Fabrication of Functionalized Graphene Coated OTFT
Humidity and Chloride Ion Sensors for Detecting
Corrosion Precursors in Metallic Structures

by
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A thesis submitted to the Faculty of Graduate and Postdoctoral Affairs in partial
fulfillment of the requirements for the degree of
Master of Applied Science

Electrical and Computer Engineering
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Abstract

Corrosion monitoring has been the focus of structural health monitoring due to its damaging effects on metallic structures. Early detection of environmental factors responsible for corrosion can reduce maintenance related expenses. There is growing interest in developing compact and low-cost thin film sensors with high sensitivity to corrosion precursors. In this work, chemical sensors are fabricated using solution processed C_{60} organic thin film transistors (OTFTs) coated with functionalized graphene oxide for humidity sensing and functionalized graphene nanoparticles for Cl^{-} detection. The fabricated OTFTs exhibit good carrier mobilities and current ON/OFF ratios reaching 1.2 cm^{2}/V.s and 5x10^{3}, respectively. The rGO coated OTFT humidity sensor is designed for qualitative measurements, and it exhibits a relative responsivity for dry to surface wetness transition of 122.6\%, with a response time of 20 ms. Chemically functionalized hydrogenated graphene coated OTFT is used for Cl^{-} ion sensing which yielded sensitivity of 4%/ppm to ultrafine ionic concentrations.
Co-Authorship

The scientific content presented in this thesis was developed by the Organic Sensors and Devices Lab at Carleton University (2019-2021) with the collaboration of the National Research Council of Canada, and presented in one published review paper and one submitted manuscript (under review), referenced below.

The work presented in reference A, is a comprehensive overview of corrosion forms in aircraft structures and state of art graphene based sensing mechanisms for corrosion monitoring. The overview on aircraft corrosion forms and mechanism was presented by Dr. Lucy Li at the Institute of Aerospace Research (NRC). The literature review on existing corrosion sensing mechanisms and potential graphene based sensing approaches was carried out by the thesis author in collaboration with Prof. Ravi Prakash at Carleton University.

The submitted manuscript (reference B) describes novel corrosion sensors based on solution processed n-type organic thin film transistors coated with functionalized graphene detecting surface moisture and low concentration of chloride ions. It establishes their viability in low cost, non-destructive corrosion monitoring and prevention approaches for the safeguard of aircraft structural integrity.

The experimental work presented in this thesis and manuscript B was conducted by the author in collaboration with Dr Siziwe Bebe, under the supervision of Prof. Ravi Prakash. Material selection, synthesis and device fabrication process was developed by the author under the guidance of Prof. Ravi Prakash and Dr. Siziwe Bebe. Device fabrication including electrode patterning and material deposition was carried out by the author with the assistance of Dr. Siziwe Bebe. Device electrical characterization and experimental data collection and analysis was performed by the author of this dissertation.

Acknowledgments

First of all, I would like to express my gratitude to Prof. Ravi Prakash for providing me the opportunity to be part of his team and work on fascinating projects, for his mentorship, continuous encouragement and never ending patience. Words could not express my appreciation. Special thanks to Dr. Lucy Li at the National Research Council Canada for sharing her expertise on corrosion forms and mechanisms and for great discussions on corrosion management and sensing approaches. Our year and a half long collaboration was invaluable in the development of the corrosion sensors.

I would also like to thank Dr. Siziwe Bebe who spent innumerable hours assisting me during material synthesis and characterization as well as device fabrication, and for always being available with great advice and guidance.

Furthermore, I would like to thank Robert Vandusen and Angela Mccormick at Carleton microfabrication lab who assisted me throughout the device microfabrication and physical characterization. The training they provided me would certainly help me advance in my professional career, for which I am truly grateful.

Special thanks to my research team at the Organic Sensors and Devices Lab, in particular, Ivan Amor for his continued support and assistance in experimental setups, and Roslyn Massey for sharing her expertise on organic electronics.

Last but certainly not least, I would like to thank my parents and my siblings for their constant support, encouragements and for believing in me during times I could not believe in myself.
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<td>Acoustic Emissions</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>ALD</td>
<td>Atomic Layer Deposition</td>
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<tr>
<td>BG</td>
<td>Bottom Gate</td>
</tr>
<tr>
<td>BGBC</td>
<td>Bottom Gate Bottom Contact</td>
</tr>
<tr>
<td>BGTC</td>
<td>Bottom Gate Top Contact</td>
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<tr>
<td>CELIV</td>
<td>Charge Carrier Extraction by Linearly Increasing Voltage</td>
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<tr>
<td>DI</td>
<td>Dark Injection</td>
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<tr>
<td>DI</td>
<td>De-Ionized</td>
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<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
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<tr>
<td>FTIR</td>
<td>Fourrier Transform Infrared Spectroscopy</td>
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<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IDT</td>
<td>Interdigitated Transducer</td>
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<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
</tr>
<tr>
<td>IPES</td>
<td>Inverse Photoelectron Spectroscopy</td>
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<tr>
<td>LOR</td>
<td>Lift-Off Resist</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
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<tr>
<td>OFET</td>
<td>Organic Field Effect Transistor</td>
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<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
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<tr>
<td>OPT</td>
<td>Organic Phototransistor</td>
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<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
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<td>OTFT</td>
<td>Organic Thin Film Transistor</td>
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<tr>
<td>OSC</td>
<td>Organic Semiconductor</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapour Deposition</td>
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<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
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<td>PES</td>
<td>Photoelectron Spectroscopy</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PPV</td>
<td>Poly(p-phenylene vinylene)</td>
</tr>
<tr>
<td>PR</td>
<td>Photoresist</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>rGO</td>
<td>reduced Graphene Oxide</td>
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<tr>
<td>SAW</td>
<td>Surface Acoustic Wave</td>
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<tr>
<td>SCLC</td>
<td>Space Charge Limited Current</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SHM</td>
<td>Structural Health Monitoring</td>
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<tr>
<td>TG</td>
<td>Top Gate</td>
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<tr>
<td>TGBC</td>
<td>Top Gate Bottom Contact</td>
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<tr>
<td>TGTC</td>
<td>Top Gate Top Contact</td>
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<tr>
<td>TOF</td>
<td>Time of Flight</td>
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<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
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<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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<td>X-ray Emission Spectroscopy</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>$\delta$</td>
<td>Loss angle</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity</td>
</tr>
<tr>
<td>$\mu_{FET}$</td>
<td>Field effect carrier mobility</td>
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<tr>
<td>$\mu_{\text{lin}}$</td>
<td>Carrier mobility in the linear regime</td>
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<tr>
<td>$\mu_{\text{sat}}$</td>
<td>Carrier mobility in the saturation regime</td>
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<td>$C_i$</td>
<td>Effective capacitance per unit area of OTFT stack</td>
</tr>
<tr>
<td>$d$</td>
<td>OTFT stack thickness</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent Series Resistance</td>
</tr>
<tr>
<td>$g_m$</td>
<td>Transconductance</td>
</tr>
<tr>
<td>$I_{DS}$</td>
<td>Drain-source current</td>
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<td>$I_{DS,\text{lin}}$</td>
<td>Drain-source current in the linear regime</td>
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<td>$I_{DS,\text{sat}}$</td>
<td>Drain-source current in the saturation regime</td>
</tr>
<tr>
<td>$I_{GS}$</td>
<td>Gate-source current</td>
</tr>
<tr>
<td>$L$</td>
<td>Channel length</td>
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<tr>
<td>ON/OFF</td>
<td>Current ON/OFF ratio</td>
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<tr>
<td>$R$</td>
<td>Responsivity</td>
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<tr>
<td>$S$</td>
<td>Sensitivity</td>
</tr>
<tr>
<td>$V_{DS}$</td>
<td>Drain-source voltage</td>
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<td>$V_{GS}$</td>
<td>Gate-source voltage</td>
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<td>$V_{Th}$</td>
<td>Threshold voltage</td>
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<td>$W$</td>
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1 Introduction

1.1 Background

Structural health monitoring (SHM) is a growing discipline focused on studying the behaviour of civil and mechanical engineering structures such as bridges, oil and gas pipelines as well as aerospace structures. It involves the collection and analysis of data about the condition of structures throughout their entire lifecycle that facilitate the design and implementation of efficient prevention and maintenance programs [1, 2]. SHM has been the focus of growing interest by government agencies and private industries due to the increasing age of existing civil, mechanical engineering and aerospace structures and their life-safety and economic impact [2]. These structures require exhaustive and expansive maintenance and repair protocols to preserve their integrity as well as their safety and prevent eventual catastrophic failures. SHM systems have the potential to ensure the safety and integrity of such structures, while alleviating maintenance and repair costs by adopting an as-needed maintenance approach instead of scheduled maintenance and preventing unscheduled maintenance as well [1]. The goal of SHM protocols is to monitor operational conditions and factors affecting and indicative of structural damage which can be classified in three categories outlined in Figure 1. Physical factors include stress and stain, cyclic loading and mass loss. whereas chemical and environmental factors are related to the presence and concentration of pollutants, acidity, pH variations, high levels of humidity and temperature fluctuations [3].

Traditionally, the adopted detection approaches rely on the use of distributed and standalone sensor systems that detect structural defects such as cracks and corrosion, and critical operating conditions being stress, strain, vibrations and cyclic loading. These methods include enhanced visual inspection, mass loss measurements using sensors such as elec-
Figure 1: Classification of factors affecting the structural integrity of metallic structures [3].

Electrical resistance, radiography, ultrasonic sensors, galvanic corrosion sensors among others [3]. These sensing approaches can only assess physical damage and fail to account for the chemical and environmental factors that contribute to the onset of metal degradation such as corrosion. Numerous studies have shown that the durability of civil, mechanical engineering and aerospace structures are significantly affected by the environmental conditions in which they operate. These conditions include temperature, humidity, pressure, acidity and pollutants which are the precursors of numerous types of defects such as corrosion events (pitting, intergranular, exfoliation. . . ), hydrogen attack and fatigue [4]. In literature, various emerging environmental sensing approaches have been suggested which offers in situ and continuous monitoring of various environmental parameters affecting the health of structures. They can be integrated within structures and provide real-time information about the operating and environmental condition auspicious to structural defects and failure [5]. Such detection methods are based on emerging sensing mechanisms, such as optical, chemiresistive, capacitive, acoustic and potentiometric sensing [5]. These sensing mech-
anisms can be used in distributed systems and wired and wireless networks comprising
stand-alone sensors and sensor nodes that include multiple sensors targeting a wide range
of parameters simultaneously, all connected to a common processing unit to minimize the
complexity of the network and reduce the installation and maintenance costs [6, 7]. New
approaches rely on the use of semiconductor material used as the active component or the
sensing component or both. Since the discovery of organic semiconductors, significant re-
search has been devoted to the fabrication of organic electronics and optoelectronics and
their implementation in chemical and optical sensing [8]. Organic semiconductors are an
ideal candidate for the fabrication of environmental sensors owing to their high sensitivity
and selectivity stemming from their unique electronic and chemical properties. Moreover,
their exceptional physical properties allow for the development of miniaturized and flexible
sensors while preserving their high performance [8].

1.2 Sensing Mechanisms

Currently, there is a variety of sensors used in structural health monitoring which are based
on various sensing mechanisms having both strength and weaknesses depending on the
targeted application. These sensors can be classified in terms of the sensing mechanism by
which they operate, namely, optical, resistive, capacitive, acoustic and potentiometric. In
this section, a comprehensive overview of existing and novel sensing techniques applicable
in SHM are presented along with a description of their sensing mechanisms, their strengths
and limitations.

1.2.1 Optical Sensors

Optical Sensing is a mechanism by which targeted parameters or analytes are detected and
monitored by recording the optical response of the sensor. In this technology, the sensing
response depends strongly on the optical response of the sensor in terms of frequency, polarization and wavelength, which can be converted into an electrical signal [9]. In SHM application, the most common optical sensors are fiber optic-based sensors as they possess powerful analytic capabilities, able to provide remote and distributed monitoring information about various analytes and parameters throughout the entire lifecycle of the structure [6, 9]. Fiber optic-based sensors are essentially optical fibers in which the cladding is made of or coated with materials sensitive and selective toward certain chemicals, temperature, pressure and other physical properties. In the presence of measurands, the refractive index of the fiber core changes, which in turn, affect the frequency, wavelength or intensity of the optical signal propagating inside the fiber core [6, 10]. Currently the most common fiber optic-based sensing technologies suitable for structural health monitoring are intrinsic fiber optics and fiber gratings. Intrinsic fiber optics use the interaction between the evanescent field and fiber cladding, which induces a change in the intensity of the propagating optical signal as shown in Figure 2(a). Fiber grating on the other hand, produces discreet spectral loss in the propagating optical signal brought by periodic perturbation in the refractive index of the fiber core as illustrated in Figure 2(b) [11]. Fiber grating based sensing monitors the shift in the spectral dip in the event of structural deformation or the presence of target analytes affecting the periodic grating and the refractive index of the fiber cladding, respectively [10].

Fiber optic-based sensors are promising candidates for environmental sensing in SHM due to their high sensitivity, low transmission loss, low power consumption and small footprint. However, the deployment of fiber optic-based sensors has been hindered by the fragility of optical fibers and their propensity to misalignments and bending during installation and maintenance activities [10].
1.2.2 Resistive Sensors

Resistive sensing is a mechanism by which information about structural parameters and chemical analytes presence and concentration are provided in the form of electrical resistance [13]. Resistive sensing is an established technology used in a wide range of application including temperature and gas sensing, as well as train gauges and chemical sensors. Resistive sensors can be realized with a variety of configurations depending on the target application. In gas or chemical sensing, a set of interdigitated electrodes (Figure 3(a)) is made of or coated with a conductive or semiconductive sensing material that reacts chemically with specific chemical compounds and responds to their presence and change in concentration in the form of change in surface resistivity [14, 15]. Similar to gas sensors, temperature sensors employ intrinsic metallic filaments or filaments coated with conductive and semiconductive materials (shown in Figure 3(b)) that experience changes in resistance resulting from the effect of temperature on the electron mobility in the filaments [13]. Strain sensors, also known as gauge sensors (Figure 3(c)), on the other hand, rely on change in electrical resistance caused by mechanical deformation resulting from strain, stress, pressure. . . etc. [13].
Resistive sensing is a valuable technology for structural health monitoring due to its sensing capabilities, design simplicity, compactness and low cost. It can be used for a wide range of smart sensors targeting parameter and analytes critical for maintaining the safety and durability of metallic structures [13]. However, the reliability of resistive sensors is limited by its high-power consumption, limited sensing range and susceptibility to vibrations, temperature, magnetic interference and sound and air pressure. Moreover, resistive sensors are not suitable for long-term measurements as time and temperature drifts are substantial [18].

1.2.3 Capacitive Sensors

Capacitive sensing is a popular sensing technology used for many applications including intelligent human interfacing, displacement measurements, non-destructive testing and chemical and biomedical sensing [19]. Its popularity stems from capacitive sensors fast re-
sponse, simple and inexpensive fabrication and low power consumption, in addition to their non-destructive and non-intrusive sensing mechanism. Capacitive sensing provides information about physical and chemical parameters by measuring the capacitance between two electrodes placed in the material under test.

In the context of structural health monitoring, physical capacitive sensors are used to detect defects and physical deformities such as voids and cracks, and quantify physical parameters including shear bending, thickness, elastic modulus, stiffness, among others [20]. Common configurations used in physical sensing include parallel plate capacitors, cantilever beams, and acoustic transducers. Chemical capacitive sensors, on the other hand, detect the presence and measure the concentration of a range of analytes such as relative humidity, heavy metals and gases by monitoring the change in permittivity of sensing membranes used in conjunction with a set of interdigitated electrodes as illustrated in Figure 4 [20].

![Image](image.png)

Figure 4: Schematic diagram of interdigitated capacitor based chemical sensor. (a) Top view of the interdigitated capacitor coated with a sensing layer. (b) Cross sectional view of the interdigitated capacitor based sensor without the sensing layer [3].

Although capacitive sensors have been widely employed as physical sensing applications, their application in chemical sensing is relatively new and faces issues associated with slow response time, low output signal and short-term stability of the sensing membrane due to poisoning which affect the sensitivity, resolution and long-term stability of the sensors [21]. Furthermore, the performance of capacitor sensors is affected by electromagnetic
interference and the complexity of measurements circuitry that becomes more significant as the footprint is decreased [22].

1.2.4 Acoustic Sensors

Acoustic sensing is a non-destructive testing technique widely employed in structural health monitoring of civil and mechanical engineering structures to detect and evaluate structural deformation and loading conditions. This sensing approach employs sensors that monitor the behaviour of elastic waves traveling at the surface of the material under testing and converting the mechanical signal into an electrical signal [23]. This can be done using acoustic emission sensors or surface acoustic wave sensors. Acoustic emission sensors detect and quantify elastic transient waves emitted by solid materials experiencing structural deformation or damage, also called acoustic emissions (AE). AE sensors are essentially passive contact-type sensors composed of a piezoelectric element housed between two electrodes to transmit the generated electric signal [23]. They are commonly used to monitor loading conditions such as dynamic and static stress and strain as well as associated structural deformities, defects and crack propagation as shown in Figure 5(a) [23].

