droplet growth regime. Moreover, polarity inversion occurred at the GaN/AlN interface enabling the growth of Ga-polar GaN on N-polar AlN. GaN grown in the intermediate growth regime showed Ga polarity on both Al and N-polar AlN layers. The formation of Al-Al bonding was found to be the reason for the observed inversions in AlN and GaN layers. Thus, it is suggested that Al metal flux played a major role in controlling the polarity of AlN and hence determining the polarity of the subsequent GaN layers.
3. The narrow growth window was found to be affected by the fluctuation in Ga fluxes during the longer growth times leading to poor reproducibility of the GaN layers. The “growth window” was established by determining the region having Ga stable conditions where the surface coverage was the same despite the fluctuations in the Ga flux. The Ga bilayer was maintained using in-situ RHEED during the growth of GaN to keep an optimal III/V ratio and overcome the Ga flux fluctuations. GaN grown in this Ga stable growth conditions resulted in reproducible material properties such as smooth surface morphology, good crystalline quality and negligible tensile strains.

4. AlGa_N/Ga_N HEMT heterostructures were optimized to achieve good 2DEG properties. The AlGa_N barrier layer with an Al content of 29% and a barrier layer thickness of 25 nm resulted in the highest room temperature mobility of 1100 cm²/V.s with a sheet carrier density of 9.0×10^{12} cm⁻² grown using 1.5 μm thick Ga_N layer. AlGa_N/Ga_N HEMT device with 1.5 μm gate length exhibiting good device characteristics was demonstrated using this optimized layer structure.

7.1.2 Growth of AlGa_N/Ga_N HEMT heterostructure on Si (111) by ammonia MBE.

1. The pyrolysis or thermal “cracking” mechanism of ammonia was investigated in order to understand the growth mechanism of nitrides by ammonia MBE. The ammonia cracking efficiency increased with increasing substrate temperature and it reached saturation beyond 250 sccm of ammonia flow for both AlN and GaN layers. The cracking efficiency was found to be more sensitive to the substrate temperature than the ammonia flow.
2. The growth rate and the growth temperature were optimized at 0.13 μm/hr and 920°C, respectively to obtain AlN layers of good crystalline quality and smooth surface morphology. Unlike PA-MBE, the growth of GaN layer above 500 nm thickness directly on AlN resulted in the cracking of the epilayers due to thermal mismatch. This made it necessary to investigate the use of stress mitigating layers for the growth of thick GaN.
3. AlGa_N/AlN stress mitigating layers were studied first to alleviate the thermal mismatch induced tensile strain and obtain crack-free GaN on Si. The structural properties of GaN grown on AlGa_N/AlN were assessed as a function of AlN thickness and AlGa_N growth temperature. GaN grown on 200 nm thick AlN showed reduced dislocation density and lesser tensile strain. 3D growth regime was observed for GaN grown at lower AlGa_N growth temperature of 800 °C while higher AlGa_N growth temperature resulted in 2D growth mode. The GaN layers grown in 2D growth mode showed poorer crystalline quality and higher residual tensile strain than 3D grown GaN. The origin of tensile strain in the GaN layers was further determined by comparing the measured and the theoretically obtained strain values. The compressive strain relaxation in GaN grown in 2D growth mode was mainly due to the average plastic relaxation of the layers by dislocation looping. However, grain coalescence was found to be an additional factor for the

origin of tensile strain in 3D grown GaN. Thus, GaN layers with either 3D surface morphology or poor crystalline quality and high residual tensile strain were obtained using AlGa_N/AlN stress mitigating layers.

4. AlN/GaN stress mitigating layers were also studied. GaN layers grown using this showed 2D growth mode, improved crystalline quality and compressive strain. The 1st AlN/GaN interface assisted in the significant amount of dislocation filtering by reducing the screw-type dislocation density to about 90%. The 2nd AlN/GaN interface aided in inducing sufficient compressive stress in the subsequent GaN layers such that it compensates for the tensile strain generated during the cool down. The high lattice mismatch induced compressive strain at the 2nd AlN/GaN interface and slow relaxation process of the subsequent GaN layers owing to the low dislocation density was found to be effective in obtaining compressively strained GaN layers. Consequently, AlN/GaN stress mitigating layers were found to be a relatively better choice for the development of GaN based HEMT heterostructures on Si (111) using ammonia MBE.

The GaN layers grown using AlN/GaN stress mitigating layers were further improved by increasing the growth rate of the 1st GaN layer. The evolution of the 1st GaN layer from initial 3D nucleation to the 2D lateral growth was found to be more rapid with the increasing growth rate. This rapid transition assisted in improving the surface morphology and increasing the compressive strain in the 2nd GaN layer.

