Studies on GaN HEMT based gas sensors for low concentrations of NO₂ and NH₃

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**Studies on GaN HEMT Based Gas
Sensors for Low Concentrations of NO₂
and NH₃**

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G1503083E**

**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

2019

Studies on GaN HEMT Based Gas Sensors for Low Concentrations of NO₂ and NH₃

AKHIL RANJAN

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirements for the degree of
Doctor of Philosophy

2019

To

My late grandfather
Mr. Ramchhabila Singh

My wife & son
Mrs. Rakhee Sinha
Mr. Aditya Ranjan

“Progress is made by trial and failure; the failures are generally a hundred times more numerous than the successes; yet they are usually left unchronicled.”

William Ramsay

“What we know is a drop, what we don’t know is an ocean.”

Isaac Newton

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

23.08.2019

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Date

Akhil Ranjan

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Akhil Ranjan

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

25 Aug 2019

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Date

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Assoc Prof. K. Radhakrishnan

Authorship Attribution Statement

This thesis contains material from 4 paper(s) published in the following peer-reviewed journals and from papers accepted at conferences where I was the first author.

Chapter 4 includes 2 publications

- **Akhil Ranjan**, M. Agrawal, K. Radhakrishnan and N. Dharmarasu, AlGaIn/GaN HEMT based high-sensitive NO₂ gas sensors, Japanese Journal of Applied Physics (JJAP), 2019, 58 SCCD23.
- **Akhil Ranjan**, M. Agrawal, K. Radhakrishnan and N. Dharmarasu, AlGaIn/GaN HEMT based high-sensitive NO₂ gas sensors, International workshop on Nitrides Semiconductors, Nov 12-16, 2018, Kanazawa, Japan.

The contributions of the co-authors are as follows:

- I co-designed this project with Prof. K. Radhakrishnan and performed all laboratory works including mask design, sensor fabrication, measurements and preparation of manuscript drafts.
- Prof. K. Radhakrishnan provided the initial project direction, assisted in the interpretation of results and edited the manuscript drafts.
- Dr. M. Agrawal assisted with the measurement setup and edited the manuscript drafts.
- Dr. N. Dharmarasu assisted with the epilayer growth and characterization, initial fabrication of devices and edited the manuscript drafts.

Chapter 5 includes 2 publications

- **Akhil Ranjan**, M. Agrawal, K. Radhakrishnan and N. Dharmarasu, Effects of various functionalization layers on ammonia gas sensing using AlGaIn/GaN high electron mobility transistors, International Journal of Nanotechnology (IJNT), 2020.
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The contributions of the co-authors are as follows:

- I co-designed this project with Prof. K. Radhakrishnan and performed all laboratory works including mask design, sensor fabrication, measurements and preparation of manuscript drafts.
- Prof. K. Radhakrishnan provided the initial project direction, assisted in the interpretation of results and edited the manuscript drafts.
- Dr. M. Agrawal assisted with the measurement setup and edited the manuscript drafts.
- Dr. N. Dharmarasu assisted with the epilayer growth and characterization, initial fabrication of devices and edited the manuscript drafts.

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Table of Contents

Statement of Originality	iv
Supervisor Declaration Statement	v
Authorship Attribution Statement.....	vvi
Acknowledgments	viii
Abstract	xiii
List of Figures	xviii
List of Tables	xxx
List of Abbreviations	xxii
Chapter 1 Gas sensors: State of the art	1
1.1 Need for gas sensors	1
1.2 NO ₂ and NH ₃ hazards	2
1.3 Existing NO ₂ and NH ₃ gas sensors	4
1.3.1 Metal oxide semiconductor sensors	6
1.3.2 Polymer sensors	9
1.3.3 Electrochemical cell sensors	11
1.4 Gas sensor performance metrics	13
1.5 Recent advances of NO ₂ and NH ₃ sensors.....	15
1.6 Objective and thesis organisation	17
Chapter 2 AlGaN/GaN HEMT Sensor.....	21
2.1 GaN material properties	21
2.1.1 Applications.....	24
2.2 AlGaN/GaN HEMT	26
2.2.1 2DEG	26
2.2.2 AlGaN/GaN HEMT gas sensor.....	28
2.2.3 Advantages of AlGaN/GaN HEMT gas sensors	31
2.2.4 Substrates for GaN based heterostructures	32
2.3 Interdigitated electrodes	35
2.4 Functionalization layers.....	37
Chapter 3 Epilayer growth and gas sensor fabrication.....	40
3.1 Growth and characterization of AlGaN/GaN HEMT	40

heterostructure	40
3.2 Growth and characterization of AlN/GaN/AlN HEMT	45
heterostructure	45
3.3 Mask design	47
3.4 Fabrication process	51
3.4.1 Techniques for device fabrication	52
3.4.2 Fabrication steps for GaN HEMT based sensor	55
3.5 Gas sensing measurement procedure	64
Chapter 4 Pt/AlGaIn/GaN HEMT based NO₂ sensor	68
4.1 Background	68
4.2 NO ₂ sensing at room temperature	69
4.2.1 Heat induced recovery	70
4.2.2 Sensing mechanism	71
4.3 Relative humidity influence	73
4.4 NO ₂ sensing at elevated temperature	75
4.4.1 NO ₂ sensing at 300 °C	75
4.4.2 Analysis of NO ₂ sensing performance at 275 °C	77
4.5 Temperature effects on NO ₂ sensing	82
4.5.1 Response and recovery times	82
4.5.2 Sensitivity	86
4.6 Effects of functionalization layer dimensions on the NO ₂	89
4.7 Summary	91
Chapter 5 AlGaIn/GaN HEMT based NH₃ sensor	93
5.1 Background	93
5.2 Pt functionalization layer	95
5.2.1 Thickness effect	95
5.2.2 NH ₃ sensing at room temperature	99
5.2.3 NH ₃ sensing at 275 °C	101
5.2.3.1 Sensitivity as a function of concentration	102
5.2.4 Temperature effect on NH ₃ sensing	103
5.3 Pd functionalization layer	108
5.3.1 NH ₃ sensing at room temperature and 275 °C	108

5.4 Ag functionalization layer	110
5.4.1 NH ₃ sensing at room temperature and 275 °C	110
5.5 Comparative analysis among various functionalization layers	113
5.6 Summary.....	115
Chapter 6 Pt/AlN/GaN/AlN HEMT based gas sensor.....	116
6.1 Background.....	116
6.2 NO ₂ sensing at room temperature	118
6.3 NO ₂ sensing at 275 °C	119
6.3.1 Sensitivity and response time as a function of NO ₂ concentration	123
6.4 NH ₃ sensing at room temperature and 275 °C	125
6.5 Summary.....	128
Chapter 7 Conclusions and recommendations	129
7.1 Conclusions	129
7.1.1 Pt/AlGaN/GaN HEMT based NO ₂ sensor.....	129
7.1.2 AlGaN/GaN HEMT based NH ₃ sensor	131
7.1.3 Pt/AlN/GaN/AlN HEMT based gas sensor	133
7.2 Recommendations for future work	134
7.2.1 Functionalization layers.....	135
7.2.2 Fine-tune epi-structure and device dimensions.....	136
Author's Publications.....	138
References	140

Abstract

In recent decades, the demand for gas sensors has increased rapidly because of their large-scale use in medical instruments, automobiles and laboratories. For example, nitrogen dioxide (NO₂) and ammonia (NH₃) are found to be among the main constituents of exhaust gases and harmful air contaminants. Inhalation and long-term exposure to these gases can cause health issues and may result in life threatening conditions. Hence, there is a need to detect low concentrations of NO₂ and NH₃. GaN based sensors are gaining momentum due to their unique properties, such as high electron mobility, mechanical stability and wide bandgap that allow high thermal resistance and the ability to withstand harsh chemicals, gaseous and the corrosive environments. Furthermore, AlGaIn/GaN high electron mobility transistors (HEMTs) are extremely sensitive due to the proximity of two-dimensional electron gas (2DEG) to the sensing surface and their high sheet carrier concentration ($\sim 10^{13} \text{ cm}^{-2}$), thereby enhancing the detection sensitivity. Surface charges vary due to the interaction of the environmental conditions such as temperature and humidity leading to the modulation of 2DEG.

This thesis presents the fabrication and characterization of GaN HEMT based gas sensors with Pt, Pd and Ag functionalization layers that can sense low concentrations of NO₂ and NH₃ for a large range of concentrations and temperatures. The sensing mechanisms

corresponding to the temperature dependent response of these gases have been explained in detail. It was found that the Pt/AlGaIn/GaN HEMT based sensors sensed and recovered completely to the steady state value when exposed to various concentrations of NO₂ at temperatures above 275 °C. A high sensitivity of 5.1 % with the corresponding ΔI of 1.72 mA was achieved for 10 ppm NO₂ at 275 °C, which is better than the reported results of 1 %, but at a higher temperature of 300 °C. A sensitivity of 1.2 % was obtained for a very low NO₂ concentration of 50 ppb in this study, which is the lowest NO₂ concentration sensed by Pt/AlGaIn/GaN HEMT based sensor. The large surface area of the interdigitated electrodes and the catalytic property of Pt functionalization layer enabled high sensitivity for low NO₂ concentrations of < 10 ppm. A rapid response time of < 2 min and a recovery time of < 5 min were obtained for all the concentrations which are comparable to or better than the reported results.

In this NO₂ sensing studies, the activation energy values of 0.33 eV/ion and 0.64 eV/ion were obtained for response and recovery times, respectively, which are lower than the reported values of 0.9 eV and 1.0 eV respectively, for open gate AlGaIn/GaN HEMTs. The lower values obtained in this study are mainly due to the presence of Pt functionalization layer, which enhances the reactivity due to its catalytic properties.

Low concentration (< 50 ppm) sensing of NH_3 over a wide temperature range of 30 - 275 $^{\circ}\text{C}$ using AlGaIn/GaN HEMT based gas sensors with Pt functionalization layer has been systematically studied and other functionalization layers that have not been previously studied such as Pd and Ag have also been investigated. While the current decreased (ΔI is negative) when the sensor was exposed to different concentrations of NH_3 at room temperature, it increased (ΔI is positive) above 200 $^{\circ}\text{C}$. This phenomenon of ΔI being negative at lower temperatures and positive at higher temperatures has not been reported thus far.

At low temperature (30 $^{\circ}\text{C}$), NH_3 is adsorbed in a molecular form on Pt surface and donates free electrons to produce negative potential at the Pt/AlGaIn interface leading to a decrease in the current. However, NH_3 gets dissociated into positively charged hydrogen ions (H^+) at high temperature (>200 $^{\circ}\text{C}$). This results in positive surface potential causing an increase in the current. The observed phenomenon was validated by plotting Arrhenius plots for two different regions and relating the activation energy with the mechanism. The sensor with the Pd functionalization layer exhibited higher sensitivity at 275 $^{\circ}\text{C}$ as compared to Pt and Ag sensors due to higher hydrogen affinity of Pd. The sensor with the Ag functionalization layer was found to respond quickly to the change in NH_3 concentration and demonstrated faster response and recovery times (< 3 min) as compared to other sensors using Pt and Pd. This is attributed to the oxidized Ag surface which creates a favourable site for the adsorption

of NH_3 gas. After the adsorption, charge transfer from NH_3 to Ag occurs quickly leading to faster response and recovery times.

Having studied the AlGaN/GaN HEMT based sensors, further efforts were made to investigate Pt/AlN/GaN/AlN HEMTs for NO_2 and NH_3 sensing. This is the first time that thin barrier AlN/GaN/AlN HEMT has been demonstrated as a gas sensor. The sensitivity obtained by this sensor was lower than that obtained for Pt/AlGaN/GaN HEMT based sensor. However, the Pt/AlN/GaN/AlN HEMT based sensor was found to respond quickly to the change in the NO_2 concentration. The respective mechanisms have been illustrated.

List of Figures

Fig. 1.1 Gas sensors used in various fields and different sources of air pollutants	2
Fig. 1.2 Schematic diagram of metal oxide gas sensor.	7
Fig. 1.3 Schematic diagram of polymer gas sensor.	9
Fig. 1.4 Schematic diagram of electrochemical cell gas sensor.	11
Fig. 1.5 Transient response showing ΔI	15
Fig. 2.1 Stick-and-ball structure of GaN (wurtzite).	22
Fig. 2.2 Schematic of (a) AlGaIn/GaN heterostructure and (b) resultant band diagram of the heterostructure.....	27
Fig. 2.3 Schematic cross section of Pt/AlGaIn/GaN HEMT-based NO ₂ gas sensor.....	29
Fig. 2.4 Schematic of interdigitated electrodes.	35
Fig. 3.1 Schematic cross section of AlGaIn/GaN HEMT heterostructure.	41
Fig. 3.2 (a) An optical microscope image of the AlGaIn/GaN HEMT heterostructure top surface and (b) the corresponding AFM image.....	41
Fig. 3.3 Schematic diagram of contactless Hall measurement method.....	43
Fig. 3.4 HR-XRD ω -2 θ GaN (004) rocking curve scan of AlGaIn/GaN heterostructure.	44
Fig. 3.5 Photograph of the AlGaIn/GaN heterostructure grown on 100-mm Si (111) wafer.	45
Fig. 3.6 Schematic cross section of AlN/GaN/AlN HEMT heterostructure.	46
Fig. 3.7 (a) An optical microscope image of AlN/GaN/AlN HEMT heterostructure top surface and (b) the corresponding AFM image.....	46
Fig. 3.8 The schematic cross section of GaN based heterostructure with the interdigitated electrode ohmic contacts.....	49
Fig. 3.9 The schematic cross section of GaN based heterostructure with the ohmic contact and pad layer.	50
Fig. 3.10 The schematic cross section of GaN based heterostructure with the ohmic contact and functionalization layer.....	51
Fig. 3.11 Process flow of complete GaN HEMT sensor fabrication process.	55

Fig. 3.12 Schematic of (a) photolithography of the mesa layer, (b) ICP RIE etching and (c) photoresist removal process.	57
Fig. 3.13 Etching depth measured using Dektak.	57
Fig. 3.14 Microscope image of the sample after mesa isolation.	58
Fig. 3.15 Schematic of ohmic contacts.	59
Fig. 3.16 Microscope image of pre-annealed ohmic contact fabricated structure.....	60
Fig. 3.17 Resistance versus separation between the adjacent contacts of TLM structures.....	60
Fig. 3.18 Schematic of ohmic contacts and pad layer.	61
Fig. 3.19 Schematic of ohmic contacts, pad layer and functionalization layer.....	63
Fig. 3.20 Microscope image of the post-annealed fabricated device.	63
Fig. 3.21 Photograph of the wire bonded IC package.....	64
Fig. 3.22 Schematic diagram of the gas sensor measurement setup. ...	64
Fig. 4.1 Transient response of the sensor at RT for different NO ₂ concentrations.	70
Fig. 4.2 Transient response of the sensor for 10 ppm NO ₂ at RT with the heat-induced recovery at 300 °C.	71
Fig. 4.3 Schematic diagram of AlGaIn/GaN heterostructure showing the surface charges and 2DEG.	72
Fig. 4.4 Sensitivity and ΔI as a function of RH for 5 ppm of NO ₂	73
Fig. 4.5 Transient response of the sensor at 300 °C for different NO ₂ concentrations.	76
Fig. 4.6 Transient response of the sensor at 275 °C for (a) different NO ₂ concentrations and (b) 50 ppb of NO ₂ concentration.....	78
Fig. 4.7 Sensitivity and ΔI as a function of NO ₂ concentration at 275 °C.	80
Fig. 4.8 Response time as a function of NO ₂ concentration at 275 °C. .	81
Fig. 4.9 Response and recovery times as a function of temperature for 6 ppm NO ₂	83
Fig. 4.10 Arrhenius plots of (a) recovery time and (b) response time, for 6 ppm NO ₂	85
Fig. 4.11 Sensitivity and ΔI as a function of temperature for 10 ppm NO ₂	86

Fig. 4.12 (a) Sensitivity and (b) ΔI as a function of temperature for different concentrations of NO_2	87
Fig. 4.13 Arrhenius plot of sensitivity for 10 ppm NO_2	88
Fig. 5.1 Sensitivity as a function of Pt layer thickness at RT and 275 °C for 50 ppm NH_3	96
Fig. 5.2 SEM images of Pt layer with the thickness (a) 10 nm (b) 15 nm and (c) 20 nm.	97
Fig. 5.3 Statistics of pore size distribution of Pt layer with the thickness (a) 10 nm (b) 15 nm and (c) 20 nm.....	99
Fig. 5.4 Transient response of the sensor at RT for different NH_3 concentrations.	100
Fig. 5.5 Transient response of the sensor at 275 °C for different NH_3 concentrations.	101
Fig. 5.6 Sensitivity as a function of NH_3 concentration at RT and 275 °C.	103
Fig. 5.7 ΔI as a function of temperature for 50 ppm NH_3	104
Fig. 5.8 Arrhenius plots of ΔI in the temperature range of (a) 30 - 150 °C and (b) 200 - 275 °C.	107
Fig. 5.9 Transient response of the sensor for different NH_3 concentrations at (a) RT and (b) 275 °C.....	109
Fig. 5.10 Sensitivity as a function of NH_3 concentration at RT and 275 °C.	110
Fig. 5.11 Transient response of the sensor for different NH_3 concentrations at (a) RT and (b) 275 °C.....	112
Fig. 5.12 Sensitivity as a function of NH_3 concentration at RT and 275 °C.	112
Fig. 6.1 Energy band diagram of AlN/GaN/AlN HEMT.	117
Fig. 6.2 Transient response of the sensor at RT for different NO_2 concentrations.	119
Fig. 6.3 Transient response of the sensor at 275 °C for different NO_2 concentrations.	120
Fig. 6.4 Sensitivity as a function of NO_2 concentration at 275 °C.	124
Fig. 6.5 Response time as a function of NO_2 concentration at 275 °C.....	124
Fig. 6.6 Transient response of the sensor for different NH_3 concentrations at (a) RT and (b) 275 °C.....	126
Fig.6.7 Sensitivity as a function of NH_3 concentration at RT and 275 °C.	126

List of Tables

Table 2.1 Properties of wurtzite GaN at room temperature.....	23
Table 2.2 Comparison of physical properties and the 2DEG of the corresponding hetero-junction interface of GaN with conventional semiconductors at room temperature.....	24
Table 2.3 Comparison of existing NO ₂ and NH ₃ gas sensors with AlGaIn/GaN HEMT based gas sensor.....	32
Table 2.4 Comparison of properties of different substrates used for GaN Growth.....	34
Table 2.5 Functionalization layers for different types of gas sensors.....	38
Table 3.1 2DEG properties and their values.....	43
Table 3.2 2DEG properties and their values.....	47
Table 4.1 Comparison of key parameters of Pt/AlGaIn/GaN HEMT based NO ₂ gas sensors.....	79
Table 4.2 Comparison of NO ₂ sensing performance having variable gate dimensions.....	90
Table 5.1 Comparison of Pt/AlGaIn/GaN HEMT and Schottky based NH ₃ gas sensors.....	102
Table 5.2 Comparison of sensing performance of Pt, Pd and Ag functionalization layers for 50 ppm NH ₃ concentration.....	114
Table 6.1 Comparison of key parameters of GaN HEMT based NO ₂ gas sensors.....	121
Table 6.2 Comparison of key parameters of GaN HEMT based NH ₃ gas sensors.....	128

List of Abbreviations

2DEG	Two-dimensional electron gas
AFM	Atomic force microscopy
DI	De-ionized
DIP	Dual in-line package
HEMT	High electron mobility transistor
HR-XRD	High resolution X-Ray diffraction
IC	Integrated circuit
ICP-RIE	Inductively coupled plasma reactive ion etching
MBE	Molecular beam epitaxy
MFC	Mass flow controller
MOCVD	Metal organic chemical vapour deposition
MOS	Metal oxide semiconductor
ppb	Parts per billion
ppm	Parts per million
RH	Relative humidity
RMS	Root mean square

RT	Room temperature
sccm	Standard cubic centimetre per minute
SEM	Scanning electron microscopy
SMU	Source measurement unit
TLM	Transmission line model

Chapter 1 Gas sensors: State of the art

1.1 Need for gas sensors

In recent decades, the demand for gas sensors has increased rapidly because of their large-scale use in medical instruments, automobiles and laboratories. These sensors have been installed in buildings, military camps, public places and other strategic locations to keep people safe from the toxic gases. Gas sensing technology has gained increased attention, especially for applications in which the detection of gases is imperative for human health and safety.