Surface acoustic wave (SAW) sensors monitor the behaviour of applied surface acoustic waves traveling through the material under test. Similar to the AE sensors, SAW sensors consist of a piezoelectric material patterned with two sets of interdigitated transducers (IDTs) acting as the transmitter and the receiver. The transmitter IDTs convert the applied radio frequency signal into a mechanical wave that propagates through the surface of the material, whereas the receiver IDTs convert the traveling mechanical wave into an output radio frequency signal [5]. Piezoelectric materials are intrinsically sensitive to strain and temperature allowing SAW sensors to be used for related applications. However, SAW sensors can be used as chemical sensors by depositing chemical active films onto the piezoelectric layer. The sensing film modify the frequency, amplitude and/or velocity of the trav-
eling acoustic waves in the presence of targeted analytes such as relative humidity, heavy metals, and other pollutant [5].

![Diagram of acoustic wave sensor](image)

(a) Acoustic Emissions sensing mechanism [24]. (b) Surface Acoustic Wave sensor [3]

The described acoustic sensing technologies are advantageous in structural health monitoring for both structural and environmental parameters due to their small footprint, low power requirements, ease of fabrication and compatibility with moving parts. They can be connected in both wired and wireless modes; the latter requires the use of radio frequency antenna which reduced the complexity of distributed networks when a large number of sensors are in use. However, the high frequency circuitry requirements for acoustic sensing results in significant noise, reducing thereby, the sensitivity and reliability of the sensors [5].

### 1.2.5 Thin Film Transistor Sensors

Electrochemical sensing is considered one of the earliest electroanalytical measurement approaches used in the extraction and evaluation of chemical and biological systems. This approach is aimed at converting chemical responses of specific materials into a measurable electrical response [25]. Electrochemical sensing is based on electrochemistry mechanism which essentially involves charge transfer between an electrode and a transconductance element in solid or liquid phase. Electrochemical detection employs a diversity of chemical
recognition elements, predominantly, semiconductor materials which can be chemically modified to enhance their specific binding capabilities and catalytic activities [25]. However, most electrochemical sensors require aqueous electrolytes which make them rather bulky and susceptible to environmental contamination. The need for complete encapsulation may be a limiting factor for their integration in environmental sensing for structural health monitoring [26]. These issues could be addressed using solid state sensors such as thin film transistors, and meet the demand for efficient, environmentally stable and minia-turised sensors that could be easily integrated into structures.

Thin film transistors (TFT) are one of the most commonly used devices for chemical sensing. As the name suggests, TFT sensors are essentially transistors consisting of a thin film semiconducting channel, a source and drain electrodes, as well as a gate insulator as shown in Figure 6 [27]. The conductivity of the semiconducting channel is modulated by varying the applied electric field between the source and drain electrodes at a specific gate voltage. TFTs have been extensively used in integrated circuits applications, where they are used as operational amplifiers, voltage variable resistors and digital switches, among others. They have recently received significant interest in chemical and biochemical sensing application due to their high sensitivity, fast response, small footprint and simple fabrication. Environmental/chemical sensing can be achieved using TFTs in which the gate insulator material has chemical affinity toward targeted ions or is coated with an ionophore material. The sensor’s response is in the form of output current generated by the transistor channel. As target analytes reversibly binds with the gate insulator, they modulated the drain current and the surface potential [28].

In structural health monitoring applications, TFT sensors have the potential to monitor and quantify environmental parameters that are critical to structural integrity such as relative humidity, acids and hydrogen as well as parameters indicative of early signs of potential damage such as pH and metal ions. However, the performance of theses sensors depends
strongly on the ionic activity of the semiconductor channel and on the catalytic and chemical stability of the sensing material.

Organic thin film transistors (OTFT) have attracted significant attention since the past two decades owing to their low cost, simple fabrication and high sensitivity. Such devices are capable of detecting a wide range of analytes like ambient gases, ions, and biomolecules among others. They are advantageous over other sensors like chemiresistors or capacitive sensors due to their current amplification capabilities that enhances the device sensitivity. Furthermore, they generally exhibit faster response, require less power and are easily integrated in complex circuits. OTFTs small size and device architecture allow for their implementation in multiparameter sensing systems comprising OTFT arrays to detect multiple species simultaneously using common interrogation system as in the case for sensor nodes [7].

Commercialization and large-scale implementation of OTFTs in sensory platforms has been hindered by the environmental instability of organic semiconductors. Exposure of such materials to ambient environments, including humidity, temperature and ultraviolet radiation during device fabrication and operation was found to be the leading cause of the declining sensor performance, instability and short shelf life.
1.3 Motivation

Currently, environmental factors are rarely included in SHM protocols and are limited to temperature, pressure and relative humidity. Studies have suggested that the presence of chloride ions and high levels of humidity offer the right conditions for corrosion onset, which have a significant impact on the integrity and durability of metallic structures. Chloride ion thresholds for corrosion initiation has been identified to be within the range of 100 ppm and 3500 ppm depending on the type of metal alloy, temperature and pH [30, 31]. Early on detection of these agents can prevent damage, lower maintenance costs and extend the life of structures. The motivation behind this work is to develop robust low cost chemical sensors to address the lack of sensing approaches targeting environmental conditions favorable for corrosion events.

TFT chemical sensors have the potential to fill in the gap in SHM by providing a sensory platform for chemical agents responsible of metal degradation, in particular, Chloride ions and humidity. Compared to other emerging technologies, they are advantageous in terms of high sensitivity, fast response time, low power consumption and small footprint. Furthermore, they are low cost, compatible with modern electronics and easily integrated in complex circuits.

The advent of organic semiconductors has opened new perspectives for the deployment of low cost and diverse TFT sensors. The abundance, diversity and excellent electronic and structural properties of organic materials allows for the development of low cost OTFTs using low temperature and energy efficient processing techniques with performance comparable to their inorganic counterparts. While p-type OTFTs have been the focus of much interest in the research community and underwent considerable success, the progress of n-type OTFTs have been lagging due to the environmental instability of n-type semiconductors and low carrier mobility stemming from electron trapping.
The work reported in this thesis is intended to explore the feasibility and performance of n-type OTFTs using simple and low-cost fabrication techniques. The OTFTs are solution processed and feature fullerene C\textsubscript{60} as the active channel material and a novel organic gate insulator that preserves the semiconductor environmental stability and at the same time allows for effective channel modulation. Applications of the proposed solution processed OTFTs in sensory platforms are achieved through the implementation of graphene derived materials as sensing components. Herein, reduced graphene oxide and hydrogenated graphene are employed as the OTFTs sensing elements for humidity and Cl\textsuperscript{-} ions, respectively. These sensing materials are obtained by simple chemical functionalization routes that increases the chemical reactivity and selectivity of graphene without fully compromising its exceptional electronic and structural properties. This work demonstrates the achievability of low-cost solution processed n-type OTFTs and their applicability in chemical sensing using graphene derived materials. The sensors performance demonstrates the practicability of OTFTs and graphene derived material in addressing the lack of environmental sensing in SHM. The featured device architecture and materials allow for large scale fabrication and easy integration to new and existing structures. Graphene excellent and unique electronic, chemical and mechanical properties lay the groundwork for the development of a panoply of organic chemical sensors targeting a wide range of environmental factors with the aim of preserving the integrity of metallic structures and minimizing repair and maintenance costs.
1.4 Thesis Organization

This thesis consists of eight chapters and they are organized as follows: Chapter 2 is a brief review of organic semiconductors and classification including their chemical and electronic structures and the corresponding charge transport mechanisms, with special attention given to fullerene $C_{60}$ and graphene derived materials. Chapter 3 provides necessary background information on device architecture and operation of OTFTs along with characterization methods of the fundamental figures of merit. An outline of structural materials of the proposed OTFT sensors as well as detailed fabrication procedure adopted are presented in Chapter 4. Chapter 5 describes the characterization methods used to determine the physical, chemical and electrical properties of the fabricated OTFTs. Characterization results and experimental data analysis pertaining to the operation of $C_{60}$ OTFT, humidity and Cl⁻ sensors are presented and discussed in Chapter 6. Finally, conclusions and future work are presented in Chapter 7 and Chapter 8, respectively.
2 Fundamentals of Organic Semiconductors

Organic semiconductors are a class of solid materials composed mainly of carbon and hydrogen atoms. Their discovery dates back to the late 1800s where they were considered insulating materials. After the discovery of their electrical conductivity in 1950s it, much attention was drawn toward the use of organic semiconductors in the fabrication of electronic and optoelectronic devices [32]. Since then, a new research field emerged motivated by the unique electronic properties of organic semiconducting materials as well as their abundance, low fabrication costs, solution processability, and mechanical flexibility. These properties, combined with scientific progress, lead the way to significant improvements in the performance of organic semiconductor-based electronics, which made them comparable to their inorganic counterparts in term of carrier mobility, responsivity and output current [8]. Organic semiconductors have nowadays the potential to be used in a broad range of electronic and optoelectronic applications such as, organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), organic phototransistors (OPTs), as well as organic photovoltaics (OPVs). The success of such devices is also due to improvements in fabrication techniques such as deposition conditions, growth rate optimization and chemical functionalization. In addition, the diversity of organic materials and their electronic functionalities continues to broaden the range of potential applications including sensing technologies such as chemical, biochemical and environmental sensing for SHM [33].

Organic semiconductors (OSCs) are essentially carbon materials that exhibit a combination of mechanical properties associated with organic materials and semiconducting properties. Semiconducting properties refer to the optical absorption and emission in the visible spectral range, as well as the display of a level of conductivity in ambient conditions necessary for the operation of semiconductor devices such as organic thin film transistors (OTFTs)
and phototransistors (OPTs) [34]. Contrary to inorganic materials in which molecules form strong covalent bonds, molecules in organic materials are weakly bonded by van der Waals forces. The molecular structure of organic materials is characterized by two types of inter-molecular bonds shown in Figure 7: \( \sigma \)-bonds and \( \pi \)-bonds. \( \sigma \)-bonds are formed between two adjacent atoms through sp\(^2\)-hybridization, whereas \( \pi \)-bonds form between unpaired electrons throughout the entire structure by the conjugation of the sp\(_{2}\)-orbitals [35].

![Diagram of sigma and pi bonding in organic materials](image)

Figure 7: Sigma and pi bonding in organic materials [36].

The nature of the intermolecular bonds is responsible for the unique combination of mechanical and electronic properties of organic semiconductors. The weak intermolecular binding associated with organic materials provides molecules a level of freedom to move with respect to each other and allows them to easily separate in response to thermal energy. Hence, organic materials are more ductile than their inorganic counterparts, have low melting points and require lower processing temperatures [37]. Organic semiconductors, being a subclass of organic materials, exhibits the same physical properties in terms of flexibility, tensile strength and low energy processability, in addition to insulating properties associated with the physical separation between molecules and the localized bonding orbitals within the individual molecules that restrict the mobility of electrons [35]. Nevertheless,
the electronic properties of OSCs are governed by the $\pi$-bonded conjugated structure which allow for the delocalization of electrons in the direction perpendicular $\sigma$-bands and hence, determine the intrinsic electronic properties such as charge transport, Fermi energy conditions and bandgap [38]. Unlike inorganic materials where the semiconducting properties depend strongly on the quality of the band structure, semiconducting behaviour is intrinsic in OSCs where such electronic properties are entrenched in molecules and does not depend on the crystal arrangement. Consequently, effects of grain boundaries, impurities and defects are not as significant in organic materials as in inorganic materials and so allows for simpler and low-cost processing [39].

Organic semiconductors have a band structure analogous to that of inorganic semiconductors, where the Lowest Unoccupied Molecular Orbital (LUMO) is analogous to the conduction band and the Highest Occupied Molecular Orbital (HOMO) to the valence band. The HOMO-LUMO is the energy required to excite an electron from the HOMO to the LUMO and is analogous to the bandgap energy in inorganic semiconductors as shown in Figure 8 [40]. Charge carrier transport in organic materials is due to overlapping of molecular $\pi$-orbitals as well as $\pi^*$-orbitals (anti-bonding). Electron transport occurs at the lower unoccupied molecular orbital (LUMO), whereas hole transport occurs in the highest occupied molecular orbital (HOMO) [40].

The charge carrier transport mechanism has been largely debated as the nature of charge transport depends strongly on the morphology of the organic material, namely, the molecular structure and the packing [41]. Two distinct mechanisms are used to describe the charge carrier transport in organic semiconductors, namely, band transport and hopping transport. They essentially depend on the degree of order of the organic semiconductor which can be classified in two classes: small molecules and conjugated polymers [40].
2.1 Small Molecules

Small molecular crystals are materials with low molecular weight, low viscosity and a structural order that allows for manipulation of the material’s morphology. They can be viewed as a close and regular stacking of identical molecules tied together by intermolecular interactions i.e. \( \pi-\pi \) interaction, as illustrated in Figure 9(a) [41]. This class of materials include anthracene, tetracene, and pentacene, fullerene and other aromatic compounds. The prevalent charge carrier transport mechanism in small molecule organic semiconductors falls under the band transport model where charge carriers (electrons or holes) move along the energy bands in the absence of defects and traps as demonstrated in Figure 9(b). The mobility of charge carriers is enhanced by the large width of the energy bands that allows the carrier to be freely transported [42]. Compared to other organic semiconductors, small molecules show higher carrier mobilities due to their long-range periodic order and their ability to form relatively large crystals and organized polycrystalline films. However, they require complex processing and deposition techniques such as chemical vacuum deposition to achieve high levels of structural order and purity, and may be prone to environmental degradation [35].
2.2 Conjugated Polymers

Conjugated polymers, are long chain molecules resulting from bonding of source compounds (monomers) with relatively higher molecular weight [41]. The polymers are formed by iteratively repeated monomers over the entire network and bonded to each other by covalent bonds as shown in Figure 10(a). Examples of commonly used organic conjugated polymers in electronics are Polyaniline (PANI), Polyparavinylene (PPV) and PEDOT among others. The charge carrier transport mechanism in conjugated polymers is dominated by the interactions along the chains while the interaction between the chains are generally considered negligible [41]. In this class of organic semiconductors, the conduction follows the hopping regime shown in Figure 10(b), due to dislocations within the molecular structure where carriers are trapped in potential wells formed by the dislocated segments. As a result, trapped carriers have to hop from one well to another for conductivity to occur [42]. Compared to small molecules, conjugated polymers have lower charge carrier mobility due to the high structural disorder and low purity, but they are more advantageous in terms of large scale processability as they are soluble in a wide range of organic solvent, structural stability and tunable electronic properties [41].
2.3 Buckminsterfullerene

Fullerenes are a class of carbon allotropes that are essentially symmetrical nanocarbon molecules forming hollow spheres, tubes, or ellipsoids [44]. They consist entirely of carbon atoms arranged in polygons and are named based on the number of molecules that makes up their structure as shown in Figure 11 [45]. Fullerene, also known as Buckyballs, have attracted much attention in the scientific field due to their high thermal conductivity and structural strength, in addition to their potential application in electronics, nanotechnology and material science. The expansive diversity of fullerene molecules has given rise to new materials with unique chemical properties and advanced electronic properties.[45].

The most common fullerene molecule used in electronic and optoelectronic applications is Buckminsterfullerene, known as C_{60}. It was discovered by Kroto et al in 1985 and has been heavily investigated as a semiconducting and active material in organic photovoltaics and thin film field effect transistors [46]. C_{60} is an n-type semiconductor produced
from graphite by laser ablation and arc-discharge technique. It is the most stable fullerene molecule, has high electron affinity and high charge transport capabilities, as well as large linear optical responses [46]. These properties stem from a combination of structural and electronic properties which depend strongly on material purity, processing techniques, film morphology and ambient conditions. Fullerenes can exist in zero-, one-, two and three-dimensional forms as well as a variety of structures, namely, spherical, nano-tubes and polymers. They can be crystalline, polycrystalline and amorphous and have insulating as well conducting properties [47].

