Fluorinated Graphene Oxide Based Chemiresistive Gas Sensor Targeting NH_3 and Other Analytes Under Atmospheric Conditions

by

Ivan Amor

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Abstract

Emergence of graphene-derived highly functional materials has transformed chemical and biological sensing. Several novel approaches utilizing chemical modification of graphene oxide (GO) were investigated and implemented using these materials in sensor fabrication for the detection of chemical analytes such as volatile organic compounds (VOC). The detection methods rely on using functionalization of modified graphene derivatives to target select analytes and produce a quantifiable, distinguishable electrical response. In this work, an in-house hydrothermal fluorination technique to synthesize fluorinated-GO (FGO) suspension was developed. The FGO material was drop coated in its solution phase onto interdigitated electrodes to create a chemiresistive gas sensor. An ultra-low-level detection of NH_3 (~ 2.26 ppm) was observed by the chemiresistive sensor which was extended to detect acetone and distinguish between their individual transient responses. The sensor system is fully integrated and miniaturized making it suitable for point-of-care, continuous health monitoring applications in exhaled breath testing.

Co-Authorship

The content of this scientific body of work has been developed at the Organic Sensors and Devices Laboratory at Carleton university in 2019-2021. This work has produced one published conference paper, and one special issue conference paper submission (in progress).

These described FGO chemiresistive sensors were able to quantify and distinguish noticeable responses to changes in select gas concentration. The sensitivity, specificity, reliability, are all established with a low-cost synthesis fabrication process. The first conference paper describes a novel FGO chemiresistive sensor able to detect ammonia and acetone in ultra-low concentrations and its viability for point-of-care, non-invasive health monitoring. The second paper is in submission progress and pertains to the same work with a focus on the hybrid implementation of the sensor onto a custom printed circuit board (PCB) for data acquisition and production on flexible polymer substrates.

This experimental work presented in this thesis with references A and B were in collaboration with the author, research supervisor Prof. Ravi Prakash, Dr. Siziwe Bebe and Bruno Gamero at the Organic sensors and devices laboratory (OSDL) at Carleton University. The graphene material was kindly provided by Brian Kennedy from KennedyLabs. Electrode patterning was carried out by the Carleton University nanofabrication team led by Mr. Rob Vandusen, with material deposition carried out with assistance Dr. Siziwe Bebe. Development of these deposition techniques was created and carried out by Dr. Siziwe Bebe and Prof. Ravi Prakash. The readout circuit was built by the author, and Bruno Gamero. Data analysis was then performed by the author. Custom PCB design was carried out by the author with the assistance of Mr. Nagui Mikhail.

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List of Abbreviations and Symbols

Abbreviations		Symbols	
1D	One-Dimensional	Φ_{bn}	Height of I-layer
2D	Two-Dimensional	Φ_m	Metal Semiconductor Barrier Height
BZ	Brouillin Zone	Φ_{bn}	Barrier Height of the Metal-Semiconductor Interace
CAD	Computer Aided Design	$\Delta\Phi$	Total Energy Barrier Height
CFGO	Chemically Fluorinated Graphene Oxide	Φ_0	Activation Energy Level of Fermi-level to Conduction Band
CH	Carbon-Hydrogen Bond	Δ	Potential Across the Interface
CO	Carbon Monoxide	ε	Minimum Tensile Strain
CP	Conductive Polymer	$\Delta L/L$	Normalized Material Change of Length
CVD	Chemical Vapour Deposition	C_2H_5OH	Ethanol
DA	Dopamine	C_{cell}	Cell Capacitance
DC	Direct Current	C_{DL}	Double Layer Capacitance
DFT	Density Functional Theory	CH_4	Methane
DI	De-Ionized	D_s	Density of Interface States
DIP	Dual In-line Package	$[e]_S$	Electron Concentration
DLD	Delay Line Detector	E_F	Fermi-level Energy
DOS	Density of States	$E(k)$	Low Energy Spectrum Representation in Graphene
FET	Field Effect Transistor	G	Electrode Overlap Gap
FGO	Fluorinated Graphene Oxide	H_2	Hydrogen
FGO30	30% Fluorinated Graphene Oxide	H_2O	Water
FGO49	49% Fluorinated Graphene Oxide	H_2S	Hydrogen Sulfide
FTIR	Fourier Transform Infrared Spectroscopy	i	Current
GO	Graphene Oxide	I_O	Output Current
rGO	Reduced Graphene Oxide	K	Dirac Point
HC	Hydrocarbon	δ_*	Neighbouring Vectors in Graphene
HF	Hydrofluoric Acid	K_C	Cell Constant
IC	Integrated Circuit	L_D	Debye length
IDE	Interdigitated Electrode	N_2	Nitrogen
I-layer	Interface Sensing Layer	NADH	Nicotinamide Adenine Dinucleotide
IPA	Isopropyl Alcohol	N_d	Carrier Concentration
IR	Infrared	NH_3	Ammonia
KBr	Potassium Bromide	NH_4^+	Ionized Ammonia
MEFS	Metal-Embedding Flexible Substrate	NO_x	Nitric Oxide
MIF	Metal Ion Free Developper	NO_2	Nitrogen Dioxide
MIP	Molecularly Imprinted Polymer	O	Oxygen
MOX	Metal Oxide sensor	O_2	Oxygen (gaseous form)
O	Oxygen	Q_{sc}	Space Charge Density of the Semiconductor
PCB	Printed Circuit Board	Q_m	Space Charge Density of the Metal
PEDDOT	Poly(3,4-ethylenedioxythiophene)	ρ	Resistivity
PMMA	Poly(methy methacrylate)	ΔR_g	Resistance Change Due To Presence of Target analyte
POC	Point-of-Care	$ \Delta R/R (\%)$	Normalized Resistance Change in percentage
PSS	poly(4-styrenesulfonic acid)	R_s	Resistance
PSS2	2nd sample of poly(4-styrenesulfonic acid)	R_L	Lead Resistance
PSS3	3rd sample of poly(4-styrenesulfonic acid)	R_O	Initial Resistance
pSi	Passivated Silicon Substrate	R_{sol}	Resistance of the Solution
PTFE	Polytetrafluoroethylene	R_{sat}	Resistance at Saturation
PVA	Polyvinyl Alcohol	R_{Tot}	Total Resistance
QHE	Quantum Hall Effect	Ω	Resistance in Ohms
SAW	Surface Acoustic Wave	S/cm	Conductivity, Siemens per centimetre
SdHOs	Shubnikov-de Haas oscillations	SO_2	Sulfur Dioxide
SEM	Scanning Electron Microscope	V_b	Built-in Voltage
SMO	Semiconductor Metal Oxide	ϕ	Electrostatic Potential
SMU	Source Monitoring Unit	∇	Del/Gradient Operator
SPI	Serial Programming Interface	V_2O_5	Vanadium(V) oxide
SS	Silicon Substrate	V_s	Voltage
UA	Uric Acid	V_g	Gate Voltage
UV	Ultraviolet	σ_{xy}	Hall Conductivity
VOC	Volatile Organic Compound	ρ_{xx}	Resistivity
W	Width	V_O	Output Voltage
XPS	X-ray photoelectron spectroscopy	WO_3	Tungsten Trioxide
		x	Semiconductor Electron Affinity

Chapter 1: Introduction

Gas sensing devices are crucial sensors that identify and monitor the presence of certain volatile gaseous analytes. Applications for these sensors primarily include detection of toxic gases, vehicle emissions, and breath analysis for medical health monitoring. These devices employ a miniature, solid-state architecture that rely on interface to gas interaction, whose chemical and electronic properties change and can be measured and quantified electronically. A chemiresistor consists of a material deposited on top of parallel electrodes that change electrical properties due to exposure to atmospheric presence of interactive analytes. Chemical interaction between the top sensing layer and gaseous analytes adsorbed onto the surface can be quantified by measuring the electrical resistance on the electrodes that are addressed [1].

These sensors have been widely adopted to detect harmful, toxic gases within the atmosphere. The sensing layer on a chemiresistor is deposited on top of two electrodes, or an interdigitated electrode array (IDE) and the resistance is then measured. The resistance of the sensing material modulates proportionally to the exposure to a certain targeted analyte. The interactions between the target analyte and the sensing surface can indicate the presence of the target molecule and in addition has the capabilities to identify the specific concentration of the analyte within the atmosphere based on the distinct changes in conductivity. Working characteristics of a chemiresistor are adopted from general chemical sensors which include a receptor and transducer element. The receptor element is the segment where the reaction occurs thus modifying the chemical and electrical properties of the layer. These chemical properties then can be measured by the transducer element that converts the energy and transports it to the electrode underneath that provides

a quantifiable electrical signal [2]. Chemiresistive sensors have also been deployed for environmental sensing and medical point of care applications due to their high selectivity, sensitivity, small footprint, low operating temperatures, and ease of fabrication.

Figure 1. Principle operation of a chemical/biosensor

Some materials that have chemiresistive properties are metal-oxide (MOx) semiconductors, conductive polymers (CP), nanomaterials and nanostructures such as graphene and carbon nanotubes (CNTs) [3].

1.1 History

In the late 1960s, there have been reports of semiconductor materials changing conductivity based on exposure to the atmosphere realized in the form of olfactory transduction. Rosenberg et. al discovered that the interaction energy between a certain odorous molecule and the sensing layer must be weak, representing a minimal value of the product of Boltzmann's constant and temperature (kT) that allows rapid change in signal when the material is exposed to a different molecule [4]. The weak interaction would produce a distinguishable effect on the sensing layer due to the number of molecules adsorbed. Chemical interactions were attributed electronically to the change in conductivity due to

the increase of the charge density carriers in the membrane of the sensing material. These effects were first realized to produce a distinct change in signal in relation to exposure to an olfactory molecule.

The first commercialized chemiresistive sensor in 1970 incorporated a MOx sensing layer for carbon monoxide, combustible gas, and other toxic gas detection applications [5]. The research around these sensors has grown exponentially due to their solid-state nature and the choice of materials such as polymers and organic films. Various material parameters such as film geometries, thicknesses, and microstructure configurations have been produced to investigate improvements on specificity where they are inherently sensitive to reducing gases. Many discrete thick-film sensors have been deployed since the 1990s for industrial applications such as medical, automotive, and environmental air quality monitoring. Sensors from the Capteur product line provided accurate sensitivity and selectivity on a combination of metal oxides as opposed to single composition metal oxides to detect ammonia, hydrogen, carbon monoxide and other reducing gases [6]. Electronic nose chemiresistive sensors have been commercially available throughout the 1990s, however their expensive prices and complex miniature footprint restricted them to be deployed as a compact, convenient chemical sensing option [7].

By the 2000s more commonly examined properties of the MOx chemiresistor, moreover for tin and zinc-oxide, have been investigated for sensitivity and selectivity for small footprint microsystems as the material can be tuned to focus on these parameters [5].

Currently the development of semiconductive sensing materials have led to innovations in materials processing. Emerging technologies can dictate the drastic changes

in sensor design and capabilities in terms of smaller footprint with high sensitivity and specificity in sensor design [8].

1.2 Types of Gas Sensors

Gas sensors can be used to observe different properties of specific targeted gases [9]. A wide variety of materials such as MO_x, CPs and CNTs are used for gas sensing applications. MO_x requires higher operating temperatures to yield higher sensitivities but lack selectivity and have large power requirements. The ability to operate at room temperature, and to incorporate conducting polymers into sensing devices is limited by material degradation [10]. CNTs may operate at room temperature and have high sensitivity, but long recovery time and the intricacy of processing and fabrication techniques put them at a disadvantage.

A comparison between these sensors can be demonstrated in the following table:

Table 1. Comparison of gas sensing technologies [8]

Type	Electrochemical	Optical	Chemiresistive
Cost	Low	High	Low
Lifetime	Short	Long	Long
Sensitivity	High	High	High
Selectivity	Good	Excellent	Poor
Response time	Quick	Quick	Quick
Footprint	Medium	Large	Small

The comparison between the three major gas sensing technologies and its parameters: electrochemical, optical, and chemiresistive are compared in Table 1. The electrochemical sensor has been the standard in the gas sensing domain as it has been

extensively researched and implemented. However, their short lifetime and high temperature requirements are a major limitation. Optical sensors have optimal sensitivity, selectivity, and shelf-life however, they are costly and require a larger footprint. Chemiresistors generally have lower selectivity compared to the other sensors but are low cost and easy to fabricate which are major contributors to their widespread adoption [8]. The ability to modify the sensing layer properties to focus on a specific target analyte gives chemiresistors another advantage and ability to compensate for poor selectivity.

Table 2. Types of Electronic Gas Sensors

Sensor	Diagram	Features
Metal oxide semiconductive sensor (MOx)	<p>Diagram of layer-by-layer composition for a MOx device from an Au-loaded In₂O₃ sensor. [11]</p>	<ul style="list-style-type: none"> • High sensitivity, • Response at elevated temperatures of 150-400°C.
Electrochemical Sensors	<p>Diagram of an electrochemical sensor. [12]</p>	<ul style="list-style-type: none"> • High sensitivity, • Low power consumption, • Small footprint, • Specificity towards analytes.
Chemiresistive Sensors	<p>Diagram of a Chemiresistive gas sensor.</p>	<p>Parameters dependent on the electronic change in the sensing layer:</p> <ul style="list-style-type: none"> • Sensitivity, • Responsiveness, • Specificity

1.2.1 Field-Effect Transistors (FET) Sensors

FET sensors are a type of commonly found gas-sensing device. It is a simple, cost-effective device due to its simple fabrication process, its portability and sensitivity. A FET sensor consists of a semiconductor with a sensing channel material and two metal electrodes served as the source and drain. Different gate biases control the channel conductance and can be modulated [13]. Gas detection is realized by the change in drain current before and after gas exposure. The electronic structure of the sensing material will change due to the adsorption of gas molecules onto the surface and, hence changing its conductance [14]. Different gases such as: CO, NO, NH₃, NO₂, SO₂, H₂, are the many types of gas analytes that can be targeted.

