APPLICATION OF ELECTROSPUN THIN FILMS FOR SUPRA-MOLECULE BASED GAS SENSING

by

Amir Hossein Khoshaman
B.Sc., Sharif University of Technology, 2009

THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCES

in the
School of Engineering Science
Faculty of Applied Sciences

© Amir H. Khoshaman 2011
SIMON FRASER UNIVERSITY
Summer 2011

All rights reserved. However, in accordance with the Copyright Act of Canada, this work may be reproduced, without authorization, under the conditions for Fair Dealing. Therefore, limited reproduction of this work for the purposes of private study, research, criticism, review and news reporting is likely to be in accordance with the law, particularly if cited appropriately.
APPROVAL

Name: Amir Hossein Khoshaman
Degree: M.A.Sc
Title of Thesis: Application of Electrospun Thin Films for Supra-Molecule Based Gas Sensing

Examining Committee:

Chair: Dr. Albert Leung, P.Eng
Professor

Dr. Behraad Bahreyni, P.Eng
Senior Supervisor
Assistant Professor

Dr. Paul C.H. Li
Supervisor
Professor

Dr. Ash Parameswaran, P.Eng
Internal Examiner
Professor

Date Defended/Approved: 9 August 2011
Partial Copyright Licence

The author, whose copyright is declared on the title page of this work, has granted to Simon Fraser University the right to lend this thesis, project or extended essay to users of the Simon Fraser University Library, and to make partial or single copies only for such users or in response to a request from the library of any other university, or other educational institution, on its own behalf or for one of its users.

The author has further granted permission to Simon Fraser University to keep or make a digital copy for use in its circulating collection (currently available to the public at the “Institutional Repository” link of the SFU Library website (www.lib.sfu.ca) at http://summit.sfu.ca and, without changing the content, to translate the thesis/project or extended essays, if technically possible, to any medium or format for the purpose of preservation of the digital work.

The author has further agreed that permission for multiple copying of this work for scholarly purposes may be granted by either the author or the Dean of Graduate Studies.

It is understood that copying or publication of this work for financial gain shall not be allowed without the author’s written permission.

Permission for public performance, or limited permission for private scholarly use, of any multimedia materials forming part of this work, may have been granted by the author. This information may be found on the separately catalogued multimedia material and in the signed Partial Copyright Licence.

While licensing SFU to permit the above uses, the author retains copyright in the thesis, project or extended essays, including the right to change the work for subsequent purposes, including editing and publishing the work in whole or in part, and licensing other parties, as the author may desire.

The original Partial Copyright Licence attesting to these terms, and signed by this author, may be found in the original bound copy of this work, retained in the Simon Fraser University Archive.

Simon Fraser University Library
Burnaby, British Columbia, Canada

revised Fall 2011
ABSTRACT

Methods for preparation of high-quality thin films for fabrication of selective supra-molecular based gas sensors are proposed. Several thin films were developed for sensing of methane, ammonia, volatile organic gas compounds, and humidity. The thin films were deposited using a custom-made electrospraying set-up. Using this system, we employed suitable metal-organic framework materials to fabricate sensors for detection of organic vapours at different concentrations for the first time to the best of our knowledge. Cryptophane A was synthesized and incorporated in thin films that were deposited on the surface of quartz resonators in two different ways of electrospinning using siloxane polymers and spin-coating (followed by exposure) with SU-8 for methane sensing. The detection limit of the fabricated sensors is lower than the best reported values for similar sensors. Thin films of different ratios of poly(vinyl alcohol) and poly(acrylic acid) were electrospun and used for effective detection and sensing of ammonia and humidity. The results of this thesis lay the foundation for the development of low-power multi-gas sensors.

**Keywords:** Gas sensing, Gravimetric Sensor, Electrospraying, Electrospinning, Metal Organic Framework.
DEDICATION

To that eternal being from whom came forth this ancient current of the world, that root of all the branches of knowledge, to that shining truth which turns the mind to the Atman within, to that splendid being we meditate, may it enlighten our minds, AUM…
ACKNOWLEDGEMENTS

At the onset, I would like to convey my heartfelt gratitude to my senior supervisor Dr. Bahreyni. Working under his supervision has undoubtedly been one the greatest opportunities of my life. Without his unceasing advice and effective solutions to the problems that I came across, I would have never been able to accomplish the works of this thesis. Other than helping me in my project, he has spent a tremendous amount of time teaching me some of the most vital means that a researcher and an engineer should be equipped with. In this limited space, I will not be able to list his countless support.

I am deeply grateful to my co-supervisor, Dr. Li for all of his help and support during this project. He has always been available to assist me and his suggestions have been crucial for development of my thesis.

I would like to express my utmost thankfulness to Dr. Parameswaran for being on my committee and reading my thesis as well as all the support that he has shown me throughout the years of my master’s studies.

I am sincerely thankful to Dr. Leung for being the chair of my committee and reading my thesis. Furthermore, I honestly appreciate Dr. Merbouh for his assistance in synthesis of one of the materials, in addition to his invaluable comments for preparation of one of the publications.
I would also like to appreciate the guidance I received from my B.Sc. supervisor, Dr. Bijan Rashidian at Sharif University of Technology.

I am eternally indebted to my best friends, Jessica, Payam and Omid.