2.3.1 Atomic Structure and Electronic Properties of Buckminsterfullerene

Buckminsterfullerene is the purest form of organic semiconductors known, whose molecular structure is made of 60 carbon atoms arranged in the shape of a soccer ball made of hexagons and pentagons as illustrated in Figure 12. The carbon atoms in this molecular system are arrange in 20 hexagons and 12 pentagons with carbon atoms forming C=C double bonds between adjacent hexagons and C-C single bonds between hexagons and pentagons [48]. Each carbon atom has 6 electron, two of which are core electrons and the remaining four contribute to the valence molecular orbitals. Three of the latter electrons participate in the formation of $\sigma$-bonds while the remaining electron form delocalized $\pi$ molecular orbitals extending over the entire surface of the molecule [49]. $C_{60}$ is viewed as a fully sp$^2$ bonded three dimensional system with perfect $\pi$ orbital overlap alignment in contrast to planar carbon allotrope like graphene [50]. $C_{60}$ is generally considered as a conjugated molecule organic semiconductor as the fullerene molecules bond to form well-defined molecular crystals in a Face-Centered Cubic (FCC) lattice characterized by weak intermolecular interactions through van der Waal bonds. The van der Waal interactions between $C_{60}$ molecules give rise to a charge carrier transport dominated by the hopping mechanism [51].
The relative environmental stability of C\textsubscript{60} is attributed to the geodesic structures and electronic bonding factor. Unlike other organic semiconductors, it is distinguished by the absence of dangling bonds which prevent any interaction with its environment. However, the bent sp\textsuperscript{2} C=C double bonds (shown in Figure 12) result in a hybridization between planar and tetrahedral due to strained structures with relative reactivity [53, 51, 48]. Solid pristine C\textsubscript{60} molecules are electronically neutral and the HOMO-derived band is totally filled giving rise to a molecular semiconductor with energy band gap of 2.3 eV. On the other hand, the partially filled LUMO orbital promotes strong affinity toward electrons of 2.8 eV. The electron affinity is enhanced by the abundance of delocalized states making it an attractive candidate for n-type thin film electronic devices like thin film transistors (TFTs) and FET with high electron mobility [49].

C\textsubscript{60} thin films are commonly prepared using chemical vapour deposition (CVD) and solution deposition [54]. In ideal conditions, C\textsubscript{60} forms crystalline thin films, but the film morphology and degree of crystallinity depends strongly on the deposition technique, the surface of substrate on which it is grown, and the deposition rate and conditions as well as the purity of C\textsubscript{60} powder. Obtaining highly ordered crystalline C\textsubscript{60} thin films requires the use of substrates with weak surface bonding such as passivated silicon (SiO\textsubscript{2}), Gallium Ar-
senide (GaAs) and gold, among others [55]. In addition, the substrate temperature should be high enough to enhance the mobility of the molecules during the nucleation of the initial monolayer and the ensuing film growth [55]. It is well established that a deposition at high temperature and low rate results in large grain size. The grain size, along with the film crystallinity, degree of order have a significant impact on the charge carrier mobility in the thin film which, in turn, determines the performance of the electronic device [56].

2.4 Graphene and Chemical functionalization

Since the discovery of graphene in 2004, it has generated tremendous interest among available 2-D materials. Its morphological characteristics, combined with its unique electronic and mechanical properties have been attracting significant interest in the field of electronics. Graphene is a 2D organic semiconductor material, initially produced by mechanically exfoliating graphite into one atom think layers [57]. The resulting thin films have high aspect ratio, zero effective mass, are highly flexible, robust and transparent. In addition, graphene exhibits excellent electronic charge mobility, high electrical and thermal conductivity, wide optical absorption spectrum. This unique combination of properties makes graphene an excellent candidate for wide range of applications in integrated circuitry, optical and chemical sensing and energy storage, to name a few [44].

2.4.1 Atomic Structure and Electronic Properties of Graphene

Graphene is another interesting carbon allotrope, made entirely of carbon atoms. At the atomic level, graphene monolayer structure is a planar honeycomb lattice where carbon atoms are packed such that they form a hexagon unit cell as shown in Figure 13(a) [44]. Carbon atoms have four valence electrons that can take part in the formation of chemical bonds. In graphene, each carbon atom forms three covalent bonds with adjacent atoms at an
angle of $120^\circ$ ($\sigma$-bonds) [44]. This is done by promoting a 2s electron to a 2p orbital which results in formation of hybridized orbitals leading to a $sp^2$-hybridized honeycomb lattice [38]. The remaining valence electron in the unhybridized 2p-orbital in each carbon atom of the lattice bonds with other unpaired electrons and forms $\pi$-bonds, creating thereby half filled $\pi$-bands as shown in Figure 13(b) [44]. The strong $\sigma$-bonds in graphene thin films are responsible for the binding energy and physical properties, namely, flexibility and high tensile strength. Whereas $\pi$-bonds allow for the delocalization of electrons in the direction perpendicular to $\sigma$-bands and hence, determine the intrinsic electronic and optical properties of graphene such charge transport, Fermi energy conditions and bandgap [38]. These arrangements give rise to the unique band structure of pristine graphene monolayers.

![Graphene lattice structure](image)

Figure 13: Graphene lattice structure: (a) Graphene honeycomb lattice. (b) Position of $\pi$ and $\sigma$-bonds in graphene honeycomb lattice [44]. (c) Graphene energy band structure [38].

The electronic band structure of graphene consists of a valence band and a conduction band which meet at two district point know as Dirac points (Figure 13(c)). The physics of graphene is governed by the structure of the $\pi$-band in the vicinity of the Dirac points. At equilibrium, the gapless nature of graphene is a direct result of electrons from carbon atoms filling the valence band entirely while the conduction band remains empty. As a consequence, the fermi level is located at the energy level of the charge neutrality points (Dirac
Points) and it is equal to zero. The superior electrical conductivity of graphene is attributed to the hexagonal lattice and binding configuration. The planar hexagonal lattice offer little resistance to the motion of electrons along the monolayer and the propagation of electrons is facilitated by the ballistic transport of the charge carriers in graphene. Therefore, electrical conductivity of graphene at room temperature is comparable to that of superconductors at extremely low temperatures. Thermal conductivity is supported by the same process where phonon are transported throughout graphene lattice by the charge carriers and benefit from the high carrier mobility in graphene. Therefore, graphene monolayers are excellent thermal conductors, surpassing all other carbon allotropes and copper. However, the use of pristine graphene in chemical and gas sensing is limited by the absence of functional groups crucial to gas and molecule absorption, its gapless nature and the complexity of large scale fabrication. These shortcomings can be resolved through performance enhancement techniques such as chemical functionalization.

### 2.4.2 Chemical Functionalization of Graphene

The exceptional electronic and chemical features of graphene along with its low cost of production and synthesis spurred interest in investigating and tailoring methods to modify the electronic and physical properties of graphene for various applications such as chemical and gas sensing. Surface modification has been widely used for the chemical functionalization of graphene as it allows for the product to be further processed through simple solution deposition techniques and prevent agglomeration of graphene monolayers without modifying their intrinsic properties. In chemical sensing applications, chemical functionalization is an established technique to enhance the chemical affinity and sorption of pristine graphene layers through exposure to active functional groups including hydroxyl, epoxide, oxygen, hydrogen and fluorine. These chemical species bond with carbon atoms in graphene and modify its chemical affinity and electrical conductivity which can
be translated to electrical or optical response depending on the electronic device used. It is an economically viable process applicable for large scale fabrication of graphene derived materials such as graphene oxide (GO), reduce graphene oxide (rGO) and hydrogenated graphene [59].

### 2.4.2.1 Graphene Oxidation and Reduction

Graphene oxide is a graphene derived material produced via oxidation as shown in Figure 14. GO synthesis is conducted by functionalizing graphene with hydroxyl (-OH) or carboxyl (C=O) groups, via a process known as chemisorption. Theses chemical species bond with delocalized sp² electrons in carbon atoms and form sp³ bonds [58]. The presence of the functional groups at the edges of graphene layers improves the solubility in water and organic solvent and renders the material insulating and extremely hydrophilic. The hydrophilic nature of GO is conducive to applications in humidity sensing as GO readily expands in the presence of water resulting in a change in the dielectric constant [59]. Furthermore, the flexibility of GO can be improved by increasing the amount of oxygen-containing functional groups resulting in enhanced modulus of elasticity and toughness, which is advantageous in flexible sensors [60].

![Figure 14: Schematic illustration of GO and rGO synthesis approach](image)

The implementation of GO in thin film transistor-based sensors is disadvantageous due to its insulating properties and the fact that sensing mechanism of TFT-based sensors depends
on conductivity measurements. Reduced graphene oxide (rGO) represents a suitable trade-off between the electrical conductivity of graphene and the chemical reactivity of GO [58]. rGO is the product of reduction of graphene oxide, by which GO is partially reduced by the controlled removal of oxygen-containing groups from the surface of GO layers using simple treatments, namely, chemical, thermal and photochemical reduction, shown in Figure 14 [60]. This process restores the inherent electrical conductivity of graphene while maintaining the solubility in water and organic solvents and chemical reactivity characteristic to GO. Consequently, rGO is considered as promising in chemical and gas sensing applications due to its simple and low cost synthesis, electrical conductivity, thermal stability and particularly due the fact that its electronic properties are strongly affected by gas molecules [58].

The underlying mechanism associated with humidity sensing using rGO lies in the fact that water molecules are absorbed at the surface of rGO membrane. The absorbed water molecules bond with the hydroxyl by a single hydrogen bond and get ionised due to the effect of the electrostatic force through the Grotthus chain reaction shown below. As a result, the local hole concentration increases as more water molecules bond with rGO. Being a hole carrying material, the increase in hole density enhances the electrical conductivity of rGO as it is exposed to water molecules [58, 60].

\[ H_2O + H_3O^+ \rightarrow H_3O^+ + H_2O \]  

(1)

In TFT sensors, rGO can be used as the sensing material and the changes in conductivity associated with exposure to varying levels of humidity is translated into change in electrical response. rGO-based humidity sensors are known to be highly sensitive and have fast response owing to the 2D structure of graphene allowing for ballistic carrier transport [58].
2.4.2.2 Graphene Hydrogenation

Hydrogenation of graphene is a method by which graphene is chemically functionalized to modify the electronic properties and enhance its chemical affinity toward chemical analytes. Graphene hydrogenation products include graphane which is a fully hydrogenated form of graphene, and hydrogenated graphene being a partially hydrogenated form of graphene [61]. Graphene hydrogenation is a covalent bonding process in which hydrogen atoms form covalent bonds with carbon atoms at the surface of the graphene lattice. Accordingly, the chemisorption of hydrogen atoms disrupts the structure of graphene matrix leading to the hybridization of $sp^2$ bonds into $sp^3$ and the formation of C-H bonds as illustrated in Figure 15 [62].

![Figure 15: Schematic representation of the $sp^2$ hybridization breakdown upon hydrogen adsorption in graphene. [63].](image)

There are conceptually two main methods for the synthesis of hydrogenated graphene, namely, gas phase approaches which include plasma hydrogenation and thermal cracking, and wet chemical approaches being, Birch and electrochemical reduction [62]. The selection of the hydrogenation route has an effect of the degree of hydrogenation which, in turn, has a direct influence on the properties of the end product. In fact, gas phase approaches are able to fully hydrogenate graphene, whereas wet chemical approaches can only achieve partial hydrogenation [61].

Hydrogenated graphene has been extensively investigated in electronic and optoelectronic
applications as hydrogenation converts the gapless graphene into a wide and tunable gap semiconductor with enhanced photoresponse associated with longer exciton lifetime [62]. In addition, hydrogenated graphene is an excellent candidate for hydrogen storage, for energy storage applications, owing to the reversibility of the hydrogenation process, low toxicity and low cost processing [62].

Although the chemical affinity of hydrogenated graphene has not been considerably investigated, studies suggested that the C-H bonds in hydrogenated graphene may exhibit chemical reactivity [64]. It has been reported that hydrogenated graphene displays selectivity toward ions such as Cl\(^-\), F\(^-\) and Br\(^-\) [65]. The sensing mechanism behind the ion selectivity of hydrogenated graphene rely on the formation of ionic bonds between hydrogen cation and the target anions though Coulomb coupling [65]. Since hydrogenated graphene has an excess of positive charges it can be regarded as a p-type material. As it is exposed the Cl\(^-\) ions, the formation of ionic bonds reduces the amount of free positive charges and therefore, its conductivity. Hence, the degree by which the electrical conductivity of the hydrogenated graphene is reduced is proportional to the concentration of Cl\(^-\) ions to which it is exposed to and makes it an excellent transducer for Cl\(^-\) ion sensing applications.
3 Fundamentals of Organic Thin Film Transistors

Thin film transistors are a class of chemical sensors that employ field effect transistors to detect the presence and measure the concentration of chemical species. TFT sensors are essentially thin film transistors where the active channel or the gate, depending on the TFT configuration, is designed such that it has chemical affinity toward the target chemical species. Typical TFT responses are in the form of a change in the output signal: current and voltage, and a shift in the threshold voltage. The performance of TFT sensors depends strongly on the sensitivity and chemical reactivity of the sensing material and the ability of the TFT to convert the chemical reaction into an electrical signal, which in turn, depends on the characteristics of the transistor in terms of ON/OFF ratio, charge carrier mobility and threshold voltage among others.

In this chapter, OTFT architecture and configurations are presented. Device operation and performance metrics are described and characterization methods used for the extraction of figures of merit are discussed.

3.1 OTFT Architecture and Fundamental Operation

Organic thin film transistors are three-terminal electronic devices comprising of an organic semiconductor channel, a gate dielectric, source and drain electrodes and a gate electrode as shown on Figure 16. In general, the layers are arranged in two main configurations: Top-Gate (TG) and Bottom-Gate (BG), which are, in turn, further classified in terms of the contacts location as Top-Contact (TGTC, BGTC) and Bottom-Contact (TGBK, BGBK) as illustrated in Figure 16 [66]. Each configuration reveals advantages and drawbacks pertaining to fabrication processes and device performance. In terms of carrier mobility, BGTC and TGBC configurations achieve higher charge carrier mobilities than the other two, as the
influence of the energy barrier height is less pronounced [67]. Nonetheless, the deposition of top contact in BGTC may damage the surface of the semiconductor. In terms of processability, BGBC is suitable for low-cost and large-scale fabrication as the gate, source and drain electrodes are prefabricated and the semiconductor layer is deposited at the last step, which can further lower the likelihood of the OSC/electrodes and OSC/dielectric interfaces to be affected by additional processing steps [68]. However, the semiconductor remains exposed to the environment, which may lead to environmental degradation and contamination. In contrast, TGBC configuration offers a total encapsulation of the semiconductor and preserves its integrity and at the same time, can be fabricated using large scale printing techniques on rigid and flexible substrates [66, 68].

![OTFT device configurations](image)

Figure 16: OTFT device configurations. (a) BGBC. (b) BGTC. (c) TGBC. (d) TGTC [66].

OTFT devices are operated by polarizing the gate, either positively or negatively, depending on the majority charge carriers of the semiconductor. Figures 17(a) and (c) illustrate the operation of n- and p-type OTFT devices, for a n-type (p-type) semiconductor, the majority carrier are electrons (holes) and the gate must be positively (negatively) polarized. This is done by applying a gate-source $V_{GS}$ voltage and a drain-source voltage $V_{DS}$. 
The gate-source voltage forces the free charges at the semiconductor/dielectric interface to counterbalance the change in charge brought by the applied gate voltage. This equivalent to shifting the LUMO and HOMO levels up or down depending on the polarity of the semiconductor. For a n-type device, a positive gate bias aligns the LUMO levels with the fermi level of the metal contact which remains constant. For a p-type device, a negative gate bias forces the HOMO levels to align with the metal fermi level [69]. The applied drain-source voltage drives the majority carriers to move from the source to the drain and allows the current to flow through the conducting channel and be collected at the drain electrode [66].

Figure 17: Schematic representation of OTFT operation, electric field lines and carrier channel energy level diagrams. (a) n-type OTFT. (b) n-type organic semiconductor carrier channel energy level diagrams and electron transport through the semiconductor. (c) p-type OTFT. (b) p-type organic semiconductor carrier channel energy level diagrams and hole transport through the semiconductor [70].

In theory, mobile charge carriers can be introduced to the semiconductor channel at $V_{GS}=0V$. In practice, a nonzero $V_{GS}$ is required to obtain flat band conditions. More often than not, the LUMO and HOMO energy levels do not match the Fermi level of metal contacts.
causing a dipole due to charge transfer between the metal and the semiconductor, and the apparent energy band bending described in Figure 17(b) and (d) [69].

The “field effect” behaviour of OTFTs stems from the dependence of the drain-source current ($I_{DS}$) on the charge density in the active channel, which, in turn is modulated by the electric field applied between the gate and source electrodes [66]. The mode of operation of TFTs and the corresponding channel charge density profile are dictated by the threshold voltage ($V_{TH}$) which is the minimum gate voltage necessary to achieve channel conduction and at the same time identifies the points of transition between the different modes of operation. Figure 18 illustrates the channel carrier density profile corresponding to each operation regime of OTFTs. In the linear regime, the carrier concentration in the channel is uniform and increases linearly as long as $V_{DS}$ does not exceed ($V_{GS} - V_{TH}$).