The operating principle features the interaction of oxygen atoms that are adsorbed onto the surface sensing material which either permits or restricts current flow based on the interaction. The presence of reducing gases lowers the surface density of adsorbed oxygen and permits current flow within the material. These devices typically operate at elevated temperatures where oxygen adsorption on the surface is enhanced by the acquisition of free electrons. The depletion layer dictates sensitivity as it encapsulates the semiconductor material. The higher the depletion region can extend around the area of each particle, the higher the achieved sensitivity would be if the region encloses the target particles. The energy band structure is represented by a distribution of conduction band electrons for a semiconductor with increased adsorbed oxygen molecules. The surface electron concentration $[e]_s$, and the resistance change from steady state can be derived [15]:

$$[e]_S = N_d e^{\left(-\frac{1}{6} \left(\frac{a}{L_D}\right)^2 - p\right)} \quad (1)$$

where L_D is the Debye length, N_d is the carrier concentration, a is normalized with respect to L_D , and p is dependent on the exposed gas.

FET gas sensors channel current changes proportional to the gate material modulation due to a change in adsorbed oxygen concentration. Adsorbed oxygen present in ambient conditions will be trapped resulting in carbon monoxide (CO) and results in a decrease in R and correlates to the concentration. This detection method is commonly found in tin dioxide-based materials (TiO_2).

1.2.2 Impedance Sensors

The impedance sensor is a mixed potential sensor and determines the impedance change in which a sinusoidal voltage is applied, and the current is measured to calculate the impedance in the frequency domain [16]. This sensor uses solid-state impedance spectroscopy to measure the response over certain frequencies from kilohertz to gigahertz.

The sensitivity of this sensor can range from the parts per million to higher concentrations. The design features sensing electrodes which are usually comprised of a noble metal, a metal oxide and layered materials and does not require a reference electrode for air. Impedance sensors have been used for detecting small concentrations of various gases such as hydrocarbons, NO_x , CO, and humidity [17].

1.2.3 Optical Sensor

Optical gas sensors provide another method to detect specific analytes by analyzing the infrared (IR) or spectrum close to IR by detecting vibrational or rotational atomic transitions [18]. Determining the presence of gases is conducted by the sensing of optical

fibres that transmit an input beam and await feedback information from a gas cell to a detector.

Chemical species possess strong absorption in the Ultraviolet (UV) and IR spectrums and these absorption lines show specificity towards certain analytes. Optical gas detection is based on the Beer-Lambert law [19]:

$$I = I_0 e^{(-\alpha l)} \quad (2)$$

Where I is the light transmitted through the gas cell, I_0 is the incident light applied on the cell, α is the absorption coefficient of the sample, and l is the optical pathlength. The absorption coefficient is the product of the gas concentration and the specific absorptivity of gas ϵ [20]. Optical detectors do not need to output a beam by gratings or prisms but determine specific gas selectivity deriving information from the molecule at a specific wavelength [18].

1.2.4 Heterojunction Sensors

These novel gas sensors attempt to improve some of the disadvantages of a single material type gas sensor. The heterojunction consists of both p-type and n-type semiconducting material, and thus can be enhanced through the reactions at the interface of two components. Example target gases that have been detected by heterojunction sensors are O_2 , H_2 , H_2O , NO_2 , and C_2H_5OH [21]. When gases are adsorbed onto its surface, the structure of the interface is change and thus modifies the charge-transfer attributes. This then affects the current flow characteristics across a current rectifying heterojunction [22].

1.2.5 Surface Acoustic Wave Sensors

Surface acoustic wave (SAW) sensors as small gas sensors provide high sensitivity and low cost by detecting the change in amplitude, frequency and velocity of a surface acoustic

wave induced at the input transducer. The changes of physical and/or chemical properties are introduced by the reaction between sensing materials and gas molecules, this then affects the acoustic wave profile. The SAW gas sensing mechanism relies on the material interaction with adsorbed gas as it modulates the amplitude of the output waves. Selectivity of these sensors depend on the property enhancements that can modify chemical parameters [23].

1.3 Sensing Materials

Chemiresistive and electro-chemical (polymer) sensors provide optimal sensitivity, short response times and are low cost but are limited to their poor selectivity. Other sensing materials such as CNTs can also be used due to their high adsorption capacity, high surface to volume ratio and greater sensitivity. However, their limitations include their high cost and complicated fabrication processes [26].

Electrochemical MOx sensors require fewer environmental constraints where they can operate in ambient temperatures due to their intrinsic, thick-film composition, that can be modified to fit the sensing needs along with a heating element to elevate operational temperatures. This allows for the ability to control the sensing element composition and tune it for unique materials and stimulates specific catalytic reactions [27]. MOx sensors with cross-sensitivity properties can be achieved with recent advancements in the material composition. New improvements like a three-array sensor deposited on a ceramic heater, prove to have the system embedded onto a single monolithic package and thus demonstrating a smaller footprint for data acquisition purposes [28]. The electrical conductivity of these sensing materials is sensitive to the presence of gas particulates which are adsorbed onto the surface, catalyzing a reaction [29]. These transition metal oxides

have d_0 and d_{10} orbital configurations and allow for the gas sensing mechanism to be formed on metal oxides such as V_2O_5 , WO_3 , TiO_2 , and d_{10} formulates on transition metals such as ZnO and SnO_2 [30]. In general, n-type metal oxide semiconductors possess properties such as: chemical stability, modifiable transport characteristics, and large excitation binding energy. The difference between n-type and p-type films is that the n-type sensitivity can be increased with reducing gases while the p-type decreases upon exposure. So, p-type sensors have lower working temperatures than n-type sensors [31]. N-type oxide semiconductive surfaces are used up to 90% more due to their higher charge mobility than those of a p-type sensor [28].

CPs are highly interactive materials when exposed to gas. Changes in conductivity can be identified to be multiple orders of magnitude higher when exposed to a target analyte when compared to its initial state [32]. Conductivity is not present in the initial state, but it was observed that charge carriers form under oxidizing, p-type doping, or reducing, n-type doping. This change in charge carriers can be observed by the change in electrical and optical properties regarding the doping concentrations in the polymer [33, 34].

1.4 Gas Sensing Mechanisms

The main sensing mechanism in gas sensors relies on two major functions- the receptor and transducer as stated previously. A shift in the state of equilibrium occurs due to the presence of targeted analytes and creates the surface oxygen on the sensing element.

Table 3. Resistance changes for different material under the presence of gas in n-type and p-type materials. [35]

Material	Reducing Gas	Oxidizing Gas
n-type	Decrease in Resistance	Increase in Resistance
p-type	Increase in Resistance	Decrease in Resistance

More commonly used materials for MOx: such as TiO₂, ZnO, SnO₂ have a band gap of 2-4 eV, have more donor electrons in the conduction band and exhibit n-type semiconductive behaviour. Other materials such as NiO, CuO act as p-type sensors [36].

The chemical reaction formula for an n-type material is:

Where O₂⁻surface is the oxygen surface boundary and e⁻bulk are the electrons in the substrate. The response for oxidizing gases is the opposite. The resistance changes proportionally in the presence of increasing oxidizing or reducing gases according to Table 2. The sensitivity can be determined by ΔR, measuring the initial resistance under ambient conditions R₀, and the change in resistance R after exposure to the targeted analyte. Using a 2D (two-dimensional) material such as graphene as a semiconductor shows to be ambipolar and can be either p or n-type material based on an induced external electrostatic potential or chemical doping [37]. Therefore, it can be used to specifically target either oxidizing or reducing analytes based on its distinct interaction.

1.5 Motivation

Chemiresistive gas sensors demonstrate excellent properties in terms of sensitivity and selectivity. This makes them ideal candidates for non-invasive health monitoring. The market for small footprint, low-cost health monitoring devices is continuously evolving. Devices that provide ‘real-time’ instant feedback, with optimal sensor properties are highly regarded and ideal for point-of-care or wearable applications. The ability to track and record a subject’s condition without having to be present is also an added benefit. Different

algorithms and processing techniques can be employed to enhance and evaluate more specific data pertaining to a subject's health and can outline any underlying conditions.

The interest surrounding targeting VOCs such as high impact markers like ammonia and acetone, allows for specific physiological condition monitoring. Commercial sensors exist for detecting ammonia in ranges above 10 ppm, however they are not adequately sensitive for healthcare centric applications. Clinical studies showed that the presence of ammonia in exhaled breath samples indicates pathological conditions pertaining to kidney and liver diseases [38]. Pre-dialysis conditions exhibit ammonia concentration ranges in exhaled breath to be 1.5-2 ppm [39, 40]. Acetone is also crucial for monitoring conditions such as diabetes. Studies have shown that persons with diabetes would exhibit acetone concentrations of > 1.8 ppm in exhaled breath [41]. This puts an emphasis on highly sensitive gas sensing devices in ultra-low concentrations to characterize and target vital gaseous analytes in exhaled breath.

1.6 Thesis Organization

This work is focused on extending the application to a near market ready, small footprint device fabricated using low-cost techniques. Graphene oxide functionalization is performed using a commercial and in-house synthesis fluorination methods. Sensor implementation with a custom circuit board design is carried out to observe the viability of incorporating them in compact prototype configurations on inert flexible polymers for point of care applications.

The organization of this thesis is outlined below. A comprehensive literature review on the notion of targeted gas sensing is presented in Chapter 2. Existing research on chemiresistive gas sensors is discussed here, detailing the prevalent sensing techniques

with different materials and the obstacles in configuration and implementation for specific gas sensing. In Chapter 3, the idea behind the selection of graphene and its derivative GO, is examined based on their electronic properties, and the ability to have the chemical affinity of GO tuned toward NH_3 and ketones by fluorination. The IDE design criteria and response are also investigated. Chapter 4 describes the overall experimental approach and setup. Material synthesis, novel device fabrication, and custom circuit board design are discussed. The setup for both ideal and low concentrations is described, and the testing methodology for both conditions is explored. Chapter 5 presents the results obtained for the FGO based chemiresistive sensors. The conductivity data for the sensors using novel materials, gas sensing metrics upon exposure to ambient, burst, and ultra-low concentrations of NH_3 , and the response of the sensor when exposed to ketones such as acetone are all delineated. The conclusion and future work discuss the overall outcomes from this project and further outlook towards the integration of these devices for a point of care system. Finally, the appendix provides the design overview for the custom board components.

Chapter 2: Literature Review

Gas sensors have been investigated throughout the research community and many advances have been made towards improving responsiveness, selectivity, and sensitivity through modifications, primarily of the sensing layer. Improving the sensor composition focuses on fabrication techniques that incorporate novel materials. These material improvements will be used to modify chemical and electrical properties and augment the sensing mechanism.

Chemiresistive sensors have been deployed as gas sensors that feature a top layer sensing element which interacts with a targeted analyte. The top film polymer conductive properties would change upon exposure to a specific gas and thus producing a change in electrical resistance. Motivation behind research of these gas sensing devices is for use in environmental monitoring, food processing, and medical diagnosis applications [42, 43, 44]. Among these applications, detecting medical diseases using techniques such as exhaled breath analysis has garnered much attention due to its non-invasive nature and real-time feedback [45, 46]. Human breath contains many trace particulates such as, oxygen, nitrogen, carbon dioxide, and ammonia to name a few. These ultra low concentration ranges feature in the ppb to the hundreds of ppm range [47].

Previous works focusing on use of chemiresistors demonstrate the benefit of sensing a targeted analyte within the environment due to the ability to configure layer properties of the sensor. Common materials featured on chemiresistive sensors are MOx, CNTs, and CPs. These materials all have unique optimal sensing properties but come with trade-offs associated with high temperature requirements, complex and expensive fabrication methods, and poor selectivity [48, 49]. Graphene-based chemiresistors offer

versatile performance stemming from graphene thick 2D composition, high surface-to-volume ratio, and augmented carrier mobility. Adsorption of targeted gas on graphene produces a noticeable change in the electrical conductivity [50].

2.1 Chemiresistor Device Architecture

Chemiresistive gas sensing devices are fabricated by coating an IDE structure with a top-thin film that acts as the sensing layer. These thin films are used to bridge the gap between two electrodes. The conductivity of the film provides a channel for the electrons to flow, and a change in conductivity can be realized due to the change in electronic properties of the sensing layer when interacting with targeted gas molecules [51].

IDEs are ideal for gas sensing applications due to its linearity when biased at steady state, sensitivity, low-cost production, and high surface to volume ratio [52]. Chemiresistive gas sensors consist of inorganic substrate materials with metal IDEs that are patterned on an interface between the sensing layer and the production of electrical signal due to their high integrity and conductivity. IDEs provide a maximum functional area of contact between the sensing layer and then output an electrical signal [53]. Types of IDE sensors are mechanical and chemical structures that react to a change in influencing conditions such as force, or environmental concentrations. Carbon based electrodes are great alternatives to metal electrodes and can offer a low-cost solution for fabricating IDE devices on flexible polymer substrates. Their excellent electrical properties such as capacity, energy, and power density have put them at the forefront of organic energy storage systems [54]. Together with their electrochemical performance they are great candidates to be incorporated in organic sensors.

IDE Chemical sensors can be represented by two categories: capacitive and resistive sensors. Capacitive sensors consist of a dielectric material that senses the change in capacitance from interaction. Resistive chemical sensors detect the change in electrical properties of the sensing layer resulting in a change in resistance when exposed to a target analyte. The current flow within the material when biased at a certain voltage, changes the conductivity of the material when exposed to different concentrations of the targeted analyte. The electrodes are arranged in a serpentine structure which take advantage of the large gap such that the electrodes can be modelled as resistors in parallel. Figure 2 shows a common design of an IDE structure where the top sensing film will react and demonstrate this phenomenon.

Figure 2. Interdigitated electrode structure.

Dimensions of the IDE structures dictate the sensing operation of the device. A large gap between electrode corners do not contribute to the sensor performance. But since this is the path of least resistance for current flow, most of the current will be found in this area. Therefore, optimization of the overlap gap G , between electrodes must be optimized to output an accurate reading [53]. Optimization of the serpentine electrode structure can

be expressed as a fraction of the electrode gap thickness over the sum of the gap and electrode thicknesses. It was observed that to achieve maximum efficiency, electrode fingers can be lengthened and overlap gap will increase [53].

2.2 IDE Fabrication Techniques

IDEs consisting of these serpentine electrodes can be fabricated on a semiconductor or an insulating substrate such as Silicon Dioxide (SiO_2) or pSi. The insulating layer can be grown hydrothermally to prevent an electrical connection between the sensing material and the substrate. The electrodes can be patterned onto the substrate by depositing metal such as chromium, gold, or aluminum to create the conductive structure.

Figure 3. Process flow of IDE fabrication through conventional photolithography. Reproduced from [52].

Sputtering is a physical vapor deposition (PVD) method where the target material is ejected and deposited onto a substrate. Two common forms of sputtering are direct current magnetron sputtering and electron beam evaporation. Direct current magnetron sputtering features an ionized gas to inject an influx of atoms onto a target (source) material to be sputtered off onto the substrate [55]. Electron beam sputtering transforms target material into a gaseous state.