Thank you to my friends at IMuTS lab particularly Alborz and Sadegh for their help and collaboration.
# TABLE OF CONTENTS

Approval .................................................................................................................. ii

Abstract ................................................................................................................... iii

Dedication ................................................................................................................ iv

Acknowledgements ................................................................................................. v

Table of Contents ................................................................................................... vii

List of Figures ......................................................................................................... xi

List of Tables .......................................................................................................... xv

List of abbreviations .............................................................................................. xvi

List of symbols ....................................................................................................... xviii

1: Introduction ......................................................................................................... 1

2: Gas-sensing technologies ..................................................................................... 6

2.1 Optical gas sensors ............................................................................................. 8

   2.1.1 Laser diode based gas sensors ................................................................. 11

   2.1.2 Photoacoustic spectroscopy ................................................................... 12

   2.1.3 Quantum cascade lasers ........................................................................ 13

   2.1.4 Cavity ringdown spectroscopy ............................................................... 14

   2.1.5 Ellipsometry ............................................................................................ 15

   2.1.6 Surface Plasmon Resonance ................................................................. 17

2.2 Conductive polymer gas sensors .................................................................... 20
7.2 Synthesis of MOFs ................................................................. 129
7.3 Applications of MOFs .............................................................. 130
  7.3.1 Adsorption and purification of gases ........................................ 131
  7.3.2 Gas separation ..................................................................... 131
  7.3.3 Gas storage ......................................................................... 131
  7.3.4 Catalysis ............................................................................ 132
  7.3.5 Sensing applications ............................................................ 133
7.4 Experiment setup .................................................................... 135
  7.4.1 Thin film fabrication .......................................................... 135
  7.4.2 Gas experiment set-up ......................................................... 139
7.5 Results and discussions ............................................................. 141
  7.5.1 Frequency response measurement and film qualities ............... 141
  7.5.2 Response to VOCs .............................................................. 141
    145
  7.5.3 Minimum detectable range .................................................. 146
8: Conclusions ............................................................................. 148
8.1 Future work ............................................................................ 152
Appendix A: Oscillator circuits ....................................................... 156
8.2 Pierce oscillator: ...................................................................... 159
Bibliography ................................................................................. 161
LIST OF FIGURES

Figure 2-1: Block diagram of ellipsometry set-up.......................................................... 16
Figure 2-2: Schematic of a gas sensor based on SPR. ...................................................... 19
Figure 2-3: Most common conductive polymers in gas sensing technologies .............. 21
Figure 2-4: The equivalent circuit of conductive film based on the works of
           Hwang et al. [58] ................................................................................................. 24
Figure 2-5: Structure of chemiresistors ............................................................................ 31
Figure 2-6: The equivalent circuit of associated with a chemiresistor [70]............... 32
Figure 2-7: Schematics of FET transistors for gas sensing applications ..................... 33
Figure 2-8: Schematic of a diode chemical gas sensor .................................................... 34
Figure 3-1: Structure and packaging of a QCM. ............................................................... 45
Figure 3-2: Simplified equivalent circuit of a QCM. ....................................................... 50
Figure 3-3: Propagation of APM-SH mode in a thin substrate. ................................. 56
Figure 3-4: The symmetric and anti-symmetric Lamb modes in a thin plate. ............. 60
Figure 4-1: Schematic of a typical electrospinning set-up........................................... 68
Figure 4-2: Formation of Taylor cone at electrospinning (bottom)/electrospraying
           (top) processes .................................................................................................. 69
Figure 5-1: Molecular structures of PVA and PAA ......................................................... 77
Figure 5-2: The electrospraying set-up used in this work..........................................................79

Figure 5-3: A crystal electrospun with 15 % m/v PAA for a long time for presentation purposes...............................................................................................................................80

Figure 5-4: Block diagram of the gas experiment set-up..........................................................90

Figure 5-5: Frequency response of electrospun with PAA/PVA ratio of 30 % .....................91

Figure 5-6: SEM images of PAA/PVA film at two magnitudes.............................................91

Figure 5-7: The frequency change as the crystal (PAA/PVA film) is successively exposed to 100ppm concentration of ammonia and nitrogen. .........................93

Figure 5-8: Change in frequency vs. ratio of PAA in a PAA/PVA solution ....................94

Figure 5-9: Frequency change of PAA/PVA film vs. concentrations of ammonia (ppm) ..............................................................................................................................95

Figure 5-10: The response of PAA/PVA film to humidity....................................................96

Figure 5-11: The response of PVA film to 50 % humidity...................................................97

Figure 6-1: General structure of cryptophanes (I) and the structure of CrypA (II)........103

Figure 6-2: Three step method for synthesis of CrypA............................................................104

Figure 6-3: Two step method for synthesis of CrypA .............................................................105

Figure 6-4: Procedure used for synthesis of CrypA in this work, starting with vanillin ((i): BrCH2CH2Br, NaOH/EtOH, (ii): NaBH4, EtOH (iii): HCOOH ) .................................................................................................................................106

Figure 6-5: NMR results for compound (VIII) ......................................................................107

Figure 6-6: NMR results for compound (IX) .......................................................................108

Figure 6-7: NMR results for CrypA (II) ...............................................................................109
Figure 6-8: SEM images of Crystal D at two different magnitudes ........................................... 115

Figure 6-9: SEM images of the film on Crystal E at two different magnitudes ............. 116

Figure 6-10: Frequency response of QCMs coated with three different films. The
curves are shifted by resonant frequency, \( f_0 \) to the right in order to
have the same peak .................................................................................................................. 116

Figure 6-11: Response of Crystal D to 2.5 % methane concentration. ..................... 118