![Figure 18: Schematic representation of OTFT modes of operation.](image)

When $V_{DS}$ is increased, the charge density becomes nonuniform and its profile decreases from the source to the drain until it becomes “pinched” at $V_{DS} = V_{GS} - V_{TH}$ where the drain region is completely depleted of charge carriers and the potential difference between the
gate and the drain region becomes zero. Beyond that point, further increase in $V_{DS}$ shifts the pinch point toward the source and the constant conductive channel resistance prevents the generation of additional drain current which is said to be saturated [70, 69]

3.2 OTFT Electrical Characterization and Figures of Merit

The performance and properties of OTFTs are investigated by observing the current-voltage response under constant gate bias, known as the output characteristic and the current-voltages response under constant drain-source voltage, known as the transfer characteristic. In this section, the scope of discussion is limited to the characterization of n-type TFTs which is the focus of the thesis work.

Figure 19(a) illustrates typical output characteristic of a n-type TFT and displays the change in output current ($I_{DS}$) in response to change in output voltage ($V_{DS}$) under a pre-set gate-source voltage. The transfer characteristic, shown in Figure 19(b) describes the change in $I_{DS}$ with respect to change in $V_{GS}$ under constant $V_{DS}$ [66].

![Figure 19: Electrical characterization of n-type OTFTs. (a) Output characteristic depicting the change in $I_{DS}$ with respect to $V_{DS}$ at constant $V_{GS}$. (b) Transfer characteristic showing the evolution of in $I_{DS}$ as a function of $V_{GS}$ at constant $V_{DS}$ [71].](image)

The output characteristic reveals the evolution of the drain-source current $I_{DS}$ with respect to the drain-source voltage $V_{DS}$ and to the gate-source voltage $V_{GS}$. The output curve
is characterized by two distinct regions: linear and saturation regimes. In these regimes, the drain source current are modeled by equation 2 and 3, where, \( \mu \) is the charge carrier mobility, \( C_i \) is the effective capacitance per unit area, \( L \) and \( W \) are the channel length and width and \( V_{th} \) is the threshold voltage [66]. In the linear regime, \( I_{DS} \) increases linearly with increasing \( V_{DS} \). Here, the OTFT operates as a gate voltage controlled variable resistor and the output current is represented by equation 2. In the saturation regime, the electric field generated along the channel by the applied drain-source voltage exceeds the gate bias and the associated drain current saturates due to charge depletion near the drain contact regions and is described by equation 3 [72]. OTFT output characteristic is also dependent on the applied gate bias where \( I_{DS} \) is proportional to \( V_{GS} \) in both the linear and the saturation regimes as the applied gate bias \( V_{GS} \) modulates the charge density in the channel [68].

\[
I_{DS,lin} = \mu_{in} \frac{C_iW}{L} (V_{GS} - V_{Th} - \frac{V_{DS}}{2})V_{DS} \quad \text{For} \quad |V_{DS}| < |(V_{GS} - V_{Th})| \quad (2)
\]

\[
I_{DS,sat} = \mu_{sat} \frac{C_iW}{2L} (V_{GS} - V_{Th})^2 \quad \text{For} \quad |V_{DS}| > |(V_{GS} - V_{Th})| \quad (3)
\]

The effective capacitance per unit area \( (C_i) \) corresponds to the equivalent intrinsic capacitance of the OTFT stack which includes the semiconductor and the dielectric layers. The total capacitance of an OTFT can be described as the equivalent capacitance of capacitors connected in series as shown in Figure 20.

![Schematic diagram of the equivalent capacitance of an OTFT.](image)

Equation 4 describes the effective capacitance per unit area of an OTFT where \( C_{SC} \) is the
semiconductor capacitance, $C_{\text{die}}$ is the capacitance of the gate dielectric interface.

$$C_i = \left( \frac{1}{C_{\text{SC}}} + \frac{1}{C_{\text{die}}} \right)^{-1}$$  \hspace{1cm} (4)

In addition to intrinsic capacitances, extrinsic capacitances can originate from source-drain capacitive coupling, traps at the semiconductor-dielectric interface and fringing field effects. However, at low operating voltages, extrinsic capacitances can be regarded as negligible compared to the intrinsic ones and their effects can be further minimized by optimizing the channel length, the source and drain geometry as well as the semiconductor-dielectric interface [73].

The transfer characteristic illustrates the dependence of the drain-source current $I_{DS}$ on $V_{GS}$ under constant $V_{DS}$ and it is used to determine OTFT performance metrics, namely, threshold voltage ($V_{th}$), carrier mobility ($\mu$), transconductance ($g_m$) and current ON/OFF ratio ($I_{on}/I_{off}$) [66].

Equations 2 and 3 indicate the strong dependence of OTFTs operation on the threshold voltage, transconductance, current ON/OFF ratio and the carrier mobility. These parameters are critical indicators of the performance of the devices and are assessed using the output and transfer curves.

### 3.2.1 Threshold Voltage

The threshold voltage $V_{th}$ is the minimum gate-source voltage for the charge carriers to accumulate at the dielectric interface and hence induce a noticeable channel current. Several graphical methods have been suggested for the determination of $V_{th}$, and the most common method uses linear interpolation where $V_{th}$ magnitude corresponds to the gate voltage intercept of the linear interpolation of $\sqrt{I_{DS}}$ as a function of $V_{GS}$ [71]. The magnitude of the
threshold voltage is influenced by the presence of crystal defects, impurities and surface roughness at the semiconductor-dielectric interface. A high $V_{th}$ is indicative of impurities and defects leading to charge trapping cites which need to be filled before a noticeable current can be induced [66, 68]. High $V_{th}$ can also be attributed to high contact resistance stemming from large barrier height between the active channel and metal contacts [68].

3.2.2 Transconductance

Transconductance (or transfer conductance) ($g_m$) refers to the change in drain current in response to change in gate voltage. It is a valuable measure of the performance of OTFT-based devices as it is an expression of the amplification gain that the devices are capable of delivering. The transconductance is also an indirect measure of how fast an OTFT can switch between ON and OFF states and the minimum gate voltage that is requires to do so [74]. The higher the transconductance the faster the OTFT can switch ON and OFF and the lower the gate voltage requirements. The transconductance can be extracted from the transfer characteristics by taking the derivative of the drain current with respect to change in the gate voltage as shown in Figure 21(a). It is often used graphically and analytically to determine the carrier mobility in the linear region [74].

3.2.3 ON/OFF Current Ratio

The ON/OFF current ratio ($I_{ON}/I_{OFF}$) is defined as the ratio of the maximum drain current during the ON-state to the current during the OFF-state [41]. It is a critical OTFT parameter studying the effect of gate leakage current on the performance of the device. The ON-current is attributed to the applied gate voltage and is dependent on the carrier mobility and gate capacitance, whereas the OFF-current is associated with the leakage current through the gate. Ideally, the leakage current should be kept a low as possible compared to the drain
current in the ON-state for device optimal performance [40]. $I_{ON}/I_{OFF}$ is extracted from the transfer characteristic by plotting the drain current against gate voltage in a semilogarithmic scale as shown in Figure 21(b).

![Figure 21: Typical OTFT (a) transconductance and (b) ON/OFF ratio as a function of gate-source voltage $V_{GS}$ [74].](image)

### 3.2.4 Charge Carrier Mobility and Characterization Techniques

Charge transport mechanism and efficiency is of paramount importance in the design and performance evaluation of thin film transistors. Charge transport characteristics are defined by the molecular structure and crystallinity of the OTFT active channel that falls under either small molecules or conjugated polymers that display distinctive charge carrier transport modes, namely, band transport and hopping transport respectively. However, knowledge of these attributes is not sufficient to predict the performance of OTFT as it depends on the degree of crystallization, presence of defects as well as purity of the organic semiconductor [75]. Charge carrier mobility is an important parameter impacting the performance of organic thin film transistors to which efficient charge transport is especially critical as it determines the speed at which charge carriers move through the semiconductors under an applied electric field, as well as the generated current. Currently, there are numerous methods used in the characterization and measurement of charge carrier mobility and the most
commonly used for organic semiconductors are Field Effect Transistor (FET) model, Time of Flight (TOF), Space Charge Limited Current (SCLC) and Charge Carrier Extraction by Linearly Increasing Voltage (CELIV).

Field Effect Transistor (FET) Model

Field effect transistor-base method makes use of FET configurations (top gate or bottom gate) to measure the charge carrier mobility of the active channel. The charge carrier mobility is extracted from the transfer characteristic curve previously described. In the linear regime the mobility is deduced from the transconductance $g_m$ and thus from the transfer characteristic using equation 5 where, $g_m$ corresponds to slope of the linear fitting of $I_{DS}$ in the linear regime.

$$
\mu_{lin} = \frac{L}{W C_S V_{DS}} g_m \quad \text{For} \quad V_{DS} < (V_{GS} - V_{Th}) \tag{5}
$$

In the saturation regime, on the other hand, the charge carrier mobility is estimated by extracting the slope of the square root of the drain current versus the gate-source voltage at constant drain voltage, using equation 6 [76].

$$
\mu_{sat} = \frac{2L}{W C_S} \left( \frac{\partial \sqrt{|I_{DS}|}}{\partial V_{GS}} \right)^2 \quad \text{For} \quad V_{DS} > (V_{GS} - V_{Th}) \tag{6}
$$

This extraction method is based on the assumption that carrier mobility in thin film transistors is temperature and field effect independent, which is inaccurate as most organic semiconductors exhibit such dependence. Nonetheless, useful estimation of the carrier mobility can be obtained [76]. The carrier mobility in the saturation regime is usually larger than in the linear regime due to the difference in the electrical field distribution. In addition,
it is affected by several factors including, and not limited to, presence of defects in the semiconductor and at the channel-dielectric interface morphology, contact resistance at the source and drain, dielectric surface chemical structure and morphology and permittivity of the gate insulator [76, 40].

**Space Charge Limited Current**

Charge carrier mobility extraction using SCLC technique employs the diode configuration where the semiconductor material is sandwihced between two electrodes as shown in Figure 22(a). One electrode is used to inject electrons or holes and the other is used as the injection blocking contact [76]. The carrier mobility is estimated by applying a step voltage at the injection contact and observing the generated current transient shown in Figure 22(b). The current transient illustrates the increase of current due to the increase of applied voltage as the front carriers move rapidly toward the counter electrode, reaching a maximum which corresponds the maximum charge density attained when the electrostatic field prevents the injection of additional carriers [40]. Beyond that point, the current density decreases until it reaches the equilibrium state analogous to charge dynamic equilibrium [76].

![Diagram](image)

Figure 22: Dark Injection Space-Charged Limited Current. (a) Measurement setup [40]. (b) Current transient [76].
The estimation of carrier mobility depends on the type of injection adopted, namely dark injection (DI) or trap-free injection. In dark injection mode, the carrier mobility is estimated using equation 7. Where $t_{tr}$ is the free carrier transient time, $V$ is the applied step function voltage and $d$ is the channel thickness. The carrier transient time is determine using equation 8, where $\tau_{DI}$ corresponds to the peak in the current transient in Figure 22(b) [76].

$$\mu = \frac{d^2}{V t_{tr}}$$  \hspace{1cm} (7)

$$\tau_{DI} = 0.787 t_{tr}$$  \hspace{1cm} (8)

In the trap-free injection mode, the carrier mobility is estimated using equation 9 assuming the material does not display field dependence, where $\varepsilon$ is the dielectric constant of the active layer and $\varepsilon_0$ is the permittivity of the vacuum [40]. In the case where the carrier mobility is field dependent at high electric fields, equation 10 is used. Where $\gamma$ represents the field dependence as function of temperature and is determined using equation 11 where $K_B$ is Boltzmann constant, and $T_0$ is equal 600 K [76].

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu V^2 d \frac{V^2}{d^3}$$ \hspace{1cm} (9)

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu e^{0.89 \left( \frac{V}{d} \right)^2} \frac{V^2}{d^3}$$ \hspace{1cm} (10)

$$\gamma = B \left( \frac{1}{K_B T} - \frac{1}{K_B T_0} \right)$$ \hspace{1cm} (11)

Compared to the FET method, The SCLC technique is more accurate as it does not require the use of a dielectric layer and is not affected by the morphology of the interface between the semiconductor and the dielectric layer nor the operational regime (linear and saturation). However, it requires a thin conductive layer between the semiconductor and
the injection contact to maintain an injection barrier of no more than 0.3 eV. Furthermore, the required thickness of the semiconductor layer should be between 200nm and 2um [76].

**Time of Flight Method**

Estimation of carrier mobility using Time Of Flight (TOF) method uses similar experimental setup as for SCLC, where the semiconductor material is placed between two transparent or semitransparent electrodes. This method relies on photoexcitation of charge carriers and requires a channel thickness of at least 1µm [76]. The mobility is extracted using photogenerated current transient resulting from subjecting the semiconductor sample to short laser pulses near one electrode which creates excitons at the surface of the material as illustrated in Figure 23(a). The photogenerated carriers are separated by the applied electric field and move toward one of the electrodes depending on the polarity of the electric field. The current as a function of time, is then recorded using an oscilloscope [40]. Figure 23(b) depicts the resulting current transient in which two distinctive types of response can be observed depending on whether the carrier transport is dispersive or non-dispersive.

![Figure 23: Time Of Flight Method. (a) Measurement setup [40]. (b) Photogenerated Current transient [76].](image)

When the charge carriers reach the back electrode, the photocurrent drops and displays a characteristic plateau region. Non-dispersive materials display a “knee” in the characteris-
tic response at the transient time $t_{tr}$ [76]. The carrier mobility is estimated using equation 12, where $t_{tr}$ is the transient time, $d$ is the thickness of the semiconductor layer and $V$ is the applied voltage. The presence of density traps and the variation in their depths is characteristic to disordered semiconductors and may result in a dispersive response without the expected plateau region. The dispersive photocurrent response is, therefore, plotted in a double logarithmic format in which the observed inflection point corresponds to the transient time [77].

$$\mu = \frac{d^2}{V_{tr}}$$  \hspace{1cm} (12)

TOF method have been successfully used in determining the mobility of both electrons and holes in organic and non-organic materials. The main requirements of this technique is associated with the laser pulse absorption depth which should be short enough that the excitons are concentrated within the thin film thickness. The transient time and RC-time constant should also be smaller than the dielectric relaxation time of the photogenerated carriers and the transient time, respectively [76].

**Charge Carrier Extraction by Linearly Increasing Voltage**

CELIV is a measurement technique used to estimate doping-generated charge carrier mobility in semiconductors. Similar to TOF, the mobility of charge carriers is estimated by extracting the time it takes for the current to reach the maximum value which is to the time it takes a sheet of charge carriers near one electrode to reach the other electrode [78]. It is more advantageous compared to TOF as it does not require transparent electrodes and is not limited by the film thickness as semiconductor samples do not have to be optically thick. CELIV is carried out by applying a triangular pulse voltage to the semiconductor film sandwiched between an injecting electrode and a blocking electrode as illustrated in Figure 24(a). Current transient is then measured using an oscilloscope and features a peak
in the current as displayed in Figure 24(b). The charge carrier mobility is estimated using equation 13 where $t_{\text{max}}$ corresponds to the current peak, $A$ is the voltage rise speed and $d$ is the sample thickness [78].

$$\mu = \frac{3 t_{\text{max}}}{2 d^2 A}$$  \hfill (13)

Figure 24: Carrier Extraction by Linearly Increasing Voltage (CELIV) (a) Measurement setup. (b) Current transient [79].

CELIV is a favoured mobility extraction method for organic materials with low mobilities and is the only known method for direct measurement of mobility in disordered materials [78]. However, CELIV measurements require sufficient amount of free charge carriers in the sample under study which can be introduced by either doping or by photoexcitation using an optical sources like lasers. The accuracy is also limited when the sample under study is an ambipolar semiconductor which makes it difficult to distinguish between electrons and holes [78].

### 3.2.5 Electronic Structure and Bandgap Energy Characterization

The investigation of the electronic structure of organic semiconductors is particularly critical to the performance of organic field effect transistors as it determines the energy band structure of the active channel, the electronic properties at the metal/OSC interface and the energy band gap of the semiconductors. The accurate modeling and prediction of these
properties requires appropriate experimental and theoretical information for the exploita-
tion of the full potential of organic-based devices. Various methods have been employed
to investigate energy band structure of semiconductors and the metal/semiconductor inter-
face properties. They combine experimental techniques with well established models to
extract the critical properties. These methods include and not are not limited to, Photoelec-
tron Spectroscopy (PES), X-ray Photoelectron Spectroscopy (XPS), and a combination of
X-ray Emission and Absorption Spectroscopy (XES, XAS).