Photolithography is also used to pattern IDEs onto a substrate. It uses photoactive polymer materials and specific UV wavelength that produces a patterned material layer [56]. Wet etching and lift-off are the more common patterning methods that are used. Photomasks are used to achieve the exact electrode pattern. Drawbacks show that the wet-etching process takes longer to produce, is lower resolution and compromises edge integrity. But the benefits include longer shelf-life in repeated processes, better photo-masking and are cost effective [57]. Lift-off does however offer fewer fabrication steps with a single lift off to pattern. Residues that are more difficult to remove become easier to extract in the absence of the etching step [58].

Inkjet printing is an additive fabrication process that has been used as an alternative method for low-cost devices. The ability to produce micro-patterns on flexible substrates, such as polymers are ideal for disposable electronics. Ink-jet printing allows for drop-on-demand fabrication which drops a precise amount of solution-based material to be fabricated onto the substrate [55].

2.3 Substrate Conductivity

Chemiresistors can be deployed on various substrates. They are more commonly found on regular silicon substrates for typical IC fabrication and for ease of system-level integration.

But for applications such as wearable or disposable electronics, they are fabricated on inert polymer substrates that are inherently non-conductive. Flexible electrodes printed on polymer requires high electrical conductivity along with mechanical robustness. Therefore, a thin-film coating of a conductive material will aid in decreasing the sheet resistance of the material and augments its conductivity.

Flexible devices require durable properties under twisting, folding, and stretching conditions. The minimum tensile strain (ϵ) where it is defined as $\Delta L/L$ where ΔL is the change in material length over the initial length, is required to be at least 10%. The demand of wearable organic devices such as solar cells, thin film transistors, and flexible touch sensors benefit from being on a strong conductive material [59, 60].

Improving the conductivity of electrodes on flexible inert substrates can be done by incorporating metal grids on an organic substrate with thermal evaporation or a shadow mask seen on organic solar cells [61]. However, thicknesses are limited due to the organic layer underneath being extremely thin and thereby potentially causing a short circuit between the metal grids and the layer. Moreover, a costly and complex method of adding an intermediate insulating layer can prevent this discrepancy [62]. An innovative process of fabricating electrodes was investigated by metal-embedding flexible substrate (MEFS) and has been closely looked at in recent literature. The process involves trench-like patterns and is removed by chemical-mechanical polishing, but it proved to be expensive [63, 43]. Jung et al. reported a method to overcome adding an insulating layer by using a combination of metal-embedding into the flexible plastic substrate and ultrathin transparent electrodes leading to high optical transmittance of 93% at 550 nm, high conductivity at $13 \Omega/\square$, and a flexible bending radius of $\sim 200 \mu\text{m}$. This fabrication method proved to perform

like devices fabricated on a glass substrate and did not demonstrate any degradation at maximum material strain [64].

CPs such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on rigid metal oxides have played a critical role in creating electrode property enhancements on transparent substrates, with augmented hole transport layers, and electroactive layers [65]. PEDOT:PSS is an optimal candidate as a CP because of its tuneable electrical conductivity, work function, and flexibility. It is widely adopted in the fabrication of numerous devices such as photovoltaics (PVs), displays, organic transistors and bio sensors [66, 67, 68]. These CPs have great attributes such as uniformity and roughness <2.0 nm regardless of the underlying substrate being plastic or glass. This has enabled a monolayer interface that is easily applicable for transistor applications that no other material could achieve [65]. Pristine PEDOT:PSS typically has a direct current (DC) conductivity (σ) of no more than 1.0 S/cm [69], but when modified, these films can achieve values up to 4000 S/cm through doping of strong acids, and ionic liquids [70, 71]. CP films also have typical work functions of 4.8-5.4 eV that is ideal for enhanced charge transfer and injection with fast kinetics, these films are preferably used in optoelectronics as a p-type contact layer [65].

2.4 Chemiresistive Material Layers for Gas Sensing

The novelty attributed to a chemiresistor is its sensing layer. The sensing layer interacts with the target analyte and goes through a chemical reaction where the electronic properties are modified and can be observed and characterized. Different materials would provide optimal sensor characteristics based on the sensing application.

CPs as a 3D organic micro and nanostructure are sensing layers that are typically employed in electronic nose arrays. The polymer would incorporate a template and interact with a target analyte and change conductivity. The sensor arrays are simple to fabricate however its high cost makes them harder to implement [72]. The use of CPs in chemical and biosensors is used due to its intrinsic affinity towards acidic or basic species that catalyze redox reactions [32]. Interaction specificity can be tuned by modifying receptor sites on the polymer and provide high signal amplification compared to single molecular monomer receptors [73]. Sensor response using conductometric techniques is the most common method of transduction for chemo- and bio sensors due to the small interactions that cause a chain reaction in the CP wire. These can then be setup in sensor configurations and combined into multiple sensing arrays that would provide optimal sensitivity [74, 32]. The disadvantage of this sensor is that selectivity is limited due to it being highly interactive. The CP would interact with exposed impurities and conductivity would change. To increase selectivity on the CP, a molecular imprint (MIP) can be employed to enhance response, and this creates the active site vacancy in a CP needed where the specific targeted analyte would be trapped and consequently enhancing molecular interaction [75].

A 1D composite layer such as CNTs possess excellent properties due to the interaction of the nanotubes with functional (carboxyl and ammino groups), metallic nanoparticles and polymers that allow them to be robust active chemical sensors [76]. However, their high cost- and complex fabrication process makes them difficult to employ as widely adopted sensors.

Figure 4. Working principle of nanomaterial-based sensor arrays. Chemiresistors with a) monolayer-capped particles, b) single-wall carbon nanotubes, c) conducting polymers, d) metal oxide film. [77]

A MOx layer on top of an interdigitated structure in the presence of gas is enhanced by a chemical adsorption of oxygen ions in the air and creates surface acceptor sites (O^- , O^{2-} , O_2^-) [78]. A heating element is implemented to catalyze these reactions at higher temperatures. The surface then traps the targeted molecules, and hence the n-depletion region increases. Oxidation and reduction happen at the surface of the thin film of the sensor and thereby modifying the electrical resistance by changing its conductivity [48].

The barrier between the metal and semiconductor is the main feature of the interaction between the semiconductive sensing layer and the electrodes (I-layer). The I-layer properties influence the built-in potential voltage V_b and the barrier height Φ_{bn} [79].

The energy band diagram is modified when a metal makes contact with the semiconductive layer. The contact area, and an increased barrier height from the semiconductor material to the metal electrodes results in lower conductivity [80]. The Schottkey junction, is represented by the metal semiconductor barrier Φ_m , Φ_{bn} is the barrier height of the metal-semiconductor interface, $\Delta\Phi$ is the added energy from the barrier height to promote electrons to the conduction band, Φ_0 is the total activation energy from the fermi-level and the conduction band from Φ_{bn} and $\Delta\Phi$, V_b is the built in potential, Δ is the

potential across the interface, and x is the electron affinity of the semiconductor, Q_{sc} and Q_m are the space charge densities of the semiconductor and metal respectively [81].

In ideal cases, the barrier height on the metal semiconductor work functions Φ_m , should be greater than the electron affinity x of the semiconductor, and for a p-type it should be less. More holes will be present in the valence band and can be represented as:

$$\Phi_{bn} = \Phi_m - x \quad (4)$$

But in practical situations the interference between the metal semiconductor is due to the surface from other states [81], metal induced gap states [82], and due to the interface of chemical reactions between metal and semiconductor atoms [83]. Cowley and Sze formulated an approximation for the barrier height [82]:

$$\Phi_{bn} = \gamma(\Phi_M - x) + (1 - \gamma)(E_g - \Phi_0) - \Delta\Phi \quad (5)$$

where,

$$\gamma = \varepsilon_i(\varepsilon + e^2 x_m D_s) \quad (6)$$

Where x_m is the thickness of the I layer, and D_s is the density of interface states. But when $D_s = 0$ it is relatively the same as the ideal case in Equation 4.

The surface of the semiconducting metal oxide adsorbs the gas molecule and reduces the potential barrier by promoting electrons to the conduction band and promotes the flow of electrons and carrier mobility [84]. When reducing gases interact with the surface, the ion and charge replenishment of the charge carrier density occurs in the conduction band [85]. And when oxidizing gases interact with the surface, the reverse phenomenon happens, and the resistance increases on an n-type material.

MOx gas sensors have remained at the forefront of gas research as improvements are required due to challenges regarding the limited selectivity, and higher heating power requirements (150-400 °C) that makes them difficult to employ in miniaturized configurations and integrated sensor networks. Methods to overcome these limitations have been investigated such as: using micromachined heaters to decrease the power consumption [86], and preparation of nanocrystals for solid state gas sensing techniques [87].

The use of graphene, a 2D material has been receiving more recognition for gas sensing applications due to its single atomic layer which is ideal for gas adsorption [88]. The electrical response, high surface-to-volume ratio, and low noise levels makes graphene a viable candidate for gas sensing applications. Chemical modification of graphene is essential for targeting specific analytes, requiring oxygen groups being present for targeted sensing [89].

Pristine graphene demonstrated drawbacks in lower sensitivity and response time. Functionalization of graphene composites such as GO has been investigated to improve graphene gas sensing capabilities by reshaping the surface chemistry and electrical response. Tang et al. reported that a fluorine atom, which is more electronegative than oxygen, introduced into the surface chemistry of GO would influence the hydrogen binding in GO and the surface adsorption of hydroxyl and epoxy functional groups would be enhanced [90]. Intermolecular distances between the O from GO and the H from NH₃ will be reduced and increases electron transfer for higher responsiveness and sensitivity. Reduced graphene oxide (rGO) is the formation of GO that is processed by chemical, thermal and other methods that reduces oxygen content and creates vacancies. As a result,

GO is a material produced by oxidation of graphite which leads to increased intermolecular spacing and room for functionalization of the base planes of graphite [90].

2.5 Extended Applications in Targeted/Specific Gas Sensing

Targeting specific analytes while maintaining a non-invasive, miniature footprint is paramount in applications where sensors can provide instant feedback while maintaining specificity and selectivity.

To broaden the scope of these devices in other sensing categories, they can be applicable in other domains such as environmental monitoring. The requirement for gas sensors stems from building regulations in an enclosed space such as a house or industrial area. More specifically, monitoring the concentrations of hazardous gases such as hydrocarbons, CO, CO₂, O₂, and their concentrations [91]. These sensing units are commonly connected to a broader platform of other sensors to determine the potential gas leaks within the environment. Gas sensors can be deployed within the network to determine the presence of various analytes while being able to be used independently as a separate sensor monitoring node or part of an overall sensor network [92].

A catalytic gas sensor has the same operational principle as many commonly available gas sensors but tailored to immediately detect targets. It consists of two elements: a detector, and a compensator. The detector element consists of a catalytic material that will detect combustible gases, and the compensator element remains inert and not interact with the gas. A Wheatstone bridge is typically employed as a variable resistor maintains equilibrium of the detection circuit. When a combustible gas is identified, the resistance of the detector will change and produces an observable signal. These devices tend to produce a linear signal with respect to the targeted gas concentration.

Chemical agents and other volatile substances for non-intrusive medical monitoring can be detected through exhaled breath as opposed to invasive methods. Exhaled breath contains around 1000 unique VOCs that are products of metabolism. Discharged gases from exhaled breath such as NO_x, NH₃, H₂S, acetone, ethanol and various others can be identified and correlated to diagnose various diseases [93]. It is possible to also determine different nutritional levels of patients due to the lack or excess of any detected chemical component in the breath sample.

Specificity and sensitivity of unique gases can distinguish detection in categories to specify different physiological conditions. Recently, gas exchange for more in-depth medical measurements such as ionic and proton mass spectroscopic methods use analyzers to measure the concentration of oxygen and nitrogen in an exhaled gas sample to study gases present in the blood but have proven to be more costly [93].

In summary, chemiresistive sensors have shown to exhibit optimal properties for gas sensing such as sensitivity and specificity, which are all attributed to the change in the conductivity of the top sensing layer resulting from the interaction with a targeted analyte. Among common applications of chemiresistive sensors, physiological monitoring of diseases using techniques such as exhaled breath analysis has been a targeted application for due to their miniature footprint, robust composition and simple fabrication techniques. They benefit from the ability to chemically configure and tune the sensing layer properties for specific gas detection.

Chapter 3: Theory

Gas sensing devices rely heavily on gas interaction between the interface layer and thus, solid state mechanics. The receptor and transduction functions play the major role in obtaining a unique response with respect to a targeted analyte. The transduced input is translated into an electrical output that can be used and analyzed. The stimulus is generally chemical, and the output signal is directly proportional to the induced reaction. The determination of these effects on the sensing surface dictates the quantifiable electrical signal on the sensor. Graphene would be the principal material that would be investigated due to its unique and outstanding properties for gas sensing.

The increasing interest in investigating the phenomenon behind the FGO based chemiresistive gas sensor is attributed to the tuneable properties of graphene band structure and the sensor response when functionalized graphene oxide is used as a sensing layer. Sensor parameters such as the conduction mechanism and current flow are dictated by the properties of the sensor composition and IDE configuration that are governed by theoretical background behind the conductivity changes.

3.1 Graphene Band Structure and its Electronic Properties

Graphene has rapid response and recovery time when used in gas sensing applications. Carbon has hybridized atomic orbitals like many of the first-row elements in the periodic table, attributing to the s- and p-orbitals in the secondary shell having similar energies. This can be related to form chemical bonds with unique morphologies [94, 95, 96]. Graphene features one s-orbital and two in-plane p-orbitals of carbon associated with sp^2 hybridization. The π orbitals are available above and below the graphene sheet and can form π bonds that can overlap with neighbouring graphene sheets. σ -electrons within the

material are densely bound so current conduction is negligible but π and π^* orbitals can behave like valence and conduction band electrons and dictates the planar conduction mechanism [94]. Electrons behave like pseudo relativistic particles following the Dirac equation due to linear energy dispersion in conical valleys at high symmetry Brillouin zones [94, 96, 97].