Gas sensors are used in the automotive industry to detect exhaust gases from vehicles and to control ventilation in cars and aircrafts. For safety purposes, gas sensors are also used in various applications such as fire detection, methane detection in mines, detection of toxic or flammable gas leaks in laboratories or gas pipelines and as a personal gas monitor. Furthermore, these sensors can be used to monitor air quality and pollution [1]. Moreover, the medical arena includes other critical applications of these sensors for breath analysis and disease detection. Fig. 1.1 shows the gas sensors used in various fields and different sources of air pollutants. Outdoor air pollution causes various heart diseases, such as fatal respiratory illness and lung cancer, that lead to the loss of millions of lives [2]. Various air pollutants emitted from different sources that need

to be detected are carbon monoxide (CO), carbon dioxide (CO₂), sulphur dioxide (SO₂), nitric oxide (NO), Nitrogen dioxide (NO₂) and ammonia (NH₃).

Fig. 1.1 Gas sensors used in various fields and different sources of air pollutants.

1.2 NO₂ and NH₃ hazards

The detection of air pollutants is crucial in monitoring the air quality to avoid health problems. NO₂ is found to be one of the most harmful common air pollutants and is associated with a range of indoor and outdoor combustion sources. Mobile sources such as petrol- and diesel-powered vehicles and industrial combustion generate significant outdoor sources of NO₂. The most common indoor contributors to NO₂ emissions are fuel-burning stoves used for cooking and heating systems (natural gas, propane, etc.). On a global scale, the average concentrations of NO₂

emitted per hour in indoor environments are much higher than those in outdoor environments (94 to 940 $\mu\text{g}/\text{m}^3$; 50 to 500 parts per billion) [3].

Because NO_2 is in gaseous form, its inhalation and long-term exposure can lead to the development of wheezing, asthma, bronchitis in children and can hamper lung growth [4]. In fact, NO_2 was found to have a more significant effect on people with existing respiratory and cardiovascular conditions. Numerous epidemiological studies have indicated that an increase in the concentration of ambient NO_2 can lead to an elevated risk of cardiovascular mortality [5]. Furthermore, nitrate aerosols, which form an essential component of hazardous airborne particles with a diameter of 2.5 μm or less, contain NO_2 as the primary source [6]. Moreover, nitrogen oxides lead to the formation of acid rain and ground level ozone, which is a key component of smog [7]. The World Health Organization has established an annual limit for exposure of NO_2 to 40 $\mu\text{g}/\text{m}^3$ – equivalent to 20 parts per billion (ppb). But, this limit is often exceeded in many of the urban areas. Thus, the regulations that govern NO_2 , particularly in automobiles, are becoming increasingly strict [8]. Hence, there is a need to detect low concentrations of NO_2 in various applications. In addition to NO_2 , ammonia (NH_3) is among the main constituents of exhaust gases and harmful air contaminants.

NH_3 is widely used in various industries such as the oil and gas, fertilizer, chemical and refrigeration industries. At room temperature, it is colourless, flammable and has a typical pungent odour. Inhalation of or exposure to high concentrations of NH_3 can cause severe irritation to the eyes, skin, nose, respiratory tract, moist skin and mucous membranes and can sometimes result in life threatening conditions [9]. In addition, the inhalation of NH_3 causes olfactory fatigue or adaptation. Exposure to a level as low as 500 parts per million (ppm) can be fatal due to its highly toxic nature. The current Occupational Health and Safety Administration Permissible Exposure Limit (OSHA PEL, USA) is 25 ppm in the gaseous phase [10]. Hence, the detection of NH_3 at low concentrations is essential to monitor gas release in industry and the environment.

1.3 Existing NO_2 and NH_3 gas sensors

There are various ways such as electrochemical cells, semiconductor and photonic based approaches, through which pollutant gases are detected. Specifically, the photonic based approach has various advantages such as high sensitivity and stability, longer lifetime and shorter response time. Moreover, the performance of these sensors is not affected by environmental variations or catalyst poisoning. However, the high cost of these sensors limits their practical applications. This approach is based on spectroscopic analysis which involves absorption and emission spectrometry. The working principle of the absorption spectrometry is

based on the gas concentration dependent absorption of the photons [1]. The emission spectrometry is based on the fact that the excited atoms emit photons and return to the ground state. Based on this working principle, photonic crystal fibre and tunable laser diodes have been used for sensing various gases such as NH_3 , CO_2 and CH_4 .

The function of a gas sensor is to detect and quantify the concentration of a specific gas in the environment. The basic operation of a gas sensor involves the transfer of electrons or photons when the sensor is exposed to the analyte. During the sensing process, when any of the physical/optical properties such as mass, resistance, capacitance, conductivity, work function, refractive index or optical path length gets altered, this change is measured and correlated to the gas concentration.

Traditional techniques such as mass spectrometry and gas chromatography are expensive, time consuming, complex as well as bulky in size [11]. In order to overcome the limitations posed by these sensors, the solid-state gas sensors have been developed, commercialized and used in various applications. The solid state gas sensors have an edge in terms of their low cost, small size and the ability to detect a large number of analytes at very low concentrations in the order of ppm and ppb range. These sensors have a simple device structure that includes the sensing materials with an anode and a cathode

on the top [12]. However, the operation of these sensors involves various complexities. It is difficult for these simple gas sensors to selectively detect a wide range of gaseous species. Furthermore, their output response can be affected by various parameters such as temperature, pressure, humidity and other ambient contaminants [13]. These factors limit the possibility of realizing a universal sensor that can be employed in a number of gas sensing applications. Hence, the predictable ambient environment and the type of gases must be considered in the selection of a sensor for practical applications. Various kinds of NO₂ and NH₃ gas sensors have been studied in the past based on metal oxide semiconductors, polymers and electrochemical cells [14-19].

1.3.1 Metal oxide semiconductor sensors

Metal oxide semiconductors are the most commonly used sensors. When these sensors are exposed to the target gas, the conductance of the oxides gets altered and the variation in the conductance is a direct function of the concentration of the gas [12]. The basic operating principle of this type of sensor is based on the redox reaction, which involves the chemical reaction between the molecules of the exposed gas and the oxygen ions (O⁻) of the material's surface. These reactions modify the electronic properties of the oxide surface, which in turn varies the resistance of the sensors. The resistance variation can be measured directly or indirectly to confirm the detection of a particular gas. The

schematic diagram of the metal oxide semiconductor gas sensor is shown in Fig. 1.2. The chemical reaction of the sensitive layer (O^-) occurs at a high temperature and the likelihood of gas molecule adsorption on the oxide surface is enhanced at high temperatures, which increases the sensitivity of these sensors. Hence, metal oxide sensors have an operating temperature in the range of 200°C to 500°C [1].

Fig. 1.2 Schematic diagram of metal oxide semiconductor gas sensor.

WO_3 has been shown to be an excellent material for NO_2 sensing because it has much greater sensitivity than the other metal oxide based sensors [20, 21]. Tamaki et al. demonstrated the response of a WO_3 based sensor to the NO_2 concentration within the range of 0.01 to 100 ppm [22]. However, high sensitivity with a steady response can only be acquired when these sensors are operated at elevated temperatures ($>200^\circ C$). In fact, the highest sensitivity and minimum cross-sensitivity of the WO_3 based sensor are achieved only when the operating temperature is raised

to 350°C [21]. The development of a WO₃ based sensor that can detect concentrations less than 0.01 ppm was also reported by Williams et al. [14]. However, its sensitivity was found to be strongly related to the operating temperature, and the temperature had to be closely monitored and controlled. This requirement for continuous heating while sensing results in high power consumption (>200 mW). A sensor based on thin film metal oxide of SnO₂ has been reported, which can be used as an NH₃ gas sensor for detecting 100 ppm concentration [15]. Various metal oxide-based NH₃ gas sensors have been shown to exhibit gas sensing property only at elevated temperatures of >200°C [23]. Moreover, a sensor based on ZnO thick film has been used to sense NH₃ within a concentration range of 10 to 150 ppm [24].

Metal oxide based semiconductor gas sensors have been most successful for commercial applications as they are cheap and are available in small sizes. They also exhibit rapid reactivity and high efficiency when suitable additives are applied. However, they have several limitations such as high operation temperature, which results in additional complexity and an increase in the power consumption relative to other sensors that could function at the ambient temperature. Moreover, these sensors require longer recovery time, which limits their use for applications where gas concentrations vary rapidly. In addition, these sensors cannot survive harsh environmental conditions and suffer from

other limitations such as poor selectivity, dependence upon air humidity and poor compatibility with integrated circuit fabrication [25]. Furthermore, degradation of the thin-film metal oxides causes the device characteristics to drift over a long operation period as a result of high thermal stress encountered in harsh and corrosive environments [26].

1.3.2 Polymer sensors

The basic working principle of the polymer based gas sensors involves the conversion of physical properties such as mass, resistance and conductivity into an electrical signal output when the sensor is exposed to the gas. The schematic diagram of the polymer gas sensor is shown in Fig. 1.3.

Fig. 1.3 Schematic diagram of polymer gas sensor.

Polypyrrole thin film has been used for highly sensitive NO₂ gas sensing in the range of 10 to 100 ppm [17]. Hui Li et al. [27] demonstrated the response of alkyl and alkylthio-thiophene polymer to NO₂ concentrations between 1 and 5 ppm. A sensor based on sensitive polyaniline film was reported as an NH₃ gas sensor for concentrations of 100 ppm [28]. The development of a polypyrrole coated TiO₂/ZnO nanofiber based sensor that can detect NH₃ concentration of 450 ppm has also been reported [17]. The porous structure of nanofibers presents superior sensing properties because of their large surface area. In addition, polymer sensors are suitable candidates for the detection of volatile organic compounds in vapour form, which are commonly used as constituents in domestic products and in the industrial processes.

The various advantages of these polymer based sensors include low fabrication cost, simple and portable structure, high sensitivity and the ability to operate at room temperature leading to lower energy consumption. The sensor with polymer polarization filters has been reported with a power consumption of 15 mW [29]. However, these sensors suffer from limitations such as moderate lifetime, poor selectivity, long term instability and irreversibility.

1.3.3 Electrochemical cell sensors

Gas sensors based on electrochemical cells are used to detect the concentration of a particular gas via oxidation and reduction of the target gas at an electrode. An electrochemical sensor consists of two or three electrodes. The first is the working (sensing) electrode, which makes contact with the electrolyte and the target gas through a porous membrane. The second is the counter electrode that balances the reaction at the working electrode. The electric potential of the sensing electrode is maintained with the third electrode or reference electrode. The schematic diagram of the electrochemical cell gas sensor is shown in Fig. 1.4.

Fig. 1.4 Schematic diagram of electrochemical cell gas sensor.

This type of gas sensor functions basically like a battery, in which the target gas is accountable for the complete battery reaction. The target gas

diffuses via porous membranes to the working electrode where oxidation or reduction reactions occur, leading to the generation of the electrical signal. The electrolyte then transports the generated electrical current between the counter and the sensing electrode. The increase in concentration enhances the rate of the electrolytic process at the sensing electrode, leading to a current that is directly proportional to the concentration of the gas. Hence, this type of electrochemical cell acts as a gas sensor by measuring the current between the two electrodes.

Dali Van et al. [18] demonstrated the response of ZnO nanostructures/porous silicon based electrochemical sensors to NO₂ concentrations from 0.1 to 1 ppm. The nanosheet exhibits better sensing properties due to its large surface area. The development of a micromachined thin film solid-state electrochemical sensor that can detect NO₂ concentrations of less than 1 ppm has also been reported [30]. Furthermore, a sensor based on electro-synthesised polypyrrole film has been used as an NH₃ gas sensor that can detect concentrations of lower than 10 ppm [19]. B. A. Mishima et al. [31] demonstrated the response of propylene carbonate to NH₃ concentrations between 60 and 100 ppm.

Electrochemical sensors generally exhibit high selectivity with linear output, low power requirements and good resolution. The power consumption of integrated micro-potentiometric electrochemical sensor

has been reported to be lower of about 5 mW [30]. However, they only work in a narrow temperature range, have a limited lifetime, poor sensitivity, bulky and usually more expensive [32]. The performance of these sensors is likely to get affected by the working environment as well [1].

1.4 Gas sensor performance metrics

The GaN HEMT based gas sensors sense the gases by measuring the device current changes with and without the gas to be sensed under certain bias condition. The performance of the studied sensor was analyzed with respect to several parameters. Each factor is well-defined and illustrated with respect to the gas sensing applications. Each parameter is characteristically a function of various factors such as temperature and gas concentrations.

1. Change in current (ΔI) is denoted as $\Delta I = I_{\text{Test gas}} - I_0$, where I_0 is the initial current of the device under the bias when no sensing gas is exposed to except the reference dry N_2 , and $I_{\text{Test gas}}$ is the steady-state current of the device when a constant flow of certain concentration of test gas (e.g., NO_2 or NH_3) is applied. ΔI is defined as shown in Fig. 1.5.

2. Sensitivity (S) of the gas sensor is defined as the ratio of the change in current (ΔI) to the initial current under dry N_2 (I_0) for a particular concentration of the test gas.

$$S_{Test\ gas} = \frac{\Delta I}{I_0} \times 100 \%$$

3. Selectivity is the sensor's ability to respond to a particular gas without interference from other gases. It is defined in terms of the relative change in response, which can be caused by the test gas and other gases.
4. Response time (τ_r) is evaluated between the time intervals corresponding to 10% and 90% of the initial current under dry N_2 and the final current under the test gas exposure. This parameter is used to evaluate the transient response when the sensor is exposed to the test gas.
5. Recovery time (τ_R) is calculated in a manner similar to the response time when the gas is turned off and dry N_2 is applied to the chamber. This parameter is used to evaluate the sensor's transient response when the test gas is turned off.
6. Reset temperature (T_{reset}) is the minimum temperature at which the sensor recovers completely to the steady state value when the supply of test gas is turned off and dry N_2 is applied.
7. Reproducibility is the sensor's ability to obtain a consistent response when exposed to the same concentration of the test gas

under similar operating conditions over a consecutive number of cycles.

8. Responsivity (R) is used to compare the performance of the sensors having different sensing areas. It is given as $\Delta I / (A \times \Delta C)$, where ΔI is the change in current, A is the sensing area and ΔC is the change in concentration of the test gas.

Fig. 1.5 Transient response showing ΔI .

1.5 Recent advances of NO₂ and NH₃ sensors

This section contains a brief overview of the prospective materials that can be used for low concentration NO₂ and NH₃ gas sensing. The advantages and shortcomings of various NO₂ and NH₃ gas sensors have been reviewed in the previous section (1.3). Low cost, reproducibility,

sensing accuracy and possible integration with the existing electronic circuits (based on silicon) make these sensors a preferred choice [33]. However, they are unable to sustain in harsh environmental conditions such as high temperature, pressure, and chemically corrosive ambient. They also get etched in some of the harsh acidic and base environments [34, 35].