**Photoelectron Spectroscopy**

PES is among the simple technical methods used in the investigation of the electronic struc-
ture and particularly the energy bands of semiconductors by measuring the relative energies
of electrons. It employs ionization radiations to induce photoelectric effect and measure the
kinetic energy of ejected electrons which can be directly related to the binding energy be-
tween the electron and the atom [80]. Determination of semiconductor band gap energies
require knowledge of the band energy levels of either sides of the fermi level, which can
be done using a combination of PES subclasses, namely Ultraviolet Photoelectron Spec-
troscopy (UPS) that determines the position of the valence band of the semiconductor, and
the Inverse Photoelectron Spectroscopy (IPES) to determine the position of its conduction
band. UPS is based on "photon-in electron-out" technique and is performed by subjecting
the semiconductors to UV rays with photons energy ranging between 10 eV to 45 eV, in an
ultra-high vacuum environment [80]. The ejected electrons are collected and their binding
energy is measured as a function of the incident photon energy. IPES uses "electron-in
photon-out" methodology where the surface of a semiconductor is subjected to electron
excitation. The impinged electrons recombine with unoccupied states resulting in emission
of photons [80]. The emitted photons are then collected and the binding energy is measured
as a function of the incident electron energy. The UPS and IPES binding energy spectra are
plotted against the incident energy relative to the fermi level on the same plot and the difference between the UPS onset energy and the IPES inset energy corresponds to the energy band gap, as shown in Figure 25. [81, 82].

Figure 25: UPS and IPES spectra as a function of the energy relative to Fermi level. [82].

UPS/IPES technique is a simple and inexpensive method to investigate the electronic structure of semiconductors as it provides a complete picture of the energy levels, electron affinity and ionization energy at the surface of the material, in addition to the work function and transport bandgap [80]. However, EPS techniques rely on the use of optical sources which can damage the material and produce inaccurate results [83].

**X-ray Spectroscopy**

X-ray spectroscopy is another experimental and analytical method widely used in the study of the electronic structure of semiconductors. This technique is similar to PES methods previously described but it is based on the interactions, of electrons and x-rays, namely; Compton Scattering and Auger process. Compton scattering occurs when and electron is ejected from the conduction band when it collide with x-rays. The kinetic energy of the ejected electron depends on the binding energy between the atom and the electron at the
valence band. Auger process occurs when an electron from the valence shell moves toward the conduction band to fill the hole left by the ejected electron. To conserve energy, an Auger electron is emitted from the valence band at a kinetic energy related to the binding energy at the conduction band [84]. The binding energy at the valence and conduction energy levels are measured using XAS and XES, respectively. The band gap corresponds to the difference between conduction band maxima and the valance band maxima as demonstrated in Figure 26 [85].

![Figure 26: Band gap estimation using XAS and XES spectra.][85]
4 OTFT Design, Materials and Fabrication

The objective of the project is to design and fabricate a fully organic field effect transistor chemical sensors for the detection of surface moisture and chloride ions. The selection of materials and processing methods is centered around low cost and simple fabrication while achieving high performance, high sensitivity and robust devices. The OTFT configuration selected for chemical sensors is TGBC as it minimizes the exposure of the semiconducting material to contaminants and at the same time, exposes the sensing gate layer to the surrounding environment. The device is deposited on a rigid insulated substrate. The OFET metal contacts (source and drain) configuration is designed using CAD tools and patterned on the substrate using negative lift-off process, while the TFT device is solution processed by means of layer-by-layer deposition technique. The sensing functionalities are achieved by coating the OTFTs gate layer by a chemically active material on which the gate metal contacts are deposited via physical vapour deposition.

4.1 Device Architecture

The selection of the OTFT configuration and design are based on the fact that C$_{60}$ is prone to contamination and photodegradation. A TGBC configuration protects the semiconductor material from environmental doping and UV-light exposure. In this layout (shown in Figure 27), the semiconducting layer (C$_{60}$) is deposited on a passivated rigid substrate and coated by a dielectric layer. The dielectric is then coated with a conductive layer followed by a sensing layer having chemical affinity toward the target analytes. Finally, the gate metal electrode is evaporated on the top of the conductive layer. The source and drain contacts are designed such that the aspect ratio, i.e. the ratio of the channel width to the channel length (W/L) is greater than 10 to obtain distinctive linear, pinch off and saturation regions in the
output characteristics, and at the same time, minimize metal contact resistance and gate voltage requirements [86]. The effect of the aspect ratio on the device performance, hence the scalability, is further investigated by varying the channel length and/or the channel width. Transistors with varying aspect ratios (10 - 50), channel lengths (10μm - 25μm) and widths (100μm - 1000μm) were designed using L-edit CAD tools and arranged in a circular cluster as shown in Figure 27(c). The corresponding top gate metal structure was designed such that multiple transistors are addressed simultaneously and the gate is in close proximity to each transistor to minimized losses. Figure 27(d) is a image of the shadow mask used for top gate metal physical evaporation and was also designed using L-edit CAD suite tools.

Figure 27: C₆₀ OTFT device architecture. (a) Cross sectional view of the OTFT layout structure. (b) Top view of the OTFT layout. (c) OTFT cluster arrangement. (d) Top gate shadow mask.

4.2 Materials

The selection of materials used in the fabrication process was focused on organic materials properties in term of conductivity, dielectric properties, solubility and environmental
stability. Their processability, safety and availability were taken into account to ensure simple and reproducible fabrication process providing a good range of OFETs for testing and optimization.

**Substrate**

The OTFT devices are deposited on a p-doped passivated silicon wafer. Silicon offers great convenience for device fabrication and characterization due to its robustness and low cost. While surface passivation allows of the isolation of individual transistors within the same wafer and at the same time protects the silicon wafer from degradation. In addition, characterization of devices fabricated on passivated silicon provides a reliable gauge on the transferability to flexible substrates. The passivation of silicon is obtained when a thin oxide layer is thermally grown on the surface of the silicon wafer using Plasma Enhanced Chemical Vapour Deposition (PECVD) or Atomic Layer Deposition (ALD). Both techniques are carried out in a process chamber containing the silicon wafer and use an Si precursor and oxygen source such as O₂. The precursors react with each other, bond with the wafer and form a silicon oxide layer (SiO₂). The reaction by-products are then removed from the process chamber [87].

**Active Channel Material**

The selected OTFT active channel material is fullerene C₆₀ which is a conjugated molecule organic semiconductor with large electron affinity. The solution deposition of C₆₀ requires the use organic solvents to preserve the organic nature of the device. Fullerenes have generally low solubility in organic solvents commonly used in OTFTs fabrication. The constrains around the selection of organic solvents are related to the toxicity of the solvent and solubility of C₆₀ in it. C₆₀ is soluble in low toxicity organic solvents such as toluene
and benzenes. Ortho Dichlorobenzene (1,2 Dichlorobenzene) is an organic solvent derived from benzene and it is a preferred solvent for fullerene due to its non-polarity, where a maximum solubility of 24.6 mg/ml can be achieved. The C_{60} solution is prepared by placing the C_{60}-1,2 dichlorobenzene mixture in an ultrasonic sonicator for a one to two hours. It is stirred overnight at a speed of 400-500 rpm and filtered. However, using high concentrations of C_{60} in the solvent, even below the solubility limit, does not result in complete dissolution, as clumping of particles is observed after annealing at the boiling temperature of 1,2 dichlorobenzene as shown in Figure 28(a). The observed clumping of C_{60} particles impacts the uniformity of the deposited film and creates defects that act as trapping cites that lower the performance of the OTFT. To circumvent the solubility issue, the concentration of C_{60} in 1,2 dichlorobenzene has to be decreased until a relatively uniform film with little to no clumping is achieved.

![Figure 28: Microscopic image of C_{60}-1,2 dichlorobenzene film at different concentration. (a) 20mg/ml. (b) 15mg/ml. (c) 12mg/ml. (d) 9mg/ml.](image)

Figure 28 shows microscopic images of the deposited C_{60}-1,2 dichlorobenzene at different concentrations and after complete evaporation of the solvent. At low concentrations, the absence of clumped particles allows the formation of uniform films of and promotes the full crystallization of C_{60}. 

51
Gate Dielectric

The selection of dielectric materials is an important part of OTFT design as gate dielectrics have a significant influence on the charge transport which determines the overall performance of the OTFT. Polymeric dielectric materials have attracted much interest due to the increase in popularity of organic electronics. Compared to inorganic dielectrics, polymeric dielectrics are soluble in water, can be processed using low temperature and energy efficient techniques. The molecular structure and intrinsic flexibility of polymer based dielectrics allow for simple functionalization and molecular engineering to target specific applications and make them compatible with organic semiconductors and flexible substrates [88].

In an OTFT, the function of the dielectric layer is to modulate the charge transport as the conductive channel forms due to charge accumulation at the semiconductor-dielectric interface under constant gate bias. The transport of the injected charge carriers is greatly influenced by the dielectric layer as it occurs in the few layer of the semiconductors in the vicinity of the interface between the semiconductor and the dielectric layer. As such, a dielectric material should have insulating properties to limit current leakage and energy dissipation, and high breakdown strength to ensure the integrity of the material under high electric fields [88].

The gate dielectric layer of the designed C_{60} based OTFT is a multilayer polymer dielectric composed of poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). PVA is an organic polymer favoured in the fabrication of organic electronics due to its high dielectric constant, low temperature, solution processability as well as mechanical flexibility, low toxicity and biodegradability. The superior insulating properties of PVA lowers operational power requirements of OTFT devices and its high solubility and mechanical flexibility facilitate thin film processing and integration in thin film and flexible devices [89]. However, the
hydrophilic nature of PVA has a negative effect on the performance of n-type OTFTs as it exposes the semiconductor to H₂O and O₂ which results in electron trapping and restrain charge transport. PMMA is another type of dielectric polymer with good insulating properties, high solubility and mechanical flexibility. It has lower dielectric constant than PVA but it is hydrophobic in nature, which can provide the semiconductor protection against water and oxygen molecules while preserving the dielectric properties of the PVA [90]. The integration of PEDOT:PSS on top of PMMA is based on the fact that the latter has poor electrical conductivity and the performance of OTFTs depends on good conductivity between the metal gate electrode and the gate dielectric. PEDOT:PSS is an established highly conductive conjugated polymer having good film forming properties, capable of producing smooth films, requires low processing temperatures, compatible with organic electronics and environmentally stable [91]. Using PEDOT:PSS as a conductive layer in OFETs enhances the performance of the devices and its porous structure provides a stable matrix for the organic doping agents used for chemical sensing platforms like graphene derived materials.

4.3 Fabrication

Processing and fabrication presented in work were conducted at Carleton University Fab Lab and Wet Lab facilities in two sequential portions: substrate metal patterning followed by thin film structure deposition. Substrate metal patterning was performed via a combination of negative lift-off using ultra violet photolithography, and physical evaporation. Whereas thin film deposition was achieved using layer-by-layer solution deposition.

Lift-off is a procedure in which materials are patterned using a sacrificial layer, where patterns are defined using a photolithography mask. It is a commonly adopted technique for lower level contact, interconnects as well as gate metal electrodes. Unlike direct etch,
lift-off process can be used for most metals including those that are difficult or cannot be dry-etched, is more economical, compatible with most materials and circumvents damage and residues associated with dry etching [92]. Metal lift-off process is carried out by creating an inverse image of a predesigned mask on a material. A photoresist (PR) is applied to the surface of the material and exposed to UV rays through a photolithography mask resulting in specific lift-off profile. Metals are then deposited onto the patterned PR using physical evaporation techniques. Finally, the resist is removed with a solvent leaving behind metal directly deposited on the patterned regions. In metal lift-off processes, positive or negative resists or a combination of both is used. Negative resists are generally preferred for metal lift-off as they achieve reproducible undercuts which prevent the resist from covering the sidewalls of the undercut and result in easier and significantly shorter exposure time than positive resists. However, some negative resists become cross-linked at high temperatures and require stronger solvent which may damage the metal and the patterned material. In addition, negative resists produce tapered undercuts when used for wide openings and makes the subsequent lift-off more difficult [92].

4.3.1 Metal Patterning

The substrate metal patterning procedure consists essentially of four distinct steps: wafer surface preparation, resist deposition, resist exposure and development and finally metal evaporation and lift-off. The fabrication process illustrated in Figure 29 was performed in a clean room environment at 22°C and 40% relative humidity.

P-type passivated silicon wafer with 500 ±10 µm thickness was subjected to O₂ Plasma Preen treatment for 5 min to remove any organic and nonorganic residues from the surface of its surface. The wafer was further cleaned with N₂ gas and baked at 100°C for 10 min to remove water molecules absorbed at the wafer surface from exposure to air humidity.
A thin film of Bis(trimethylsilyl)amine (HMDS) was spin coated on the surface of the wafer to enhance chemical adhesion between the resist and the silicon wafer, at a spin speed of 1000 rpm for 10s and spread speed of 4000 rpm for 30s followed by a soft bake at 115°C for 60s. The wafer was allowed to cool down to room temperature before the lift-off resist (LOR 5B) was spin coated at 1000 rpm for 10s and spread at 1500 rpm for 30s. The wafer was then baked on a hotplate at 190°C for 5 min and the surface of the LOR carefully inspected for defects and presence of whiskers which were removed by plucking using tweezers and cleaned with N₂ gas to remove particulates. Photoresist (S1811) was deposited onto the LOR layer at a spin speed of 1000 rpm for 10s and spread speed of 3000 rpm for 30s and soft baked at 115°C for 60s. After this, the photoresist was ready for patterning.

The photoresist was patterned with the aid of a UV lithography system using the pre-designed masks shown in Figure 27(c). The wafer was placed on a vacuum chuck and aligned with the photomask. A beam of UV light with energy of about 260mj and wavelength of 365 nm transferred the pattern on the photomask onto the wafer for a duration
of 40 to 60s. The photoresist was developed by immersing the wafer in MF321 developer until the photoresist was removed which takes approximately 45s. The wafer was then examined under a microscope to ensure that the LOR was not overdeveloped in the process which usually create a large undercut.

The metal deposition was performed after exposing the patterned wafer to O₂ Plasma Preen to remove any remaining PR residues. 200 nm of Chromium was deposited using E-Beam evaporation at a rate of 5 Å/min. Two PG remover baths were prepared and kept at a temperature of 60°C. The metal patterned wafer was immersed in the first bath until most of the metal is lifted-off. The wafer was then transferred to the second bath for 10 min or until the remaining metal was completely removed. Finally, the wafer was rinsed with DI water for 5 min and dried with N₂.

4.3.2 Material Synthesis

Fullerene C₆₀ (sublimed, 99.9% purity), 1,2 Dichlorobenzene, PVA, ethylenediamine, PEDOT:PSS, sodium:Pottasium alloy (Na-K (1:3)), fluoro-graphite, isopropanol, ethanol and n-Hexane were obtained from Sigma Aldrich. Graphene nanoplatelets (GnP) and rGO were acquired from Kennedy Labs and PMMA from DuPont. Deionized (DI) water was supplied by Carleton University microfabrication lab.

OTFT Active Channel Material: Fullerene C₆₀

The OFET semiconductor material was prepared by dissolving C₆₀ in 1,2 dichlorobenzene at a concentration of 9 mg/ml. The solution was sonicated for 1 hour and placed in a magnetic stirred at 400 rpm at room temperature for 2 hours. The solution was then filtered using a PVDF syringe filter with 0.22μm pore size to remove any remaining undissolved particles. The resulting solution is semitransparent and has a purple colour as shown in
Figure 30(a).

(a) C$_{60}$ in 1,2 dichlorobenzene solution. (b) Hydrogenated graphene wet chemical synthesis apparatus.

**Chloride Ion Sensor Functional Material: Hydrogenated Graphene**

Hydrogenated graphene was chemically synthesized in-house using modified Birch method. Briefly, 2.33g of 1:3 Na-K alloy and 5ml of ethylenediamine were added into a 50 ml three necked round bottomed flask under nitrogen atmosphere and stirred until a blue mixture was obtained. Meanwhile, a solution of 43mg of fluorographite in 5 ml of ethylenediamine was sonicated for 30 seconds. The fluorographite-ethylenediamine suspensions was then added to the flask through a gastight syringe and stirred under nitrogen atmosphere at room temperature for 2h as shown in Figure 30(b). Isopropanol (10 ml) was added using a peristaltic pump at rate of 5ml/h until the blue colour disappears. After the Na-K alloy was completely exhausted, the mixture was dispersed in 50 ml of de-ionized water and extracted with n-hexane after which the mixture was filtered through a 0.22 µm nylon membrane. After washing the resulting brown cake product alternatively with n-hexane and alcohol, it was dried overnight under vacuum at 60°C.
4.3.3 Deposition Process

The OTFT structural materials deposition procedure is illustrated in Figure 31 below. The patterned passivated silicon substrate was put through a four step cleaning process, starting with acetone wash, followed by isopropyl alcohol (IPA) and DI water, and dried with nitrogen gas in order to remove organic material residues and water molecules absorbed at the surface. The OTFT fabrication procedure was performed under a fume hood with the aid of Laurell Tech spin coating apparatus under nitrogen atmosphere.

$C_{60}$ in 1,2 dichlorobenzene solution was spin coated onto the substrate at 500 rpm for 8s and spread at 2000 rpm for 45s. The coated substrate was annealed under vacuum (26.5 Torr) at 150°C for one hour and cooled down to room temperature under vacuum. The reason behind using a vacuum oven of annealing stems from the fact that $C_{60}$ is very susceptible to contamination and its performance as a semiconductor is affected by the presence of impurities. A vacuum oven decreases significantly the level of contamination and the same time the slow cool down provides the material ample time to fully crystallize and form uniform thin films.