Effective mass is dependent on the second derivative of energy with respect to electron momentum. The Dirac points in a material is represented as the transition between the valence and conduction bands in an energy diagram but arranged as a honeycomb lattice made of hexagons. Since the derivative of a linear function is zero, electrons have zero effective mass near the Dirac boundaries. Graphene being a zero-gap semiconductor where electrons travel at constant speed, indicates that electrons are closely bound, forming strong sigma bonds between carbon atoms [94, 97]. Graphene can be structurally represented by six cones and its Fermi level can be found the converging point. This indicates a low electrical conductivity in pristine graphene.

Graphene is a 2D material that is composed of a single layer of carbon atoms oriented in a honeycomb lattice that serves as the base structure for its material derivatives [98]. Device applications such as high speed, radio frequency systems have been looking to implement thermal and electrically conductive composites to enhance electronic properties [99]. Many novel materials such as quantum dots and rare earth metals have been investigated to enhance the performance of electronics, however their high cost, complex, limited availability and synthesis methods make them difficult to be widely adopted [100, 101]. Graphene demonstrates extraordinary electronic properties and shows unique characteristics with Dirac fermions, quantum Hall effect (QHE), and the ambipolar

electric field effect [102, 103]. The quantum hall effect stems from the Dirac fermions that have unique behaviours in a magnetic field [104].

Figure 5 shows the view of crystalline structures of graphene in mono, bi- and multi- layer formations in Figures 5 a) and c), and their corresponding band structures in Figures 5 b) and d). A unit cell would contain carbon atoms A (red) and B (blue) for a monolayer of graphene, and A₁ and A₂, and B₁ and B₂ for the bilayer. The lines represented in b) and d) demonstrate the band structure of graphene materials and the difference going from monolayer and bilayer with an adjacent influencing electric field. The solid and shifted lines show the resultant energy band structure in the presence of an influencing electric field due to an adjacent graphene layer [96].

Figure 5. a) Diagram of a monolayer graphene, c) bi-layer graphene, e) trilayer of graphene, and their corresponding band diagrams in b), d), f). [96]

The electronic properties of graphene are attributed to the crystallinity of the material and is the main driver of experimental focus on graphene compared to other 2D materials.

Electrons in graphene have paths where the movement of electrons would be unhindered, and interaction would remain constant as it is a gap-less material [104].

Figure 6. Electronic properties of graphene showing a) the Hexagonal lattice structure (left) and the Broullin zone (right); b) Graphical representation of the ambipolar electric field in a single layer of graphene. [104]

Graphene is essentially carbon atoms oriented in a hexagonal structure [102]. In Figure 6 a), a triangular lattice is shown with two base atoms would form a honeycomb lattice structure. The unit vectors of the lattice can be demonstrated as [104]:

$$a_1 = \frac{a}{2}(3, \sqrt{3}), a_2 = \frac{a}{2}(3, -\sqrt{3}) \quad (7)$$

Two carbon atoms feature a distance of 1.42Å and the reciprocal vectors of the lattice structure is:

$$b_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad b_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (8)$$

And the two points K and K' are at the edge of the graphene Broullin zone (BZ), also known as Dirac points, and are essential parameters pertaining to the physics of graphene.

The positions in the space can be shown as [104]:

$$K = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right), \quad K' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right) \quad (9)$$

And the nearby neighbouring vectors as,

$$\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = -a(1, 0) \quad (10)$$

While the other six nearest neighbours are positioned at $\delta'_1 = \pm a_1, \delta'_2 = \pm a_2, \delta'_3 = \pm(a_2 - a_1)$. The electronic structure of graphene can be characterized and predicted through simulation from the density functional theory (DFT) [104]. The properties of graphene and different adatoms (lithium, sodium, hydrogen, potassium), density of states (DOS), geometry, and work function can also be calculated using DFT [105, 106].

The ambipolar nature of graphene is shown in Figure 6 b) showing the change in Fermi energy E_F in response to the variable gate voltage V_g in a conical low energy spectrum representation $E(k)$ [104, 107]. The material exhibits either n or p-type behaviour based on the biasing voltage. The Fermi level of the material is dictated by the biased gate voltage and switches between the valence and conduction bands. The charge carrier mobilities are high with values being over $15000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in ambient conditions and the concentrations of electrons and holes can be continually switched in $n (10^{13} \text{ cm}^{-2})$ [103, 108].

Figure 7. Hall Conductivity for double layer graphene σ_{xy} (red) and resistivity ρ_{xx} (green) vs. carrier concentration. [104]

QHE is another element that demonstrates the outstanding electronic properties of graphene. Due to its high temperature stability range, its QHE is 10 times broader than other 2D materials [104]. The massless fermions and their reactions in a magnetic field is more pronounced at the high field limit, where Shubnikov-de Haas oscillations (SdHOs) develop into the QHE [103]. Figure 7 shows the Hall conductivity as σ_{xy} and the resistivity ρ_{xx} of graphene is represented with electron or hole concentrations in a constant magnetic field. Distinguishable QHE plateaus in the graph are represented but do not behave as:

$$\sigma_{xy} = \left(\frac{4e^2}{h} \right) N \quad (11)$$

Where N is an integer. The plateau is seen at the value at $\left(\frac{2e^2}{h} \right)$, and the progression through:

$$\left(\frac{4e^2}{h} \right) \left(N + \frac{1}{2} \right) \quad (12)$$

Where the plateaus happen at half-integer ν [104]. The lowest hole in graphene ($\nu = -\frac{1}{2}$), and the lowest electron ($\nu = +\frac{1}{2}$) Landau Level needs the same number of carriers to move through adjoining levels. Figure 7 would show the σ_{xy} of a graphite composing of two graphene layers and the presence of a quantized level at zero E, is shared by electrons and holes is an accurate depiction of the unique QHE [104, 107].

3.2 Electronic Tuneability of Graphene

The unique properties of graphene make it suitable for a variety of applications that require a specific response. It can be modified such that its electronic response demonstrates a specific reaction to a target species for sensor applications.

Modifications of the energy band in graphene can be through the composition of bulk graphite. Electron hopping parameters play an essential role in the structure, and tight binding calculations would show that a tri-layer stack of graphene seen in Figure 5 e). The adjacent layers are oriented such that an A_2 atom is in between both B_1 and B_3 atoms [96]. This would lead to show that the top of the energy levels of the valence band overlaps with the bottom of the conduction band, leading to finite density of states [37]. Moreover, when the interlayer symmetry is disrupted by an external orthogonal electric field, the low energy parabolic extremes would shift to lower energies as seen in Figure 5 f). A disorder broadened energy window leads would increase the band velocity at the Fermi-level ($E=0$) [37], and increases the overlap of the conduction and valence bands [109, 110]. The opposite occurs in bilayer graphene as the band gap opening induced by the interlayer symmetry is broken [96].

Moreover, doping with catalytic noble ions is highly established in chemical sensor research. The advantage of doping with noble metals argument adsorption, albeit with fewer carriers and lower noise that can make changes discernable in the ultra-low concentration (sub-ppm, ppb) ranges. Augmented chemical affinity and selectivity also can be attributed to the functionalization of graphene [111, 112]. Charge carrier concentration by an induced magnetic field, morphology deformations or other external influencing factors can be used to optimize atomic interactive sensitivity.

3.3 Properties of Graphene Oxide

Dangling bonds help facilitate chemisorption of target molecules on the graphene surface. Hence, graphene modification by functionalization with polymers or metals stimulates surface adsorption with the target gas species [113].

Graphene oxide as a non-conductive material has been heavily investigated and been incorporated in various oxidizing/reducing interaction that that are implemented in hybrid materials [114, 115]. The addition of oxygen in graphene allowed graphene to be synthesized into thin film sheets and allowed the expansion for graphene composites. A number of studies have researched the chemical structure of GO, however, a complete model has not yet been achieved. Probabilistic models from Lerf-Klinowski and Dékány have considered the hydration behaviour of GO to have a carbon plane surrounded with hydroxyl and epoxy (1,2-ether) functional groups. There is also an abundance of carboxylic acids along the sheet edge, along with organic carbonyl defects [116, 117]. GO films exhibited high conductivity with sheet resistances of 276-2024 Ω/sq [115].

S. -H. Kang et al. reported XPS data of samples of GO and the C1s peaks are at 284.5, 285.5, 286.5, and 288.9 eV, each associated with C-C, C-N, C-O, and O-C=O groups, respectively [115]. Differences in the C-O ratios of the oxygen functional groups of the GO led to different oxygen concentrations present within the film [115, 118]. Binding energy peaks at 286.5 eV and 288.9 eV for C-O and O-C=O respectively, show a large amount of oxygenated carbon structures. The exfoliation process can be shown as [115]:

The anodic oxidation of water produces hydroxyl and oxygen radicals within the graphene. Hydroxylation along with oxidation of raw graphite by the radicals influences the dissolution of carbon atoms from the anode and leads to the oxidative cleavage of expanded graphene that generates GO [119, 115]:

3.4 Graphene Oxide Chemical Functionalization

Electrical conductivity can be enhanced by chemically functionalizing graphene. This process modifies the surface of graphene monolayers and exposes them to active functional groups [120]. Functionalization of graphene promotes adsorption of target species that cause changes in the material properties resulting in electrical change in resistance [121].

Chemical functionalization is conducted through chemisorption in which an exposed chemical species bonds with dangling sp^2 electrons in carbon atoms and form sp^3 bonds. As a result, the hexagonal lattice structure of graphene and the π bands is disrupted. This method of precisely modulating the chemical composition of graphene allows for the enhancement of its electronic properties which can be reversed through chemical desorption. Hence, feasible for large scale fabrication [120]. Functional groups that are compatible with graphene chemical functionalization are hydroxyl, epoxy, oxygen, hydrogen, and fluorine [122, 123]. These chemical functionalization methods are paramount in modifying the properties to tune GO for diagnostic applications. The reactive functional groups found in GO can be tuned and functionalized with different electroactive species [123, 124]. These covalent functionalization groups can diminish non-specific binding that occurs in pristine graphene [123]. Chemical functionalization would fine-tune

the characteristics of GO and increases specific interaction leading to augmented electrochemical properties.

3.5 Graphene Oxide Reduction and Fluorination

Graphene is an excellent 2-D material that has high charge mobility. Young's modulus, and high surface to volume ratios. The material's surface atoms would be featured in the composition of active sites within the material that can be involved with molecular interactions.

The gas sensing mechanism is reliant on the exposure to different target species and targeted sensing analytes act as dopants as it interacts with the graphene sensing layer and its localized electronic conductivity changes accordingly. The addition of oxygen into graphene would create GO and thus sp^2 bonding would be heavily interrupted as there is a huge decrease in the conductivity of GO compared to pristine graphene.

Reduced graphene oxide (rGO) is the formation of chemically processed GO and/or other methods to create oxygen vacancies which leads to increased intermolecular spacing and room for functionalization of the base planes of graphene.

Reducing graphene oxide by fluorination offers several advantages, owing to the low polarity of C–F bonds and the high polarity of oxygenic groups, characteristics of FGO could be tuned by controlling both the carbon-fluorine, C–F and carbon-oxygen, C–O ratios.

Figure 8. Oxidation of graphene to create graphene oxide and reduction and fluorination to form FGO.

This makes FGO a suitable candidate for replacing MO_x based materials in chemiresistors. Another benefit is that FGO can be produced using cost-effective chemical methods, and in high yields from the inexpensive graphite raw material. In addition, due to its hydrophilic nature, stable aqueous colloids can be formed to facilitate the assembly of macroscopic structures by simple, low-cost solution deposition processes [126, 127]. Oxygen or fluorine atom concentration can be tuned for different target analytes and end products [128].

Fluorination of GO can be achieved by chemically vapour deposited (CVD) plasma or other reactive gases onto graphene, but this process is more complicated overall. Another advantage of using FGO for gas sensing is the high electrocatalytic activity (augmented electron transfer), and specificity towards certain analytes due to the presence of these C-F bonds [129]. First-principles calculations can estimate the adsorption energies, charge distributions, and the configurations of NH₃ and NO₂ molecules on GO and chemically fluorinated graphene oxide (CFGO). The calculations prove that functionalization of GO results in augmented sensitivity, selectivity, and reversibility are present at room temperature [88].

GO which is graphite with an expanded interplanar distance due to the repulsion of oxygen groups that are introduced, have been investigated for mass production in liquid form [126]. GO has attracted attention due to its properties such as diverse oxygen functional groups and various morphologies [130]. Oxygen reactivity and its specific hetero atoms such as fluorine or nitrogen, promotes the interaction at oxygen acceptor sites. This makes GO versatile for various uses such as sensor catalyzing material [131]. GO demonstrates high reactivity in catalyzing a reaction as an oxidizing agent. Research

regarding the control of oxygen functional groups and morphology in GO is very encouraging. However, there are limitations such as the control of oxygen functional groups. A reducing agent such as hydrazine would remove all oxygen functional groups [132]. Processes such as heat treatment may lead to restacking and deficits in the carbon structure which would lead to undesired electrical and chemical response. Fluorination on the other hand is time and process efficient method of controlling the oxygen functional groups [133]. Fluorine provides an ideal substitute for C-O bonds due to it having a lone electron pair [126].

From literature, Park et. al determined fluorination weakens the binding of GO and hence the presence of the F adatom reducing the intermolecular distances between the O group and the H in NH_3 [126]. This suggests that the O group in the GO, actively facilitates in the adsorption of NH_3 molecules by breaking one of the two bonds on the GO surface. As the O group is attracted to the H of the NH_3 , the hydrogen enhances adsorption. The distance between the H of the hydroxyl (OH) and the N of NH_3 is reduced resulting in a stronger hydrogen bond between them.

Hence, the fluorine adatom enhances binding with NH_3 and is adsorbed onto the GO surface, as it binds strongly with both O and OH groups. This change in the response is attributed to the lower Fermi level of GO and the increased number of holes in the GO after fluorination, which is helpful for NH_3 gas retention.

The low fluorine (F) content that augments the electron transfer from electrode to biomolecule (or vice versa) will neither significantly affect the electrical conductivity nor the wetting properties of graphene [134]. The fluorine adatom introduced into GO is suggested that the fluorine-carbon bond and the Fermi level change of FGO exhibits the

necessary characteristics for gas sensing [88]. Additionally, fluorination can be used to control pores and surface area of GO [135].

Fluorination for gas sensing introduces a sensitivity targeted towards specific analytes that can be realized electronically and characterized in a unique profile that the sensor exhibits from specific interaction. FGO demonstrates excellent sensing properties for a wide range of biomolecules such as ionized ammonia (NH_4^+), unionized ammonia (NH_3), gaseous NH_3 , nicotinamide adenine dinucleotide (NADH), ascorbic acid (AA), uric acid (UA), and dopamine (DA). Hill et al. reported that improvements to sensitivity can be associated to efficient device design [94]. It was found that a larger surface area can increase adsorption sites and thus optimize material sensitivity to short exposures and the detection of ultra-low concentration levels.