Recently, several wide bandgap semiconductor materials have attracted great interest for application in gas sensing to mitigate some of the limitations associated with metal oxide, polymer and electrochemical cell-based sensors. The investigated materials include ZnO, diamond, GaN and its alloys. ZnO and diamond based NO₂ sensors can sense low concentrations with high sensitivity. However, ZnO nano-particles based sensors might measure erroneously as their initial current (I_0) and the leakage current in the circuit are usually of the same order (in μA) [36-38]. Moreover, the measurement time of ZnO nano-particles based sensors and diamond FET sensors is several hours and have slow response and recovery times [36, 39, 40]. GaN based sensors are gaining momentum due to their unique properties, such as the wide bandgap material that allows high thermal resistance and the ability to withstand harsh chemicals, gaseous and corrosive environments [7, 41]. Furthermore, GaN based materials exhibit greater carriers' mobility and thermal conductivity as compared to that of ZnO, which is beneficial for the high

temperature sensing applications [42]. GaN based high electron mobility transistors (HEMTs) are potentially interesting for sensors due to the proximity of two-dimensional electron gas (2DEG) to the sensing surface and their high sheet carrier concentration, which makes them extremely sensitive to the gases. Hence, lower detection limit and faster response time can be achieved with these sensors. Moreover, continuous heating is not required in these sensors, which allows for lower power operation. Hence, they can be used to develop devices that can sense low concentrations of NO_2 and NH_3 in the harsh and corrosive environments.

1.6 Objective and thesis organisation

The following objectives were set to realize GaN HEMT based gas sensors that can sense low concentrations of NO_2 and NH_3 , in this research.

- 1> NO_2 sensing using AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and platinum (Pt) functionalization layer, and to study the influence of relative humidity on NO_2 sensitivity.
- 2> NH_3 sensing using AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and to study the effects of various functionalization layers such as Pt, Pd and Ag.

- 3> To operate the sensors over a wide range of temperatures to investigate the temperature dependent sensing mechanism for both NO₂ and NH₃ gases.
- 4> To demonstrate AlN/GaN/AlN HEMT based gas sensors for NO₂ and NH₃ sensing applications for the first time.

These objectives were accomplished and are addressed in this thesis.

This thesis consists of seven Chapters organized as follows:

The thesis starts with **Chapter 1**, which describes the motivation to conduct research in the field of NO₂ and NH₃ gas sensors and a description of various sensing parameters. In addition, this Chapter describes the existing NO₂ and NH₃ gas sensors and their comparative assessment. This Chapter also outlines the research gaps in this area and lists the primary objectives of the thesis work.

Chapter 2 presents a literature review that outlines the importance of GaN HEMT based devices for gas sensing. A brief review is also presented on various functionalization layers that can be used for detecting different gaseous species and the importance of Pt, Pd and Ag as functionalization layers for NO₂ and NH₃ gas sensing.

Chapter 3 discusses growth and characterization results of two different GaN HEMT heterostructures employed in this study. Mask layouts

designed for the fabrication of GaN HEMT based gas sensors are presented. The complete device fabrication process to achieve GaN HEMT based gas sensors is discussed. This Chapter also describes the experimental set up for gas sensing that was used to evaluate the performance of NO₂ and NH₃ gas sensing.

Chapter 4 discusses the results obtained for the Pt/AlGaIn/GaN HEMT based gas sensors. The gas sensing performance of NO₂ is evaluated with respect to variation in concentration, temperature and relative humidity. Various parameters such as sensitivity, response and recovery times are analysed for a wide range of temperatures. The adsorption/desorption sensing mechanism that corresponds to each result is extensively illustrated with reference information gathered from the literature.

Chapter 5 presents the NH₃ gas sensing performance over various concentrations and temperature ranges using AlGaIn/GaN HEMT based gas sensors. A comparative analysis of various parameters is performed for three different functionalization layers: Pt, Pd and Ag. This Chapter also describes the temperature dependent sensing mechanism for NH₃.

Chapter 6 discusses the results obtained for Pt/AlIn/GaN/AlIn HEMT based gas sensors. This structure has been used as a gas sensor for the first time. The gas-sensing performance of this sensor for NO₂ and NH₃ is assessed with respect to the variation in gas concentration and

temperature. A comparative analysis of the results with respect to Pt/AlGaIn/GaN HEMT based gas sensors is performed and described in detail.

Finally, **Chapter 7** provides a summary of this thesis and presents an outlook for the prospective future scope of work using GaN HEMT based gas sensors.

Chapter 2 AlGaN/GaN HEMT Sensor

2.1 GaN material properties

In recent times, interest in III-nitride based sensors has increased both in the field of gas sensing and ion detection. It may be attributed to advancements in the material growth and novel device fabrication technologies that have made GaN based semiconductors as possible candidates for gas sensing applications. GaN based materials are particularly attractive due to their unique properties including high electron mobility, mechanical stability and the ability to sustain harsh environmental conditions such as high temperatures and chemically corrosive environments. A comprehensive understanding of the GaN crystal structure and its properties will aid in understanding the operating principles and sensing mechanism of various GaN based gas sensors.

GaN based materials exist mainly in two types of crystal structures: wurtzite (hexagonal or α) and zinc blende (cubic or β). The wurtzite structure is energetically more favourable than the zinc blende structure and has greater stability at room temperature. Fig. 2.1 shows the standard wurtzite structure of GaN.

Fig. 2.1 Stick-and-ball structure of GaN (wurtzite) [43].

Table 2.1 lists the physical, thermal and electronic properties of wurtzite GaN at room temperature. The large binding energy of 9.12 eV/atom between gallium and nitrogen atoms renders high chemical and mechanical stability to GaN. Moreover, with a high melting point (2500 °C), GaN-based structures exhibit high thermal stability.

One of the fundamental characteristics of GaN that differentiates it from other well-developed semiconductors such as Si and GaAs is its polarization effects: spontaneous and piezoelectric. Table 2.2 compares the physical properties of GaN to those of other conventional semiconductors at room temperature (300 K). The wide bandgap of GaN

based devices allows high temperature operation. High saturated peak electron velocity results in higher switching frequency leading to faster response. Furthermore, AlGaIn/GaN HEMTs exhibit high 2DEG density which is very close to the sensing surface resulting in the enhancement of detection limit and response time. Moreover, the relatively better thermal conductivity of GaN is favourable for better heat dissipation.

Table 2.1 Properties of wurtzite GaN at room temperature [44].

	Properties	Value
1	Melting point (°C)	2500
2	Energy gap (eV)	3.40
3	Intrinsic carrier concentration (cm ⁻³)	~10 ¹⁶
4	Electron effective mass	0.2 m ₀
5	Hole effective mass	0.8 m ₀
6	Electron mobility (300 K) (cm ² V ⁻¹ s ⁻¹)	1245
7	Hole mobility (300 K) (cm ² V ⁻¹ s ⁻¹)	<20
8	Binding energy (eV)	2.22
9	Static dielectric constant	8.9

Table 2.2 Comparison of physical properties and the 2DEG of the corresponding hetero-junction interface of GaN with conventional semiconductors at room temperature.

	Properties	Si	GaAs (AlGaAs/ InGaAs)	InP (InAlAs/ InGaAs)	GaN (AlGaN/ GaN)
1	Bandgap energy (eV)	1.11	1.42	1.35	3.40
2	Saturated peak electron velocity ($\times 10^7$ cm/s)	1	2.1	2.3	2.7
3	2DEG sheet electron density (cm^{-2})	NA	$<4 \times 10^{12}$	$<4 \times 10^{12}$	20×10^{12}
4	Thermal conductivity (W/cm.K)	1.50	0.50	0.70	>1.70

2.1.1 Applications

After the successful demonstration of GaN based blue light emitting diodes two decades ago, more attentions are paid to GaN based materials. Since then, researches in this area have grown rapidly and have resulted in the development of high frequency/high power transistors such as HEMTs that could operate at high temperature, light emitting diodes, laser diodes and photodetectors. In 1993, Asif Khan et al. first demonstrated a HEMT based on AlGaN and GaN heterojunctions [45]. Since then, extensive researches have been done in developing high frequency and high power devices for microwave and telecommunications

applications, with state-of-the-art performances [46, 47]. However, another important application of AlGaN/GaN heterostructure based devices that has not been explored much is for the gas sensing technology [48]. These advanced applications with the GaN based materials are possible because of their unique material properties.

GaN based gas sensors are potentially suitable for applications in automobiles, aircraft, fire detectors, exhaust diagnosis and monitoring emission from the industrial processes due to their unique properties as discussed in section 2.1. The electrical properties of these gas sensors change by the adsorption of any gas on the surface and return to their original state after the gas is desorbed. Thus, no sensor material is consumed during the sensing process, which leads to a long life expectancy. Furthermore, the chemically inert nature of GaN based gas sensors allows to overcome the issue of poisoning or burning of the chemical sensor when it is exposed to high gas concentrations. In addition, these sensors can possibly detect several types of pollutants such as oxidising and reducing gases ranging in concentration from the low range of ppm to high combustible levels [49]. This eliminates the need to use multiple sensors and also simplifies system design and maintenance. Moreover, GaN based sensors can withstand high flux/energy radiations, which make them suitable for the satellite industries. The combination of relatively good thermal management of

GaN based materials due to their better thermal conductivity along with high radiation hardness of the GaN based sensing technology reduces the overall weight and thus the high cost required for the space applications.

2.2 AlGaN/GaN HEMT

The 2DEG property of AlGaN/GaN HEMT makes it a prospective candidate for various gas sensing applications. The formation of 2DEG in AlGaN/GaN heterostructure, working principles and advantages of the AlGaN/GaN HEMT based gas sensors are discussed in the subsequent sections.

2.2.1 2DEG

The coherent growth of a wide bandgap AlGaN barrier on the top of a narrow bandgap GaN channel of a HEMT structure results in the development of 2DEG at the AlGaN/GaN interface. Both materials exhibit spontaneous polarization due to the existence of wurtzite crystal structure, which is non-centro-symmetric in nature. Moreover, the coherently grown AlGaN barrier induces additional strain at the heterojunction interface and results in strain-induced piezoelectric polarization. The combined effect of both of these polarizations results in a dipole of charges that are induced at the interface and the surface of the AlGaN barrier layer, as shown in Fig. 2.2 (a).

Fig. 2.2 Schematic of (a) AlGaN/GaN heterostructure and (b) resultant band diagram of the heterostructure [50].

The net polarization induced charge density $\sigma_{POL}(x)$ at the hetero-interface is represented by Eq. 2.1.

$$\sigma_{POL}(x) = P_{SP}(x) + P_{PE}(x) - P_{SP}(GaN) \text{ C.m}^{-2} \quad \text{Eq. 2.1}$$

where ' x ' is the mole fraction of the constituent element in the barrier. For example, ' x ' represents 'Al' mole fraction in the $Al_xGa_{1-x}N$ barrier layer. $P_{SP}(x)$ and $P_{PE}(x)$ are the spontaneous and piezoelectric polarizations of the barrier layer, respectively, and $P_{SP}(GaN)$ represents the spontaneous polarization of the GaN buffer. The contribution of piezoelectric polarization due to the GaN buffer is negligible because this layer is almost relaxed in the AlGaN/GaN-based heterostructure [50].

The polarization field induces a net positive charge at the AlGaN/GaN interface, which causes energy bands to bend in the AlGaN layer towards the interface. The difference in the conduction band energy between

AlGa_N and Ga_N at the heterojunction interface results in the development of a quantum well. The developed positive charges at the heterojunction interface drive electrons into the quantum well, which can move freely in two-dimensions while tightly bound in the third dimension. Hence, the confined electron gas is named as 2DEG [50]. Fig. 2.2 (b) shows the typical band diagram of the AlGa_N/Ga_N heterostructure, including the quantum well and the presence of 2DEG. It is interesting to note that donor like surface states are the source of electrons to compensate for the polarization induced positively charged sheet carrier density. Subsequently, 2DEG is formed at the AlGa_N/Ga_N interface [51].

2.2.2 AlGa_N/Ga_N HEMT gas sensor

Fig. 2.3 shows a schematic cross-section of the AlGa_N/Ga_N HEMT based gas sensor. The 2DEG channel is connected to the two ohmic contacts (source, drain), and the drain voltage is applied between these two terminals, while no external voltage is intentionally applied to the gate. Pt has been used as a functionalization layer in Ga_N HEMT based gas sensors due to its high catalytic property. The gas gets dissociated into ion at the Pt surface, when the sensor is exposed to the gas. These ions interact capacitively with AlGa_N surface and diffuse via pores or grain boundaries on the Pt surface. The electrostatic interaction that arises due to the adsorption of the gas on the surface induces an electric potential

that acts as the gate voltage. Thin functionalization layer is desired for the gas sensors since the thin layer will have larger pores which facilitate the diffusion of gaseous molecules/ions. Significance of Pt functionalization layer and its morphologies are discussed in detail in sections 2.4 and 5.2.1. The interaction of gaseous molecules/ions on the surface of AlGa_N/Ga_N HEMT alters the surface state and has a direct effect on the carrier concentration in the high mobility 2DEG region, resulting in a significant change in the device output current. This change in current is capable of sub-ppm level detection with the response time on the order of minutes or seconds [52].

Fig. 2.3 Schematic cross section of Pt/AlGa_N/Ga_N HEMT based NO₂ gas sensor.

The equation for the drain current as a function of gate voltage (V_{gs}), drain voltage (V_{ds}) and other HEMT parameters is represented by Eqs. 2.2 and 2.3.

$$I_{ds} = \frac{\epsilon_N \mu_n W_g}{2L_g d} \left[2(V_{gs} - V_{th})V_{ds} - V_{ds}^2 \right] \quad \text{Eq. 2.2}$$

$$I_{ds} = W_g q v(x) n_s(x) \quad \text{Eq. 2.3}$$

where I_{ds} is the drain current, W_g is the gate width, L_g is the gate length, $v(x)$ is the carrier velocity and $n_s(x)$ is the sheet carrier density. It is evident from Eqs. 2.2 and 2.3 that the drain current is dependent upon the applied gate voltage, mobility and sheet carrier density.

Unlike MOSFET devices, the AlGaIn/GaN HEMTs can achieve 2DEG without intentional doping, resulting in higher electron mobility in the undoped GaN layer. 2DEG being highly sensitive to any slight alteration on the surface, the concentration in the order of ppm and ppb range of the analytes can be detected [53]. Thus, AlGaIn/GaN HEMTs should enhance the detection sensitivity compared to the other existing sensors [54] discussed in Chapter 1.

2.2.3 Advantages of AlGaN/GaN HEMT gas sensors

The work function based sensors such as Schottky diodes and HEMTs can be used for hydrogen sensing [55], but only a few reports have demonstrated the use of these sensors for NO₂ and NH₃ detections. GaN based heterojunction and Schottky diodes have already been reported for NO₂ and NH₃ sensing [8, 56, 57]. However, HEMTs have an edge over Schottky diodes as sensors due to their larger output current, which leads to a higher ΔI and a lower limit of detection [49]. Further, the response and recovery times of AlGaN/GaN HEMT based sensors are only a few minutes. It has been proven experimentally that sensors based on heterostructures provide greater sensitivity than the devices fabricated on simple GaN layers due to the presence of 2DEG near the surface [58]. In addition, AlGaN/GaN HEMTs are extremely sensitive to the surface charge and variations in the environmental conditions, due to the proximity of 2DEG to the sensing surface and their high sheet carrier concentration (on the order of 10^{13} cm^{-2}), thereby enhancing the detection sensitivity [54]. AlGaN/GaN HEMT is highly selective as found in the literature [7, 59, 60]. Table 2.3 compares the existing NO₂ and NH₃ gas sensors on important parameters such as sensitivity, selectivity and response time [7, 16-18, 26, 29, 30, 38, 41, 61-67]. AlGaN/GaN HEMT based sensors yield relatively lower magnitude of sensitivity even when ΔI is significant in mA range since I_0 of these sensors are higher in mA range. Hence, there is a

trade-off between sensitivity and ΔI . Thus, it is not meaningful to compare the magnitude of sensitivity among different sensor technologies.

Table 2.3 Comparison of existing NO₂ and NH₃ gas sensors with AlGaIn/GaN HEMT based gas sensor.

	Parameters	Electro-chemical cells	Polymers	Metal oxides	AlGaIn/GaN HEMTs
1	Sensitivity	Moderate	High	Moderate	High
2	Selectivity	Poor	Poor	Moderate	High
3	Response time	Moderate (5-15 min)	Fast (1-15 min)	Fast (1-15 min)	Fast (1-5 min)
4	Life-time	Limited	Moderate	Long	Very long
5	Power consumption	Low (~5 mW)	Low (~15 mW)	High (>200 mW)	Low (μ W range)
6	Size	Bulky	Small	Small	Small

2.2.4 Substrates for GaN based heterostructures

The native substrates for epitaxial growth of GaN based heterostructures are very expensive and available only in smaller sizes. Due to these limitations, heteroepitaxial growth of GaN is more favourable using foreign substrates such as sapphire, SiC and Si.

GaN epi-layer growth on the sapphire substrate has already attained a maturity stage. However, there are various limitations of using sapphire

substrates such as its lattice mismatch (15%) and thermal mismatch (30%) with GaN leading to the compressively strained layer and its incompatibility with other growth/deposition processes in the semiconductor foundries.

SiC substrate is a preferred choice for GaN epi-layer growth due to its lower lattice mismatch (3%), thermal mismatch (20%), and high thermal conductivity, which is beneficial to dissipate the heat generated during the device operation. However, the growth on SiC substrates suffers from various limitations such as high cost and the availability of substrates in smaller sizes. Moreover, the growth of GaN layer on the SiC substrate is tensile strained.

Si is the most widely used semiconductor material for the electronics applications. Growth of GaN epi-layer on Si(111) substrate is more favourable due to the availability of large diameter wafers up to 12", lower cost of production, acceptable thermal conductivity (1.5 W/cm.K at 300 K) and possible integration with existing CMOS technology. However, the growth of GaN on Si(111) substrate is challenging due to the high lattice mismatch (17%) and thermal mismatch (54%) which induce high tensile strain during the growth and cool down, resulting in cracking of the epi-layers [50]. Furthermore, the device performance also gets hampered due to the presence of high dislocation density in the GaN layer. Despite, the

challenges faced during the growth, various efforts have been made to develop the GaN growth on Si substrates in order to fully exploit the advantages of using Si as the substrates. Many promising results have been published in the literature related to the GaN growth on Si substrates [68, 69]. Various properties of different substrates used for GaN growth have been compared in Table 2.4.