The multilayer dielectric composed of PVA (2% in DI water) and PMMA was achieved by spin coating the materials at 500 rpm for 10s spreading at 3000 rpm and 1000 rpm for 40s, respectively. PVA and PMMA were both soft baked on a hot plate at 90°C for 30 min and 110°C for 10 min, respectively. This process is beneficial as it evaporates water present in the materials and enhances surface bonding between $C_{60}$ and PVA and between PVA and PMMA. However, the hydrophobic nature of PMMA makes the deposition of PEDOT:PSS, which is suspended in water, rather challenging. This issue was avoided by surface modification using UV/ozone. Exposing PMMA to UV/ozone leads to oxidation of the polymer by generating hydrogen-bond doners that facilitate bonding with the coating polymer [93]. The hydrophilicity of PMMA after UV/ozone exposure was investigate in
terms of contact angle after UV/ozone exposure at various duration. It was found that UV/ozone treatments have considerable impact on the hydrophilicity of PMMA after only 5 to 7 min exposure.

The gate conductive polymer is essentially composed of PEDOT:PSS and 0.1% graphene nanoplatlets suspension in PEDOT:PSS. The layering of conductive polymers was the same for both material and consisted of spinning at 500 rpm for 8s and spreading at 1000 rpm for 40s follows by a 10 min soft bake at 90°C. The OTFT device was tested before and after the deposition of the metal gate electrode. It was observed that performance of the device decreases significantly after the metal gate evaporation accompanied by an increase in gate leakage current. This was possibly due to metal particles penetrating the OTFT stack and possibly creating leakage current path. It was possible to reduce the effects of metal evaporation by adding a second layer of PEDOT:PSS and protecting the semiconductor and the gate dielectric from metal doping and minimizing thereby, the leakage current. For the OTFT sensors fabrication, graphene:PEDOT:PSS layer was replaced by rGO:PEDOT:PSS for the humidity sensing and Hydrogenated graphene:PEDOT:PSS for chloride ion sensing.
0.1% suspensions were prepared and sonicated for 2 hours prior the deposition process. Each suspension was spin coated onto the PEDOT:PSS layer using the same process as graphene:PEDOT:PSS.

The top gate metal electrode was deposited on top of the conducting polymer. This was achieved by thermal evaporation of 200 nm of chromium at a rate of 5Å/min through the shadow mask shown in Figure 27(d). The OTFTs were then ready for characterization and testing.

### 4.4 Fabrication Challenges

The challenges faced during the fabrication process were mostly related to adhesion issues between organic and inorganic materials. When Si/SiO₂ substrates are exposed to ambient air, water molecules and other species bond with the surface and prevent the adhesion of C₆₀ to the surface. This issue was more pronounced when using n-type Si substrates which, in theory, should not happen as the substrate is passivated. The reason is unknown at this stage and further investigation is required. To overcome this problem, the substrates were treated with oxygen plasma and hard baked at 200°C for 2 min to remove any traces of water and impurities before starting the deposition process.

The second challenge was related to the thermally evaporated top gate electrode. As the Cr was deposited on the PEDOT:PSS conductive layer, the poor uniformity of the film resulted in nonuniform metal layers that were easily damaged during the probing process. This issue was resolved by increasing the thickness of the conductive layer which resulted in more robust gate metal contacts.
5 Characterization

The performance of OTFTs is generally described in terms of figures of merit which are key device parameters extracted through characterization. Here, the OTFT characterization is conducted in three steps. First, hydrogenated graphene is chemically characterized to obtain insights on the success of the synthesis procedure and the degree of hydrogenation of graphene. Then, physical characterization involves the direct extraction of carrier mobility in fullerene C$_{60}$ as well as capacitance estimation of the OTFT stack. Finally, electrical characterization is used to extract the performance metrics of the OTFT as an electronic device.

5.1 Chemical Characterization

Chemical characterization of hydrogenated graphene was carried out using XPS and Fourier Transform Infrared Spectroscopy (FTIR) to identify chemical bonds in the molecules.

In XPS experiments, electrons at the surface of the material under study are excited using X-ray beams. The excited electrons release photoelectrons at specific energies which, upon analysis, provide information about the surface chemistry and chemical binding of the material. The presence and oxidation state of chemical species is indicated by peaks in XPS spectra at specific binding energies. When atoms in the material under study bind with chemical species, the observed peaks undergo a shift caused by a change in the binding energy of the core electrons [94]. Hydrocarbon bonds are typically identified by a peak in the C 1s spectra at binding energies in the range of 284 eV-285 eV. Small deviations from the expected value and broadening of the spectrum may occur due to exposure to air as well as N$_2$ gas during chemical synthesis [95, 96]. However, XPS is unable to distinguish between C-C bonds and C-H bonds and should be used in conjunction with other
characterization techniques such as FTIR.

FTIR uses similar principle to identify chemical bonds of a molecule or a material using infrared light. In this configuration, the infrared absorption of the material is mapped out by identifying distinctive molecular fingerprints associated with specific chemical bonds [97]. Types of chemical bonds in a material can be identified by the presence of stretched absorption peaks in the FTIR spectra at specific wavelengths. Saturated C-H bonds are typically indicated by peak stretching at wavenumbers numbers below 3000 cm\(^{-1}\) [98].

Hydrogenated graphene XPS data was collected using AlK\(_\alpha\) radiation at 1486.69 eV (150 W, 10 mA), charge neutralizer and a delay-line detector (DLD) consisting of three multi-channel plates. Survey spectra were 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 to confirm the hydrogenation of the graphene. To further verify the hydrogenation, Fourier transform infrared spectroscopy (FTIR) was performed on a ABB Bomem MB-Series FTIR spectrometer, with resolution of 8 cm\(^{-1}\), using a KBr pellet method. Scanning was from 400 to 4000 cm\(^{-1}\). Transmittance spectra for both graphene and hydrogenated graphene were obtained, and peaks examined and analyzed.

### 5.2 Physical Characterization

Physical characterization was essentially used to obtain physical parameters and properties that influence the performance of OTFTs. Here, the properties sought for are the morphology and the thickness of the layered films morphology, in addition to the energy band gap and charge carrier mobility of the semiconductor.
5.2.1 Thin Film Morphology and Thickness Measurements

Quantitative measurements of the surface topology and cross-sectional parameters of the OTFT structural layers were obtained using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). AFM and SEM are powerful imaging tools often used together for physical characterization of thin film semiconductors and polymers.

AFM is a powerful tool capable of providing three dimensional images of a wide range of materials, as well as quantitative characteristics of the surface texture and morphology. The measurements are conducted by placing the sample in contact with the AFM tip. The tip is oscillated at a resonance frequency and predefined constant amplitude depending on the type of material under study. The tip scans the surface of the sample and generate an three dimensional image along with measurements of surface roughness which is calculated in reference to the mean plane [99].

Herein, the surface topology and roughness of the C₆₀, rGO:PEDOT:PSS, Gr:PEDOT:PSS, hydrogenated graphene:PEDOT:PSS films were imaged by scanning a 50µm x 50µm areas at multiple locations of the samples. The samples were prepared following the fabrication procedure outlined in Section 4.3.3.

SEM imaging makes use of electrons to produce magnified images of the surface and cross section of materials. SEM has a high resolution and high penetration depth capable of producing high quality magnified images of specimens and detect changes in material structure and composition. SEM imaging is conducted by focusing a beam of electrons with the aid of lenses toward the specimen. Electrons and X-rays ejected from the samples are collected and used create a magnified images of the sample. Unlike AFM, SEM imaging is conducted under vacuum and requires the samples to be conductive [99].

In this study, SEM was used to examine the morphology of C₆₀ thin film after annealing and
to estimate the thickness of the fabricated OTFT individual structural layers by scanning the cross section of the samples. The samples were prepared using the same method described in Section 3.3.3 and were coated with a layer of gold to increase their conductivity prior imaging.

5.2.2 Charge Carrier Mobility Characterization

The characterization of the charge carrier mobility of the C$_{60}$ channel was performed using two methods: Charge carrier Extraction by Linearly Increasing Voltage (CELIV) and Dark Injection Space Charge Limited Current (DI SCLC) described in Chapter 3. Both approaches require the same sample preparation procedure, where the semiconductor is sandwiched between a charge injection electrode and a charge blocking electrode. The selection of metal used for electron injection and blocking is based on the electron work functions of the metals compared to energy level of C$_{60}$ LUMO (4.7 eV). Charge injection required a low workfunction metals whereas charge blocking requires high workfunction metals. Chromium has an electron workfunction of 4.7 eV and was used as the electron injecting electrode [100]. Whereas nickel was used as the electron blocking electrode as it has an electron workfunction of 5.01 eV [101]. C$_{60}$ samples were prepared and deposited on nickel coated passivated silicon substrate following the same procedure previously described. A thin film of PEDOT:PSS was deposited on C$_{60}$ for conductivity enhancements purposes followed by chromium electrode deposited by vacuum thermal deposition. The experiments were carried out by applying a voltage step function for DI SCLC and a ramp function for CELIV between the electrodes using a function generator. The signal was applied at frequency of 5 Hz and pulse width of 150 ms. The current transient was probed using a series resistance of 1Ω and displayed on an oscilloscope.
5.2.3 Bandgap Characterization

Energy bandgap of the synthesized C$_{60}$ film was characterized using XPS. This approach is based on a method proposed by Zhu et al. where the badgap of a semiconductor is estimated by measuring the valence band offset of a heterojunction built using the material under study [102]. The binding energy spectra of each material in the heterojunction is measured using XPS and the resulting offset between the valence band maxima corresponds to the bandgap of the material sandwiched between the substrate and the top layer [102]. Herein, a heterojunction was fabricated using C$_{60}$ and PEDOT:PSS and deposited on chromium coated substrate. The XPS spectra of the individual layers are expected to feature an offset between the HOMO of C$_{60}$ and that of PEDOT:PSS, which corresponds to the bandgap of C$_{60}$. This experiment was conducted by the Canadian National Research Council in Ottawa. The C$_{60}$ film was prepared following the same process described in the fabrication section. It was spin coated on a passivated silicon substrate on which a 200 nm layer of chromium was evaporated. A thin layer of PEDOT:PSS was then spincoated onto the C$_{60}$ film and baked at 90°C for 10 minutes.

The binding energies of C$_{60}$ and PEDOT:PSS HOMO maxima were measured using the PHI Quantera SXM XPS system with monochromatic Al-K$_{\alpha}$ with x-ray source of 1486.69 eV (150W, 10 mA). The sweeps were performed from -5 to 1200 eV at a step size of 1 eV and a pass energy of 160 eV.
5.3 Electrical Characterization

5.3.1 Dielectric Characterization

The dielectric properties of the OTFT stack were estimated with the aid of a Agilent 4294A impedance analyzer. The OTFT stack was processed and deposited between two chromium plates to emulate the structure of the device. The frequency was swept between 500 Hz and 10 kHz at an applied peak to peak voltage of 1 V. The dielectric properties of the stack were characterized by measuring the real and imaginary components of the capacitance and the series resistance. These parameters were used to estimate the dielectric losses of the structure represented by $\tan \delta$ and described by equation 14. Where, ESR is the equivalent series resistance and $X_C$ the reactance of the capacitor. The relative permittivity $\varepsilon_r$ of the structure was evaluated using equation 15, where $C$ is the measured stack capacitance, $d$ the stack thickness and $\varepsilon_0$ the permittivity of free space.

$$\tan \delta = \frac{ESR}{X_C} \quad (14)$$

$$\varepsilon_r = \frac{Cd}{\varepsilon_0} \quad (15)$$

5.3.2 OTFT Sensors Voltage-Current and Response Characterization

The electrical characterization was conducted with the aid of a probing station connected to Hewlett Packard 4155 A Semiconductor Parameter Analyser shown in Figure 32 and data collected using IC-CAP device modeling software. The fabricated OTFTs were characterized by extracting the output characteristic and the transfer characteristic. The testing was conducted in dry and dark environment to prevent photodegradation and contamination.
The output characteristic refers to the change in the drain-source current ($I_{DS}$) with respect to the drain-source voltage ($V_{DS}$) while applying a forward gate bias ($V_{GS}$). For this purpose, a $V_{DS}$ DC voltage sweep was conducted between -2V and 20 to 30V at a step size of 50mV at a constant gate bias. The effect of the gate bias were further investigated by conducting a $V_{DS}$ sweep while varying $V_{GS}$. Gate current leakage ($I_{GS}$) was also measured and plotted along with the output characteristic. It is an important property as it describes the OTFT current losses through the gate.

The transfer characteristic relates $I_{DS}$ to the applied $V_{GS}$ at constant $V_{DS}$. Herein, $V_{GS}$ is swept between -1V and 5 V while $V_{DS}$ is kept constant at 50 mV, 100mV and 200 mV. The transfer characteristic was used to determine the OTFT figures of merit including the threshold voltage, the charge carrier mobility and the current ON/OFF ratio.

The response of the OTFT humidity sensor was tested by comparing the output and transfer characteristic and measuring its current transient before and after exposure to high levels of humidity. The tests were performed in a gas chamber equipped with $N_2$ and water vapour inlets. The sensors were first exposed to $N_2$ gas to remove ambient gases. The sensors output and transfer characteristics were obtained before and after exposure to water vapour using the same testing procedure as OTFTs. The transient response was obtained at $V_{DS}$=
5V and $V_{GS} = 1V$ at which the OTFT operates in the linear regime.

The sensitivity of the chloride ion sensor was determined by comparing the output characteristic before and after exposure to various Cl$^-$ concentrations in aqueous solutions. NaCl in DI water solutions with concentrations in the range of 3 ppm to 75 ppm were prepared and deposited on the surface of the OTFT top gate with the aid of a pipette. After complete evaporation of water, $V_{DS}$ sweep was applied at constant $V_{GS} = 1V$ and $I_{DS}$ curves, before and after exposure to Cl$^-$, were compared.

Finally, the sensor temperature drift was investigated by measuring the transfer characteristic at increasing temperatures. The sensor was placed on a Peletier cooler regulated thermal chuck (Figure 33) and its output current measured at $V_{GS}$ sweep between -1V and 5V and constant $V_{DS}= 200$mV. The temperature was increased from 25°C to 50°C and measurements were recorded at 5°C increments after thermal equilibrium was reached.

Figure 33: OTFT thermal drift measurement apparatus using Peltier cooler thermal chuck.
6 Experimental Results and Discussion

6.1 Chemical Characterization of Hydrogenated Graphene

Confirmation of hydrogenation of graphene is observed in the results of both XPS and FTIR spectra (Figure 34(a) and (b)). Hydrogenation is confirmed in the XPS spectra where a shift in the C1s spectra is visible from 284 eV in graphene to 287 eV in hydrogenated graphene. Given that XPS can not distinguish between C–H and C–C bonds, the FTIR transmittance spectra comparison of both graphene and hydrogenated graphene confirms sp$^3$ C-H hybridization. Hydrogenation of graphene is validated by to C-H stretching vibrations peaks at wave numbers $\sim$2852 cm$^{-1}$ and $\sim$2923 cm$^{-1}$ and an intense C-H bending peak at $\sim$1122 cm$^{-1}$ on the hydrogenated graphene and relatively weaker or nonexistent on graphene. A stronger C-C skeletal vibration at $\sim$1629 cm$^{-1}$ for HG compared to the one on graphene confirms a destruction of the C=C in the formation of C-H to leave more C-C.

![Figure 34: Chemical characterization of hydrogenated graphene vs pristine graphene. (a) XPS C 1s (b) FTIR Spectra.](image-url)
6.2 Physical Characterization

AFM was used to inspect the surface topology and packing density of the layered materials, while SEM was used to study the morphology of the deposited materials and measure their individual thicknesses. Figure 35(a) is a microscopy image of the spin coated C\textsubscript{60} film after annealing and shows a relatively uniform layer with few defects associated to particle clumping. The SEM image of the same film shown in Figure 35(b) reveal well arranged grains of C\textsubscript{60} molecules. Unfortunately, the poor quality of the image does not allow for the measurement of grain size nor the separation between the grains. The surface topology of C\textsubscript{60} film was studied using 2D and 3D AFM images shown in Figure 35(b). The spin coated C\textsubscript{60} has a smooth surface with a spot-like crystalline morphology and root mean square roughness (R\textsubscript{q}) of 6.67 nm. This was confirmed by the cross-sectional SEM image (Figure 35(d)) which displays the C\textsubscript{60} channel layer deposited on SiO\textsubscript{2}/Si substrate with relatively smooth and uniform film with thickness of \(~\sim\) 120 nm.