3.6 Sensor Response

Solid-state gas sensors typically have rapid, reversible response after interaction room temperature compared to metal-oxide sensors. The resistance of the device increases with analyte concentration but is non-linear below the threshold saturation level of the material. The sensor response can be shown as [136]:

$$\frac{1}{\Delta R_g} = \frac{K + C}{K(R_{sat} - R_0)} \quad (15)$$

Where ΔR_g is the difference in resistance in the presence of a target analyte ($\Delta R_g = R_g - R_0$), c is the analyte concentration, K is the binding constant, R_0 is the initial resistance, R_{sat} is the resistance at saturation. Gas permeability involves three phases: adsorption, diffusion, and desorption. The adsorption phase adsorbs gas onto the surface, diffusion is

where the analytes disperse throughout the membrane, and desorption features the molecules moving to a lower concentration gradient [136].

3.6.1 IDE Array Response

Interdigitated electrodes incorporating a sensing medium in between the IDEs forms a capacitive effect and the principal phenomenon can be based on two parallel plate capacitors configured as an array. The physical properties of the electrodes can be represented by thermodynamic and conductivity models [137]. The thermodynamic aspects of the sensor can be attributed to the relationship between the concentrations of the sensing component in the adsorption of targeted particles. The polymer adsorption then causes the physical thickness of the sensing layer to increase, and conductive properties are modified with respect to the change in conductivity. The conductivity model describes the relationship between the spacing density (intermolecular distances between particles) of the sensing film and the conductivity with respect to change in the exposed targeted analytes. These two models combined can quantify the conductivity and thus the resistivity of the device [137].

The conductivity model for chemiresistive sensors can be derived by combining effective media theory and percolation theory [137, 138], and thus creating a model that correlates the resistivity to the intermolecular distance in the sensing layer:

$$\frac{f \left(\rho_c^{-\frac{1}{k}} - \rho_m^{-\frac{1}{k}} \right)}{\rho_c^{-1/k} + A \rho_m^{-1/k}} + \frac{1 - f \left(\rho_c^{-\frac{1}{k}} - \rho_m^{-\frac{1}{k}} \right)}{\rho_c^{-1/k} + A \rho_m^{-1/k}} = 0, A = \frac{1 - f_c}{f_c} \quad (16)$$

Here f_c is the critical volume fraction of the percolation of the low resistance threshold, ρ_c is the resistivity of the low resistance phase, ρ_p is the resistivity of the high resistance

phase, f is the fraction of the volume of the low resistance phase, and k is an exponential constant [137].

Resistivity is an intrinsic property of the sensing material that is independent of specific geometry. Resistance on the other hand is dependent on surface area, and can be represented on flat electrodes attached to parallel, opposite sides by:

$$\rho = \frac{RA}{L} = \frac{VA}{iL} \quad (17)$$

Where R is the resistance, A is the cross-sectional area, L is the length between electrodes, V is the voltage applied between electrodes, and i is the current flow.

A simplified 3D model of a polymer strip coating the IDEs in Figure 9 has been reduced to a 2D model as the current flow can be demonstrated as the Laplace potential equation:

$$\nabla^2 \phi = 0 \quad (18)$$

where ϕ is the electrostatic potential and ∇ is the gradient operator [137]. The solution of the Laplace equation shows the orientation of the current flow being perpendicular and non uniform as seen in Figure 9.

Increased area has shown a minimal effect on the baseline resistance of chemiresistive sensors [139]. The generation of an electric current conduction paths can be observed, and resistance can be measured between two electrodes. Total resistance can be represented by resistances in parallel:

$$\frac{1}{R_{Tot}} = \sum_{i=0}^n \frac{1}{R_n} \quad (19)$$

Figure 9. Electric fields of IDEs top view and cross-sectional view. Reproduced from [137].

An electric field also can be generated between IDEs due to the two parallel plate configurations under an applied AC voltage. The capacitive reactance would be a result of the material under AC conditions. Therefore, when the sensing element is exposed to a targeted gas analyte, the sensor dielectric constant changes and the device capacitance along with series resistance. Measuring the output voltage of the sensing element across the electrodes, its interactive properties can be quantified using the IDE structure.

Figure 10. IDEs a) 3-D configuration with sensing material b) simplified equivalent circuit. Reproduced from [140].

Figure 10 shows the cross-sectional configuration of the planar structures of the IDEs coated with a sensing material and its equivalent circuit model. The equivalent circuit in Figure 10 b) shows two double layered capacitors C_{DL} connected in series to the resistance of the material R_{Sol} . These elements are connected in parallel with the dielectric

material C_{Cell} . The contact resistances are on each of the ends of the circuit represented by R_{Lead} . The R_{Sol} can be expressed by [140]:

$$R_{Sol} = \frac{K_{Cell}}{\sigma_{Sol}} \quad (20)$$

The cell constant K_{Cell} can be shown as [140]:

$$K_{Cell} = \frac{2}{(N-1)L} \frac{K(k)}{K\sqrt{(1-k^2)}} \quad (21)$$

N and L are the number and length of the fingers, respectively. The function $K(k)$ is the elliptic integral of the modulus k that is shown as:

$$K(k) = \int_0^1 \frac{1}{\sqrt{(1-t^2)(1-k^2t^2)}} dt \quad (22)$$

where k is:

$$k = \cos\left(\frac{\pi W}{2S+W}\right) \text{ or } k = \cos\left(\frac{\pi W}{\lambda}\right) \quad (23)$$

where S and W are the interelectrode gaps between each electrode, respectively. λ is the wavelength defined [141]:

$$\lambda = 2(W+G) \quad (24)$$

C_{Cell} is the coupling term between two electrodes shown as:

$$C_{Cell} = \frac{\epsilon_0 \epsilon_{r.sol}}{K_{Cell}} \quad (25)$$

Where ϵ_0 and $\epsilon_{r.sol}$ are the absolute and relative dielectric constants of the sensing layer, respectively.

C_{DL} can be simplified as double layer capacitances that can be approximated as:

$$C_{DL} = 0.5 W L N C_{DL, Surface} \quad (26)$$

Where A is the electrode surface and $C_{DL, Surface}$ is the double layer capacitance of the electrolyte system. Note that the factor 0.5 is from C_{DL} from only half of the electrode surface. The characteristic capacitance, $C_{DL, Surface}$ is around the Stern capacitance for electrolytes with high ionic strength of values from 10-20 $\mu\text{F}/\text{cm}^2$ [142].

A chemiresistive sensor would adhere to the IDE equivalent circuit model without the capacitance values, essentially acting as an open circuit due to the main operation mode being in steady state DC. The main observation with the chemiresistive gas sensor is mainly reduced to the resistance of the layer coated on top of the IDE array (R_{sol}) and minimal contact resistance from the leads (R_{lead}).

FGO-based chemiresistive gas sensing mechanism is investigated using theoretical models that describe material and microstructure properties responsible for electrical conduction, allowing for the quantification of electrical resistance of the sensor. Tuneable properties related to graphene oxide band structure and sensor response associated with the use of functionalized graphene oxide as a sensing layer are based on mathematical representations provided in literature. Sensor parameters such as the conduction mechanism and measured current are governed by the properties of the sensor composition and IDE configuration and influence the conductivity change and sensor performance.

Chapter 4: Materials and Methods

In order to achieve a low cost, flexible, simple to fabricate chemiresistor gas sensor with reliable robust device properties and operating parameters, strategic testing and results reproduction was necessary. The IDE design, material choice, functionalization synthesis methods and experimental set up was tuned for optimal gas sensing properties such as high response, sensitivity, and selectivity, while maintaining a simple fabrication process and robust device profile ideal for repeated testing.

4.1 Sensor Fabrication

The IDE structures on the pSi substrate were layered with Poly(vinyl alcohol) PVA, PEDOT: PSS as a conductive layer, and Polymethyl methacrylate (PMMA) as a sealant/dielectric layer. A homogenous suspension of GO and the different samples of FGO (0.2mg/ml) were drop coated using a micro-pipette on each of the separate device samples. The sensor microchip was then wire bonded onto a package, that was then used to connect to a measurement circuit.

The aspect ratios of a set of IDEs are apart of the design specifications as a ratio of the channel width to channel length, W/L. Initially the designs of the IDEs were configured to maximize surface area to obtain an optimal response from the sensing layer so feature sizes of 30 and 50 were used. The overlapping electrodes have a width of 300 μm and length of 5.3 mm for an aspect ratio of 20 and an overlap width of 150 μm and length of 8mm for an aspect ratio of 50.

The IDEs used in this experiment were micropatterned using standard photolithography of 200 nm chrome layer, deposited on Silicon (Si), passivated silicon (pSi), and polyamide/Kapton substrates. The process of passivation would render the

substrate surface inert and sealing it from interaction. Exposure to residual materials would not change any conductive properties. This is typically achieved using thermal oxidation [143].

Figure 11. Left: Width and Length of a pair of IDEs. Right: Chemiresistive device cross-sectional diagram.

The first device featured a silicon substrate patterned with 200 nm chromium layer GO deposited on top creating a 200 μm layer. This provided a stack to view the effects of the device exposed to gas with out any chemical modifications to the sensing layer.

The second device used silicon substrate patterned again with 200 nm chromium layer and deposited with the various FGO samples and creating a 200 μm layer. This device setup created a configuration to test and validate the sensing layer exposed to target analytes.

The third design was fabricated on a pSi substrate with 200 nm chromium layer to form the electrodes. A layer of 500 nm PVA was deposited onto the substrate as a conductive film. A dielectric layer of PMMA was then deposited on top of the conductive layer and followed by the different samples of FGO as a top sensing layer.

The fourth design was fabricated again on a pSi substrate with 200 nm chromium layer to form the electrodes. A layer of 500 nm PEDOT:PSS was deposited onto the substrate as a conductive film. A dielectric layer of PMMA was then deposited on top of the conductive layer and followed by the hydrothermally processed of FGO as a top layer sensing layer.

Figure 12. FGO coated IDEs on pSi substrate.

4.1.1 Device Substrate Novelty

The reliance on the natural conductive properties of bulk silicon is non-ideal when aiming for the design of a flexible electronic device or a low-cost chemical detector. While in conventional silicon chemiresistors, the intrinsic conductivity is attributed to the silicon being an active device layer [144], our goal here was to achieve an ideal, active substrate using an inert base layer. A conductive layer that would enhance conductivity on an inactive substrate, would be a desirable method to employ as non-conductive materials such as glass or plastics are available at much lower cost and easier to source. This

approach would be investigated and corroborated through exposure to the targeted gas through experimental findings.

4.1.2 Substrate Usage

Experiments were conducted sensors printed on both SS and pSi substrates. Initial tests were performed to observe the response of the validity FGO sensing layer on SS. Subsequent sensor function verification experiments were carried out using pSi to verify the multilayer stack would provide the same sensitivity as a SS without having to rely on its inherent conductive properties.

4.1.3 Substrate Materials Stack Selection

The sensor design focused on the ability to fabricate on a readily available, inert substrate. pSi would emulate and mimic a low cost, polymer substrate that has a similarly high resistivity compared to silicon wafers that feature values on the lower end of 10-20 Ω (higher conductivity). They also have high thermal conductivity and frequency-independent permittivity compared to regular silicon [145]. These properties suggest pSi to be a good substrate candidate to test and in turn fabricate on low cost, non-conductive substrates that are suitable for miniature, flexible gas sensing devices. In addition, using a suitable film coating on top of these substrates lowers the overall baseline resistance and increases conductivity of the substrate.

Two conductive base layers, PVA and PEDOT: PSS were investigated to enhance the conductivity of pSi. PVA is porous and would increase the active sites of the GO/FGO coating for target molecule retention. PEDOT: PSS has a proven conformal contact with textured silicon [146], and was also investigated. PEDOT: PSS film is ideal for deposition on hydrophobic surfaces, such as a substrate due to the film being pre-deposited and

annealed. This shows PEDOT: PSS to be a thick conductive film when deposited [147]. It was then used in conjunction with the substrate layer to increase conductivity on the pSi. PEDOT: PSS is a porous material, and as a functional mechanism, may provide an unwarranted response with the targeted gas molecules. To limit interaction, a dielectric layer was then used to coat the substrate. PMMA is a synthetic resin that is derived from the polymerization of methyl methacrylate, and due to its fibrous composition, aides in the retention of gas molecules due to it creating active vacancies for molecular binding and retention, as well as possess excellent dielectric properties [148]. XPS data for PMMA has been reported and seen C1s and O1s to peak at 286 eV and 532 eV respectively [149]. PMMA film, in addition to FGO helped enhance the sensing mechanism as the PMMA would provide the necessary active sensing site micro-structures to trap targeted molecules and facilitate interaction of FGO with NH_3 . The chemiresistive sensor incorporates a novel component using readily available, inert substrate. The use of pSi in our tests was due to its low cost, non-conductive nature [146].

Gas sensors based on MOx have already shown strong attributes such as, instantaneous high gas response due to augmented charge transfer. Other influencing parameters influence the sensitivity such as: transport, catalytic activity, and surface adsorption [150]. Potyrailo et al. have shown that dielectric excitation at specific frequencies in oxide semiconductors can provide an extremely linear response with respect to gas concentrations [151]. Various sensors were studied based on n- and p-type oxide semiconductors exhibit an extremely linear correlation ($R^2 > 0.995$). Linearity was also maintained throughout a wide range of methane concentrations (CH_4). Dielectric sensing

effects also achieved to filter out external conditions such as moisture and temperature [151].

In a dielectric, the capacitance can be realized as a charge buildup from electrical potential across an insulator preventing a transfer of charge. An example of a dielectric insulator is PMMA [152]. PMMA is known to promote charge carrier mobility at the semiconductor-insulator interface due to a low trap density and has a dielectric constant of 2.8 and resistivity of $2 \times 10^{15} \Omega \text{ m}$ [153]. PMMA thicknesses found in literature tend to be 400-600 nm [154]. PMMA for chemiresistors provides a fibrous structure and low chemical affinity and would provide enhanced molecular trapping for the targeted gas [148]. PMMA stacked underneath the interaction layer therefore helps in trapping gas analytes and facilitates enhanced interaction.