GaN HEMT based gas sensors have been fabricated mostly on Sapphire substrates. Si or SiC substrates for the gas sensing applications have not been widely reported. Thus, GaN heterostructure grown on Si and SiC substrates could be explored for the gas sensing applications in this research.

Table 2.4 Comparison of properties of different substrates used for GaN growth [43].

	Properties	Sapphire	6H-SiC	Si (111)	GaN
1	Lattice mismatch (%)	15	3	17	0
2	Thermal expansion coefficient ($10^{-6}K^{-1}$)	7.3	4.5	2.6	5.6
3	Thermal mismatch (%)	25	33	52	0
4	Thermal conductivity ($Wcm^{-1}K^{-1}$)	0.5	4.5	1.5	1.3
5	Cost	Moderate	High	Low	Extremely High

2.3 Interdigitated electrodes

An interdigitated structure comprises comb-like back-to-back ohmic contact electrodes separated by a layer of semiconductor. As shown in Fig. 2.4, the adjacent fingers act as two ohmic contacts (source/drain). Alternate fingers (i.e., source contacts) are connected to one electrode. Similarly, all the drain contacts are connected to the other electrode, making each device configured in a parallel structure.

Fig. 2.4 Schematic of interdigitated electrodes.

In the past decade, interdigitated electrode based devices have gained popularity in the research field due to their inherent benefits, such as simple structure, simple planar fabrication and low capacitance per unit area due to the lateral device structure leading to a faster response speed [70]. Furthermore, the dimensions of microelectronic devices must be reduced to attain low voltage operation, which can be achieved in the interdigitated electrodes configuration by reducing the spacing between the fingers. Moreover, these sensors are less prone to production faults because damage to a single interdigitated electrode has far less effect than the interruption of a single electrode in a conventional HEMT device. Hence, HEMTs with interdigitated electrodes are preferable as they satisfy both the requirements of a sensor: a large area and reduced electrode dimensions [71]. The large surface area of interdigitated electrodes enables greater interaction between the adsorbed gaseous ions and the sensor surface, which enables the sensing of lower gas concentrations.

Interdigitated electrode based metal oxide sensors have been used to detect low concentrations of NO_2 and NH_3 . Tamaki et al. [22] have demonstrated the response of WO_3 thin film with interdigitated electrodes for sensing dilute NO_2 less than 1 ppm. The development of Nano-crystalline WO_3 with these electrodes has also been reported for sensing NO_2 in the concentration range of 50 - 500 ppb at various operating

temperatures [72]. In addition, D.V. Dao et al. have demonstrated WO_3 nanoparticles thin film with interdigitated electrodes for low concentration dilute NH_3 sensing down to 500 ppb with high sensitivity [73]. Recessed AlGaIn/GaN HEMT with interdigitated electrodes and without a functionalization layer has also been demonstrated for NO_2 sensing in the ppb range [74]. Hence, it is expected that AlGaIn/GaN HEMT with interdigitated electrodes will have better sensing properties for low concentrations of NO_2 and NH_3 .

2.4 Functionalization layers

An AlGaIn/GaN heterostructure with excellent 2DEG properties can be used for sensors with and without a functionalization layer. Due to the chemically inert nature of the surface, the AlGaIn/GaN HEMTs lack selectivity to different analytes, but this can be improved by modifying or functionalizing the surface in the gate region of the HEMT device structure. AlGaIn/GaN HEMT sensors with functionalized surface in the gate region have been reported for sensing various gases with good selectivity [7, 41]. When the sensor is exposed to the gas, the electric potential generated on the gate region modulates the drain current in HEMTs or used as the electrode for the Schottky diodes. Table 2.5 lists various functionalization layers and their corresponding detected species studied for different types of gas sensors such as HEMTs, metal oxides and Schottky diodes etc.

Table 2.5 Functionalization layers for different types of gas sensors.

	Functionalization layers	Detected species
1	Platinum (Pt)	H ₂ , NO, NO ₂ , NH ₃ [49, 58]
2	Palladium (Pd)	H ₂ , NO, NO ₂ , NH ₃ [75]
3	Silver (Ag)	NO ₂ , NH ₃ , CO ₂ [75]
4	Tin dioxide (SnO ₂)	CO, O ₂ , H ₂ , NO ₂ , NH ₃ [76-78]
5	Starch and poly-ethyleneimine (PEI)	CO ₂ [79, 80]

AlGaIn/GaN HEMT based sensors functionalized with polyethyleneimine/starch have been used for CO₂ gas sensing over a wide range of concentrations and temperatures [81]. The presence of starch enhances the absorption of water molecules (H₂O) due to its hygroscopic nature [79]. In the chemical reaction, the interaction of CO₂ with H₂O shifts the equilibrium due to the competing formation of carbonate and bicarbonate ions, thus modulating the HEMT current [82].

The sensing mechanism of the SnO₂ functionalization layer involves the adsorption of gaseous molecules on the oxide surface, leading to the depletion layer modulation, which in turn alters the oxide film's resistance. AlGaIn/ GaN HEMT based sensors are very sensitive to a change in the charge at the SnO₂/AlGaIn interface, which enables the sensing of even small changes in the concentration of the species.

Pt has been used on a large scale as a catalyst in the petrochemical, pharmaceutical, electronics and automotive industries. It has found significance as an active catalytic layer in various GaN based sensors, such as nanowires, Schottky diodes, metal oxide semiconductor diodes and AlGaIn/GaN HEMTs [83-89]. For these sensors, the Pt functionalization layer has been widely used for H₂ gas sensing [90, 91]. However, only a few studies have been reported using GaN based Schottky diodes and AlGaIn/GaN HEMTs with a Pt functionalization layer to sense nitrous oxide, NO₂ and NH₃ [57, 92, 93]. Hence, AlGaIn/GaN HEMTs with a Pt functionalization layer will be an interesting study for NO₂ and NH₃ gas sensing.

Pd and Ag have been used as functionalization layers for NO₂ and NH₃ sensing with metal oxide sensors. The Pd functionalization layer displays higher hydrogen affinity and enhanced sensitivity to H₂ gas sensing, while the oxidised Ag surface creates a favourable site for the adsorption of NH₃ gas. Thus, based on the favourable properties of Pd and Ag, it is expected that AlGaIn/GaN HEMTs with these functionalization layers would be potential candidates for NH₃ gas sensing.

Chapter 3 Epilayer growth and gas sensor fabrication

3.1 Growth and characterization of AlGaN/GaN HEMT heterostructure

AlGaN/GaN HEMT heterostructure was grown on 100 mm diameter Si (111) substrate using metal organic chemical vapour deposition (MOCVD). Trimethylgallium and ammonia were used as the gallium and nitrogen sources, respectively, with hydrogen as the carrier gas. Fig 3.1 shows the schematic cross section of the AlGaN/GaN HEMT heterostructure. The epitaxial structure consisted of AlN nucleation layer, AlGaN stress mitigating layer (1 μm), GaN buffer layer (1.1 μm), $\text{Al}_{0.29}\text{Ga}_{0.71}\text{N}$ barrier layer (18 nm) and a GaN (2.5 nm) cap layer. The typical optical microscope image and an AFM image obtained on $5 \times 5 \mu\text{m}^2$ scan area of the AlGaN/GaN HEMT heterostructure top surface sample are shown in Figs. 3.2 (a) and (b), respectively. Crack free surface of the heterostructure and a smooth surface morphology with the RMS roughness of 0.44 nm has been obtained.

Fig. 3.1 Schematic cross section of AlGaN/GaN HEMT heterostructure.

Fig. 3.2 (a) An optical microscope image of the AlGaN/GaN HEMT heterostructure top surface and (b) the corresponding AFM image.

The average sheet resistance (R_s), 2DEG mobility (μ_H) and sheet carrier density (n_s) of the AlGaN/GaN HEMT were measured using a contactless Hall measurement system. The working principle of the system is described below.

The Leighton-1600 series contactless Hall measurement system was used to measure the 2DEG properties and verify the uniformity in electrical characteristics of the heterostructure. The measurement system included a low power microwave source operating at 10 GHz, coupled to a waveguide network which directs the power to the wafer surface. The waveguide is used to transmit and receive both TE_{10} (transverse electric) and TE_{11} modes of propagation.

Initially, TE_{10} microwave is incident on the wafer surface and the reflected wave having the same polarization as the incident wave is detected by the waveguide network and measured. The sheet resistivity of the wafer is obtained by calculating the ratio of the forward and the reflected powers. The TE_{10} incident wave is rotated by 90 degrees by the “Hall effect” and generates an additional reflected mode of TE_{11} . The waveguide network also detects and measures the reflected power of the rotated TE_{11} mode, which is used to determine the mobility and sheet carrier densities of the 2DEG. The system includes a software module which is used to convert the measured microwave powers into reflection coefficient that acts as the components of the conductivity sensor. Various electrical characteristics of the wafer such as carrier concentration, mobility and sheet resistivity are extracted by this conductivity sensor [50]. The schematic diagram of the contactless Hall measurement method with TE_{10} and TE_{11} modes of operation is shown in Fig. 3.3.

Fig. 3.3 Schematic diagram of contactless Hall measurement method [50].

Table 3.1 lists the average 2DEG properties. There will be an influence of the edge threading dislocations on 2DEG mobility [94]. However, we have not investigated the effects of edge dislocations on the 2DEG mobility. For the given heterostructure (Al composition and barrier thickness), 2DEG mobility and sheet carrier density is comparable with 2DEG of GaN based heterostructure from the literature [95, 96].

Table 3.1 2DEG properties and their values.

	Properties	Values
1	Average sheet resistance (R_s) [Ohm/sq.]	387
2	2DEG mobility (μ_H) [$\text{cm}^2/\text{V.s}$]	1264
3	Sheet carrier density (n_s) [$\times 10^{13} \text{cm}^{-2}$]	1.27

ω -2 θ GaN (004) rocking curve scan of the AlGaN/GaN heterostructure measured using a high resolution XRD (HR-XRD) system is shown in Fig. 3.4 along with the simulated results. The peaks in the scan corresponding to GaN, AlGaN stress mitigating layers and AlN have been indicated. GaN peak looks slightly asymmetric as compared to the others. The asymmetric peak is possibly due to the strain difference between the two layers of GaN buffer (undoped GaN and carbon doped GaN). Moreover, the Al composition of 29.5 % and barrier thickness of 17.5 nm were obtained for AlGaN barrier layer in the simulation of the XRD scan. The screw dislocation density and edge dislocation density determined are $1.07 \times 10^9 \text{ cm}^{-2}$ and $1.06 \times 10^{10} \text{ cm}^{-2}$, respectively. Fig. 3.5 shows the photograph of the AlGaN/GaN heterostructure grown on 100-mm Si (111) wafer.

Fig. 3.4 HR-XRD ω -2 θ GaN (004) rocking curve scan of AlGaN/GaN heterostructure.

Fig. 3.5 Photograph of the AlGaIn/GaN heterostructure grown on 100 mm diameter Si (111) wafer.

3.2 Growth and characterization of AlN/GaN/AlN HEMT heterostructure

AlN/GaN/AlN HEMT heterostructure was grown on 50 mm diameter SiC substrate using molecular beam epitaxy (MBE) technique. The schematic cross section of the AlN/GaN/AlN HEMT heterostructure is shown in Fig 3.6. The epitaxial structure consisted of AlN buffer layer (300 nm), GaN channel layer (65 nm), AlN barrier layer (7 nm) and a GaN (2 nm) cap layer.

Fig. 3.6 Schematic cross section of AlN/GaN/AlN HEMT heterostructure.

A typical top surface of the optical microscope image and an AFM image of $5 \times 5 \mu\text{m}^2$ scan area of the AlN/GaN/AlN HEMT heterostructure are shown in Figs. 3.7 (a) and (b), respectively. The crack free surface of the heterostructure and a smooth surface morphology with the RMS roughness of 0.44 nm have been obtained.

Fig. 3.7 (a) An optical microscope image of AlN/GaN/AlN HEMT heterostructure top surface and (b) the corresponding AFM image.

Table 3.2 lists the 2DEG properties of AlN/GaN/AlN HEMT measured using a contactless Hall measurement system.

Table 3.2 2DEG properties and their values.

	Properties	Values
1	Average sheet resistance (R_s) [Ohm/sq.]	335
2	2DEG mobility (μ_H) [$\text{cm}^2/\text{V.s}$]	509
3	Sheet carrier density (n_s) [$\times 10^{13} \text{cm}^{-2}$]	3.66

3.3 Mask design

The complete layout of the mask was designed and fabricated using Clewin3.1 software with a minimum feature size of 2 μm . The designed HEMT layouts consist of variable gate length (L_g) and drain source spacing (L_{ds}). Various layer mask-set also includes alignment marks for the optical lithography and transmission line model (TLM) patterns for the determination of ohmic contact resistance (R_c). The photolithographic mask for this project was designed with an objective to compare the various parameters of the sensors with the recently reported AlGaN/GaN HEMT based gas sensors [9, 41, 49]

The mask consisted of the following four layers:

Layer 1- Mesa isolation layer

Layer 2- Ohmic contact layer

Layer 3- Pad layer

Layer 4- Functionalization layer

All layers of the masks, respectively are discussed in the following sections:

Layer 1 Mesa isolation layer

Mesa isolation layer of the mask was designed in order to electrically isolate a particular device from the adjacent devices on the wafer. The isolation is realized by etching through the conducting layer and creating island-like platforms on which devices are fabricated.

Layer 2 Ohmic contact layer

The ohmic contact layer of the mask was designed in the form of interdigitated electrodes pattern. The schematic cross-section of GaN based heterostructure with the interdigitated electrode ohmic contacts is shown in Fig. 3.8.

Fig. 3.8 The schematic cross section of GaN based heterostructure with the interdigitated electrode ohmic contacts.

Layer 3 Pad layer

Pad layer of the mask was designed on top of two ohmic contacts of the sensors for the purpose of wire bonding to an IC package. The schematic cross section of GaN based heterostructure with the ohmic contacts and pad layer is shown in Fig. 3.9.

Fig. 3.9 The schematic cross section of GaN based heterostructure with the ohmic contact and pad layer.

Layer 4 Functionalization layer

The functionalization layer of the mask was designed between two ohmic contact electrodes, which acts as the gate for the GaN HEMTs. The schematic cross section of GaN based heterostructure with the ohmic contacts and functionalization layer is shown in Fig. 3.10.

Fig. 3.10 The schematic cross section of GaN based heterostructure with the ohmic contact and functionalization layer.

3.4 Fabrication process

Fabrication of the GaN HEMT based sensors involves various processes techniques such as organic cleaning, photolithography, etching, metallization, lift-off, rapid thermal annealing and wire bonding. The standard methods followed in each stage of the fabrication flow are discussed in the subsequent sections.

3.4.1 Techniques for device fabrication

3.4.1.1 Organic cleaning

Organic cleaning is one of the most common processes in semiconductor device fabrications, which has to be followed before almost every fabrication step. Any type of organic/inorganic particles on the sample surface may result in abnormal or failure of device operation. The sample cleanliness is also an important process step, which determines the quality and yield of the fabrication process [97]. In this research, the process of organic cleaning starts with the ultrasonic cleaning in acetone (CH_3COCH_3) at room temperature for 10 min to get rid of any organic molecules or dust on the surface of the sample. This step is followed by the ultrasonic cleaning in isopropanol (IPA) at room temperature for 10 min to remove any leftover acetone or dust. Subsequently, the samples are rinsed in DI water to remove the IPA residue and then dried using N_2 gun. Finally, the samples are baked on a hot plate at 120 °C for 5 min to evaporate any moisture present on the surface. In addition to the ultrasonic cleaning in acetone and IPA, the samples are also dipped in piranha solution in order to remove the residual photoresist or any other particles stuck to the surface.

3.4.1.2 Photolithography

Photolithography is a vital process in the fabrication cycle which results in the formation of the device pattern of the mask on the sample surface. “AZ5214E” photoresist was used in this research, which can be employed for both types of photolithography techniques, i.e. positive and negative photolithography (image reversal). Various steps involved in the complete photolithography process are sample cleaning, spin-coating of photoresist, soft bake, mask alignment, first UV exposure, hard bake, flood exposure and the developing.

After organic cleaning, the photoresist was spin coated on the sample surface with 4000 rpm for 30 sec to obtain a uniform layer of the photoresist. The spin-coating is followed by baking the sample on the hot plate at 105 °C for 2 min (soft bake), which helps to condense the photoresist. Subsequently, the selective area of the sample as defined by the mask features is exposed to UV light. Suss mask aligner MJB4 was used for the alignment and exposure. The UV exposure was followed by the hard bake at 120 °C for 2 min and the flood exposure of the sample in order to obtain the negative photolithography pattern. The final step was the development of the pattern in a controlled way and the repeated observation using an optical microscope in order to acquire the actual/desired pattern on the sample surface.

3.4.1.3 Descum and BOE etching

The Descum (O₂ plasma treatment) process step was used to remove any residual photoresist present on the developed pattern and clean the surface prior to metallization. Subsequently, the sample was dipped in the buffer oxide etchant (BOE, 6:1) for 2 min just before the metal deposition in order to etch any oxide layer.

3.4.1.4 Metallization Techniques

The metal deposition process for various contacts of the devices in the fabrication cycle was carried out using a commercial electron beam evaporation system, Edwards EL400. In this process, various metals such as Ti, Al, Ni, Au, for ohmic contacts and Pt, Pd, Ag as functionalization layers were deposited. Vacuum pressure of the order of 10^{-7} mbar was maintained in the chamber for obtaining pure metal vapour, when the accelerated electron beam is focussed on the metal source placed inside a suitable metal crucible. The thickness of the metal layers deposited on the samples is measured by a sensor, which is located at the same level as the samples.