Figure 6-12: Response of Crystal E to 2.5 % methane concentration. ..................... 119

Figure 6-13: Responses of Crystals D and E to different concentrations of
methane .................................................................................................................................. 120

Figure 6-14: Responses of Crystals D and E to different levels of relative
humidity ................................................................................................................................. 121

Figure 7-1: Schematic of vertical electrospraying used for generation of thin MOF
films ....................................................................................................................................... 138

Figure 7-2: Gas-sensing set-up used for VOC measurement ........................................... 140

Figure 7-3: normalized frequency response of the crystals .............................................. 142

Figure 7-4: SEM photos of the electrosprayed MOF crystals on the substrate .......... 143

Figure 7-5: The response of the drop-casted film to saturated IPA vapor .................... 144

Figure 7-6: Response of the electrosprayed film to IPA, acetone and THF .................. 145

Figure 7-7: Response of the electrosprayed film to different concentrations of
VOCS ....................................................................................................................................... 146

Figure 7-8: Response of the electrosprayed film to 50 % humidity level ..................... 147

Figure A-1: series combination of a crystal with a resistor .............................................. 157
Figure A-2: Colpitts oscillator circuit diagram..........................................................158

Figure A-3: Miller oscillator circuit diagram .............................................................158

Figure A-4: Pierce oscillator circuit diagram ...........................................................159

Figure A-5: Schematic of the oscillator used in this project......................................160
LIST OF TABLES

Table 2-1: Summary of the properties of common gas sensors [66].......................... 40

Table 6-1: Summary of the properties of the crystals coated for methane sensing ...... 122
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>ANN</td>
<td>Artificial Neural Network</td>
</tr>
<tr>
<td>APM</td>
<td>Acoustic Plate Mode</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CPs</td>
<td>Conductive Polymers</td>
</tr>
<tr>
<td>DFB</td>
<td>Distributed Feedback</td>
</tr>
<tr>
<td>E-nose</td>
<td>Electronic Nose</td>
</tr>
<tr>
<td>FAW</td>
<td>Fibre Acoustic Wave</td>
</tr>
<tr>
<td>FM</td>
<td>Flowmeter</td>
</tr>
<tr>
<td>FPW</td>
<td>Flexural Plate Waves</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HV</td>
<td>High Voltage</td>
</tr>
<tr>
<td>IGFET</td>
<td>Insulated Gate Field-Effect Transistor</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
</tr>
<tr>
<td>MDC</td>
<td>Minimum Detectable Concentration</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal Organic Framework</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal-Oxide Semiconductor</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal-oxide-semiconductor field-effect transistor</td>
</tr>
</tbody>
</table>
PAA      Poly(acrylic acid)
PAni     Polyaniline
PAPBA    Polyaminophenylboronic Acid
PCB      Printed Circuit Board
PDMS     Polydimethylsiloxane
PPy      Polypyrrole
PTH      Polythiophene
PVA      Poly(vinyl alcohol)
QCL      Quantum Cascade Lasers
QCM      Quartz Crystal Microbalance
SAW      Surface Acoustic Wave
SEM      Scanning Electron Microscope
SH-APM   Shear Horizontal Acoustic Plane Mode
SPR      Surface Plasmon Resonance
TDLAS    Tunable Diode Laser Absorption Spectroscopy
THF      Tetrahydrofuran
TIR      Total Internal Reflection
TLC      Thin Layer Chromatography
TSM      Thickness Shear Mode
UV       Ultraviolet
VNA      Vector Network Analyzer
VOC      Volatile Organic Compound
LIST OF SYMBOLS

\( h_q \) Thickness of the quartz crystal

\( h_s \) Thickness of the thin film

\( I_0 \) Intensity of incident light

\( K_m \) Adsorption equilibrium constant

\( N_i \) Concentration (molecules per unit volume)

\( \frac{P_1 \cos \theta_0}{2} \) Legendre polynomial of order \( \frac{1}{2} \)

\( R_m, L_m, C_m \) Motional resistance, inductance and capacitance

\( S_0, A_0 \) First symmetric and anti-symmetric Lamb modes

\( T_x \) Tensile component of in-plane stress

\( U_k \) Kinetic Energy

\( U_p \) Potential Energy

\( V_0 \) Potential of the equipotential surface

\( k_{ph} \) Photoacoustic spectroscopy cell constant

\( r_p \) Reflected \( p \) component

\( r_s \) Reflected \( s \) component

\( \gamma_n \) Wavenumber for SAW propagation along \( x \)-axis

\( \mu_q \) Shear modulus of quartz
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_q$</td>
<td>Density of quartz</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Mass density of the deposited film</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Ratio of occupied sites in Langmuir equilibrium</td>
</tr>
<tr>
<td>$B$</td>
<td>Bending stiffness of the elastic isotropic plate</td>
</tr>
<tr>
<td>$I$</td>
<td>Intensity of transmitted light</td>
</tr>
<tr>
<td>$N$</td>
<td>Harmonic number</td>
</tr>
<tr>
<td>$Q(P,T)$</td>
<td>Reaction quotient ratio</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$S(\lambda)$</td>
<td>Recorded signal in photoacoustic spectroscopy</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature in Kelvin</td>
</tr>
<tr>
<td>$f, f_0$</td>
<td>Frequency, resonant frequency</td>
</tr>
<tr>
<td>$l$</td>
<td>Optical path length</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons exchanged in the reaction</td>
</tr>
<tr>
<td>$u$</td>
<td>Displacement</td>
</tr>
<tr>
<td>$v$</td>
<td>Wave velocity</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Wave attenuation</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Emf of the reaction</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Reflectance ratio</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Fraction of light absorbed by a single molecule</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Phase shift along the loop in an oscillator circuit</td>
</tr>
</tbody>
</table>
1: INTRODUCTION