PMMA was chosen as a sealant layer due to its fibrous composition and very low chemical affinity. The thin film stack aids in the retention of gas molecules, possesses excellent dielectric properties [148], and therefore proved helpful in trapping analyte molecules and facilitated interaction of FGO with NH_3 .

4.2 IDE Device Patterning Steps

4.2.1. Negative Lift-Off patterning

This method of nano device fabrication would pattern the metal layer without the etch step. It is beneficial in reducing device fabrication steps and can lift the strain on substrates that cannot withstand aggressive patterning procedures.

Lift-off patterning was employed for regular and passivated silicon substrates. A passivated silicon substrate would allow for device fabrication without the reliance on the

intrinsic conductive properties of regular silicon. A negative photoresist was used for the lift off procedure and can be demonstrated in Figure 13 [155].

A silicon wafer was prepared by cleaning It in an oxygen plasma for one minute. Microwave generated plasma is used on the oxygen plasma to clean surfaces free of any debris.

The photoresist was patterned using a photomask on the substrate. The sensitivity of the photoresist used was under the 350 nm range. The photons would interact with the salt and creates hexafluoroantimonic acid and breaks up the epoxy groups in the resin monomers [155]. These monomers then have an increased thermal energy after exposure.

After exposure the patterning procedures, the substrate must be heated to polymerize all monomers that were activated. The substrate was heated to 65°C on a hot plate for 1 minute and ramped up to 95° C for 5 minutes.

Development of the system was grown using photoresist and using 50 ml of the metal ion free (MIF) 200 developer. The process lasts for 4-5 minutes and visually verified under a microscope for any process variations or deformities. Metal Deposition was performed using a Physical Vapour deposition machine [156].

Metal etching would place the substrate faced upwards in a beaker of 50 ml of etchant solution for 3-5 minutes. The chips were then verified using a microscope to guarantee that the etching process was successful. The resist resulted in the micron thickness and the metal resulted in an order of magnitude less as 300 nm was used in the liftoff process.

The photoresist strip was performed using the mechanical process using a sonicator bath as the ultra-sonic waves produces would successfully remove the photoresist from the surface. The photoresist solution was placed inside the sonicator along with the substrate for 10 s. This process involves the stripper solution interacting/resonating and removing the polymers of the photoresist, also removing redundant metal, and leaving only the interdigitated electrode array.

Figure 13. Device fabrication with negative lift-off process

4.3 FGO Synthesis Methods

Two separate synthesis methods are used to make Fluorinated Graphene Oxide (FGO). The use of a commercial fluorinating agent was used for the comparison with an in-house fluorination methodology. Products of the different processes were then characterized. The resultant products are compared by studying the ammonia analyte sensing performance. Validation of sensor performance and multi-analyte sensing capabilities were studied using the inhouse methodology FGO product.

XtalFluor-E (XtalFluor), Hydrofluoric acid (HF), Sodium hydrogen carbonate were acquired. De-ionized water was obtained from local micro fabrication lab on-site

regeneration system. A specialized Teflon beaker with a specially formulated stabilized Polytetrafluoroethylene (PTFE) carbon base to aid in heating.

4.3.1 XtalFlour Preparation Method

XtalFluor-E 2 g of and 2 mL of 2 mg ml⁻¹ GO are suspended in 48% HF solution. The mixed solution is then boiled at 180 °C for 2 h. The reaction is quenched with sodium hydrogen carbonate (5%), washed a few times with de-ionized water and sample dried.

Figure 14. XtalFlour-E chemical structure. [157]

4.3.2 Hydrothermal FGO preparation method (In-house HF Fluorination)

GO (50 mg) is dispersed in 20 ml of deionized water ultrasonically, after which 5 ml of different concentrations of HF (49%, 30%, 10%) are added with gentle stirring for different batches. The mixture is stirred on a hot plate at 150 °C for 20 h. The resulting solution is quenched using sodium hydrogen carbonate (5%), centrifuged and washed a few times with de-ionized water. The final product was freeze-dried.

4.3.3 Chemiresistor Coating Procedure

FGO/GO is suspended in DI water at a concentration of 0.2mg/ml. The suspension is sonicated until homogenous. IDE arrays on a silicon substrate (SS) and pSi were used. The pSi is coated with 200nm PVA (Spread 5sec/100rpm Spin 45 sec/1000rpm) – pSi1 for a set of experiments, 500nm PEDOT:PSS (spread; 5 sec/100rpm Spin 45 sec/1000rpm) followed by a coating of 200nm PMMA (spread 5 sec/500 Spin 30 sec/4000rpm) – pSi2

for a set of experiments and 400nm PMMA coating (5 sec/500rpm Spin 30sec/2500rpm) – pSi3 for another set. Chemiresistor measurements are performed before coating and after each coating layer of the different conductive materials. A suspension of GO is then drop coated on one IDE each of SS (Silicon Substrate), pSi1, pSi2 and pSi3. The different suspensions of FGO (FGO49 and FGO-XtaFluor are drop coated on the 2 IDEs of SS.

Drop coating was carried out using a micro-pipette as this helps suspension to stay on the electrode area. A small volume of 0.75 μ l is dropped on the IDE at a time, with evaporation in between to a total volume of 3 μ l per coat. The different, polymer conductive enhanced, passivated IDEs, PSS2 and PSS3, FGO49, is drop coated with a total volume of 15 ml at 5ml at a time as these are 5 times bigger than the SS IDEs. Chemiresistor measurements are carried out on different electrodes. The coated IDEs are then exposed to NH_3 for a known period for SS and similar concentration ranges for PSS2 and PSS3. Chemiresistor measurements are carried out immediately after exposure on each sensor. The experiments are repeated to show reproducibility and result analysis was performed.

4.4 Sensor Packaging and Integration

4.4.1 Custom Printed Circuit Board Design

A printed circuit board was designed to be featured on a small-footprint package for the potential of use with non-invasive, point-of-care, exhaled breath monitoring. This custom board would be able to house the packaged sensor securely while having all the integrated components on the same board for data acquisition and readout purposes.

This board design was centred around the miniaturization and optimization of the sensor integration. The components consisted of a packaged sensor on a pin grid array housing wire bonded to the chip and instrumentation amplifier to observe the sensor

resistance change through a signal when connected to the voltage divider circuit. The signal processing circuit was based on an Arduino nano featuring an ATMEGA 328P microcontroller.

The coated sensor chip was wire bonded onto a pin grid package with a silicone bubble to encapsulate and protect the breakout wires from any external influence or damage. The package was then soldered to the through-hole vias for connection to the circuit and secure housing to the board. This implementation can further extend the capabilities of the sensor as it can be incorporated as a regular dual in line package (DIP). Traces that run out of the die would break out to the wire bonded pins and connect to the rest of the circuit board via through hole soldering mounts. It is important to consider that the contacts should have low resistance as they should not contribute parasitic elements that may influence the signal. The packaged die also requires design considerations that centre around physical and elemental factors pertaining to the chip. The pin grid array gives ample exposure to the targeted environment but can be susceptible to other ambient factors such as moisture, heat, and biological contaminants that is exposed from the sensor being used for exhaled breath in a point-of-care setting. Encapsulating the dye and incorporating an exhaust hole as found in pressure sensors can be incorporated for a more robust package design. The board has through hole pins where the sensor packaged onto a pin grid array can slot in easily. This makes the PCB design modular as the sensor component can be easily interchangeable.

The resistance of the sensor acts as a secondary resistor in a voltage divider circuit as the signal is amplified by setting the gain of the instrumentation amplifier *AD 620* to 10 V/V. The amplifier requires a minimum operating voltage of $\pm 2.8\text{V}$, and a voltage

converter was used to provide the necessary voltage supply for the amplifier with $\pm 5V$. According to the data specifications of the amplifier, the 3dB cut-off frequency at around 120 kHz has a low-noise flat band of 0.28 μV p-p [158]. An RC low pass-filter was designed for up to 120 kHz and was fed to the input of the amplifier and was employed to attenuate higher-frequency interference in the signal and improve performance. Since the constraints of the ATMEGA 328 has only a 10-bit ADC, this maps voltages from 0-5V in integer values of 0 to 1023, which yields a 4.9mV resolution per unit. Therefore, to ensure that the voltage readings are sufficient, the design for this voltmeter was designed to read up to 12V to compensate and allow room for detecting different increasing or decreasing linear voltage profiles. This was done by using a voltage divider of 47 k Ω and 33 k Ω . The output voltage of the amplifier was then measured at 9600 baud for a normal serial to USB interface by the microcontroller portion of the circuit.

A 16-bit ATMEGA 328P on-chip microcontroller was implemented along with all necessary components commonly found in an open-source Arduino-nano device. The board configuration having the microcontroller on-chip allows for less signal interference and quick readout. Using the standard Arduino programming interface, the code can be flashed easily to measure and capture the data that would be then sent to a connected computer.

The implementation of using an ATMEGA microcontroller can upload a barebones, custom bootloader using the serial programming interface (SPI) that can be configured to feature only the specific data processing and acquisition code to keep the readout simple and as efficient to display accurate and quick concentration level results by differentiating different linear profiles with specific target gas.

Figure 15. PCB board design with detailed board components

The motivation to create a board with sensor integration leans on intention to miniaturize and implement the design on a flexible polymer substrate as a wearable device. Board integration was designed to capture and storing data with a focus centred on the voltage dividing circuit where the sensor acts as a second resistor in the circuit. The initial resistor is set to fit within the desired voltage division to output 0.5V. This would then be amplified to 5V and then varies with respect to gas exposure and then captured on the microcontroller. This circuit was designed to simply focus on the electrical response of the sensor's exposure to gaseous analytes while maintaining a relatively miniature footprint that would be transferable from a rigid to a flexible substrate.

4.5 Experimental Procedure

4.5.1 Experimental Setup

The initial experimental setup is shown in Figure 16 a). NH_3 and N_2 gases were released into the stainless-steel test chamber and used to verify the concept of targeted gas sensing in an ideal, controlled environment. The packaged sensor was placed inside the gas chamber. A vacuum pump was used to achieve a chamber pressure of ≤ 0.00533 kPa (40

mTorr). The ammonia gas cylinder with a rated concentration of 22.6 ppm, was then attached to the chamber with a needle valve to control the flow of gas released into the chamber with added precision. A flow of ammonia gas was released for 3 minutes by opening the needle valve at around 15%. The nitrogen gas was used to dilute the ammonia and return to atmospheric baseline readings. In certain control experiments, a commercial Honeywell Ammonia Gas flow sensor (MIDAS-E-NH3) was introduced in the setup to measure and correlate the ammonia concentration to the response of the chemiresistive gas sensor. In following experiments, the sensor was exposed to an ultra-low concentration of 2.26 ppm of ammonia to verify its performance in a pseudo point-of-care environment for exhaled breath analysis.

Figure 16. a) Schematic of the experimental setup. b) Closed-lid chamber and c) Open-lid chamber setup with the integrated circuit on the PCB.

4.5.2 Experimental Procedure: Data Capture and Analysis

The data was captured with respect to the voltage of the amplifier V_O over time and was used to characterize the normalized change in resistance defined as $|\Delta R/R|$ (%): where ΔR is the resistance change with respect to the baseline resistance R before exposure to ammonia.

The FGO-based sensor was exposed to a steady flow of ammonia in a closed environment then extensively verified in an open chamber in an ambient setting to mimic practical health monitoring applications. Responsiveness and selectivity of the devices in these conditions were validated in significantly lower gas concentrations. Experiments were repeated in an open chamber with ammonia gas flow at concentrations below 2.26 ppm on top of the sensor surface, to mimic exhaled breath sensor response under atmospheric pressure conditions.

The FGO-based sensor was exposed to acetone to verify its cross-responsive performance. Acetone, an oxidizing agent which features binding mechanisms with FGO are consistent with oxidizing reactions as weakly bound fluorine ions change the electronic properties and it provides an opposite, but equal response. This results in a higher overall resistance and lowers conductivity. The experiment was conducted in a controlled environment with both the FGO and GO sensors exposed to acetone in closed, and open lid situations to verify performance under ideal, and ambient conditions.

4.5.3 Material Characterization for FGO

Fourier transform infrared spectroscopy (FTIR) is performed on several GO and FGO (XtalFluor) and FGO (In-house) samples using a KBr pellet method, scanning from 400 to

4000 cm^{-1} . Absorption and Transmittance spectra are analysed to compare efficacies of GO functionalization methods.

The X-ray photoelectron spectroscopy (XPS) data was collected using AlK_{α} radiation at 1486.69 eV (150 W, 10 mA), charge neutralizer and a delay-line detector (DLD) with three multi-channel plates. Survey spectra are recorded from -5 to 1200 eV at a pass energy of 160 eV (number of sweeps: 2) using an energy step size of 1 eV and a dwell time of 100 ms. High resolution spectra for F1s, O1s, and C1s are recorded in the appropriate regions at a pass energy of 20 eV (number of sweeps: F1s, 15; O1s, 5; C1s, 5) using dwell time of 300 ms and 0.1 eV step size.

Characterization results from the FTIR and XPS are detailed in the results and discussion section. The experimental methods described in this chapter are focused on investigating cost-effective fluorination methods for the sensing material, circuit design and sensor implementation for the FGO based chemiresistor. The sensor design is based on a reliable robust device profile.

The IDE design, material choice, functionalization synthesis methods and device characterization were strategically pursued to verify gas sensor properties such as sensitivity and selectivity, while maintaining a simple fabrication process ideal for repeated testing which can be transferred to a non-invasive system.

Chapter 5: Experimental Results and Discussion

The fabrication and testing of these chemiresistor devices along with the functionalized graphene sensing layer were analyzed and tested. Qualitative and quantitative analysis evaluations for the devices were conducted for ideal and ambient conditions. Individual sensor performance was observed to characterize the sensor properties when exposed to target analytes and for multi-analyte detection. The device fabrication process was optimized and then integrated into a full-scale data acquisition and capture system with a miniature footprint circuit board, readily accessible for market use.

5.1 Device Optimization Results

The device optimization has established a beneficial fabrication process to create devices that are exemplary candidates for extended and repeated use that is low cost. The high surface-to-volume ratio and low settling time of the functional layer makes the devices robust and simple to fabricate. The ability to also print and fabricate these devices on inert substrates replicates the viability of having these devices on flexible substrates allowing them to be used in point-of-care medical applications.