3.4.1.5 Lift-off

The lift-off process involved the removal of the developed photoresist along with metal layers deposited on top of it. The samples were soaked

in acetone and a low intensity ultrasonic cleaning was applied in order to peel off the photoresist from the patterned sample surface. Subsequently, the samples were rinsed in IPA followed by DI water, and observed under an optical microscope to accomplish the desired metal pattern on the sample surface.

3.4.2 Fabrication steps for GaN HEMT based sensor

The complete sensor fabrication process employed in this work consists of several modules: the mesa isolation, ohmic contact layer, pad layer and functionalization layer deposition followed by wire bonding in the IC package. The process flow of the complete GaN HEMT sensor fabrication process is shown in Fig. 3.11. Each step is discussed in detail in the subsequent sections.

Fig. 3.11 Process flow of complete GaN HEMT sensor fabrication process.

3.4.2.1 Mesa isolation

Mesa isolation is required in order to electrically isolate a particular device from the adjacent devices on the sample. In order to realize the electrical isolation, 2DEG channel should be etched which is usually located around 20-30 nm below the surface. The positive photolithography of the mesa layer was performed, and the obtained pattern was covered with photoresist. The patterned photoresist acts as a mask during the mesa etching process. The area between the two mesa patterns was etched down to 150 nm by the inductive coupled plasma-reactive ion etching (ICP-RIE) process. It was followed by removal of the photoresist layer present on the mesa pattern. After mesa etching, the final pattern was obtained on which ohmic contact layers need to be deposited. The schematic of photolithography of the mesa layer, ICP RIE etching and photoresist removal process are shown in Figs. 3.12 (a), (b) and (c), respectively. The desired mesa etching depth was measured and confirmed by the Dektak profiler, which is shown in Fig. 3.13 for a typical measurement. The optical microscope image of the sample after the mesa isolation step is shown in Fig. 3.14.

Fig. 3.12 Schematic of (a) photolithography of the mesa layer, (b) ICP RIE etching and (c) photoresist removal process.

Fig. 3.13 Etching depth measured using Dektak.

Fig. 3.14 Microscope image of the sample after mesa isolation.

3.4.2.2 Ohmic contact layer deposition

The ohmic contacts are deposited in order to form an electrical connection to the semiconductor. The first step of the fabrication process was the alignment of the ohmic layer mask with the sample having the etched mesa patterns. The mask alignment was followed by the negative photolithography process to define the drain and source ohmic contact regions. Subsequently, the ohmic contact electrodes were realized by the deposition of Ti/Al/Ni/Au (20/120/40/50 nm) metal stack. The following

step was the standard lift-off process to obtain the desired metal patterns. The schematic and microscope image of the ohmic contacts are shown in Figs. 3.15 and 3.16, respectively. The lift-off process was followed by the rapid thermal annealing at 825 °C under nitrogen ambient for 30 sec. The ohmic contact quality is determined by R_c , which was obtained by the four-point transmission line method (TLM) measurement. The R_c value of $<1 \text{ } \Omega.\text{mm}$ was achieved, which confirms the good quality of the ohmic contacts. Resistance as a function of separation between the adjacent contacts of TLM structures is represented in Fig. 3.17.

Fig. 3.15 Schematic of ohmic contacts.

Fig. 3.16 Microscope image of pre-annealed ohmic contact fabricated structure.

Fig. 3.17 Resistance versus separation between the adjacent contacts of TLM structures.

3.4.2.3 Pad layer deposition

The gold wire bonding is challenging on the annealed surface due to its high surface roughness. Hence, a pad layer is required on top of the ohmic contact which provides a smooth surface and larger pad area, suitable for wire bonding. The pad layer fabrication included the mask alignment, negative photolithography process, deposition of Ti/Au (25/300 nm) metal layer and the lift-off in order to obtain a pattern on top of the ohmic contacts. The schematic containing the ohmic contacts and pad layer is shown in Fig. 3.18.

Fig. 3.18 Schematic of ohmic contacts and pad layer.

3.4.2.4 Functionalization layer deposition and wire bonding

Several sensor devices were fabricated by depositing Pt functionalization layer of different thicknesses: 20 nm, 15 nm and 10 nm in the open gate region. In addition, different set of devices were also fabricated with 10 nm of Pd and Ag functionalization layers. It has been reported that NH_3 sensing needs the presence of pores, which may not be formed in thick Pt layer. Hence, this particular range of Pt thickness was selected with the view that pores will form when the thickness of the Pt layer is small, which will allow the diffusion of gas and its adsorption at the surface. The relation between the thickness and sensitivity has been discussed in detail in section 5.2.1. The schematic containing the ohmic contacts, pad layer and functionalization layer is shown in Fig. 3.19. During the initial cycles of fabrication, Pt had a weak adhesion with the top surface and it used to peel off during the lift-off process. Many cycles of depositions were investigated and one additional step, i.e. post bake after development at 120 °C for 2 min was implemented in order to achieve good adhesion of Pt with the surface. The fabricated devices were wire bonded to a 16-pin dual in-line package (DIP) for the gas sensing studies. The typical microscope image of the complete fabricated device and photograph of the wire bonded IC package are shown in Figs. 3.20 and 3.21, respectively.

Fig. 3.19 Schematic of ohmic contacts, pad layer and functionalization layer.

Fig. 3.20 Microscope image of the post-annealed fabricated device.

Fig. 3.21 Photograph of the wire bonded IC package.

3.5 Gas sensing measurement procedure

Fig. 3.22 shows the schematic of the gas sensor measurement setup used in this work to evaluate the gas sensing performance of the sensors. Various components of the gas sensor setup are indicated in the diagram. The functions of different components and the interconnections among them have been described in the following paragraphs.

Fig. 3.22 Schematic diagram of the gas sensor measurement setup.

The gas sensing measurements for the sensors need to be carried out in a well-controlled ambient and in a chamber of fixed volume in order to avoid the interference due to numerous influencing factors. The measurement ambient corresponding to these requirements is maintained inside the closed measurement chamber. The sensor was mounted with good thermal contact on the heater stage in this stainless-steel measurement chamber. The sample temperature was changed using a Linkam THMS600 heating stage and a temperature controller. The ohmic contacts (source/drain) of the sensor were connected to the two probes of Keithley 236 SMU system via the crocodile clips. The gas sources of dry N₂ (reference gas) and NO₂ / NH₃ (test gas) were connected to the measurement chamber via a gas blender. The flow rate of the gases to the blender was controlled using MFCs. All the measurements were conducted at the atmospheric pressure with a flow rate of 500 sccm. There were various channels connected to the gas blender through which the test gas, reference gas or wet air were introduced into the chamber based on the measurement requirements. The variations of the gas concentration, measurement temperature and relative humidity (RH) for the different measurement conditions were controlled by a Labview recipe. Various gas concentrations can be achieved by diluting the test gas with dry N₂ in a calculated ratio.

The experiments were carried out by applying a constant bias of 5 V across the source and drain of the HEMT sensors and measuring the sample's current. Initially, the chamber was purged with dry N₂ and a steady state response was obtained. Any variation in the steady state response due to the exposure of the gas can be attributed to the gas detection only, since all the influencing factors such as the pressure, RH and gas flow rate were kept under control. For each concentration, the response under dry N₂ was taken as the baseline with respect to the response obtained under the test gas for the evaluation of the device current change (ΔI) and sensitivity. Each experimental measurement was verified using minimum of 3 to 5 samples.

In order to evaluate the effect of RH on the test gas sensitivity, the wet air generated by bubbling dry N₂ gas through DI water flask was mixed with the test gas at the appropriate ratio in the gas blender before introducing into the measurement chamber. The calculated flow of the wet air corresponding to the specific RH was purged into the chamber to attain a steady state response before introducing the test gas. This was essential to ensure that the change in response due to the test gas does not interfere with the RH response. Under these conditions, the test gas and RH induced change in the current was measured. Subsequently, the sensor was heated to a higher temperature in order to recover back to its initial condition. The periodic heating causes the gas desorption and

inhibits the humidity induced baseline variation. It was followed by changing the RH inside the chamber and exposing the sensor to the gas for the next measurement. This procedure was repeated for each RH and the sensitivity was calculated.

Chapter 4 Pt/AlGaIn/GaN HEMT based NO₂ sensor

4.1 Background

The GaN based Schottky diode with Pt functionalization layer was shown to exhibit a sensitivity of 3.2 % for 450 ppm NO₂ concentration [93]. A sensitivity of 10% for 1000 ppm of NO₂ using Pt/AlGaIn/GaN HEMT based sensor was also reported [59]. Furthermore, AlGaIn/GaN HEMT based sensors with Pt functionalization layer demonstrated NO₂ sensing in the range of 900-100 ppm [49], down to 10 ppm with sensitivity of 1% [41]. Moreover, the relative humidity (RH) has been found to play a significant role in gas sensing as the sensitivity of NO₂ gets affected when it interacts with the sensor surface in the humid environment [74]. The influence of varying RH (0 to 80%) on the NO₂ sensing has been studied using recessed AlGaIn/GaN heterostructure based open gate sensors, nitrogen doped graphene nanosheets and Cr-doped TiO₂ [74, 98, 99]. It was observed that the presence of RH had profound impact on the output response for these materials. The RH is known to be high (> 50%) in some of the major cities such as Singapore where it varies in the range of 70 - 90 %. Thus, NO₂ sensing study has to be carried out by varying RH of the measurement environment which simulates the real-time air quality monitoring condition.

However, the influence of RH on NO₂ sensing has not been explored much using AlGaIn/GaN HEMT based sensors. The sensor operating temperature is also important, as discussed in Chapter 1, section 1.4, on the critical parameters of recovery, sensitivity, response and recovery times. In this Chapter, NO₂ sensing of low concentration (<10 ppm) at different temperatures (30-300 °C) and RH (0-90 %) using AlGaIn/GaN HEMT based gas sensors on silicon substrate, with interdigitated electrodes and Pt functionalization layer, is systematically studied. The schematic cross section of the AlGaIn/GaN HEMT heterostructure is shown in Fig 3.1, Chapter 3.

4.2 NO₂ sensing at room temperature

The response of the Pt/AlGaIn/GaN HEMT to less than 10 ppm NO₂ with dry N₂ as the reference gas was measured at room temperature (30 °C). Fig. 4.1 shows the transient response of the sensor at different NO₂ concentrations of 10 - 4 ppm. The current decreased when the sensor was exposed to different concentrations of NO₂. However, it did not recover back completely when NO₂ was turned off while maintaining the supply of reference N₂ gas only. Sensitivity of 1.2 % with the corresponding ΔI of 0.5 mA were obtained for 10 ppm of NO₂.

Fig. 4.1 Transient response of the sensor at RT for different NO₂ concentrations.

4.2.1 Heat induced recovery

The sensor was heated to the temperatures ranging from 30 to 300 °C during the recovery cycle. For example, the typical transient response of the sensor for 10 ppm NO₂ at room temperature (RT) with the recovery at 300 °C is shown in Fig. 4.2. A large decrease in the current was observed when the sensor was heated to 300 °C. The sensor recovered at this temperature and returned back to its steady state during the cool down. Hence, the heating induced gas desorption has led to the recovery of the sensor at the elevated temperature.

Fig. 4.2 Transient response of the sensor for 10 ppm NO₂ at RT with the heat-induced recovery at 300 °C.

4.2.2 Sensing mechanism

It is known that NO₂ gets dissociated into NO and oxygen ion (O⁻) when it is exposed to Pt layer at 30 °C resulting in high-coverage of oxygen on the Pt surface [100, 101]. The negatively charged oxygen ions interact capacitively with AlGaIn and diffuse via pores or grain boundaries on the Pt surface and get adsorbed at the Pt/AlGaIn interface [49]. In both cases, the presence of these ions generates negative surface potential which compensates the existing positive charges on the AlGaIn surface. This results in the depletion of 2DEG causing the current reduction. Similarly,

NO molecule having one unpaired electron gets adsorbed as a free radical resulting in negative surface potential, thereby contributing to further reduction in the current [41, 49]. The schematic diagram of AlGa_xN/GaN heterostructure showing the surface charges and 2DEG is shown in Fig. 4.3. The desorption of NO is reported to start at 30 °C, while the desorption of oxygen takes place only above 180 °C [102]. Hence, the sensor recovered only partially at RT and was found to completely recover at 300 °C due to the generation of sufficient thermal energy which causes the desorption of O⁻ ions.

Fig. 4.3 Schematic diagram of AlGa_xN/GaN heterostructure showing the surface charges and 2DEG.

4.3 Relative humidity influence

The influence of RH (0 to 90 %) on the sensitivity at 5 ppm NO₂ was studied at RT and is illustrated in Fig. 4.4. It can be observed that the RH affects the NO₂ sensitivity and exhibits an increasing trend with the increase of RH, similar to other NO₂ gas sensors [74, 99, 103].

Fig. 4.4 Sensitivity and ΔI as a function of RH for 5 ppm of NO₂.

When the sensor is exposed to the humid environment, its surface is covered with only a very thin layer of water with a thickness of up to a few monolayers [104]. The chemical reactions between the adsorbed species and the water layer are mainly accountable for the change in the sensitivity. The variation in sensing response may be due to the interaction of NO with H₂O leading to the formation of other species such as HNO₂ and HNO₃, which get adsorbed and participate in the sensing mechanism [105]. The increase of relative humidity yields more H₂O molecules, which further enhances the number of reaction by-products and sensing response. However, the actual chemical reaction of NO₂ with such a thin layer of water resulting in the increase of the sensitivity with the increase of RH needs further investigation.

The periodic heating results in sensor recovery from gas exposure and inhibits the humidity induced baseline variation [74]. Furthermore, it can be referred from Fig. 3.1 that GaN cap is grown on top of the AlGaIn barrier to prevent the oxidation effects. Thus, there should not be any issue with the oxidation effects. Hence, it can be summarized that the presence of RH influences the sensitivity and it should be compensated during NO₂ sensing in the real applications. A trend of relative sensitivity as a function of relative humidity is obtained. The obtained sensitivity trend can be used in the real world applications to offset the measured values. Based on the calibration data, a simple algorithm can be used to analyze the data.

4.4 NO₂ sensing at elevated temperature

4.4.1 NO₂ sensing at 300 °C

In addition to the measurements at RT, the response of the Pt/AlGaIn/GaN HEMT based sensor was also measured at an elevated temperature of 300 °C for NO₂ concentrations less than 10 ppm. At this temperature, the sensor functioned and recovered completely to the steady state value when exposed to various concentrations of NO₂. Fig. 4.5 shows the transient response of the sensor at different NO₂ concentrations of 0.5 - 10 ppm. The current decreased when exposed to different NO₂ concentrations, but recovered when NO₂ was turned off. This phenomenon of the decrease in current upon exposure to NO₂ and the recovery in presence of reference gas was already explained in section 4.2.2. It can be observed that the reference current is lower at a higher temperature. With the increase of operation temperature, electron phonon scattering increases which results in the reduction of electron mobility in the 2DEG channel [49]. Hence, the initial current decreases at a higher temperature.

Sensitivity of 2 % with the corresponding ΔI of 650 μ A were obtained for a very low NO₂ concentration of 0.5 ppm. A high sensitivity of 5.5 % with the corresponding ΔI of 1.8 mA were achieved for 10 ppm NO₂ at 300 °C,

which are higher than the reported values for Pt/AlGaIn/GaN HEMT based sensors under similar measurement conditions [41].

Fig. 4.5 Transient response of the sensor at 300 °C for different NO₂ concentrations.

Further, the response of the Pt/AlGaIn/GaN HEMT based sensor was measured at the temperatures ranging from 30 to 300 °C. The device sensed and recovered completely under the reference gas to steady state value when exposed to various concentrations of NO₂ at temperatures above 275 °C. Hence, the lowest temperature, i.e. 275 °C at which the sensor can recover has been fixed as the experimental temperature for further measurements.

4.4.2 Analysis of NO₂ sensing performance at 275 °C

Fig. 4.6 (a) shows the transient response of the sensor at different NO₂ concentrations of 0.8 - 10 ppm at 275 °C. A similar trend was observed, the current decreased when the sensor was exposed to NO₂ and recovered when NO₂ was turned off. The measurement was carried out at even further lower concentrations, and the minimum concentration sensed was 50 ppb NO₂. The transient response of the sensor corresponding to 50 ppb of NO₂ concentration is shown in Fig. 4.6 (b).

Fig. 4.6 Transient response of the sensor at 275 °C for (a) different NO₂ concentrations and (b) 50 ppb of NO₂ concentration.

Table 4.1 compares the key parameters of the Pt/AlGaIn/GaN HEMT based NO₂ gas sensors with the reported results of similar sensors. Sensitivity of 1.2 % with the corresponding ΔI of 400 μ A were obtained for very low NO₂ concentration of 50 ppb, which is the lowest NO₂ concentration sensed by the Pt/AlGaIn/GaN HEMT based sensors. A high sensitivity of 5.1 % with the corresponding ΔI of 1.72 mA were achieved for 10 ppm NO₂ at 275 °C, which is better as compared to other reported results summarized in Table 4.1. Interestingly, the sensor in this study was found to respond quickly to the change in the NO₂ concentration. A rapid response of less than 2 min with a recovery time of less than 5 min was obtained for all the concentrations.

The increase in adsorption rate of oxygen ions is primarily due to catalytic dissociation of NO₂ on Pt functionalization layer, which results in the

sensitivity enhancement. Furthermore, the large surface area of the interdigitated electrodes enables more interaction between the adsorbed gaseous ions and the sensor surface, enabling the sensing of low gas concentrations. The strength of the interaction between the adsorbed gaseous ions and the sensor surface is directly proportional to the surface area, which in turn leads to the enhancement in the sensitivity [106]. Hence, higher sensitivity was obtained by Pt/AlGaIn/GaN HEMT with interdigitated electrodes as compared to the conventional Pt/AlGaIn/GaN HEMT device [41].