Many researchers have directed their arduous efforts towards development of reliable gas sensing devices during the last decades. A great proportion of this surge of interest is aimed to tackle the problems arising from environmental pollutions. The drastic advancement of industrial processes has spawned generation of high levels of toxic materials and pollutants in our habitat. If not controlled properly, these gases can bring about catastrophic effects to safety and well-being of humans as well as to the environment. Consequently, reliable techniques are highly required for detection and sensing of gases depending on the circumstances that they have to operate. Many gas sensors are commercially available so far. Thanks to the advancement of nanotechnology and novel methods of increasing the sensitivity of devices, the research on numerous gas sensors has been rekindled by incorporating these novel methods.

The main objective of this thesis is the development of high quality thin films featuring many desirable characteristics such as high surface area, uniformity, nanoporosity, etc. for applications in gas sensors. We have employed supra-molecular interactions to selectively detect and sense gases such as ammonia, methane, organic vapours (i.e., acetone, tetrahydrofuran, and isopropyl alcohol) and humidity.
In Chapter 2, the significance of developing highly precise gas sensing techniques for different applications is explained and the most well-known existing gas sensing technologies are covered. Based on the interaction of each device with the target analytes, these devices have been categorized into optical sensors, conductivity sensors (e.g. metal oxide semiconductors and conductive polymer devices), electrochemical sensors, and acoustic wave sensors. The mechanisms that are employed in these devices are investigated and their advantages and disadvantages are compared with each other.

Chapter 3 is devoted to understanding the principles of piezoelectric acoustic wave devices exploiting different modes of acoustic waves such as thickness shear modes, surface acoustic waves, acoustic plate, and flexural plate modes. The benefits and downfalls of each method are explained. The emphasis is on quartz crystal microbalances that are employed in this project for gas sensing purposes.

In Chapter 4, electrospinning and electrospraying processes are introduced as effective methods for fabrication of thin films featuring favourable characteristics such as higher surface area and nanoporosity. The mechanism of electrospinning process and its applications to different areas including gas sensors is further investigated.

In Chapter 5, we present our custom-made electrospinning set-up and employ it to fabricate thin films for detection and sensing of ammonia and humidity. Detection of humidity is necessary due to its wide applications for comfort and industrial processes. The employment of automated control systems
has recently become highly popular due to falling costs and improved reliabilities. Therefore, researchers have been particularly interested in development of humidity sensing methods based on changes of one of the electrical parameters of the sensor [1]. Ammonia is a widely used substance in many industrial processes including petrochemical, pulp and paper, fertilizer and the oil industries. Furthermore, the use of ammonia has increased significantly over the last few years as a substitute for compounds, which damage the environment such as Chlorofluorocarbons (CFCs). Additionally, ammonia is considered as a highly hazardous chemical. Other than being chemically dangerous to humans, an ammonia/ammonium nitrate explosion at a fertilizer plant in Toulouse, France, killed 30 and injured more than 2,000 workers and nearby residents in 2001 [2]. Sensing films were fabricated from Poly (acrylic acid) and Poly (vinyl alcohol). The effects of different process parameters on the quality of the resulting films were investigated. We explained how the parameters of the electrospinning process were optimized based on the many experiments that were conducted. The optimized electrospun films were shown to exhibit higher sensitivity with respect to gases and their response was more reproducible. A gas sensor characterization setup was custom-built which allowed control of the gas concentrations and humidity. The response of these sensors to different levels of ammonia and humidity are investigated. Furthermore, the response of the gas sensors with films containing different ratios of the polymers is explored to obtain an optimized value for the composition of the film.
In Chapter 6, five different techniques are demonstrated that we used for fabrication of thin films to detect methane gas selectively by supra-molecular interactions. Methane is the main constituent of natural gas and is ubiquitously used in industry and house residences for heating purposes. When accumulated in a closed area, such as mines, methane causes life-threatening explosions. Therefore, development of efficient methods for detection of methane has attracted lots of attention [3]. Cryptophane A was synthesized and used as the host to trap the methane molecules inside the thin film. The adsorbed mass was detected by measuring the mass loading of the associated quartz crystal resonator. The qualities of the thin film were measured by scanning electron microscope. Their influence on the quality factors of the quartz crystals were compared from their frequency responses. The response of these devices to different concentrations of methane gas was investigated. Amid these preparation methods, two of them (i.e., spin coating of cryptophane A solution inside SU-8 followed by exposure as well as electrospinning of a polymeric solution of the host molecules) were observed to show better sensitivities compared to the previous works in the literature. The effect of humidity on these sensors was investigated as well.

Chapter 7 starts with an introduction on the highly desirable features of metal organic frameworks (MOFs) and their application for sensing of volatile organic compounds (VOCs). Measurement of volatile organic compounds has attracted a lot of attention from the researchers. Humans are constantly at the risk of exposure to these gases in our ambient environment, soil, groundwater
and workplaces [4]. Even though MOFs have been ubiquitously investigated for gas storage and separation, their extraordinary properties such as excessively high surface areas have rarely been exploited for gas sensing applications. We employed HKUST-1 MOF for detection of organic vapours. It is explained that development of a uniform film on the surface of sensors is crucial for successful detection of the analyte gases. An electrospraying set-up is employed to prepare uniform films of MOF on the surface of the crystals. Their response to different concentrations of acetone, tetrahydrofuran, and isopropyl alcohol is finally represented.