Figure 35: Surface and cross-sectional images of solution deposited C\textsubscript{60} thin film. (a) Microscopic image of C\textsubscript{60} film (x1000). (b) 2D and 3D AFM scanning image showing the surface morphology and topology of C\textsubscript{60} film. (c) SEM image C\textsubscript{60} surface (x5000). (d) SEM cross sectional view of C\textsubscript{60} film.
The thickness of the OTFT individual structural layers were determined using SEM as shown in Figure 35(d). The measured thickness of the semiconductor channel, the multi-layer gate dielectric and gate conductive layer are summarized in table 1 below.

The surface topology of the top gate layer is an important parameter determining the performance of OTFT sensors as it affects the efficiency of channel modulation by the gate. Figures 36 (a), (b) and (c) display the surface morphology of the gate conductive layers used for the OTFT and the OTFT sensors. The microscopic images show the surface of graphene, rGO and hydrogenated graphene suspensions in PEDOT:PSS after annealing. They feature particles immobilized in the suspension with particle clumping more apparent in graphene and rGO whereas hydrogenated graphene seems more uniformly disperse. AFM 2D and 3D images show films with relatively smooth surface with apparent peaks corresponding to the doping agent flakes (Gr, rGO and hydrogenated graphene) indicating that the use of PEDOT:PSS results in smooth conductive layers. The measured mean square roughness of the films are summarized in table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Mean Square Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60</td>
<td>120</td>
<td>6.67</td>
</tr>
<tr>
<td>PVA</td>
<td>125</td>
<td>-</td>
</tr>
<tr>
<td>PMM</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Gr:PEDOT:PSS</td>
<td>500</td>
<td>7.77</td>
</tr>
<tr>
<td>rGO:PEDOT:PSS</td>
<td>500</td>
<td>7.28</td>
</tr>
<tr>
<td>Hydrogenated Graphene:PEDOT:PSS</td>
<td>500</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Table 1: OTFT measured structural layers thickness and mean square roughness.
Figure 36: (top) Microscopy images (x2000), (middle) 2D AFM scanning images and (bottom) 3D AFM scanning images of functionalized top gate conductive layer: (a) Graphene:PEDOT:PSS, (b) rGO:PEDOT:PSS. (c) Hydrogenated graphene:PEDOT:PSS.

6.3 Charge Carrier Mobility Characterization

Figure 37(a) shows the current transient of the C\textsubscript{60} at different voltages measured using DIR SCLC approach, where a rapid increase in the current can be observed as the applied voltage increases reaching a point where the charge density is maximized. The well-defined maxima indicates the formation of the ohmic contact for electron injection. Beyond that point, the current density decreases until it reaches the equilibrium state analogous to charge dynamic equilibrium. The observed low saturation points and the lack of thereof, at some voltages, stems from electron trapping caused by the exposure of the substrate and the semiconductor to ambient atmosphere during the fabrication process, remnants of solvents
and other contaminants. These factors influence the energetics of metal/semiconductor interfaces and therefore, the charge injection and blocking mechanisms [103]. Figure 37(b) summarizes the electron mobilities obtained from DI SCLC measurements showing higher mobilities in the low voltage region and a saturation region at higher voltages suggesting that the electron mobility becomes independent of the applied voltage.

![Figure 37: Carrier Charge mobility characterization: (a) SCLC current transient. (b) Measured Charge mobility Vs applied voltage.](image)

The CELIV measurements were conducted in the same manner as the DI SCLC using a ramp voltage function instead of a step function. However, the measured current transient did not show a current maxima as expected. This is due to the fact that CELIV approach require the presence of charge carriers in the semiconductor. Being an organic semiconductor, $C_{60}$ has an intrinsic low carrier density which may be insufficient to achieve ohmic contact between the semiconductor and the blocking electrode. This can be circumvented by either doping the semiconductor with group V elements or inducing photoexcited carriers using an optical source. [78].
6.4 C<sub>60</sub> Bandgap Characterization

C<sub>60</sub> bandgap characterization was performed by measuring the HOMO offset of the heterojunction made of C<sub>60</sub> and PEDOT:PSS heterojunction using XPS. Figures 38(a), (b) and (c) display XPS spectra of chromium, C<sub>60</sub> and PEDOT:PSS, respectively. The CPS spectra for the individual layers were reproduced several times showing consistent results.

![Cr XPS Spectra](image1)
![C<sub>60</sub> XPS Spectra](image2)
![PEDOT:PSS XPS Spectra](image3)

Figure 38: XPS Analysis of chromium, C<sub>60</sub> and PEDOT:PSS: (a) Cr XPS spectra. (b) C<sub>60</sub> XPS spectra. (c) PEDOT:PSS XPS spectra.
XPS was then conducted on C\textsubscript{60}/PEDOT:PSS heterojunction deposited on Cr coated substrate. The results displayed on Figures 39(a) and (b) show distinctive C\textsubscript{60} and PEDOT:PSS HOMO energy levels and heterojunction interface. The heterojunction spectra displays an intact interface with consistent and reproducible spectra as shown in Figure 39(c) and features a distinct offset between the HOMO levels of C\textsubscript{60} and PEDOT:PSS shown in Figures 39(a) and (b). HOMO energy level of each material was estimated using linear interpolation indicating values of 1.5 eV and 1.1 eV for C\textsubscript{60} and PEDOT:PSS, respectively and an offset of 0.4 eV corresponding to the bandgap of C\textsubscript{60}. The calculated bandgap was not in accordance with values reported in literature (1.5 eV to 2.3 eV) [104]. Unfortunately, the approach used for C\textsubscript{60} bandgap estimation was not successful, as mapping the chromium layer spectra in the heterojunction was very challenging as shown in Figure 39(a) where the expected peak in Cr spectra is absent. This was due to incorrect charging of Cr layer while conducting the XPS analysis.

Nonetheless, XPS analysis provided valuable reproducible information about the HOMO energy level of C\textsubscript{60} and the interface spectra of C\textsubscript{60}/PEDOT:PSS heterojunction. A better approach would be to map the absorption and emission spectra using XAS and XES, respectively. The XAS determines HOMO energy level and XES indicated LUMO level. The energy bandgap can be estimated by measuring the offset between the LUMO and HOMO maxima.
Figure 39: Bandgap characterization of C\textsubscript{60} using XPS: (a) XPS spectra of C\textsubscript{60} and PEDOT:PSS showing distinctive HOMO energy levels. (b) Magnified XPS spectra of C\textsubscript{60} and PEDOT:PSS showing the edges of HOMO levels. (c) XPS spectral of the interface between C\textsubscript{60} and PEDOT:PSS.
6.5 OTFT Electrical Characterization

6.5.1 Dielectric Characteristics

The capacitance of the fabricated OTFT stack is equivalent to the individual capacitances of the structural materials outlined in Table 1 connected in series as shown in Figure 40.

![Diagram of OTFT stack capacitances](image)

Figure 40: OTFT stack equivalent capacitance layout featuring the structural layers individual capacitances connected in series.

The capacitance profile at frequencies between 500 Hz and 10kHz along with dielectric losses represented by the tanδ where the loss angle δ is depicted in Figure 41(a). tanδ is essentially a quantitative measure of the energy loss at the operating frequency and is described by equation 13.

The tested structure shows minimal losses at low frequencies and maximum loss of about 0.3 at 1 MHz with an average of 0.031 over the testing frequency range. Figure 41(b) describes the distribution of the impedance and the phase angle over the measured frequency change where it can be observed that the phase angle remains close to -90° throughout the entire frequency range which is indicative of capacitive behaviour.

The geometric capacitance of the OTFT stack was extracted at high frequencies in the vicinity of 10 kHz where the capacitance saturates and was estimated at 7.82 nF/cm². The
Figure 41: Capacitance characterization of OTFT stack. (a) Capacitance per unit area Vs frequency. (b) Z-theta Vs Frequency.

The corresponding relative permittivity of 17.2 was calculated using equation 15 where, C is the capacitance per unit area, d the thickness of the stack and $\varepsilon_0$ the permittivity of vacuum.

### 6.5.2 Current-Voltage Characteristics

To ensure the viability of the fabricated OTFTs as chemical sensors, their current-voltage characterization was conducted and analyzed by examining their output and transfer characteristics and extracting the performance metrics.

**Output Characteristic**

The output characteristic of the OTFT with graphene:PEDOT:PSS as the gate conductive layer is shown in Figure 42(a). OTFT exhibit a clear n-type transistor behavior and possesses obvious linear and saturation regions at higher gate bias. The OTFT turns on at $V_{DS}$ of approximately 2 V and is independent of the applied gate bias. The output current $I_{DS}$ increases as the gate bias $V_{GS}$ is increased. This is a demonstration of the effective channel modulation introduced by the gate dielectric. The apparent current saturation occurs at $V_{DS}$
between 13 V and 18 V. The observed hysteresis in the saturation voltages as the device channel is modulated can be explained by the environmental instability of C_{60} which influence the device performance after repeated measurements. The OTFTs current loss was measured in the output characteristic and represented by the gate leakage I_{GS} shown in Figure 42(a). The fabricated OTFTs have a visibly very low leakage current compared to the output current which is evidence of low charge trapping, good semiconductor-dielectric interface and excellent dielectric properties of the OTFT stack.

![Output Characteristic](image1)

(a)

![Output Characteristic](image2)

(b)

Figure 42: Output Characteristics of the fabricated OTFTS. (a) Output characteristic at constant gate bias VGS range of 80 mV to 1 V. (b) Parametric sweep of output characteristic against OTFT aspect ratio at VGS=1 V.

The scalability of the fabricated OTFT was evaluated by characterizing the output of devices with different aspect ratios. Figure 42(b) shows the scalability of the OTFT with channel length of 750 μm, where the output characteristic of OTFTs with increasing aspect ratios were compared. As expected, the I_{DS} increases with decreasing channel length which is in accordance with the FET model described by equations 2 and 3. The OTFTs exhibit relatively the same behaviour where they turn on at V_{DS} of 1 V and saturate at approximately 25 V. These results demonstrate effect of the channel length on the output current of the OTFT, where more compact devices exhibit higher output currents but are more challenging to fabricate.
The output characteristic demonstrates that the fabricated OTFT behaves like an n-type transistor with distinct linear and saturation regions depending on the applied gate bias. The apparent increase in channel current with respect to increasing gate bias is indicative of efficient channel modulation stemming from good dielectric properties of the OTFT stack. Furthermore, the low gate leakage current and its independence of the applied gate voltage substantiate the uniformity of solution processed C_{60} film and significantly good semiconductor-gate dielectric interface.

**Transfer Characteristic**

The transfer characteristic describes the variation in I_{DS} in accordance with the gate bias at constant V_{DS} and is used to determine performance metrics of devices, namely, threshold voltage, charge carrier mobility and current ON/OFF ratio which are summarized in Table 2 below. The transfer characteristic of the fabricated OTFTs is displayed in Figure 43 showing a parabolic growth at low gate voltages and relative saturation at higher gate voltages. The OTFT response to increasing V_{DS} of 50 mV, 100 mV and 200 mV is also displayed. The OTFT does not show a significant dependence on V_{DS} showing a slight decrease in the output current with increasing V_{DS}. Ideally, the drain current increases as V_{DS} is increased due to the dependence of I_{DS} on V_{DS} in the linear region. This behaviour can be attributed to gate bias stress caused by repeated measurements often observed in organic devices.

The effective gate voltage control over I_{DS} is demonstrated by the transconductance displayed in Figure 44. The transconductance represents the gain in I_{DS} for every incremental change in V_{GS}. This shows that the OTFT I_{DS} increases as V_{GS} increases until it reaches a saturation point at I_{GS} \sim 3.5V.

The threshold voltage at constant V_{DS} values was measured from the linear extrapolation of
the slope of $\sqrt{I_{DS}}$ as most organic semiconductors do not exhibit a distinct linear response to increasing gate voltage. The OTFTs exhibit positive thresholds values that increase with increasing $V_{DS}$. The low $V_{th}$ exhibited by the OTFTs implies that the transistor channel start conducting at very low applied voltages, which is particularly desirable in sensing application.

The field effect charge carrier mobility was determined based on the standard FET model
and was extracted from transfer curve. Since $V_{DS}$ is much smaller than $V_{GS}-V_{Th}$ the OTFT operates in the linear regime, hence $\mu_{FET}$ is determined using equation 16 below where $\delta(I_{DS})/\delta(V_{GS})$ refers to the slope of the linear region of the curve.

$$\mu_{FET} = \frac{L}{W C_S V_{DS}} \left( \frac{\partial I_{DS}}{\partial V_{GS}} \right)$$

(16)

The calculated field effect mobilities are relatively good compared to reported values for organic TFTs which is suggestive of excellent charge injection and charge transport stemming from good metal-semiconductor and dielectric-semiconductor interfaces. These results demonstrate that the solution processed OTFT exhibit excellent charge carrier mobilities at low drain source voltages. The calculated mobilities at constant $V_{DS}$ are summarized in Table 2. The apparent decrease in charge carrier mobility confirms the assumption that the observed $I_{DS}$ decreases with increasing $V_{DS}$ is due to channel degradation with cyclic measurements which intensifies electron trapping and hinders the charge transport.

The current ON/OFF ratio is a measure of the switching capabilities of OTFTs which compare the current output in the “ON” and “OFF” states. It is measured by taking the ratio of the maximum current delivered by the OTFT at high gate voltages to the current at $V_{GS}$ below the threshold voltage. Herein, the current ON/OFF ratio of the fabricated OTFTs is extracted from the transfer characteristic where $I_{DS}$ is plotted in logarithmic scale as shown in Figure 43.

The estimated current ON/OFF ratio of the fabricated OTFT are relatively low compared to values reported in literature ($\sim 10^3$). This is due to high leakage current when the devices are in the “OFF” state and to the fact that the applied $V_{DS}$ is not large enough to minimize the effects of the gate leakage.
Table 2: OTFT Performance Parameters.

<table>
<thead>
<tr>
<th>$V_{DS}$</th>
<th>$V_{Th}$ (V)</th>
<th>$\mu_{eff}$ (cm$^2$/V.s)</th>
<th>$I_{ON}/I_{OFF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mV</td>
<td>1.15</td>
<td>1.2</td>
<td>3.73x10$^2$</td>
</tr>
<tr>
<td>100 mV</td>
<td>1.3</td>
<td>0.6</td>
<td>5x10$^3$</td>
</tr>
<tr>
<td>200 mV</td>
<td>1.35</td>
<td>0.25</td>
<td>4.5x10$^2$</td>
</tr>
</tbody>
</table>

The results discussed in this section describe the operation of the solution process C$_{60}$ OTFTs and the critical performance metrics. The behaviour of the fabricated devices is characteristic to n-type transistors with distinct linear and saturation region displayed in the output characteristic. The OTFTs turn on at the same voltage of 2V regardless of the applied gate bias and undergo little to no leakage current. The scalability of the OTFT was demonstrated proving the dependence of the output current on the channel width and confirming that higher currents can be obtained through shorter channel widths. The analysis of the transfer characteristics allowed for the determination of the operation regime of the tested device and the estimation of figures of merit (summarized in Table 2). The OTFTs were characterized at low voltages to test their suitability in low power requirement sensing platforms. The OTFTs operate in the linear regime, have low threshold voltages and exhibit excellent charge carrier mobilities. However, the calculated current ON/OFF ratio is relatively low due the presence of high leakage current when the devices are in the “OFF” state. This could be explained by the environmental instability of organic materials as well as contamination, environmental and photodegradation due to repeated measurements. Nonetheless, the analysis results demonstrate that relatively stable and efficient solution processed n-type OTFTs are achievable through design optimization and gate dielectric enhancements and limiting exposure to ambient environments during fabrication and operation.
6.6 Sensor Performance

The structural properties and the operational performance of the designed C$_{60}$ OTFT makes it viable option for chemical sensing applications. OTFTs can offer qualitative and quantitative chemical sensing of target analytes while preserving integrability, small footprint and low power consumption. The realization of low cost, high sensitivity chemical sensors rely on the nature of the sensing material in terms of chemical affinity and reactivity, sensitivity and processability. In this context, graphene is an established material for the realization of highly reactive materials for sensing applications owing to its excellent electrical and thermal conductivity, mechanical properties and processability. Chemical functionalization of graphene allows for the realization of a range of materials with chemical affinity toward specific analytes depending on the functionalization route.

In this work, rGO and hydrogenated graphene were used as the sensing material for humidity and Cl$^-$ ions, respectively. The graphene conductive layer used in C$_{60}$ OTFTs was replaced by rGO and hydrogenated graphene. The idea behind developing the aforementioned sensors rises from the challenge of detecting Cl$^-$ ions in the presence of high humidity due to the reactivity of organic material to water molecules. The humidity OTFT sensor was designed for qualitative measurement purposes to detect the presence of surface moisture, while Cl$^-$ ions sensor was used to provide quantitative measurements of Cl$^-$ ions concentrations.