Table 4.1 Comparison of key parameters of Pt/AlGaIn/GaN HEMT based NO₂ gas sensors.

Temp. (°C)	NO ₂ (ppm)	I ₀ (mA)	Sensitivity (%)	Response time/ Recovery time (s)	Reference
275	0.05	33.8	1.2	107/ 117	This work
275	10	33.9	5.1	56/ 285	
300	10	33.0	5.5	48/115	
300	10	35.0	1.0	360/ 300	[41]
400	1000	5.0	10.0	-	[59]
300	900	44.0	33.0	1620/-	[49]

4.4.2.1 Sensitivity as a function of concentration

The sensitivity and ΔI as a function of NO_2 concentration (0.8-10 ppm) obtained at 275 °C is shown in Fig. 4.7. The sensitivity gradually increases as a function of the increasing concentration of the gas. The increase in the concentration results in the adsorption of a greater number of dissociated gaseous ions which results in the enhancement in the sensitivity [107].

Fig. 4.7 Sensitivity and ΔI as a function of NO_2 concentration at 275 °C.

4.4.2.2 Response time as a function of concentration

The response time as a function of NO₂ concentration (0.8-10 ppm) obtained at 275 °C is shown in Fig. 4.8. The response time shows a gradually decreasing trend as a function of the increasing concentration of the gas. The value of response time reduced from 98 sec to 56 sec when the NO₂ concentration was increased from 0.8 to 10 ppm. The decrease in the response time may be attributed to the increase of adsorption rate due to the occupation of more vacant adsorption sites with higher concentration [108].

Fig. 4.8 Response time as a function of NO₂ concentration at 275 °C.

4.5 Temperature effects on NO₂ sensing

In order to further investigate the impact of temperature on the NO₂ sensing performance of the devices, the behaviour of various sensor metrics such as sensitivity, response time and recovery time were studied at different temperatures.

4.5.1 Response and recovery times

In order to analyse the temperature effect on the transient response behaviour, the response and recovery times of the sensor were obtained for each operating temperature for a fixed concentration of 6 ppm NO₂. It was found that the response and recovery times showed a gradually decreasing trend as a function of the increase in temperature as illustrated in Fig. 4.9. A rapid response of 48 sec with a recovery time of 115 sec was obtained at 300 °C. The decrease in the response time at higher temperature is attributed to the enhanced dissociation of NO₂ on the Pt layer and the availability of more O⁻ ions. Furthermore, the desorption of gaseous ions also gets enhanced at higher temperatures resulting in the decrease of recovery time [49].

Fig. 4.9 Response and recovery times as a function of temperature for 6 ppm NO₂.

4.5.1.1 Activation energy

The activation energy is defined as the minimum energy required to initiate any process such as gas dissociation, adsorption or desorption. It is a key parameter for the gas sensing mechanism and can be an important tool to validate the performance of the sensing material [109].

The Arrhenius plots consisting of the logarithmic of recovery and response times as a function of the inverse of temperature ($1000/T$) are presented in Figs. 4.10 (a) and (b). Linear fitting was performed and a straight line was obtained in each case, which demonstrates that the response and

recovery mechanisms are governed by a thermally stimulated process [110]. The thermal process can be described experimentally by the Arrhenius equation as expressed in Eq. 4.1.

$$\tau = A. \exp \left[\frac{-E_a}{RT} \right] \quad \text{Eq 4.1}$$

Where τ is response/recovery time, E_a is the activation energy of adsorption/desorption, R is the universal gas constant, T is the temperature in Kelvin and A is a constant.

Taking logarithmic on both sides results in an equation in the form of $y = mx + C$, as expressed in Eq. 4.2.

$$\ln (\tau) = \left[\frac{-E_a}{RT} \right] + \ln A \quad \text{Eq 4.2}$$

where, $y = \ln (\tau)$, $x = 1/T$, $m = E_a/R$ and $C = \ln A$

Slope (m) has been extracted from the best fit of the Arrhenius plot, as shown in Fig. 4.10. Subsequently, by substituting the value of R , E_a was obtained in J/mole and has been converted to eV/molecule.

The activation energy can be expressed as (Eq. 4.3):

$$E_a = -RT \times [\ln(\tau) - \ln(A)] \quad \text{Eq. 4.3}$$

The values of 0.33 eV/ion and 0.64 eV/ion were obtained for response time activation energy (E_a) and recovery time activation energy (E_d) respectively. E_a and E_d are the activation energies of adsorption and

desorption of O^- ions, respectively [98]. E_a of 0.33 eV is comparable with literature since the activation energy for adsorption of oxygen on Pt surface has been reported in the range of 0.22-0.47 eV [111]. Furthermore, the activation energy of response and recovery times for NO_2 sensing with open gate AlGaIn/GaN HEMT have been reported to be 0.9 eV and 1.0 eV, respectively [112]. The lower values obtained in this study are mainly due to the presence of Pt functionalization layer, which enhances the reactivity due to its catalytic properties [113].

Fig. 4.10 Arrhenius plots of (a) recovery time and (b) response time, for 6 ppm NO_2 .

4.5.2 Sensitivity

The effect of temperature on the sensitivity was investigated in the temperature range of 30 to 300 °C for 10 ppm NO₂ as shown in Fig. 4.11. A gradual increase in the sensitivity was observed as a function of the temperature due to the enhanced dissociation of NO₂ at higher temperature and more adsorption of ions on the sensor surface. However, at higher temperatures, the desorption of gaseous ions also increases, generating more vacant adsorption sites on the surface of Pt functionalization layer, which further enhances the adsorption rate [49, 114].

Fig. 4.11 Sensitivity and ΔI as a function of temperature for 10 ppm NO₂.

Sensitivity and ΔI as a function of temperature for different concentrations ranging from 2 - 10 ppm are shown in Figs. 4.12 (a) and (b), respectively. As expected, the sensitivity and ΔI display an increasing trend with the increase in concentration as well as temperature.

Fig. 4.12 (a) Sensitivity and (b) ΔI as a function of temperature for different concentrations of NO₂.

4.5.2.1 Activation energy

The Arrhenius plot of sensitivity obtained for 10 ppm NO₂ is shown in Fig. 4.13, and the activation energy obtained is 0.085 eV/molecule. The obtained activation energy may correspond to the energy of the rate-limiting step for the dissociation of NO₂ gas into O⁻ ions, rather than diffusion-limited as diffusion rate of molecules/ions is generally high. The activation energy indicates the ability of interaction between the surface states and adsorbed gaseous ions at an operating temperature [115]. A low value of activation energy denotes that relatively lower energy is required to initiate any process resulting in the enhanced dissociation and the interaction at the surface. Hence, a smaller value of activation energy is an indication of higher sensing response.

Fig. 4.13 Arrhenius plot of sensitivity for 10 ppm NO₂.

4.6 Effects of functionalization layer dimensions on the NO₂ sensing

The dimensions of the Pt functionalization layer (gate) is an important parameter in the gas sensing since the gate surface directly interacts with the gaseous species. Hence, there is a need to investigate the impact of gate dimensions on gas sensing performance. For this purpose, four different sensors having the same number of interdigitated fingers (10 fingers) and variable gate dimensions were fabricated. These sensors had a fixed gate width (W_g) of 60 μm , while L_g varied as 6, 8, 10 and 12 μm . The response of these sensors was measured at 275 °C for 10 ppm NO₂ and their respective sensing parameters were evaluated. Table 4.2 lists the various performance parameters corresponding to different values of L_g and gate area (sensing area).

It can be observed that the initial current (I_0) of HEMTs has an increasing trend for decreasing values of L_g [41]. Moreover, it was found that the sensor with a larger sensing area ($W_g \times L_g$) yields a higher value of ΔI , since a larger area facilitates better interaction of the gas. Further, with the increasing gate length, the enhancement in sensitivity was observed due to both the factors, i.e. increase of ΔI and decrease of initial current (I_0). It can be observed from the values listed in Table 4.2, increase of ΔI is less pronounced while the decrease of I_0 is more effective accounting for larger variation in sensitivity with the increasing L_g . The responsivity is

another performance parameter, which is used to compare the performance of the sensors having different sensing areas. Interestingly, the responsivity was found to decrease with the increasing of L_g , indicating that higher performance of the sensor is achieved for the sensor with shorter L_g . The decrease in responsivity is mainly caused due to the larger sensing area with increasing L_g .

Based on the investigations conducted in this study, it can be summarized that the sensor with the shortest gate length exhibits the lowest sensitivity, but it has the highest responsivity. Thus, a trade-off should be made in designing the gate length of the sensor in order to have a right balance between the sensitivity and responsivity of the device. Because of this consideration, the devices having 10 μm gate length were mainly used in this thesis work.

Table 4.2 Comparison of NO_2 sensing performance having variable gate dimensions.

Gate length (μm)	Sensing area ($\times 10^3 \mu\text{m}^2$)	I_0 (mA)	ΔI (mA)	Sensitivity (%)	Responsivity $\text{mA}/(\text{cm}^2 \times \text{ppm})$
6	7.2	74.6	2.886	3.9	4008
8	9.6	69.6	2.980	4.3	3104
10	12.0	61.1	3.120	5.1	2600
12	14.4	49.6	3.558	7.2	2470

4.7 Summary

AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and Pt functionalization layer were characterized for NO₂ sensing at RT. The sensor was able to sense but unable to recover completely at this temperature. Subsequently, it was heated up to 300 °C during the recovery cycle, and the heating induced gas desorption has led to the recovery of the sensor. The influence of RH on NO₂ sensitivity was studied at RT and it was found that the sensitivity has an increasing trend with the increase in RH. The mechanisms for current decrease during the exposure of the gas and influence of the relative humidity on NO₂ sensitivity were investigated.

The response of the sensor was measured at various temperatures ranging from 30 to 300 °C. It was found that the sensor sensed and recovered completely to the steady state value when exposed to various concentrations of NO₂ at the temperatures above 275 °C. A high sensitivity of 5.1 % with the corresponding ΔI of 1.72 mA were achieved for 10 ppm NO₂ at 275 °C, which are higher than the reported values for Pt/AlGaIn/GaN HEMT based sensors under similar measurement conditions. The large surface area of the interdigitated electrodes and the catalytic property of platinum functionalization layer enabled high sensitivity for low NO₂ concentrations of < 10 ppm. A rapid response time

of less than 2 min and a recovery time of less than 5 min were obtained for all the concentrations. The sensitivity and response time were obtained as a function of NO₂ concentration at 275 °C. It was found that the sensitivity shows a gradually increasing trend, while the response time shows a gradually decreasing trend as a function of the increasing concentration of the gas.

The behaviour of various parameters such as sensitivity, response and recovery times were investigated as a function of temperature. The Arrhenius plots obtained demonstrate that the sensing mechanisms are governed by a thermally stimulated process. The activation energies for sensitivity, response and recovery times were calculated and the respective sensing mechanisms have been explained. Based on this study, Pt/AlGaIn/GaN HEMT based sensor with interdigitated electrodes is found to be a prospective candidate for low concentration NO₂ sensing with high sensitivity.

Chapter 5 AlGaN/GaN HEMT based NH₃ sensor

5.1 Background

AlGaN/GaN Schottky based sensor using Pt functionalization layer exhibited a high sensitivity of 1307 % for 35 ppm NH₃ in the temperature range of 30-150 °C [57]. However, the output current in nA range is unfavourable for the sensor, since the leakage current in the circuit may be of the same order [37, 38]. The lowest NH₃ concentration sensed using Pt/AlGaN/GaN HEMT based sensors is 35 ppm at room temperature (RT) [9]. However, the recovery of the sensor in the absence of NH₃ was not investigated in their work. In another study, the sensing of 0.15 ppm and 15 ppm NH₃ concentration was reported at 300 °C using the Pt/AlGaN/GaN HEMT based sensors [41]. The sensitivity of 0.2 % and 0.7 % were reported for 0.15 ppm and 15 ppm, respectively. However, the detailed mechanism for the observed trend had not been clearly explained.

AlGaN/GaN HEMT based sensors with Pd functionalization layer displays high hydrogen affinity and has enhanced sensitivity to H₂ gas. It has been reported that Pd exhibits a better catalytic property than Pt for H₂ gas sensing [116]. Due to the higher hydrogen affinity of Pd, it is expected that AlGaN/GaN HEMT with Pd functionalization layer would be a favourable candidate for NH₃ sensing at elevated temperatures. Moreover, relatively,

the lower cost of Pd makes this material more attractive for the gas sensing applications [117].

Ag has been used as a functionalization layer for NO₂, NH₃ and CO₂ gas sensing using various materials such as carbon nanotubes, SnO₂ microrods and tungsten di-sulfide nanosheets [118, 119]. It is well known that Ag has the property of getting oxidized in the normal ambient conditions. It has been reported that the oxidized Ag surface creates a favourable site for the adsorption of NH₃ gas [120]. Hence, AlGaIn/GaN HEMTs with Ag functionalization layer can be a potential candidate for NH₃ sensing.

The temperature plays a significant role on NH₃ sensing as dissociation of NH₃ is temperature dependent. It may be noted that NH₃ sensing over a wide temperature range has not been fully realized using AlGaIn/GaN HEMT based gas sensors. In this Chapter, low concentration (< 50 ppm) sensing of NH₃ over a wide temperature range of 30-275 °C using AlGaIn/GaN HEMT based gas sensors with Pt functionalization layer has been systematically studied. Other functionalization layers that have not been previously studied such as Pd and Ag have also been investigated. The sensing mechanism corresponding to the temperature dependent response of NH₃ has been explained in detail. The operating temperature of 275 °C was chosen in order to compare the results obtained from NO₂

sensing characteristics so that the HEMT based sensor can be potentially used for sensing both NO_2 and NH_3 .

5.2 Pt functionalization layer

5.2.1 Thickness effect

Morphology and thickness of the Pt functionalization layer play a significant role in NH_3 sensing. Usually, the gas gets dissociated on the Pt surface or directly adsorbed at the AlGaIn surface via pores in the Pt functionalization layer. The gases possessing permanent dipole moment such as NH_3 penetrates inside the Pt layer through the pores. Pt, NH_3 and AlGaIn surface form a triple-point configuration resulting in a polarized layer at the Pt/AlGaIn interface which modulates 2DEG and causes the current change [9]. Furthermore, it has been reported that NH_3 sensitivity is mainly caused due to the presence of pores in thin metal film and vanishes in the cases of thick and nonporous Pt films [121, 122]. Thus, a thin Pt functionalization layer bearing larger pores is recommended for the NH_3 molecules to reach the AlGaIn surface easily. Hence, there is a need to investigate the impact of the functionalization layer thickness on NH_3 sensing. For this purpose, AlGaIn/GaN HEMT based sensors with three different Pt functionalization layer thicknesses of 20 nm, 15 nm and 10 nm were fabricated. The response of all these sensors for 50 ppm NH_3 was

measured at RT and 275 °C, respectively and their respective sensitivities were calculated.

Fig. 5.1 shows the plot of sensitivity as a function of Pt layer thickness for 50 ppm NH_3 obtained at RT and 275 °C. At RT, while the sensors with 20 nm and 15 nm Pt layer thicknesses exhibited similar sensitivity of about 0.2 %, the sensor with 10 nm Pt layer thickness displayed an enhanced sensitivity of 0.51 %. Similarly, at a higher temperature of 275 °C, the maximum sensitivity was obtained for the sample with the Pt layer thickness of 10 nm. SEM images of 10 nm, 15 nm and 20 nm thicknesses of Pt layer are shown in Figs. 5.2 (a), (b) and (c), respectively.

Fig. 5.1 Sensitivity as a function of Pt layer thickness at RT and 275 °C for 50 ppm NH_3 .

Fig. 5.2 SEM images of Pt layer with the thickness (a) 10 nm (b) 15 nm and (c) 20 nm.

Pore size distribution for various Pt functionalization layer thicknesses was simulated using Image J software. After taking SEM images as input, a few image processing functions were performed to obtain a histogram which represents the number of pores in a sampling area. Fig. 5.3 shows the statistics of the pore size distribution for different Pt functionalization layer thicknesses. It was found that 10 nm thick Pt layer contains majority of the pores having the pore size in a range of $0.01 - 0.02 \mu\text{m}^2$ ($10 - 20 \times 10^3 \text{ nm}^2$). On the other hand, 15 nm and 20 nm thick Pt layers contain majority of the pores having the pore size in a range of $0.001 - 0.002 \mu\text{m}^2$ ($1 - 2 \times 10^3 \text{ nm}^2$) and $0.0005 - 0.001 \mu\text{m}^2$ ($0.5 - 1 \times 10^3 \text{ nm}^2$), respectively.

Thus, it is evident from the pore size distribution statistics that pore size increases with decreasing Pt thickness. The pore size increases slightly from 20 nm to 15 nm, while it is much larger in the case of 10 nm Pt thick layer. Hence, the sensor with a thin Pt layer (10 nm) having larger pores allows more NH_3 molecules to reach the AlGaIn surface resulting in the highest sensitivity among the three devices. Hence, the functionalization layer thickness was fixed as 10 nm in the investigation of the next set of NH_3 sensors studied.

Fig. 5.3 Statistics of pore size distribution of Pt layer with the thickness (a) 10 nm b) 15 nm and c) 20 nm.

5.2.2 NH₃ sensing at room temperature

The response of the Pt/AlGaIn/GaN HEMT sensor sample to less than 50 ppm NH₃ with dry N₂ as the reference gas was measured at RT. Fig. 5.4 shows the transient response at different NH₃ concentrations of 50 - 10 ppm. The current decreased when the sensor was exposed to different concentrations of NH₃ and it recovered to the steady state value when NH₃ was turned off. Hence, the sensor was able to sense the NH₃ gas and able to recover completely at RT. A sensitivity of 0.51 %, for a ΔI of 384 μ A, was obtained for 50 ppm NH₃. Sensitivity of 0.19 % with the corresponding ΔI of 143 μ A were obtained for a low NH₃ concentration of 10 ppm, which is the lowest NH₃ concentration sensed by the Pt/AlGaIn/GaN HEMT based sensor at RT. It may be noted that the sensitivity for 10 ppm NH₃ is low and a small change in the humidity can lead to a much larger effect. However, there is no reference report available related to the effects of humidity on NH₃ sensing for the

AlGaIn/GaN HEMTs. The humidity effect may or may not play a significant role. Further study is required to confirm on this issue.