The conclusion on the results of this work and possible improvements and future works are given in Chapter 8.

Finally, the oscillator circuits that were used for this work are presented in Appendix A.
2: GAS-SENSING TECHNOLOGIES

Due to the advent of technology and fast growth of industrial processes, we are inevitably exposed to different kinds of gases that might be perceived as an immediate threat to our welfare or they can endanger the well-being of our planet, climate, flora and fauna. Therefore, gas-sensing technology plays a crucial role in detection and measurement of the concentration of gases that are atmospheric pollutant and are hazardous to our health. Furthermore, gas-sensing technologies provide industries with reliable methods to detect and measure gas concentrations consumed or produced in industrial or medical applications. Therefore, gas sensors are an essential constituent of industrial process control or smart maintenance functionalities. Considering the tremendous applicability of gas sensors and growing demands for effective methods of detection, a whole spectrum of gas sensors with varying functionalities in terms of sensitivity, selectivity and operating conditions have been developed to fulfil these numerous needs. Applications of gas sensors include environmental, as well as industrial, medical, scientific and even domestic [5] [4] [6] [7]. The focus of this project is on development of sensitive and selective layers for sensing of methane, volatile organic compounds, ammonia and humidity.

Different performances are required from gas sensors based on the application. They can be exploited as an alarm to merely detect the presence of
a dangerous target gas and take proper actions accordingly, or they might be
used for accurate real-time measurements of the concentration of a gas or even
multiple target gases simultaneously. Consequently, the method of
measurement, size, weight and power consumption of the sensor as well as the
price are determined primarily based on the application.

In general, based on the nature of the interaction of the active part of the device
with the analyte, gas sensors can be categorized in two groups:

1) **A direct parameter of the target gas is monitored:** This type of sensing is
common in some of the optical devices where a characteristic of the gas,
such as the intensity of one of the infra-red absorption bands is measured.

2) **The gas concentration is measured indirectly:** The analytes are
absorbed/adsorbed based on chemical reactions, physical interactions or
both taking place between the active layers and the target molecules.
Subsequently, absorption /adsorption of the target molecules bring about
perturbations of certain properties of the sensor. These changes are different
depending on the type of sensor and the properties of the active layer.
Therefore, the sensor serves a transducer that converts these changes to a
measurable electrical signal. The modifications of the properties of the sensor
take place at several levels:

a. **Adsorption and absorption of target molecules can result in change of
the electrical conductivity of the sensing layer;** therefore, the changes
can be measured by monitoring conductivity. This type of transduction
leads to conductivity sensors such as conductive polymer or metal
oxide based sensors as well as some of the acoustic wave piezoelectric sensors.

b. *The interaction between the target molecules and the sensing layers bring about mass changes commonly referred as mass loading effect.* This effect can be efficiently measured using piezoelectric sensors such as quartz crystal microbalances.

c. *Optical properties of the active layer can be modulated upon exposure to the target molecules,* which can be readily detected by optical transduction mechanisms.

d. *The change in the work functions of the sensing materials* can be employed in MOSFET sensors to detect and measure the concentrations of analyte species.

e. *The change in electromotive force of a reaction or the amount of current required for catalyzed electro-dissociation of a species* is used in electrochemical sensors for measurement of different gases.

The purpose of this chapter is to provide a summary of different gas sensors and their operation mechanisms.

### 2.1 Optical gas sensors

Optical methods have been widely used for detection and quantification of different gases. One of their salient features over other sensors is that they provide contact-free measurements, and hence, reveal higher resilience in harsh
environments, which for example can contain corrosive gases [8]. These sensors can also operate at room temperature and thus are well suited to circumstances where high temperatures can lead to explosions [9]. Furthermore, by employing optical fibres, remote monitoring of an area can be carried out. Additionally, it is possible to incorporate optical sensors for multi-gas sensing applications in cases where gases show different infra-red absorption bands. Unfortunately, optical systems are relatively expensive due to the high degree of precision required for optical sensing. Another drawback of optical sensors can be related to their low level of field robustness needing frequent maintenance to keep them working [10]. Furthermore, these sensors are confined to detection of only certain gases that exhibit strong absorption bands in a desirable wavelength range that the device operates [8].

In some cases, the detection of analytes is based on the adsorption of the target molecules in a thin film, giving rise to modulation of optical properties such as refractive index, optical absorption, reflection, photoluminescence, etc. [9]. Spectroscopic methods and their plentiful varieties, however, are one of the most widespread optical sensing methods [11]. There are numerous other methods employed in optical sensing including ellipsometry, surface plasmon resonance, etc. The spectroscopic method is based on observing the optical absorption, emission, or scattering of target gas at certain wavelengths around the absorption bands of the target molecules. By monitoring the existence of a particular wavelength, the presence of the corresponding molecule can be detected. Furthermore, the intensity of absorption or other measured variables
such as emission and scattering is an indicator of the concentration of the observed species [11]. Therefore, as long as the analyte molecules show strong absorption bands within the sensor wavelength range, spectral techniques can be exploited as reliable, precise and accurate methods of detection and measurement of gases.