5.1.1 Device Patterning and Fabrication Observations

The creation of these chemiresistor devices is to optimize the interaction between the functional FGO sensing layer and the target ammonia gas. Patterning of the devices were optimized to achieve the highest gas interaction sensitivity with a quick response and reversibility. The pattern optimization was aimed to produce a suitable device aspect ratio for optimal charge transfer and realization of the change in resistance of the chemiresistor. The interdigitated electrode arrays were patterned using the L-Edit CAD design program. The optimization of the IDE array design was also centred to focus on the ease of

fabrication, and the improvement of the shelf-life and reusability of the functional materials coated onto them. Figure 18 shows the different IDE array aspect ratios for patterning. We can see that the electrode array acts as parallel resistances, and the coated fingers would contribute to $1/R$ of the total resistance $1/R_{\text{Tot}}$.

Figure 17. Microscope images of each of the coatings on IDE arrays. a) PEDOT:PSS, b) PEDOT:PSS/PMMA, c) PEDOT:PSS/PMMA/GO, PEDOT:PSS/PMMA/FGO

The patterned chemiresistors showed the highest sensitivity for the larger designed devices as the gap and overlap between the IDE fingers was optimal for electrical characterization of gas/sensing layer interaction. The designed aspect ratios of 20 and 50

showed comparable responsiveness when coated with the stacked functional layers. The structure that was mainly used for experimental analysis was the structure that a feature a width of 300 μm and length of 5.3 mm for an aspect ratio of 20 as these structures were more compact and easier to house on the pin grid array.

The material stack covered the electrode array adequately. The PEDOT:PSS was spin coated onto the metal interdigitated electrodes to increase conductivity of the substrate. The PMMA layer was then spun coated on top of PEDOT:PSS to limit interaction and seal the conductive layer. These layers were coated on top of all electrode arrays to maintain a consistency while fabricating the device.

The solution of FGO covered the array adequately as 15 μL was drop coated onto the conductive/dielectric layer stack. The process involved an intermediate settling step in between each drop coating of 5 μL to create a consistent distribution of FGO particles within the solution.

Having a high surface-to-volume ratio, FGO spreads well and had an even distribution as seen in Figure 19 b, c) on the surface of the layer stack. The sonication process also aided in the dispersion of the FGO particles that are suspended in the solution. A uniform dispersion also would contribute to an even distribution coating on top of the surface for augmented targeted sensing properties.

Figure 18. IDEs with aspect ratios of 20 and 50, respectively.

Figure 19. a) Optical microscope image of IDE chrome structure, b) Scanning Electron Microscope (SEM) image of drop casted FGO film on the IDE structure, c) SEM micrograph showing distribution of FGO micro-particles on sensor surface

5.1.2 Material Characterization

Spectra analysis for the GO and the FGO was performed and showed that the C–O bond at Wavenumber $\sim 1052\text{ cm}^{-1}$ diminishes and is replaced by another peak at $\sim 1166\text{ cm}^{-1}$. Based on literature and previous data, the resulting peak indicated the fluorination of GO due to the presence of a C–F bond. A vibration characterizing a carbonyl group C=O at wavenumber $\sim 1720\text{ cm}^{-1}$, which was originally present in the GO sample, diminishes upon the fluorination reaction using both methods (HF thermally, and the HF/Xtal Fluor). The shift of wave numbers was also noted for the bond vibration of –C=C– , $\sim 1618\text{ cm}^{-1}$ with a notable decrease in the intensity of transmittance. Intensity of the peaks associated with the carbon oxygen bonds decrease at a strong peak at $\sim 1166\text{ cm}^{-1}$, corresponding to a covalent

C–F bond, which appears in the FTIR spectrum of FGO [159], indicating that functional groups containing oxygen was replaced by fluorine. The bond C–F (sp^3) vibrates at the wave number $\sim 1082\text{ cm}^{-1}$ and is observed in the FGO spectrum. The peak at wavenumber ~ 2928 is $X=C=Y$, where X and Y can be either C or O. A C–F bond formation was additionally confirmed by the XPS data analysis. Differences between the GO and FGO decomposition XPS spectra in Figure 20 a) C1s, b) O1s and c) F1s confirmed the fluorination process.

Figure 20. a) FTIR spectra of GO fluorination with XtalFluor and with hydrothermal (Hydrother) fluorination in HF. The GO spectrum is a reference showing the different peaks that are formed due to the fluorination. The two molecular structures of GO and FGO are representative structures, showing likely fluorination positions, b) The XPS figures show the comparison between GO before Fluorination and after Fluorination for C1s, c) O1s and d) F1s. c) and d) show comparison of the different synthesis products.

Comparison of the XPS C1s spectra decomposition showed characteristic peaks at: C=C, 284 eV, C sp³, C sp², -CH 285 eV, C-O 287 eV and O-C=O 288 eV. The peak intensities of C-O and C=C/C-C display a significant increase due to the formation of various C-F bonds. The reduction of the C=O was confirmed in the FTIR spectrum and the appearance of the C-F peak. Observed in XPS, C1s of the C=O is an increase and shift in the FGO spectrum. F1s spectra Figure 20 d) shows the presence of semi-ionic C-F bonds and the covalent C-F bonds corroborated by the significant increase of C1s, C sp³, C sp², -CH peak in the FGO spectrum compared to the GO, with no notable increases in C=O and -C-O. Girardeaux & Pireaux saw that C1s and O1s to peak at 286 eV and 532 eV respectively for PMMA [149].

Since these binding energies align well with the peaks of the in-house synthesized FGO, this would suggest that a PMMA/FGO stack would enhance and augment the chemical affinity of the sensing layer and the targeted NH₃ analyte.

From the experimental results spectra, C-F bond formation was observed in both the commercial fluorination processes and that using the in-house method of synthesis would equally facilitate the formation of the FGO-NH₃ complex molecule. A comparison of the inhouse thermal synthesis of FGO and use of the commercial chemical XtalFluor is shown in Figure 20 c). The depletion and shift of the HC-O at 532 eV was observed as it is consumed in the production of C-F bonds. The graphs in Figure 20 c), d) also show a comparison of the two FGO synthesis methods products with that of GO, where the appearance of the C-F (ionic) bond is observed at 682 eV and C-F (covalent) bond at 687 eV for both synthesis methods while there is no peak at all for GO.

C-F covalent bonding is responsible for the analyte reaction hence is mostly responsible for the signal that is obtained in the sensing. From the FTIR spectra, it was also observed that in the XtalFlour spectrum, C=O and C=C bonds have diminished while there is C=C bonds still present for the hydrothermally processed FGO. This would indicate that there is more C-F covalent bonding in XtalFlour synthesis compared to the hydrothermal process.

Superior fluoride doping is apparent with the XtalFlour method as it produces more covalent C-F bonds. The hydrothermal method is a longer process but is not as harsh as the XtalFlour chemical hence not as many double bonds are broken by the reaction for the formation of the C-F covalent bonding., which is what plays an important role in the reaction with the NH₃. However, the simplicity and high yield and lower cost of the inhouse thermal process makes it more desirable.

5.1.3 Multilayer Stacks of Conductive and Dielectric Material

Table 4. Conductivity data for the sensing layer stack.

Sample	Sheet Resistance R_s ($\Omega/\square$)	Resistivity R_b ($\Omega \cdot \text{cm}$)	Conductivity σ (S/cm)
pSi (Substrate)	114.5000	0.000023	43668.12227
PEDOT:PSS	10.5987	7.41908E-06	134787.5472
PEDOT:PSS/PMMA	12.0951	1.33046E-05	75161.91756
PEDDOT:PSS/PMMA/FGO	13.5930	0.002733	365.823814

PVA was initially used due to its crystalline, stable polymer properties, however, it was not successful in lowering the baseline resistance to easily observe and differentiate the

specific chemiresistive changes which are attributed to the sensor's sensitivity and selectivity. PEDOT:PSS was effective in lowering the sheet resistance of bare pSi from $114.5\Omega/\square$ to $13.6\Omega/\square$ and baseline resistance from $1.2\text{ M}\Omega$ to $133.3\text{ k}\Omega$ and therefore achieving conductivity that is close to regular lightly doped silicon substrates at $5\Omega/\square$ [144]. This allows the inert substrates to have similar properties of silicon since the sheet resistance and conductivity values are within range. The unexpected interactive behaviour of the base layer of PEDOT:PSS is shown in Figure 21. Being highly conductive and due to its porous, conglomerated top surface, PEDOT:PSS showed susceptibility non-specific to interaction with several external environmental factors. The response with the ammonia gas was undesirable and required another coating layer to mask/prevent the interaction between the target molecules and PEDOT:PSS.

A layer of 400 nm PMMA film was used to limit the interaction of the target with the conductive underlayer. This improved the sensing mechanism and gave a response due to FGO and not from GO as desired. Full sensor baseline resistances did vary after fabrication iterations of the devices, however, it remained within $10\text{ k}\Omega$ of the original measured resistances. This was easily rectified by adjusting the first resistor in the voltage dividing circuit of the sensor read-out system.

From the results in Figure 21, the observations confirmed that adding an adequately thick layer of PMMA on top of the PEDOT:PSS, significantly improved the device responsiveness with respect to the specificity in the targeted sensing mechanism. The PEDOT:PSS base layer was rendered inactive to the exposed ammonia and the purging nitrogen gas on the PMMA layer. Having a high surface to volume ratio also enhances the

effectiveness of PMMA as it covers the entirety of the layer of PEDOT:PSS and limits interaction with the exposed gas molecules.

In this work, contact resistances are considered negligible in the data acquisition process. When transitioning forward and focusing on flexible polymer integration, these factors will be considered and accounted for. The contact resistances and parasitic capacitances from transient measurements from the substrate would be based on the structure configuration and can be decoupled. Tolerances can be modelled from the localized baseline resistivity of the novel layer stack in future device iterations.

The conductive and dielectric layer stack provides the necessary sensor modularity needed to make a viable inert, polymer substrate which would be rendered active for chemiresistive sensors. PEDOT:PSS is highly susceptible to external factors such as change in pressure, and atmospheric doping. Therefore, the dielectric layer is crucial to ensure a seal such between external factors, while providing the necessary conductivity and charge distribution as it insulates the conductive layer to observe resistance change $|\Delta R/R|$ (%) at a more appropriate sensitivity range.

Figure 21. Different substrate responsiveness coated with PEDOT:PSS (500 nm), PEDOT:PSS & PMMA (500 nm + 400 nm) with respect to ammonia exposure over time (10s intervals).

5.2 Initial Testing and Verification of Results

The initial transient results of the four tested structures were captured and delineated, shown in Figure 22 a) in an ideal, contaminant free environment of the chamber vacuum, with low level leakage and limited ammonia gas flow. The estimated ammonia flow rate onto the sensor coating was ≤ 10 ppm. The sensors were tested individually, with the test chamber being depressurized to ≤ 40 mTorr before each test. The sensors were all exposed to the gas for three minutes, followed by an instant nitrogen purge. Two minutes after the purge, the vacuum pump was reconnected to the setup to remove residual gas and prepare the chamber for the next test. The chamber pressure increases constantly throughout each test, so the effective ammonia flow was not expected to remain constant. The traditional graphene oxide demonstrated no response to the presence of ammonia as expected due to the lack of any functionalization. All three functionalized graphene oxide sensors demonstrated a visible response to the presence of ammonia. After the nitrogen purge, the voltage output approached nominal readings following reconnection of the vacuum pump.

The absolute percentage change of the resistance was then recorded as shown in Figure 22, as the actual resistance change in these tests was negative since the resistances decreased throughout exposure. The graphene oxide demonstrated no apparent change in resistance that can be attributed to the ammonia exposure within the first few minutes, whilst the three functionalized sensors all reacted within the first 10 seconds of exposure.

The resistance change would continue to rise for the first 90 seconds of each test, at which point it started to decrease as the gas flow was slowing down due to pressure build-up in the chamber. The two hydrothermally processed FGO-based sensors had similar maximum resistance changes, with the peaks being at 7.4% for 30% HF (FGO30) and 6.1% for the 49% HF (FGO49) sensors.

The XtalFluor processed sensor demonstrated a larger resistance shift with a peak change of 8.9%. The XtalFluor device also demonstrated the fastest drop in resistance change, indicating that the ammonia would unbind from the surface more rapidly. The FGO49 had the slowest drop in percent change, indicating that the presence of the double bonds was causing a retention of ammonia particles.

Following the nitrogen purge, the FGO49 also had the least amount of variation, further indicating its strong affinity for holding onto the captured ammonia particles, while the other sensors dropped rapidly. Within the first minute of turning the pump back on, all sensors had returned close to the original baseline resistance. The results demonstrate that the functionalization process introduced an electrical sensitivity in the previously unmodified graphene oxide device.

Figure 22. a) Response of FGO (30,49 %), XtaFluor, and GO to high concentration ammonia.

5.3 Sensor Function Verification

5.3.1 Comparison with a Commercial Sensor

Sensor validation was performed in conjunction with the Honeywell Midas NH_3 sensor to determine the effective sensitivity with respect to actual gas concentration. The FGO sensor responds to the ammonia almost instantaneously, within seconds of exposure while the commercial sensor only responds after the concentration has reached 9 ppm. The linear response of the chemiresistive gas sensor peaks at approximately $|\Delta R/R| = 8\%$ at being 19 ppm with the Honeywell sensor, indicating a sensitivity of $0.42\% \Delta R/R$ per ppm.

Both sensors showed an immediate response to the decreasing ammonia concentration. Within five minutes without the presence of any ammonia, the chemiresistive sensor returned to its baseline value. The FGO-based sensor shows a full resolution of sensitivity that the commercial sensor does not. The chemiresistive sensor can

show lower concentrations that then can be later correlated into actual gas concentration readings.

Figure 23. FGO-based sensor correlation with a commercial sensor.

5.3.2 Sensor Operation in Low Concentration (ambient) Conditions

Figure 24 demonstrates the sensor performance under ambient conditions. The sensor was exposed to a flow of an ultra-low concentration (2.26 ppm) of ammonia gas. To investigate material degradation effects on sensor performance, the sensor was measured right after sensor coating, and then periodically after 1, 2 and 4 days following fabrication. Each peak on the graph shows the responsiveness to the concentration of the sensor.

The newly coated sensor sample had a peak response was around 13%, and the overall change was a $|\Delta R/R|$ of $\sim 5.75\%/ppm$. The sensor demonstrated fluctuation throughout the exposure due to the solution being tested right after drop coating. The adjusted scaled percentages would demonstrate the same linear response that was modelled from previous experiments conducted in ideal conditions.