The large surface area of the interdigitated electrodes enables more interaction between the adsorbed gaseous molecules and the sensor surface, enabling the sensing of low gas concentrations, similar to NO₂ sensing as described in Chapter 4, Section 4.4.2. Hence, Pt/AlGaIn/GaN HEMT with interdigitated electrodes was able to sense the lower concentration as compared to the conventional Pt/AlGaIn/GaN HEMT configuration [9].

Fig. 5.4 Transient response of the sensor at RT for different NH₃ concentrations.

5.2.3 NH₃ sensing at 275 °C

In addition to the measurements at RT, the response of the Pt/AlGa_N/Ga_N HEMT based sensor was also measured at 275 °C for concentrations less than 50 ppm NH₃. The sensor sensed and recovered to the steady state value when exposed to various concentrations of NH₃. Figure 5.5 shows the transient response of the sensor at different NH₃ concentrations of 50 - 20 ppm. Contrary to the response at RT, the current increased when the sensor was exposed to NH₃. A sensitivity of 0.83 % with the corresponding ΔI of 393 μ A was obtained for 50 ppm NH₃.

Fig. 5.5 Transient response of the sensor at 275 °C for different NH₃ concentrations.

Table 5.1 compares the key parameters of the results determined in this study with that of the Pt/AlGa_N/Ga_N Schottky and HEMT based NH₃ gas sensors reported in the literature. The sensor in this study was found to respond quickly to the change in the NH₃ concentrations. A rapid

response of less than 3 min and a recovery time of less than 6 min were obtained for all the concentrations.

Table 5.1 Comparison of Pt/AlGaIn/GaN HEMT and Schottky based NH₃ gas sensors.

T (°C)	NH ₃ (ppm)	I ₀ (mA)	S (%)	Device / Ref.
30	50	74.3	0.51	HEMT, this work
30	10	74.3	0.19	
275	50	47.5	0.83	
30	35	21.5	–	HEMT [9]
300	15	45.0	0.70	HEMT [41]
150	35	5.4×10 ⁻⁶	1307	Schottky [57]

5.2.3.1 Sensitivity as a function of concentration

The sensitivity as a function of NH₃ concentration was obtained at RT and 275 °C as shown in Fig. 5.6. It was found that the sensitivity shows a gradually increasing trend as a function of the increasing concentration of the gas at both the temperatures, as described later in section 5.2.4.1.

Fig. 5.6 Sensitivity as a function of NH₃ concentration at RT and 275 °C.

5.2.4 Temperature effect on NH₃ sensing

The temperature effect on the response of Pt/AlGaIn/GaN HEMT based sensors was investigated from 30-275 °C for 50 ppm NH₃. As shown in Fig. 5.4, the current decreased (ΔI is negative) when the sensor was exposed to different concentrations of NH₃ at RT. With further increase in the temperature, up to ~150 °C, the current continued to decrease but the relative ΔI is smaller compared to the value at RT, as plotted in Fig. 5.7. However, the current increased (ΔI is positive) with the exposure of the gas above 200 °C and ΔI shows an increasing trend with the further rise in temperature. This phenomenon of ΔI being negative at lower temperatures and positive at higher temperatures has not been reported thus far. This phenomenon is described in the next section on sensing mechanism.

Fig. 5.7 ΔI as a function of temperature for 50 ppm NH_3 .

5.2.4.1 Sensing mechanism

It has been observed that NH_3 molecules have a low rate of decomposition at temperatures below $\sim 275^\circ C$. Consequently, the gas is adsorbed in a molecular form on Pt surfaces at lower temperatures (RT) [122]. Moreover, NH_3 molecules act as an electron donor and donate free electrons at the Pt/AlGaIn interface. The donated electrons induce negative surface potential which compensates the existing positive charges on the AlGaIn surface. This results in the depletion of 2DEG causing the current reduction as shown in Fig. 5.4. Furthermore, the recovery phenomenon was observed due to the desorption of the gas

molecules, when NH_3 was turned off and dry N_2 was supplied to the chamber.

However, at elevated temperatures ($>200\text{ }^\circ\text{C}$), the probability of decomposition of NH_3 into NH_2 and hydrogen ion (H^+) is accelerated when it is exposed to the Pt layer [123]. The positively charged hydrogen ions interact capacitively with AlGaIn and diffuse via pores or grain boundaries on the Pt surface and get adsorbed at the Pt/AlGaIn interface. These ions give rise to a positive surface potential which further augments the existing positive charges on the AlGaIn surface [7]. This results to an increase in the 2DEG and causes the current increment as shown in Fig. 5.5. At RT, there is a minimal probability of decomposition of NH_3 , but the rate of decomposition seems to increase relatively with temperature. In the temperature range of 30 to $150\text{ }^\circ\text{C}$, the current decreases due to the adsorption of NH_3 molecules countering the increase in current due to the adsorption of a smaller number of dissociated ions. Hence, the change in current (negative value of ΔI) relatively reduces with the increase in temperature up to $\sim 150\text{ }^\circ\text{C}$ as shown in Fig. 5.7. However, a gradual increase in ΔI was observed as a function of temperature due to the enhanced dissociation of NH_3 into NH_2 and H^+ at higher temperatures ($>200\text{ }^\circ\text{C}$) and more adsorption of ions on the sensor surface. As shown in Fig. 5.6, the increase in the concentration results in the adsorption of a

greater number of gaseous molecules/dissociated ions giving rise to the enhancement in the sensitivity.

5.2.4.2 Activation energy

The Arrhenius plots consisting of the logarithmic of ΔI as a function of the inverse of temperature ($1000/T$) for two different temperature regions of 30 - 150 °C and 200 - 275 °C are shown in Figs. 5.8 (a) and (b), respectively. Linear fitting was performed and a straight line was obtained in each case, which demonstrates that the response is governed by a thermally stimulated process [110].

Fig. 5.8 Arrhenius plots of ΔI in the temperature range of (a) 30 - 150 °C and (b) 200 - 275 °C.

The activation energy values of -0.18 eV/molecule and 0.612 eV/molecule were obtained for NH_3 sensing for the two regions of 30 - 150 °C and 200 - 275 °C, respectively. The two values of activation energies obtained for NH_3 sensing supports the hypothesis that the mechanism is different at different temperature ranges as discussed in section 5.2.4.1. Furthermore, the negative value of the activation energy obtained at the lower temperature region of 30 - 150 °C validates the observed trend that the response decreases with the increase of temperature. It has been explained in the thesis that NH_3 gets dissociated into a hydrogen ion, which gets adsorbed and causes the current change. The activation energy of 0.81 eV was obtained for 500 ppm H_2 sensing in 200 - 300 °C

temperature range [124]. Moreover, it has been reported that the activation energy for hydrogen adsorption decreases as a function of decreasing concentration of the gas [125]. Hence, the data present in the literature supports the value obtained in this study (0.612 eV) for 50 ppm of gas.

5.3 Pd functionalization layer

In this section, low concentration (< 50 ppm) sensing of NH_3 at RT and 275 °C using AlGaIn/GaN HEMT based gas sensors with 10 nm Pd functionalization layer thickness is demonstrated.

5.3.1 NH_3 sensing at room temperature and 275 °C

The response of the Pd/AlGaIn/GaN HEMT based sensor was measured at RT and 275 °C for concentrations less than 50 ppm NH_3 . The transient response of the sensor for different NH_3 concentrations at RT and 275 °C are shown in Figs. 5.9 (a) and (b), respectively. The trend of the measured current observed during NH_3 exposure and recovery under dry N_2 at both the temperatures are the same as that of the Pt/AlGaIn/GaN HEMT based sensors. The sensitivity values of 0.12 % and 1.2 % were obtained for 50 ppm NH_3 at RT and 275 °C, respectively. The sensitivity as a function of NH_3 concentration was obtained at both the temperatures, and the results are plotted in Fig. 5.10.

Fig. 5.9 Transient response of the sensor for different NH_3 concentrations at (a) RT and (b) 275 °C.

Fig. 5.10 Sensitivity as a function of NH₃ concentration at RT and 275 °C.

5.4 Ag functionalization layer

In this section, low concentration (< 50 ppm) sensing of NH₃ at RT and 275 °C using AlGaIn/GaN HEMT based gas sensors with 10 nm thickness of Ag functionalization layer is investigated.

5.4.1 NH₃ sensing at room temperature and 275 °C

The response of the Ag/AlGaIn/GaN HEMT based sensor was measured at RT and 275 °C for concentrations less than 50 ppm NH₃. The transient response of the sensor for different NH₃ concentrations at RT and 275 °C are shown in Figs. 5.11 (a) and (b), respectively. The trend of current observed during NH₃ exposure and recovery under dry N₂ at both the

temperatures are the same as Pt/AlGaIn/GaN and Pd/AlGaIn/GaN HEMT based sensors. The sensitivity values of 0.15 % and 0.43 % were obtained for 50 ppm NH₃ at RT and 275 °C, respectively. It can be observed from all the plots that there is a change in profile at high temperature compared to RT and the high temperature response is approximately linear with time. As discussed in section 5.2.4.1, the response at RT is caused due to the adsorption of molecular NH₃, while the response at high temperature is due to the adsorption of H⁺ ions. The H⁺ ions being smaller in size can penetrate at a faster rate leading to the approximately linear response at high temperature. The sensitivity as a function of NH₃ concentration was obtained at both the temperatures and the results are plotted in Fig. 5.12.

Fig. 5.11 Transient response of the sensor for different NH₃ concentrations at (a) RT and (b) 275 °C.

Fig. 5.12 Sensitivity as a function of NH₃ concentration at RT and 275 °C.

5.5 Comparative analysis among various functionalization layers

The functionalization layer plays a significant role on the gas sensing as the sensor response depends on the interaction of the gas molecules with different functionalization layer surfaces employed. In order to investigate the impact of different functionalization layers on NH_3 sensing performance, the behaviour of various sensor metrics such as sensitivity, response and recovery times were studied for AlGaIn/GaN HEMT based sensors with Pt, Pd and Ag functionalization layers. The attractive properties of Pd and Ag functionalization layers for NH_3 gas sensing, as discussed in section 5.1 have been validated by the evaluation of its gas sensing performance.

Table 5.2 compares various parameters of AlGaIn/GaN HEMT based NH_3 gas sensors with Pt, Pd and Ag functionalization layers for 50 ppm NH_3 concentration. Response for these sensors at RT was carried out at a constant bias of 2 V. All the three sensors exhibited similar sensitivity values at RT. However, the sensor with the Pd functionalization layer exhibited higher sensitivity at 275 °C as compared to Pt and Ag sensors. At higher temperature, the mechanism of NH_3 sensing involves the decomposition of NH_3 into NH_2 and H^+ and adsorption of ions on the sensor surface. Higher hydrogen affinity of Pd results in the adsorption of

a greater number of hydrogen ions, which contributes to the enhancement in the sensitivity.

The sensor with Ag functionalization layer was found to respond quickly to the change in NH_3 concentration and demonstrated faster response and recovery times as compared to Pt and Pd sensors. Ag being the semiprecious metal has the property of getting oxidized in the environment. Oxygen, being higher electron negative than Ag, acquires the negative charge, [120] making Ag positively charged. NH_3 , being the electron donor, is more likely to interact with positively charged Ag species. Hence, the oxidized Ag surface creates a favourable site for the adsorption of NH_3 gas. After the adsorption, charge transfer occurs quickly from NH_3 to Ag, resulting in faster response and recovery times.

Table 5.2 Comparison of sensing performance of Pt, Pd and Ag functionalization layers for 50 ppm NH_3 concentration.

Function-alization layers	Sensitivity at RT (%)	Sensitivity at 275 °C (%)	Response time (min)	Recovery time (min)
Pt	0.14	0.83	3	6
Pd	0.12	1.20	8	10
Ag	0.15	0.43	3	3

5.6 Summary

AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and Pt functionalization layer were characterized for NH₃ sensing over a wide temperature range of 30 - 275 °C. The sensor was able to sense the gas when exposed to various concentrations of NH₃ and recover completely to the steady state value upon removal. While the current decreased (ΔI is negative) when the sensor was exposed to different concentrations of NH₃ at lower temperature (< 200 °C), it increased (ΔI is positive) above 200 °C. The sensing mechanisms corresponding to the temperature dependent response of NH₃ were investigated and described.

The response of the sensor was also measured with other functionalization layers such as Pd and Ag at RT and 275 °C. The behaviour of various sensor metrics such as sensitivity, response and recovery times were compared for Pt, Pd and Ag functionalization layers and respective sensing mechanisms have been explained. Hence, it can be summarized that each functionalization layer has its own unique properties and advantages. The sensors with specific functionalization layer can be used depending upon the practical requirements.

Chapter 6 Pt/AlN/GaN/AlN HEMT based gas sensor

6.1 Background

Investigations conducted on AlGaN/GaN HEMT based sensors in this study for NO₂ and NH₃ sensing have been discussed in the previous chapters. The behaviour of various sensor metrics such as sensitivity, response and recovery times were studied for a large range of concentration and a wide range of temperatures. Having studied the AlGaN/GaN HEMT based sensors, further efforts were made to investigate and propose AlN/GaN/AlN HEMT heterostructure for NO₂ and NH₃ sensing. The schematic cross section of the AlN/GaN/AlN HEMT heterostructure is shown in Fig 3.6, Chapter 3.

AlN exhibits large conduction band discontinuity (ΔE_c) and a large polarization difference with GaN. The combination of these two properties induces high 2DEG sheet carrier density in AlN/GaN heterostructures [126]. Furthermore, large ΔE_c enables tight electrostatic and quantum confinement which forms AlN buffer layer to act as the back barrier. Moreover, 2DEG with higher electron concentration and mobility can be achieved by employing a very thin AlN barrier of around 5 nm thickness [127]. Furthermore, the unstrained AlN barrier layer grown on a coherently strained GaN channel promises to improve the reliability and transport properties of these HEMTs. The energy band diagram of AlN/GaN/AlN

HEMT is shown in Fig. 6.1. The thin AlN barrier layer employed in the structure, compared to conventional AlGaN/GaN HEMT, reduces the distance between the sensor surface to the 2DEG channel that could potentially improve the sensor performance. Among the III-nitrides, the AlN/GaN heterostructure offers a large bandgap offset for GaN channel. As a result, 2DEG carrier density developed in the AlN/GaN heterojunction ($\sim 2\text{-}5 \times 10^{13} \text{ cm}^{-2}$) is expected to be higher compared to the conventional AlGaN/GaN heterojunction ($\sim 1 \times 10^{13} \text{ cm}^{-2}$) [128, 129]. The higher thermal conductivity of AlN and 4H-SiC is likely to improve heat dissipation, thus providing greater thermal stability and lesser deterioration due to self-heating for high power devices.

Fig. 6.1 Energy band diagram of AlN/GaN/AlN HEMT.

AlN/GaN/AlN HEMT based sensor with a thin AlN barrier layer has not been studied so far for gas sensing applications. Hence, an investigation of this type of sensor for NO₂ and NH₃ sensing would be an interesting study for gas sensing applications. AlN/GaN/AlN HEMTs were fabricated using the fabrication steps explained in section 3.4.2, Chapter 3. The device having 10 μm gate length was used in this study, as mentioned in section 4.6, Chapter 4. In this Chapter, low concentration sensing of NO₂ (<10 ppm) and NH₃ (<50 ppm) using AlN/GaN/AlN HEMT based sensors with Pt functionalization layer is studied at room temperature (RT) and an elevated temperature of 275 °C.

6.2 NO₂ sensing at room temperature

The response of the Pt/AlN/GaN/AlN HEMT to less than 10 ppm NO₂ was measured at RT. Fig. 6.2 shows the transient response of the sensor for different NO₂ concentrations of 10 - 4 ppm. The current decreased when the sensor was exposed to different concentrations of NO₂. However, it did not recover back completely when NO₂ was turned off. The characteristics observed during the NO₂ exposure and recovery are found to be similar to Pt/AlGaN/GaN HEMT based sensors studied in this work (Chapter 4). A sensitivity of 0.6 % was obtained for 10 ppm of NO₂.

Fig. 6.2 Transient response of the sensor at RT for different NO₂ concentrations.

6.3 NO₂ sensing at 275 °C

The transient response of the sensor was measured at an elevated temperature of 275 °C for concentrations less than 10 ppm NO₂. The sensor sensed with the decrease in current upon exposure to NO₂ and then recovered almost completely to the steady state value when NO₂ was turned off, as shown in Fig. 6.3 for various NO₂ concentrations.

Fig. 6.3 Transient response of the sensor at 275 °C for different NO₂ concentrations.

Table 6.1 compares the key parameters of the sensor studied at 275 °C with Pt/AlGa_N/Ga_N HEMT based sensor investigated in Chapter 4. A sensitivity of 0.24 % with the corresponding ΔI of 150 μ A was obtained for a low NO₂ concentration of 0.8 ppm. A sensitivity of 0.76 % with the corresponding ΔI of 472 μ A was obtained for 10 ppm NO₂, which is lower than that obtained by Pt/AlGa_N/Ga_N HEMT based sensor. However, the Pt/Al_N/Ga_N/Al_N HEMT based sensor was found to respond quickly to the change in the NO₂ concentration. There was an improvement in the response time from 56 sec to 32 sec for 10 ppm NO₂. Moreover, a recovery time of less than 5 min was obtained for all the concentrations.

Table 6.1 Comparison of key parameters of GaN HEMT based NO₂ gas sensors.