5. The AlGa_N barrier layer was optimized at an Al content of 31% and a barrier layer thickness of 25 nm for the growth of AlGa_N/GaN HEMT heterostructure on Si. The highest room temperature mobility of 1350 cm²/Vs and sheet carrier density of $1.2 \times 10^{13} \text{ cm}^{-2}$ was achieved for this optimized structure. A stable and reproducible growth process was established to obtain high quality AlGa_N/GaN HEMT heterostructures with good uniformity. AlGa_N/GaN HEMTs with 0.3 μm gate length exhibiting good device characteristics was demonstrated using this optimized layer structure.

AlGa_N/GaN HEMTs have been demonstrated in this study on 100-mm Si (111) substrate using both PA-MBE and ammonia MBE. Both the techniques have shown their own advantages and shortcomings. The growths by PA-MBE technique was

realized at lower substrate temperatures and provided atomically flat surfaces with sub-nm roughness in the metal-rich growth regime. GaN layers with thicknesses up to 1.5 μm could be grown without the use of any stress mitigating layers. The metal-rich growth conditions could have assisted in the early relaxation of the GaN layers such that negligible relaxation occurred in the subsequent GaN leading to the compressively strained GaN. The lower growth temperature of PA-MBE could have also aided in alleviating the degree of thermal mismatch induced tensile strain in the GaN layers grown on Si. However, the early relaxation of the GaN layers and consequent limited dislocation interactions could have led to lesser dislocation reduction with resulting dislocation density in the order of 10^{11} cm^{-2} .

On the other hand, growths by ammonia MBE were done at higher substrate temperature to aid in the process of thermal “cracking” or pyrolysis of ammonia. The GaN layers exhibited mound type surface morphology with rms surface roughness ranging between 2 to 4 nm. The N-rich growth conditions are likely to cause slow compressive stress relaxation throughout the GaN leading to the development of tensile strain and subsequent cracking of the epilayers. Thus, the use of stress mitigating layers was necessary in order to obtain 1.7 μm thick crack-free buffer layer on Si by ammonia MBE. However, the process of compressive stress relaxation due to the dislocation looping and annihilation also resulted in good crystalline quality GaN layers with reduced dislocation density in the lower order of 10^{10} cm^{-2} . The reduction in the overall dislocation density by one order could be a potential reason for the higher mobility obtained for AlGaIn/GaN HEMT heterostructures by ammonia MBE compared to PA-MBE.

The process of growth optimization of AlGaIn/GaN HEMT heterostructure by PA-MBE and ammonia MBE has assisted in an in-depth understanding of the growth mechanisms. Exploring both the techniques have aided in identifying respective advantages and shortcomings. PA-MBE and ammonia MBE have been shown as potential techniques to realize AlGaIn/GaN HEMT heterostructures on 100-mm Si (111) substrate for the first time. Moreover, prototype devices have also been demonstrated using the AlGaIn/GaN HEMT heterostructures grown. This work may possibly provide useful insights and is a unique contribution towards the development of future technology on GaN on Si by MBE.

7.2 Future work

1. This dissertation focuses on the growth of Ga polar AlGaN/GaN HEMT heterostructures by PA-MBE. Recently, devices fabricated on AlGaN/GaN HEMT heterostructures grown with N-polarity have gathered much attention. The reversed polarization has several advantages such as low gate leakage, enhancement operation, low dispersion devices and improved carrier confinement. N-polar GaN may be obtained by facilitating the formation of Al-Al bonding through the insertion of optimum amount of Al metal on the surface of Al polar AlN as discussed in Section 4.3.
2. The growth of GaN using AlGaN/AlN stress mitigating layers has been discussed in Section 5.4.1. GaN grown at lower AlGaN growth temperature of 800 °C showed overall low dislocation density and low residual tensile strain. However, the only drawback is that the GaN layers exhibited 3D growth mode. However, if the 3D growth can be recovered to 2D growth mode, AlGaN/AlN stress mitigating layer can be still useful. This process may be facilitated by increasing the Ga flux. The higher Ga flux will enhance the surface diffusion aiding in the faster coalescence of the 3D columnar grains resulting in smoother 2D surface morphology.
3. Both PA-MBE and ammonia MBE growth techniques have their own advantages and shortcomings. AlN buffer layers grown on Si (111) by PA-MBE have been found to be nearly relaxed at a thickness of 120 nm. However, ammonia MBE grown AlN buffer layers exhibited residual tensile strain of ~ 0.6% at a thickness of 200 nm. Comparable strains were also observed for 200 nm and 500 nm thick AlN grown on Si (111) which indicated that AlN had reached saturation in strain relaxation for 200 nm thickness. On the other hand, GaN layers grown by ammonia MBE exhibited one order lower dislocation density compared to PA-MBE. A new structure may thus be proposed which could exploit the advantages of the growth mechanisms of both the techniques.