The equation governing absorption at a fixed wavelength is described by the Beer-Lambert law [12]:

\[ I = I_0 e^{-\sigma l N_i} \]  \hspace{1cm} (2-1)

where \( I_0 \) and \( I \) are the intensity of the incident light and the transmitted light, respectively; \( \sigma \) is cross section of light absorption by a single particle and \( N_i \) is the density (number per unit volume) of absorbing particles, and \( l \) is the length of optical path.

For detection of small concentrations of the target gas, the minimum detection limit is usually set by the intensity fluctuations of the incident source. However, there are two methods to improve the minimum detectable range limit for gas sensors operating based on absorption measurements [10]. In the first method, the frequency or wavelength of the incident light can be modulated to match a molecular absorption band of the target species. In the second method, the optical path length can be increased by changing the configuration of the set-up (e.g. by employing multipass or intracavity arrangements) [13].

The numerous developments in laser sources technologies, have led to the production of more reliable and precise instruments that can be used in gas
sensing applications with improved sensitivity and performance. With state-of-the-art lasers and other optical devices, it is possible to have highly sensitive and selective sensors for real-time and continuous measurements. Some of the advanced optical technologies that have been put into service for gas sensing applications include multipass absorption spectroscopy (MPAS) [14], cavity ring-down spectroscopy (CRS) [15], tunable diode laser absorption spectroscopy (TDLAS) [16], and photoacoustic spectroscopy (PAS) [17].

2.1.1 Laser diode based gas sensors

The laser diode absorption method, in its simplest form, is based on the comparison of the absorption at a probe wavelength (where absorption by the gas species occurs) and at a reference wavelength (chosen to be free of any absorption by the target gas or any likely contaminant) [10].

Laser diodes have the desirable feature of providing low noise levels compared to other lasers, making them suitable for high sensitivity gas sensing applications. Distributed feedback (DFB) laser diodes function in the spectrum where vibrational overtone bands of many desirable gas species such as CO, CO$_2$, CH$_4$, HCl, HF, H$_2$S, NO, N$_2$O and NH$_3$ occur. The limitations for the use of laser diodes arise primarily from interference fringes and detector noise [18]. It was found that by use of distributed feedback (DFB) laser diode with two-tone frequency modulation spectroscopy, one can improve detection limits of gases (down to ppm levels) [19].
Multipass cells can be used to obtain longer paths for the optical ray without increasing the volume. It also optimizes the position of two consecutive spots on the mirrors [10]. The active part of a multipass unit comprises of two spherical [20] or astigmatic [21] mirrors positioned opposite to each other on an optical axis. Highly sensitive devices for detection of gases can be built by incorporating multipass cells approach and using different sources, namely by using tunable diode-laser spectroscopy (TDLS). For example, sensitivities on the order of ppb have been reached for nitric acid and other smaller molecules [22]. More recently, new approaches of detecting several target molecules with different absorption bands have attracted lots of attention [10], where optical devices can be employed.

2.1.2 Photoacoustic spectroscopy

In photoacoustic spectroscopy the laser beam IR radiated at the gas molecules initially gives rise to generation of heat due to non-radiative relaxation of the excited states of gas species through phonon production [17]. The periodic heating of the target gas causes generation of acoustic waves in the photoacoustic cell which can be detected by a sufficiently sensitive microphone if the incident laser beam is modulated in the audio frequency range. The amplitude of the signal picked up by the microphone is directly proportional to absorbed incident power and thus to gas concentration in the cell [17]:

\[
S(\lambda) = k_{ph} N \sigma(\lambda) I_0
\]  

(2-2)
where $S(\lambda)$ is the recorded signal and $k_{ph}$ is a constant specified by the cell whose value is determined by calibration. Higher sensitivities can be achieved by increasing the incident power, $I_0$. Other improvements can be made by using more efficient cells or by increasing the optical path using multipass cells which can improve the detection sensitivity by up to 10 times [23]. Moreover, it is possible to use an array of microphones to improve the signal-to-noise ratio.

### 2.1.3 Quantum cascade lasers

The development of quantum cascade lasers (QCLs) has offered promising improvements on the behaviour of optical gas sensors. QCLs are semiconductor-based lasers functioning in the mid-to far- infrared range of the electromagnetic spectrum. They were first introduced by Faist et al. [24].

Conventional semiconductor lasers are based on inter-band transitions that radiate electromagnetic waves through electron-hole recombination across the material bandgap. On the other hand, QCLs have their radiation originated in inter-subband transitions in a repeated stack of semiconducting multiple quantum wells in the heterostructures [24]. In the case of conventional semiconductor laser diodes, a single photon is emitted when a high-energy electron in an excited level recombines with a hole in the valence band. The energy of this photon is determined by the difference between the energy levels of the valence and conduction bands. The energy of the photon consequently controls the wavelength that the laser is functioning. QCLs use a periodic series of thin layers of varying material composition (super-lattice) instead of employing a bulk
semiconductor material. This periodic structure introduces a varying electric potential leading consequently to varying probabilities of electron occupying different positions across the length of device. This arrangement is referred as one-dimensional multiple quantum well confinement [25] which results in formation of discrete electronic sub-bands from the splitting of permitted energy bands. Therefore, by careful tailoring of the thicknesses of the periodic structure, inversion of population between to sub-bands can take place, which ultimately leads to laser emission. Interestingly, the position of energy level is predominantly determined by the material thickness and not by the material itself. Therefore, it is possible to tune the emission of QCLs over a wide spectrum of wavelengths for the same material system [25]. Due to flexibility of QCLs, it is possible to detect the vibrational/rotational absorptions of many gases that occur in this region. These absorption bands are at least ten times bigger than their corresponding overtone and combinatory absorption bands in the near infrared region [10]. By combining QCL lasers and photoacoustic spectroscopy, it is possible to reach very low levels of concentrations (about tens of ppb) for many gases [26].