NO ₂ (ppm)	I_0 (mA)	ΔI (μ A)	Sensitivity (%)	Response time/ Recovery time (s)	Sensor
0.8	62.0	150	0.24	66/ 228	Pt/AlN/GaN/AlN HEMT
10	62.0	472	0.76	32/ 236	
0.8	33.9	924	2.72	98/ 207	Pt/AlGaN/GaN HEMT
10	33.9	1718	5.10	56/ 285	

The gas sensing mechanism, as explained in Chapter 4 for Pt/AlGaN/GaN HEMT based sensor, is expected to be similar for Pt/AlN/GaN/AlN sensor. During sensing, NO₂ molecules get dissociated into NO and negatively charged oxygen ions (O⁻). These ions get adsorbed at the Pt/AlGaN interface leading to the 2DEG variation and hence causing the current to change.

As listed in Tables 3.1 and 3.2 (Chapter 3), 2DEG sheet carrier densities in AlGaN/GaN and AlN/GaN/AlN HEMT structures are 1.27 and 3.66 $\times 10^{13}$ cm⁻², respectively. When the sensors are exposed to 10 ppm NO₂, a similar number of ions are expected to get adsorbed at the interface for both the sensors. However, 2DEG variation due to the adsorbed ions is likely to be less effective for Pt/AlN/GaN/AlN HEMT based sensors due to the higher sheet carrier density. Hence, there is a reduction in the current

change and sensitivity for Pt/AlN/GaN/AlN HEMT based sensors as compared to Pt/AlGaIn/GaN HEMT based sensors as listed in Table 6.1. However, Pt/AlN/GaN/AlN HEMT based sensors exhibit improved response time. The surface potential variation due to the interaction of gas with the sensor is the same, irrespective of thin or thick barrier. However, in the case of thin barrier (7 nm), due to the higher electric field, the electrostatic interaction between the variation in surface potential and 2DEG is much stronger which results in faster response time. This justification is based on one barrier thickness of AlN/GaN/AlN HEMT. The heterostructure growths with different barrier thickness need to be investigated for fully understanding the effect of barrier thickness on the key sensor parameters. However, there is a negative effect of using very thin AlN barrier layers. It results in higher polarization and high 2DEG density, causing a reduction in the sensitivity.

6.3.1 Sensitivity and response time as a function of NO₂ concentration

The sensitivity and response time as a function of NO₂ concentration (0.8 - 10 ppm) were obtained at 275 °C as shown in Figs. 6.4 and 6.5, respectively. As observed for Pt/AlGaIn/GaN HEMT based sensors, the sensitivity shows a gradually increasing trend as a function of the increasing concentration of the gas. The response time was found to be similar and was in the range of 64 - 68 sec for up to 2 ppm NO₂. In the low concentration range (1-2 ppm), only a minor deviation of response time is observed which may be within the measurement tolerance. Beyond this point, a sharp decrease in the response time was observed as the NO₂ concentration was increased. A rapid response time of 32 sec was achieved for 10 ppm NO₂. The decrease in response time may be attributed to the increase in adsorption rate due to the occupation of more vacant adsorption sites with higher gas concentration [108].

Fig. 6.4 Sensitivity as a function of NO₂ concentration at 275 °C.

Fig. 6.5 Response time as a function of NO₂ concentration at 275 °C.
(Curve is only for guidance to the eye).

6.4 NH₃ sensing at room temperature and 275 °C

The response of the Pt/AlN/GaN/AlN HEMT based sensor was measured at RT and 275 °C for gas concentrations less than 50 ppm of NH₃. The transient response of the sensor for different NH₃ concentrations of 50 - 20 ppm at RT and 275 °C are shown in Figs. 6.6 (a) and (b), respectively. The sensor sensed when exposed to various concentrations of NH₃ and showed recovering trend towards the steady state value. The trend of current observed during NH₃ exposure and recovery at both the temperatures is similar to that for Pt/AlGaIn/GaN HEMT based sensors. The sensitivity values of 0.08 % and 0.2 % were obtained for 50 ppm NH₃ at RT and 275 °C, respectively. The sensitivity as a function of NH₃ concentration at RT and 275 °C are shown in Fig. 6.7.

Fig. 6.6 Transient response of the sensor for different NH₃ concentrations at (a) RT and (b) 275 °C.

Fig.6.7 Sensitivity as a function of NH₃ concentration at RT and 275 °C.

Table 6.2 compares the key parameters of Pt/AlN/GaN/AlN and Pt/AlGaIn/GaN sensors for 50 ppm NH_3 . Lower sensitivity and improved response time were observed for Pt/AlN/GaN/AlN sensors compared to Pt/AlGaIn/GaN sensors. As discussed in section 6.3, 2DEG variation due to the adsorbed ions is likely to be less effective due to the higher sheet carrier density. Hence, there is a reduction in the sensitivity for Pt/AlN/GaN/AlN HEMT based sensors as compared to Pt/AlGaIn/GaN HEMT based sensors. Furthermore, Pt/AlN/GaN/AlN HEMT based sensors exhibit improved response time. The mechanism for the improved response time is same as explained in section 6.3. The obtained results are consistent with the theory explained for different device structures. Moreover, each measurement result has been confirmed with 3 to 5 devices. Hence, the probability of fabrication issues to yield an erroneous result can be ruled out. Thus, the alignment between theoretical mechanisms and experimental results indicate that the variation in response can be attributed to the differences in design only.

Table 6.2 Comparison of key parameters of GaN HEMT based NH₃ gas sensors.

Temp. (°C)	I_0 (mA)	$ \Delta I $ (μA)	Sensitivity (%)	Response time/ Recovery time (s)	Sensor
30	91.8	75	0.08	78/ 156	Pt/AlN/GaN/AlN HEMT
275	57.7	115	0.20	106/ 110	
30	74.3	384	0.51	96/ 226	Pt/AlGaN/GaN HEMT
275	47.5	393	0.83	140/ 118	

6.5 Summary

AlN/GaN/AlN HEMT based gas sensors with Pt functionalization layer were proposed and characterized for NO₂ and NH₃ sensing at RT and 275 °C. The trend of current observed during NO₂ and NH₃ exposure and recovery cycles are similar to that observed for Pt/AlGaN/GaN sensors. Lower sensitivity and improved response time were observed for Pt/AlN/GaN/AlN sensors compared to Pt/AlGaN/GaN for both NO₂ and NH₃. Thus, based on the first results obtained in this investigation, achieving a rapid response time signifies the ability of Pt/AlN/GaN/AlN HEMT based sensor to follow fast changes in gas concentrations.

Chapter 7 Conclusions and recommendations

7.1 Conclusions

This chapter summarizes the findings of systematic studies conducted for the development of GaN HEMT based gas sensors that can sense low concentrations of NO₂ (< 10 ppm) and NH₃ (< 50 ppm) over a wide range of temperatures (30 - 300 °C). The investigations include experiments carried out to evaluate the operating temperature and various sensing parameters such as sensitivity, response and recovery times. Furthermore, this study was targeted to develop a more comprehensive understanding of the sensing mechanisms due to the variation of concentrations and temperatures.

7.1.1 Pt/AlGaIn/GaN HEMT based NO₂ sensor

AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and Pt functionalization layer for NO₂ sensing were investigated. The sensors exhibited sensitivity of 1.2 % with the corresponding change in current (ΔI) of 0.5 mA for 10 ppm NO₂ at RT (30 °C), but unable to recover completely at this temperature. The sensor was heated up to 300 °C during the recovery cycle and the heating induced gas desorption has led to the recovery of the sensor. The influence of relative humidity (0 to 90%) on NO₂ sensitivity was also investigated at RT and the sensitivity has an increasing trend with the increase in relative humidity (RH). Since the

presence of RH influences the sensitivity, it should be compensated during NO₂ sensing in practical applications. The mechanisms for current decrease upon NO₂ exposure and influence of RH on NO₂ sensitivity were investigated.

It was found that the sensor sensed and recovered completely to the steady state value when exposed to various concentrations of NO₂ at the temperatures above 275 °C. Sensitivity of 1.2 % with the corresponding ΔI of 400 μ A were obtained for very low NO₂ concentration of 50 ppb, which is the lowest NO₂ concentration sensed by the Pt/AlGaIn/GaN HEMT based sensor. A high sensitivity of 5.1 % and the corresponding ΔI of 1.72 mA were achieved for 10 ppm NO₂ at 275 °C, which are higher than the reported values for Pt/AlGaIn/GaN HEMT based sensors under similar measurement conditions. A rapid response time of less than 2 min with a recovery time of less than 5 min was obtained for all the concentrations. The sensitivity and response time were obtained as a function of NO₂ concentration. It was found that the sensitivity shows a gradually increasing trend, while the response time shows a gradually decreasing trend as a function of the increasing concentration of the gas. The respective sensing mechanisms for the characteristics were illustrated.

The behaviour of various parameters such as sensitivity, response and recovery times were investigated as a function of temperature. The Arrhenius plots obtained demonstrate that the sensing mechanisms are governed by a thermally stimulated process. The values of 0.33 eV/ion and 0.64 eV/ion were obtained for response time activation energy (E_a) and recovery time activation energy (E_d), respectively. E_a and E_d are the activation energies of adsorption and desorption of O^- ions, respectively. Furthermore, the activation energy for sensitivity was calculated and the sensing mechanism was explained. Thus, Pt/AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes have been demonstrated which exhibit the enhanced sensitivity for NO_2 .

7.1.2 AlGaIn/GaN HEMT based NH_3 sensor

AlGaIn/GaN HEMT based gas sensors with interdigitated electrodes and Pt functionalization layer were characterized for NH_3 sensing. The sensor exhibited the sensitivity of 0.51 % and 0.83 % for 50 ppm NH_3 at RT and 275 °C, respectively. Sensitivity of 0.19 % was obtained for a low NH_3 concentration of 10 ppm, which is the lowest NH_3 concentration sensed by Pt/AlGaIn/GaN HEMT based sensor at RT. The sensor sensed and recovered completely to the steady state value when exposed to various concentrations of NH_3 . A rapid response of less than 3 min with a recovery time of less than 6 min was obtained for all the concentrations. The transient response of the sensors showed that the current decreased

(ΔI is negative) when the sensor was exposed to different concentrations of NH_3 at a lower temperature ($< 200\text{ }^\circ\text{C}$), while it increased (ΔI is positive) above $200\text{ }^\circ\text{C}$. At lower temperatures ($< 200\text{ }^\circ\text{C}$), NH_3 may be adsorbed in a molecular form on Pt surface and donates free electrons to induce negative potential at the Pt/AlGaIn interface leading to a decrease in the current. However, NH_3 gets dissociated into positively charged hydrogen ions (H^+) at higher temperatures ($>200\text{ }^\circ\text{C}$). This results in positive surface potential at the interface, causing an increase in the current.

Other functionalization layers that have not been previously studied such as Pd and Ag have also been investigated. The sensor with the Pd functionalization layer exhibited sensitivity of 1.2 % at $275\text{ }^\circ\text{C}$ for 50 ppm NH_3 , which is higher than that obtained using Pt and Ag. The sensor with the Ag functionalization layer was found to respond quickly to the change in NH_3 concentration and demonstrated faster response and recovery times ($< 3\text{ min}$) as compared to other sensors using Pt and Pd. The properties of Pd and Ag functionalization layers resulting in the enhanced sensing performance were investigated. The results obtained in this study demonstrate that each functionalization layer has its own unique properties and advantages. The sensors with specific functionalization layer can be used depending upon the practical requirements.

7.1.3 Pt/AlN/GaN/AlN HEMT based gas sensor

AlN/GaN/AlN HEMT based gas sensors with Pt functionalization layer were investigated for NO₂ and NH₃ sensing. This is the first time that AlN/GaN/AlN HEMT has been demonstrated as a gas sensor. The novelty comes from the device structure having 2DEG closer to the surface than the typical AlGaN/GaN HEMT. The characteristics observed during NO₂ and NH₃ exposure and recovery are found to be similar to Pt/AlGaN/GaN HEMT based sensors studied in this work. The response time as a function of NO₂ concentration was obtained at 275 °C. A rapid response time of 32 sec was achieved for 10 ppm NO₂. Thus, achieving a rapid response time signifies the ability of Pt/AlN/GaN/AlN HEMT based sensor to follow the fast changes in gas concentrations.

Lower sensitivity and improved response time were observed for Pt/AlN/GaN/AlN sensors compared to Pt/AlGaN/GaN. Since the electrostatic interaction between the variation in surface potential and 2DEG is much stronger due to the lower barrier thickness (7 nm), it results in the decreased value of response time. The 2DEG variation due to the adsorbed ions is likely to be less effective for Pt/AlN/GaN/AlN HEMT based sensors due to the higher sheet carrier density leading to the reduced sensitivity.

Thus, overall, in this thesis, GaN HEMT based gas sensors that can sense low concentrations of NO₂ and NH₃ were demonstrated. The large surface area of the interdigitated electrodes facilitates better interaction between the gas and the sensor surface resulting in the improved performance of the sensor. This study has aided in identifying the respective advantages and shortcomings of different functionalization layers for NH₃ sensing. The sensors exhibited ΔI in the range of mA and the current was found to decrease when exposed to different concentrations of NO₂ at 275 °C. Contrary to the response of NO₂, the current increased when the sensors were exposed to NH₃ and ΔI was in the range of μ A. Hence, the GaN HEMT based sensor can be potentially used for sensing both NO₂ and NH₃ at this temperature. Thus, for the first time, low concentration (<10 ppm) sensing of NO₂ was demonstrated using Pt/AlGaIn/GaN HEMT and in-depth understanding of the sensing mechanism was illustrated. Based on this study, Pt/AlGaIn/GaN HEMT based sensor with interdigitated electrodes is found to be a prospective candidate for low concentration NO₂ sensing with high sensitivity.

7.2 Recommendations for future work

This thesis focused on GaN HEMT based gas sensors for low concentrations of NO₂ and NH₃ sensing. Several optimized results have been demonstrated as part of this work. However, there are still a few aspects that are recommended to be explored further.

7.2.1 Functionalization layers

1. The technology implemented in this thesis needs to be slightly modified and can be used for sensing of other analytes besides NO_2 and NH_3 . O_2 and CO_2 sensors are needed for monitoring these gases in the breath of lung transplant patients. Furthermore, biosensors are required for the detection of various biological substances such as proteins, DNA and glucose in cells, blood or in solutions. Different materials such as Au, SnO_2 and Starch/PEI can be deposited as functionalization layers for bio-sensing, O_2 and CO_2 gas sensing, respectively.
2. ZnO nanoparticles as a functionalization layer is one of the prospective candidates for the gas sensing applications due to the favourable properties of the material such as high mobility, wide bandgap, remarkable thermal and chemical stabilities. In recent times, ZnO nanoparticles based sensors have been used to sense low gas concentrations with high sensitivity since the nanoparticles increases the effective surface area [36]. Similarly, the high surface to volume ratio and single-crystalline characteristics of the oxide nanowires enhance the sensing performance of the gas sensors [118]. Furthermore, ZnO nanoparticles prepared with a sol-gel method lowers the growth cost, and it is convenient to grow the

layer with variable porosity, thickness and grain sizes to enhance the sensing performance. Hence, the nanostructures can be grown as the functionalization layer in order to exploit the advantages of both AlGaIn/GaN HEMTs and the nanostructures.

3. Porous material has been reported as a prospective candidate for the gas sensing applications due to its large surface to volume ratio and high reactivity [130, 131]. Hence, materials such as porous Pt structures can be explored as the functionalization layer in order to further enhance the sensing performance.

7.2.2 Fine-tune epi-structure and device dimensions

1. The sensing mechanism of AlGaIn/GaN HEMT involves the interaction of gaseous molecules/ions with surface state defects that modulates 2DEG and causes current change. In order to further improve the sensing performance, the number of adsorption sites can be enhanced by surface roughening which induces surface defects and increases surface area to volume ratio [62]. Furthermore, the device dimensions can be modified to enhance the sensing performance.

2. With the optimization of epilayers using various growth condition variations, the heterostructures can be further improved. AlN/GaN/AlN HEMT heterostructure with lower sheet carrier density and thin barrier can be investigated as a gas sensor in order to achieve higher sensitivity and faster response time. The effects of varying Al composition and barrier thickness in order to optimize the 2DEG properties, can be investigated to improve the gas sensing performance.

Author's Publications

Journal publications

1. AlGaIn/GaN HEMT based high-sensitive NO₂ gas sensors.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan and N. Dharmarasu,
Japanese Journal of Applied Physics (JJAP), 2019, 58 SCCD23
2. Effects of various functionalization layers on ammonia gas sensing using AlGaIn/GaN high electron mobility transistors.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan and N. Dharmarasu,
International Journal of Nanotechnology (IJNT), 2020 (Accepted)
3. High sensing performance for low concentration of NO₂ gas using AlGaIn/GaN high electron mobility transistors.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan, N. Dharmarasu and Ravikiran Lingaparthi,
(Manuscript under preparation)

Conference proceedings

1. Pt/AlGaIn/GaN HEMT based ammonia gas sensors.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan and N. Dharmarasu,
IEEE INEC, July 3-5, 2019, Kuching, Malaysia

Conference presentations

1. AlGaIn/GaN HEMT based high-sensitive NO₂ gas sensors.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan and N. Dharmarasu,
International workshop on Nitrides Semiconductors,
Nov 12-16, 2018, Kanazawa, Japan

2. AlGa_N/Ga_N HEMT based gas sensors for harsh environments.
Akhil Ranjan, M. Agrawal, K. Radhakrishnan and N. Dharmarasu,
ICMAT, June 23-28, 2019, Singapore
3. Open-Gate AlGa_N/Ga_N HEMT Based MSM Gas Sensor Grown on Si(111) by MOCVD.
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ICMAT, June 18-23, 2017, Singapore
4. Dislocation based conduction modulation in Ga_N Schottky based MSM photodetectors grown on Si(111) by ammonia-molecular beam epitaxy.
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