In this direction, AlN buffer layers as a template can be grown on Si (111) substrate using PA-MBE technique followed by the growth of GaN layer by ammonia MBE. The relaxed AlN buffer layer can assist in stimulating higher lattice mismatch induced compressive strain in the GaN layers. The process of gradual looping and annihilation of the dislocations in the GaN layer grown by

ammonia MBE should result in improved crystalline quality. Thus, a simple AlGa_N/Ga_N HEMT heterostructure with a thick Ga_N layer exhibiting good crystalline quality can be achieved using this combination of techniques.

8. References

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9. Author's publications

9.1 Journal publications

1. Origin of tensile strain in GaN grown on AlGaN/AlN stress mitigating layers on 100-mm Si (111) by ammonia molecular beam epitaxy.
M. Agrawal, N. Dharmarasu, K. Radhakrishnan, L. Ravikiran
Journal of Crystal Growth, 2013, 378, 283-286
2. Structural properties of GaN grown on AlGaN/AlN stress mitigating layers on 100-mm Si (111) by ammonia molecular beam epitaxy.
M. Agrawal, N. Dharmarasu, K. Radhakrishnan, L. Ravikiran
Thin Solid Films, 2012, 520, 7109-7114
3. Effect of stress mitigating layers on the structural properties of GaN grown by ammonia MBE on 100 mm Si (111).
L. Ravikiran, **M. Agrawal**, N. Dharmarasu, K. Radhakrishnan
Japanese Journal of Applied Physics, 2013, 52, 08JE05
4. Demonstration of AlGaN/GaN high electron mobility transistors on 100 mm diameter Si (111) by ammonia molecular beam epitaxy.
N. Dharmarasu, K. Radhakrishnan, **M. Agrawal**, L. Ravikiran, S. Arulkumaran, K.E. Lee, N.G. Ing
Applied Physics Express, 2012, 5, 091003
5. Realization of two-dimensional electron gas in AlGaN/GaN HEMT heterostructure grown on Si (111) by PA-MBE.
N. Dharmarasu, K. Radhakrishnan, Z.Z. Sun, **M. Agrawal**
Physica Status Solidi (c), 2011, 1-3
6. Strain states of AlN/GaN-stress mitigating layer and their effect on GaN buffer layer grown by ammonia molecular beam epitaxy on 100-mm Si (111).
L. Ravikiran, K. Radhakrishnan, N. Dharmarasu, **M. Agrawal**, S. Munawar Basha
Journal of Applied Physics (in press)
7. Effect of III/V ratio on the polarity of AlN and GaN layers grown in the metal rich growth regime on Si (111) by plasma assisted molecular beam epitaxy.
M. Agrawal, K. Radhakrishnan, N. Dharmarasu, S.S. Pramana
(Communicated)

9.2 Conference contributions

1. Effect of III/V ratio on the polarity of AlN grown on Si (111) by PA-MBE.
M. Agrawal, N. Dharmarasu, K. Radhakrishnan,
International Workshop on Nitrides Semiconductors
Oct 14-19, 2012, Sapporo, Japan
2. Origin of tensile strain in GaN grown on AlGaN/AlN stress mitigating layers on 100-mm Si (111) by ammonia molecular beam epitaxy.
M. Agrawal, N. Dharmarasu, K. Radhakrishnan, L. Ravikiran,
International Conference on Molecular Beam Epitaxy
Sept 23-28, 2012, Nara, Japan

3. Effect of stress mitigating layers on the structural properties of GaN grown by ammonia MBE on 100 mm Si (111).
*L. Ravikiran, **M. Agrawal**, N. Dharmarasu, K. Radhakrishnan,*
International Workshop on Nitrides Semiconductors
Oct 14-19, 2012, Sapporo, Japan
4. Ga-bilayer controlled AlGaIn/GaN HEMT heterostructure grown on Si by PA-MBE.
*N. Dharmarasu, **M. Agrawal**, K. Radhakrishnan, Z. Sun,*
International Conference on Nitrides Semiconductors
July 10-15, 2011, Glasgow, United Kingdom
5. Growth of AlGaIn/GaN HEMT on 100 mm Si (111) by Ammonia-MBE.
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