6.6.1 Humidity Sensor

The humidity sensor response before and after exposure to water under constant gate bias of 1 V is shown in Figure 45(a). As expected, the conductivity of rGO is enhanced as a result of chemical bonding between the hydroxyl groups present in rGO and water molecules.
In both instances, the OTFT sensor turns on at $V_{DS} \approx 1$ V and exhibit current saturation at 10 V. The sensor displays a long and sharp linear response after exposure to humidity and saturates at high current $\sim 6$ folds the saturation current of the dry sensor. The increase in conductivity of the OTFT is due to increase of charge carrier density in the rGO. When rGO is exposed to water, the presence of hydroxyl groups promotes bonding with water molecules which acts as hole donors. Because rGO is a hole carrying material, the increase of hole density brought by water molecules, results in an increase of conductivity apparent in the output characteristic.

In the transfer characteristic, the sensor’s response is manifested by a shift in the threshold voltage as shown in Figure 45(b). It is evident that the sensor threshold voltage shift to a lower gate voltage which is attributed to the increase in conductivity.

![Output Characteristic](image)(a)

![Transfer Characteristic](image)(b)

Figure 45: OTFT humidity sensor I-V characteristics. (a) Output characteristic before and after exposure to humidity. (b) Transfer characteristic before and after exposure to humidity.

The dynamic response of the sensor is depicted in Figures 46(a) and (b) at constant $V_{GS} = 1$ V and $V_{DS} = 3$ V, where the OTFT operates in the linear region. The corresponding output current of 0.3 mA/cm$^2$ is considered as the baseline for sensitivity estimations. As humidity is introduced, the sensors switch to the ON state indicated by the increase in output current attributed to the increase in conductivity. It is observed that the OTFT output current increases by approximately 2 folds when the sensors switch from the OFF state.

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to the ON state. After complete removal of humidity using N₂, the sensor turns off and the output current returns to the baseline value. The sensor relative responsivity for dry to surface wetness transition ($R_{rel}$) was estimated using equation 17, where $\Delta I_{resp}$ is the change in output current after exposure to high levels of humidity above 80%RH and $I_{dry}$ is the current measured under dry conditions. The relative responsivity for dry to surface wetness transition was found to be 122.6%.

$$R_{rel} = \frac{\Delta I_{resp}}{I_{dry}} \times 100$$  \hspace{1cm} (17)

The response time and recovery time of the sensor was measured to be $\sim 20$ ms. It can also be observed that the output current undergoes a slight decrease during the ON state which can be attributed to expected OTFT degradation usually observed in organic electronics. The same is observed for the baseline current as it undergoes a slight decrease on subsequent measurements.

![Current Transient](image1.png)  \hspace{1cm} ![Current Transient](image2.png)

Figure 46: OTFT humidity sensor dynamic response. (a) Current transient before and after exposure to humidity. (b) Current transient displaying ON and OFF states, response time and recovery time measurements.

Since the humidity sensor was designed for qualitative measurements only, the sensitivity of the sensor against humidity concentration was not examined, which requires further investigation. Nonetheless, the humidity sensor displays excellent responsivity to the pres-
ence of surface moisture and exhibit fast response time and fast recovery.

6.6.2 Chloride Ion Sensor

As previously described, the chloride sensors is based on C\textsubscript{60} OTFT previously described in which the gate was functionalized with hydrogenated graphene. The sensing performance of the fabricated OTFT chloride sensor against chloride concentration is evaluated and compared to a control OTFT device with graphene conductive layer. NaCl solutions in DI water with various concentrations were prepared and deposited onto the sensors gate. The performance and response of the sensors was tested after complete evaporation of water. Figure 47(a) displays the normalized output characteristic of chloride sensors before and after exposure to increasing Cl\textsuperscript{−} concentrations at constant gate bias \(V_{GS} = 1\) V. The sensors turn on at \(V_{DS} = 2\) V which is in accordance with turn-on voltage of the OTFT and undergo a decrease in the saturation current associates with the decrease in conductivity resulting from hydrogenated graphene bonding with chloride ions. The effect of Cl\textsuperscript{−} ions concentrations is also observed in the decrease of the linear response range of the OTFT due to the decrease in charge carrier mobility attributed to the chemical reduction of hydrogenated graphene stemming from the reaction of Cl\textsuperscript{−} ions and H\textsuperscript{+} ions. Figure 47(b) depicts the response of the reference device (with graphene:PEDOT:PSS) to increasing Cl\textsuperscript{−} ions concentration. The observed response of the device does not display any dependence on Cl\textsuperscript{−} ions concentration and demonstrates that pristine graphene does not exhibit chemical reactivity to the presence of Cl\textsuperscript{−} ions. The observed change in conductivity of the reference sensor can be attributed to the absorption of water by PEDOT:PSS. Absorption of water molecules results in decohesion of PEDOT:PSS matrix and swelling of the film, which in turn increase the resistivity of film leading to a drop in conductivity [105].

The sensors response to Cl\textsuperscript{−} ions concentration was investigated by maintaining \(V_{GS} \) at 1 V and \(V_{GS} \) at 13 V at which the OTFT operates in the linear region. The measured output
current $I_{DS}$ of the sensors at Cl$^-$ ions concentrations ranging between 3 ppm and 75 ppm is displayed in Figure 48. The sensors exhibit a relative logarithmic response as expected from a TFT. The sensors output current decreases logarithmically with increasing Cl$^-$ ions concentration.

The consistency of the measurements was validated by fabricating and testing devices with various channel lengths and widths. A total of 80 OTFT chloride ion sensors with channel length ranging between 10$\mu$m and 25 $\mu$m, and aspect ratio ranging between 10 to 50, were fabricated and tested against the targeted range of Cl$^-$ concentration (3ppm-75ppm) with a success rate of 70%. The measurements pertaining to each concentration value were repeated several times to evaluate the spread of measurements and are plotted along with sensors response curve in Figure 48. The collected data for each concentration does not deviates significantly from the mean, which proves the reliability of the measurements. The sensors were tested repeatedly in a lab environment over a period of four weeks in which they remained operational for an average of two to three weeks [106].

The sensitivity of the Cl$^-$ ion sensors was estimated at concentration range of 3ppm-75ppm...
using equation 18, where $\Delta I_{\text{resp}}$ refers to the change in output current after exposure to Cl$^-$ and $I_{\text{ref}}$ is the current measured in the absence of Cl$^-$ and $C_{Cl^-}$ is concentration of Cl$^-$. The calculated sensitivity of the sensor was found to be 4%/ppm [106].

$$S = \frac{\Delta I_{\text{resp}}}{I_{\text{dry}} C_{Cl^-}} \times 100$$  \hspace{1cm} (18)

The achieved results demonstrate the potential of hydrogenated graphene in the detection of Cl$^-$ ions using OTFT sensors. The sensors are capable of detecting minute concentrations of Cl$^-$ far below reported corrosion initiation thresholds of 100 ppm to 3500 ppm, depending upon the type of metal alloy, ambient temperature, and pH [30, 31]. Furthermore, they show noticeable sensitivity to changes in concentration. The logarithmic response of the sensor provides a significant enhancement of sensitivity for low concentration. It is a specially coveted property in sensing of hazardous chemical where detection of small concentrations can prevent irreversible damage. Analysis of repeated measurement show that sensors
response does not change significantly after recurrent sweeps, which representative of the sensor reliability and robustness. Further investigation is required to determine the response time and recovery of the sensor.

6.6.3 Sensor Temperature Drift

Ambient conditions in which sensors operate has a significant influence on their performance and the accuracy of their measurements. Temperature effects, for instance, have an impact on OTFT characteristics, namely threshold voltage and mobility. Studies suggest that increasing temperature increases the charge carrier mobility and decrease the threshold voltage. These effects are attributed to thermal excitation in which electron in localized states are energized and contribute to channel conductivity along with free electrons [107]. When thermal effects are not taken into consideration, the OTFT sensor change in output gives erroneous readings and unreliable measurements.

The temperature dependence of the OTFT sensor was investigated by placing the OTFT on a Peltier cooler regulated thermal chuck and measuring the drain current with respect to \( V_{GS} \) at \( V_{DS} = 200\text{mV} \) after thermal equilibrium is reached. The sensor response to increasing temperature is depicted in Figure 49 and shows an increase in the drain current with increasing temperature along with a decrease in \( V_{Th} \). The apparent increase in conductivity is caused by thermal effects, where the \( V_{Th} \) decreases form 0.2 V at 25°C to 0.05 V at 45°C after which it starts increasing due to the degradation and breakdown of organic materials at higher temperatures. This type of behaviour is expected especially from organic OTFT due to their sensitivity to high temperatures.

In sensing applications, thermal effects can be controlled with proper encapsulation and cooling. Temperature compensation is also essential, particularly for environmental sensors, to achieve high performance uniformity over the operational temperature range of the
Figure 49: OTFT sensor transfer characteristic vs. ambient temperature illustrating the influence of ambient temperature on the OTFT drain-source current and threshold voltage.

device. This is realized through temperature calibration using a combination of empirical equations describing the change in output current and threshold voltage with respect to change in ambient temperatures and simple algorithms to calculate the reference values and adjust the sensor response accordingly.
7 Conclusion

Thin film transistor-based sensing has been found advantageous compared to other state of the art technologies, due to their simple design, small footprint, high sensitivity and fast response. It is an excellent approach to demonstrate the potential of organic materials in chemical sensory platforms. The diversity, abundance, low energy processability of organic semiconductors laid the groundwork for the development of low cost electronics and their implementation in a wide range of applications. Combining the exceptional electronic, chemical and structural properties of organic materials and the performance of TFTs makes such approach very appealing for the detection of wide range of analytes.

In this work, fullerene C₆₀ OTFT is designed and fabricated using simple and low cost solution processing techniques and its applicability in chemical sensing is demonstrated. The rationale behind using C₆₀ as the OTFT semiconducting channel material stems from the fact that, in general, mobility of electrons is much higher than that of holes and would result in faster electronic devices. However, n-type OTFTs have had much less success compared to p-type OTFTs due to the fact that electron transporting materials tend to be more environmentally unstable compared to their hole transporting counterparts, resulting in devices with low carrier mobilities. The capabilities of n-type materials as OTFT semiconducting channels can be enhanced through processing optimization, including, but not limited to, substrate surface treatment, deposition ambient conditions, dielectric stack material selection, device structure design and configuration, as well as proper packaging and encapsulation.

The extent of application is centered around environmental sensing for structural health monitoring of metallic structures due their predisposition to degradation in corrosive environments, specifically in humid conditions and in the presence of chloride ions. The sensing capabilities of the fabricated OTFT is brought up by the implementation of sensing agents
based on graphene derived materials, namely reduced graphene oxide and hydrogenated graphene. Furthermore, the chemical reactivity and selectivity of the aforementioned sensing materials to humidity and chloride ions are tested and confirmed.

The OTFT device configuration adopted in this work is a top gate bottom contact architecture. Although devices in this configuration generate less output current/voltage than other common configurations, it is the ideal option for the proposed sensor as the semiconductor material is sealed by the gate dielectric stack and protected against oxygen and environmental doping, while the gate remains exposed to the target analytes. Furthermore, the fabrication procedure becomes simpler as the structure layers are deposited consequently using spin casting and low temperature annealing which does not significantly affect the integrity of the structure.

The OTFT devices were deposited on passivated silicon substrates which are a safe choice in terms of surface uniformity, insulating properties and robustness. The source and drain metal contacts were patterned on the Si/SiO$_2$ via photolithography and negative lift-off process. Multiple structures with different aspect ratios were arranged in a circular cluster such that multiple devices can be fabricated from the same batch and the effect of channel dimensions is investigated. The patterned substrates were recycled using simple organic cleaning process and reused multiple times.

The optimized OTFTs were fabricated using 0.9% C$_{60}$ in 1, 2 dicholobenzene which gave the highest concentration and relatively good crystallization. The polymeric gate dielectric stack was comprised of PVA and PMMA in addition of a gate conductive layer composed of PEDOT:PSS and graphene:PEDOT:PSS. Finally, the gate metal contact thermal evaporated on top onto the conductive material. The top metal gate contacts were designed in accordance with the cluster design such that multiple devices can be addressed with a common gate which is placed in close proximity to each individual device.
Microscopic, SEM and AFM images of the channel material showed that the deposition and annealing process results in fully crystallized $C_{60}$ layer with uniform surface and low surface roughness which is much desired in electronics as the effect of electron trapping is minimized. Mobility characterization using DI SCLC demonstrated that $C_{60}$ layer behaves like a semiconductor but degrades rapidly due to environmental doping. Dielectric characterization allowed for the measurement of the OTFT stack capacitance which was estimated at 7.82 nF. Current-voltage characterization demonstrated that the fabricated OTFTs operate as n-type devices with distinguishable linear and saturation regions. The devices were characterized at low gate and drain voltages for output ad transfer characteristics and showed a minimum threshold voltage of 1.2 V with charge carrier mobility and current ON/OFF ratio as high as 1.2 cm$^2$/V.s and 5x10$^3$, respectively. The carrier mobility was calculated using the standard field effect method under the assumption of electric field independence and does not consider the effect of contact resistance. Furthermore, repeated measurements on the same devices show a decline in mobility due to cyclic gate bias stress effects, photodegradation and environmental doping.

The humidity and $Cl^-$ ion sensors were fabricated by replacing the graphene:PEDOT:PSS conductive layer by rGO:PEDOT:PSS and hydrogenated graphene:PEDOT:PSS. Hydrogenated graphene was synthesized in house via modified Birch method and successful hydrogenation was confirmed using XPS and FTIR. Microscope and AFM imaging conducted on the sensing layers showed a relatively smooth surface owing to the porosity and good film forming properties of PEDOT:PSS. The humidity sensor showed a high relative responsivity for dry to surface wetness transition of 122.6% with a fast response time and recovery of 20 ms. However, it was designed for qualitative measurement and its sensitivity against varying relative humidity levels was not tested. The $Cl^-$ ion sensor was tested at various concentrations and displays a logarithmic response to increasing concentration which is highly desirable as it allows for the detection of low concentrations. The sensitivity displayed by the sensors was estimated at 4%/ppm within the detection range of
The overall work of this thesis including design, fabrication and characterization is to investigate the potential of solution processed n-type OTFTs and their applicability in chemical sensing applications. Low cost and low power requirements n-type OTFTs were achieved via simple and energy efficient fabrication procedure as well as material optimization. OTFT sensors were fabricated and the sensing abilities of graphene derived materials was demonstrated. The versality of chemically functionalized graphene can be exploited to construct a systematic framework for low cost, miniaturized and highly sensitive chemical sensing.
8 Future work

The promising results obtained during this thesis work demonstrate the proof of concept of low cost chemical sensors based on $C_{60}$ as the semiconductor material and functionalized graphene as the sensing material. This simple and inexpensive fabrication process may be an attractive method for the development of chemical sensors for structural health monitoring of metallic structures. Obviously, more design and material optimization as well as characterization is required in order to increase the shelf life and reliability of these devices. The environmental instability of $C_{60}$ in particular and susceptibility to environmental doping of organic material in general can be minimized by limiting the exposure to ambient environments during fabrication and the use proper encapsulation during device operation. Ion selective membranes may enhance the performance and reliability of the sensor by allowing the passage of target analytes and blocking other elements which decreases contamination and the likelihood of false measurements. Thermal effects and gate bias stress should be taken into consideration when developing sensors and proper compensation should be designed accordingly.

Material characterization performed in this work was used to quantify material parameters governing the performance of the fabricated devices, such as, dielectric properties of the OTFT stack, threshold voltage and charge carrier mobility. It is necessary to develop a link between the material parameters and the electrical operation of the fabricated devices through device modeling to predict the performance of the device on its own and as part of an electronic circuit. Accurate equivalent circuit modeling and simulation would provide a comprehensive physical description of the designed sensors, enable prediction and simulation of device operation under various conditions and offer more design flexibility and scalability.

The multiple device cluster design and its small footprint would allow for the design of
multiparameter sensing systems such as sensor nodes. Sensor nodes are small and low powered devices with data collection and signal processing capabilities. It usually includes a micro-controller, a transceiver and a memory. The designed sensor node would comprise of multiple sensors each targeting a specific analyte among them a humidity sensor. Since chemical sensing in high level of humidity is not ideal, preventing sensors from operating in such conditions would limit skewed readings. In this system, the main function of the humidity sensor is to ensure that other sensors are operating in relatively dry conditions. As such, the humidity sensor response is captured by the micro-controller which with turn on or the other sensors accordingly. The designed nodes would be stand-alone units or part of a network of devices connected wirelessly to a common data acquisition unit. In this manner, ambient conditions affecting metallic structures would be continuously monitored a data collected and processed in real time.

The high sensitivity if the designed chemical sensors and the proposed integration strategy have the potential to detect environmental factors affecting the integrity of metallic structure before the onset of damage as well as monitor its progress at early stages. The information provided by the sensing units will allow the development of efficient prevention and maintenance protocols fo structural health monitoring.
References


[102] Y. Zhu, N. Jain, M. K. Hudait, D. Maurya, R. Varghese, and S. Priya, “X-ray photoelectron spectroscopy analysis and band offset determination of CeO2 deposited on epitaxial (100), (110), and (111)