Figure 24. Graph of the sensitivity of a coated FGO-based sensor at different periods of time.

The previously coated counterparts would demonstrate favourable results as well. An apparent 11%, 8.4%, and 9% peak sensitivity was observed during experiments for each of the sensors after 1, 2, and 4 days after coating with a $|\Delta R/R|$ of 4.86%, 3.71%, and 3.98% per ppm. The sensor response however demonstrated the same unstable readings a day after initial measurement but did settle in the following days. This can be attributed to the settling time of the sensing layer to achieve stability. The slight decrease in sensor performance was expected due to sensor storage and environmental doping. Regardless of duration between coatings, the sensors would demonstrate a rapid response back to baseline readings which indicate proper molecular discharge and quick reversibility when not exposed to the target NH_3 . The sensor showed the same desired linear characteristic in lower concentrations. pSi sensors showed slightly lower peak $|\Delta R/R|$ after coating stabilized compared to SS. This can be attributed to the lower conductivity of the material stack compared to SS.

The higher response to the exposure of ultra-low NH_3 concentration compared to ideal conditions can be attributed to a ‘trap effect’ that the PMMA sealant layer would exhibit. Since the FGO layer and the target molecules would demonstrate changes in conductivity due to specific chemical affinity between them, and the fibrous microstructures in PMMA would provide available vacancies for molecular retention with more ease. This would aid in the retention of target molecules and facilitate augmented interaction and response between the sensing layer and the target analyte.

This data validates that the sensor response remains profile over a broad concentration ranges and the sensitivity is reproducible for ultra-low concentrations ($\sim 1\text{-}2$ ppm) consistently after repeated use and after a few days of sensor fabrication. To further improve results, additional packaging components such as a sensing membrane with a small orifice is desired. Sensors can also be packaged in vacuum or low differential pressure configurations to diminish the environmental doping effects.

5.3.3 Burst Exposure

To analyze its response time and response kinetics more closely, the FGO-based sensor was exposed to ammonia gas flow (2.28 ppm) in 10 s intervals. This experiment closely emulates an exhaled breath sample collection from a subject during intermitted exhaled breath monitoring tests. The burst exposure intervals were repeated three times to view the sensor characteristics under repeated exposure to the target analyte. The sensor performed relatively well as each burst exposure of NH_3 showed a considerable response as well as each settling interval remained at a steady level. Upon first exposure, the response peaked at 6.5% and hovered around that region when the flow was cut off. Upon second exposure,

the peak change went from 6.5% to 10.5% resulting in a total change of 4%. The response then started at 9% for the third exposure and peaked at 12% for a total change of 3%.

The sensor shows promising results when exposed to burst ammonia flow. The overall changes throughout each exposure were 6.5%, 4%, and 3% respectively. The changes in response differ due to the short settling time and a slight retention of particles on the surface. The fact that the sensor response remains steady as there is no gas exposure is a great attribute that can be configured and calibrated to reflect the actual concentration of target analytes present in exhaled breath which is paramount for POC devices.

Figure 25. Sensor response to 10s interval burst exposure.

5.3.4 Demonstration of Multi-analyte Sensing Capabilities

Acetone was investigated due to its relevance in diabetes monitoring. The experiment was conducted by generating ammonia vapour as a qualitative experiment. This was conducted to verify the distinct multi-analyte chemiresistive sensing capabilities of the FGO-based sensor.

A beaker of acetone was heated on a hot plate at 56 °C and was placed into the sensing chamber. In Figure 26, device exposure to acetone vapour demonstrated the expected, opposite increasing voltage response. The overall responsiveness to ammonia $|\Delta R/R|$ (%), equal cross-response and linear correlation of the sensor was predictable and remained unchanged. The trend showed that the peak exposure from the acetone vapour occurred at 10 s.

The change in $|\Delta R/R|$ (%) reached a maximum of 1.7% for the FGO-based sensor in ambient conditions as well as the GO sensor in both open and closed environments demonstrated limited response. The device henceforth proved capable of targeting multiple, opposite analytes, and shows a distinct, predictable response which can be attributed to the selectivity of the chemiresistor device at an ultralow concentration range. Since concentration ranges of acetone in exhaled breath of people with diabetes can be as low as ~ 1.8 ppm, the sensor response fits well within the physiological monitoring range. To further verify the sensing capabilities of the coatings, the FGO and GO coated sensors were exposed to a timed-release of isopropyl alcohol and ethanol. Neither the GO nor FGO-based sensor responded to IPA or ethanol.

Since the concentration ranges of acetone in exhaled breath of people with diabetes can be as low as ~ 1.8 ppm, the sensor response fits well within the physiological concentration ranges. This data shows a proof of concept in terms of distinguishing the opposite transient response of acetone and furthermore proves to be highly promising for detecting multiple analytes, in ultralow concentrations.

Figure 26. FGO-based sensor voltage response and nominal resistance change to acetone and comparison with NH_3 .

5.4 Shelf Life and Implementation

These devices proved to be consistent after the fabrication and testing processes. However, there were minor inconsistencies with the device fabrication process that could affect the longevity and implementation of these devices in a fully packaged system.

The FGO-based sensors performed well with respect to immediate exposure of NH_3 . The time response demonstrated throughout the experiments shows good correlation and instant feedback to the increase in concentration of NH_3 and Acetone. Monitoring of clinical conditions is not dependent on constant sampling, however information intervals between readings can prove valuable in clinical diagnosis.

It was noted that the full sensor baseline resistances did vary after fabrication iterations of the devices, however, it remained within 10 $\text{k}\Omega$ of the original measured baseline resistances. This was due to the minor variations of thickness of the layer stack. When the FGO was coated, the baseline resistance of the entire sensor was measured, and the voltage divider resistance was then calibrated. This method is not sufficient for a market ready system and efforts will be made to keep fabrication processes consistent to remain within a reasonable baseline resistance range. Also, microcontroller interfacing can also be used to calibrate the circuit if there are any discrepancies.

The shelf life of the sensor showed consistent results after a few days of fabrication. This shows great potential for these sensors to remain out in normal environmental conditions without compromising the integrity of the sensing interface. The only variation was seen to be in the overall normalized resistance change and was minimal. Again, the microcontroller can adjust and set the correlation between the actual concentration and the percentage change since the trend remained linear. Overall, the sensor integration shows great promise to be a wearable, point-of-care device as it features all the necessary components that can be designed further to be miniaturized by incorporating components on both sides of the board to further reduce the overall system footprint.

The results described in this chapter establish the optimal augmented sensing properties obtained through the fluorination of graphene oxide and the novel multilayer thin film stack for specific analyte retention. The qualitative and quantitative analysis for the sensor devices were conducted under both pristine and ambient conditions and seen to perform extremely well exhibiting great response and selectivity. The device integration into a full-scale data acquisition and capture system with a miniature footprint circuit board, showed excellent preliminary results and maintained signal integrity during low-level sensing.

Conclusions

This work has investigated and subsequently implemented a series of graphene derived materials into a low-cost, small footprint chemiresistive gas sensor with exceptional, early-stage sensing capabilities that can be used to target specific markers. The novel materials used are ideal for implementation on inert, low-conductivity substrates while maintaining the same properties as these substrates are optimal for medical monitoring due to their low-cost, robust composition, and less susceptible to environmental doping.

A literature review was conducted to focus on present technologies for targeted gas sensing. The discussion described the prevalent sensing techniques with different materials and their drawbacks in design and implementation for specific gas sensing. The concept behind the use of graphene and its derivative GO was also discussed, and furthermore examined its augmented electronic properties for sensing. Tuning the chemical affinity of GO towards NH_3 and ketones by fluorination determined that it was an ideal sensing material candidate.

Primary quantitative work was put into designing the IDE array for maximize responsiveness to the interaction of the target gas and the sensor coating. The electrode designs were first designed on L-Edit CAD software with the MEMSPro package. The IDE array structures were then printed on substrates using microfabrication processes such as wet etching and lift-off. Using a pSi substrate instead of relying on regular Si conductive properties, shows the novelty of the sensor and its ability to be printed on inert flexible substrates such as polyamide. Device designs were made to have overlapping electrodes that have a width of 300 μm and length of 5.3 mm for an aspect ratio of 20. The structures had an optimal miniature design while taking advantage of the full effects of the FGO

sensing layer due to it already having a high surface to volume ratio. The longevity of these devices was explored and used repeatedly without much variation makes them optimal for repeated usage applications.

The sensing layer was an in-house synthesized FGO layer used to create gaseous molecule interaction and resultant resistance changes when exposed to the target ammonia gas. The process of fluorination would weaken the binding of GO and the presence of the F adatom which reduces the intermolecular distance between O and H groups in the target NH_3 . This interaction would reflect a decrease in resistance linearly proportional to the concentration and number of molecules involved in the interaction.

To increase conductivity and limit interaction of the exposed gas with the substrates, PEDOT:PSS and PMMA were added as a novel layer stack to limit the electrical response to only the sensing layer. PEDOT:PSS is a highly conductive layer that lowers the baseline resistance from $114.5 \Omega/\square$ to $10.6 \Omega/\square$ comparable to an inert substrate and makes resistance changes with respect to layer-analyte interaction distinguishable. PMMA as a sealant dielectric film proved that it limited interaction between the conductive underlayer and the target gas. This stack of novel material under the sensing layer renders inert flexible polymer substrates desirable for versatile and robust physiological monitoring applications.

The custom PCB to demonstrate the hybrid integrated system was designed to be featured on a small-footprint, miniature board to evolve into the use with non-invasive, point-of-care, exhaled breath monitoring devices. This PCB would be able to house the packaged sensor securely while having all the integrated components on the same platform for data acquisition and readout purposes. The board featured a low pass filter to condition

the signal and reduce voltage drift that might be mistaken as a response. Data samples were taken every second and stored locally to be processed and analyzed afterwards. This proves that the sensor packaging and integration is paramount to the viability of the entire system and its reliability on capturing data for repeated measurements.

Quantitative analysis was performed on both GO and FGO to determine the overall sensitivity of each sensing layer when interacting with the exposed analytes. GO had no reaction when exposed whereas FGO showed optimal response as it demonstrated a specific linear profile of $|\Delta R/R|$ of $\sim 5.7\%/ppm$, and the overall peak change was 13% when exposed to 2.26 ppm of NH_3 . The same linear profile was observed when exposed to acetone, as it has the same molecular affinity towards the C-F bonds and electron transfer is augmented. The change in $|\Delta R/R|$ (%) reached a maximum of 1.7% for acetone.

In conclusion, this work demonstrated a proof-of-concept hybrid integrated chemiresistive sensor that was successful in detecting an ultra-low-level concentration of 2.26 ppm of NH_3 using in-house synthesized FGO as the sensing material layer. Graphene oxide functionalization in-house techniques for fluorination was employed and proved beneficial in terms of lower cost and higher yield compared to higher temperatures and quicker processing times. The device performance was preferable to a commercial electrochemical NH_3 sensor in detection limit, sensitivity, and linearity. The design of these chemiresistor devices can be configured in a way that the sensing layer and substrate are interchangeable, which makes them advantageous. Passivated silicon emulated a low-cost, robust polymer substrate. In the future, such devices will be directly printed using 3-D printing techniques, on a lower cost substrate for large area manufacturing and for ease of integration in flexible form factors. The conductive layers of, PEDOT:PSS and PMMA

would provide necessary conductivity and limit interaction with the targeted gas. The cross-responsiveness of the sensor demonstrated that it could handle concentrations of acetone in the ~ 1 -5 ppm range which is ideal for physiological, exhaled breath monitoring of diabetes.

This work establishes a roadmap to fabricate such sensors on a low-cost polymer surface with configurable sensing layers, and to identify the presence of multiple gaseous analytes. The small footprint of the device also serves useful for smart wearable type health monitoring applications. Extensive experimental validation using a commercial gas sensor as control and ultra-low concentration of gaseous analytes verified that the FGO based chemiresistive gas sensor has a unique, target specific, transient response that can be easily analysed using simplified techniques, illustrating the versatility of these devices over traditional electro-chemical sensors.

Future Work

This work has established a platform for low-cost, non-invasive, point-of-care sensors. The FGO chemiresistive sensor proves to be an extremely viable candidate for repeated use due to its robust composition. The roadmap of this project can be further extended and has great potential to be a versatile gas sensor for multianalyte detection. The sensor packaging, and signal processing techniques can give the sensor an edge over market ready options.

The current devices are fabricated on passivated silicon substrates due to microfab limitations on handling flexible low-cost material substrates. Future iterations of these devices can be effectively patterned on flexible polymer substrates using additive manufacturing methods such as Inkjet or 3D printing. The robust composition of the multilayer stack proves as a highly innovative way to fabricate chemiresistive gas sensors and can be configurable based on the sensing need.

The sensor packaging and footprint can be further minimized when printed on the polymer substrate. The added property of flexibility can greatly reduce the system footprint and can be adequate for a smart wearable device such as a watch. A monitoring device of this calibre would sit readily available without the use of any interchangeable cartridges or components.

Furthermore, the signal output can be used to implement algorithms to identify the specific signatures pertaining to different responses to unique analytes. The response signatures can be attributed to specific maximum response with respect to time. This can be a technique used to identify the specific analyte present without having to reconfigure any of the sensing components. This can also be extended to instantly give feedback of which analyte is being detected along with its concentration.

The data gathered from the sensor can be stored on a server where physicians can remotely access information pertaining to their patient's condition and can monitor and diagnose on demand. These devices have the potential to facilitate easier patient-physician cooperation using it in a point-of-care, remote setting. This sensor also has the potential to impact markets for widespread adoption where continuous monitoring devices prove to be costly. This would allow for the option of having a low-cost wearable that would provide the necessary clinical feedback that can ameliorate the quality of life for an individual.

Appendix

A.1 FGO Based Sensor: Custom Printed Circuit Board Design Schematic

Figure 27. Schematic of custom board components.

A.2 Component Sizing

Instrumentation Amplifier Specifications: AD 620 Gain 10 V/V, Preamp Low Pass Filter designed for up to 120 kHz.

Component	Value
R ₁₁	5.489 kΩ
C ₁₅ , C ₁₃	106 pF
C ₁₄	1.06 nF
R ₁₂ , R ₁₃	10 kΩ

Filter design equations for up to 120 kHz [158]:

$$FilterFreq_{DIFF} = \frac{1}{2\pi R(2C_D + C_C)}$$

$$FilterFreq_{CM} = \frac{1}{2\pi RC_C}$$

Where $C_D \geq 10C_C$

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