2.1.4 Cavity ringdown spectroscopy

Another remarkably sensitive optical spectroscopic method is cavity ring-down spectroscopy which is based on measurement of the absolute extinction from the analytes that scatter and absorb light. This technique has been employed to detect the presence and concentration of (in the form of mole fraction) target
gases down to low levels on the order of tens of ppm [27] [15]. In this method, a laser is illuminated inside an optical cavity, which is typically composed of two highly reflective mirrors. The absorbing gas species is fed inside the optical cavity and when the laser is in resonance with the cavity mode, due to constructive interference, intensity builds up in the cavity. Subsequently, the laser is turned off and the leaking light intensity from the cavity is measured (extinction measurement). Because of the presence of highly reflective mirrors, during the exponential decaying phase, light travels in a very long extinction path (on the order of a few km) as it is reflected between the mirrors for thousands of times [28]. The decaying time is substantially reduced in the presence of a target gas with an absorption band in that range as it makes fewer bounces before complete extinction. The time constant of this decaying is calculated and directly related to the concentration of the gas species [29].

2.1.5 Ellipsometry

Ellipsometry is an optical technique well known for its use in thin film and surface characterization applications [30]. This method is based on measurement of change of polarization after the beam of light is reflected inside an optical cell containing the sample. The change in the polarization is governed by some of the properties of the sample such as dielectric tensor, refractive index and also by the thickness of the reflector. The high precision of optical ellipsometry can be well attributed to the fact that ellipsometers measure the phase and polarization of the light, and thus, unlike other optical devices are not diffraction-limited [30].
Therefore, resolutions as low as angstrom limit can be measured using ellipsometry in thin film thickness measurements. The sample should be comprised of well-defined layers of homogenous and isotropic material for ellipsometry, otherwise many parameters have to be introduced in the modeling part [31].

A typical set-up for ellipsometry is shown in Figure 2-1. The incident light is emitted by a source and subsequently polarized using a polarizer. The light is then reflected and passed through a rotating polarization detector. The angles of incidence and reflection are equal (specular optics) and the incident and reflected beams span the plane of incidence according to Snell's law [32]. The light that is polarized parallel to the incidence plane is termed as $p$-polarized and accordingly, the one polarized perpendicular to this plane is referred as $s$-polarized light. The amplitudes of reflected $s$ and $p$ components after normalization are represented by $r_s$ and $r_p$, respectively. The complex reflectance ratio $\rho$ is defined as [15]:

![Figure 2-1: Block diagram of ellipsometry set-up.](image)
\[
\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta}
\]  

(2-3)

The right hand side of this equation is another way of showing a complex number in polar format; therefore \(\tan(\Psi)\) represents the amplitude ratio upon reflection and \(\Delta\) the phase shift of the complex reflectance. One of the main features of ellipsometry is that it measures the ratio of two values, and therefore, is not significantly affected by noise fluctuations and usually does not require sample reference beams [31]. Using ellipsometry, detection limit ranges of 10 \(ppm\) can be achieved for acetone vapours [33], and by optimization of properties of the active layer such as thickness and porosity, even lower detection limits can be attained [34].

2.1.6 Surface Plasmon Resonance

Surface plasmon resonance (SPR) is the optical process in which surface plasmons in a metal film are excited by light. This phenomenon takes place when the plane-polarized light hits the metal surface under total internal reflection (TIR) conditions [35]. TIR refers to conditions where the ray of light hits the boundary of the two media at angles (with respect to the vector normal to the surface) higher than a certain value denoted by critical angle [36]. In the case of gas sensors, one of these media contains the target molecules and the other is the active layer of the sensor. If the refractive index of the other side of the boundary is lower, under TIR circumstances, no light passes through the medium and the entire light is reflected. Since surface plasmons, also referred to as surface plasmon polaritons, are electromagnetic waves travelling along the metal/dielectric
interface, this phenomenon is notably sensitive to the changes taking place on
the boundary of the metal surface such as adsorption of the molecules in the
case of gas sensors [37]. Under the appropriate circumstances, the light rays
striking at the metal/dielectric interface give rise to resonance taking place
between the mobile electrons in the conduction and outer shell bands and the
incident waves.

When the thickness of the metal layer is very thin (e.g. in the order of tens of nm)
these waves are also present on the boundary of metal and dielectric material
(i.e., evanescent waves). After the incident light reaches the critical angle, an
evanescent wave penetrates about a quarter of wavelength beyond the reflection
surface through the metal film (Figure 2-2). This penetration effect in turn leads to
a drop at the intensity of reflected lights. Resonance takes place at the moment
that momentum of the incident light is equal to the momentum of the surface
plasmon [38].

It should be mentioned that like any other transformation, both energy and
momentum are conserved in photon-plasmon transformation. The momentum of
plasmons and photons can be associated with a vector whose magnitude and
direction vary according to the angle and wavelength of the incident ray as well
as with the properties of the metal film and the refractive index of the two media.
The best candidate for the metal layer in SPR process is gold [10] as other
metals such as aluminium are more reactive and silver is more susceptible to
undergoing chemical reactions compared to gold.
SPR techniques have recently become a well-noted method for optical detection of gases. Many reports of application of SPR method for sensing applications already exist in the literature [39] [40]. In order to exploit SPR techniques for gas sensing applications and have the desired sensitivity, the metal surface is coated with a functional thin film exhibiting a chemical or physical affinity towards sorption of the target molecules. Of all the different kinds of films incorporated as sensitive layer on metal surface, conductive polymers such as polyimide are of particular interest and have been applied to fabricate selective sensors for hydrocarbons [41], humidity [42], ethanol and methanol [52].

Figure 2-2: Schematic of a gas sensor based on SPR.
2.2 Conductive polymer gas sensors

The origin of employing conductive polymers for gas sensing applications can be traced back to 1980s. Polypyrrole (PPy), polyaniline (PAni), polythiophene (PTh), and their derivatives have been used as the active layers of gas sensors [43].

Some of the favourable properties of conductive polymers (CPs) that have made them especially appealing for sensing applications are high sensitivity, short response time, and possibility of room temperature operation. Conductive polymers can be easily synthesized by chemical or electrochemical means. Additionally their structure can be easily modified through copolymerization and they offer relatively stable mechanical properties. Therefore, conductive polymers have attracted lots of attention for different applications [44].

2.2.1 Molecular structure and properties

The backbone of the conductive polymer molecule comprises of alternative single and double bonds, which generate a highly conjugated \( \pi \) electron system. Some of the most famous CP molecules used for gas sensing applications are represented in Figure 2-3.

It should be noted that the electrical conductivity of pure conductive polymers is not sufficient and doping is necessary in order to fit them to sensing applications. The possibility of doping is the main feature associated with conductive polymers that differentiated them from normal polymers [45].
The process of doping can be done by a reduction-oxidation (redox) reactions or protonation [46]. However, from the well-known CPs, protonation is only possible for PANi for which the lone pairs of electrons on the nitrogen atoms are not part of the highly conjugated electron system and their involvement does not lead to reduced stability of the extended conjugated \( \pi \) electrons of the aromatic ring. Therefore, this lone pair can be engaged as a Lewis base and attract a hydrogen ion (proton).

At the oxidation doping reaction of PPy some electrons are separated from the conjugated \( \pi \) electron system leaving some positive charges on the corresponding atoms. The resulting molecule is a cation radical which is commonly known as a polaron [47]. These polarons are accompanied by their counter ions to maintain the neutrality of charge in the overall system. It should be noted that the doping process is a reversible reaction. The doped conductive polymers have their conductivities in the range of conductors or semiconductors \( (\sigma = 1.05 \Omega^{-1} cm^{-1}) \) [48].

![Polymers](image)

**Figure 2-3: Most common conductive polymers in gas sensing technologies**
2.2.2 Preparation of conductive polymer films

Conductive polymers have been ubiquitously used for sensing applications and many efforts have been carried out to provide high-quality films of these compounds.

Electrochemical deposition is the most widespread method used to prepare films of conductive polymers. The controllability over the thickness of the film is achieved by monitoring the total amount of charge that passes through the electrochemical cell during the process [49].

Another method is dip-coating, where the substrate is plunged into a solution containing the conductive polymer [50]. This process is not very efficient in the sense that it requires a lot of the conductive polymer solution to be prepared. Additionally, there is less control over the thickness of the produced film. The dip-coating process can be refined by used of spin-coating giving rise to more control over the thickness of the deposited film [51].

Instead of synthesizing the polymer and then depositing it on the surface of substrate, the coating process can be alternatively performed by carrying out the polymerization reaction from the monomers on the surface of substrate. This method is referred as Langmuir-Blodgett technique [52].

Polymers can be further heated under vacuum conditions and deposited onto the surface of the desired substrate. This method is known as thermal evaporation and the thickness can be relatively controlled by monitoring the time of evaporation [53]. Other methods such as vapour deposition polymerization
2.2.3 Sensing mechanism

Conductive polymers serve as a medium to allow the transducer to transfer one of the characteristics of the adsorbed gas to a measurable signal. The signal is measured by detecting the change in resistivity, work function, optical absorption, resonant frequency, etc. The interactions between the target gas and sensing material are multi-fold, depending on the type of gas and properties of the operating film of the polymer.

One of the most significant interaction mechanisms that take place between the conductive polymer and the analyte species is the change of conductivity of the film which is primarily caused by modifying the doping levels of the conductive polymer as the interaction happens [56]. This change in doping levels of the conductive polymer is mainly due to a chemical redox or acid/base reaction between the conductive polymer and the target gas. The electron transference in the redox reaction between the analyte and the film gives rise to dramatic alterations of the electronic properties of the polymer such as resistivity and work function. The change in the doping level depends on the type of the doping of the conductive polymer film in addition to the nature of the gas being oxidized or reduced.

When $p$-doped electron-deficient polymers such as PPy, PTh and in some case PANi films are treated with oxidizing gases such as $NO_2$ and $I_2$, their
doping levels are increased as they gain more positive charge by transferring electrons to the reducing gases [57]. Therefore, their conductivity values are elevated accordingly. On the other hand, when the p-type polymer films are exposed to electron-rich reducing gases such as ammonia, an opposite effect takes place leading to reduction of the doping level and thus a sharp fall in the conductivity of the material [57]. The reversibility of these reactions makes conductive polymer materials particularly useful for gas sensing applications.

As illustrated in Figure 2-4, the overall resistance of the conducting film is modelled as the equivalent parallel of \( n \) resistances of value \( R \), each one comprising of the series combination of \( m \) series resistances with value \( r \). The values \( R \), \( r \), and \( n \) signify the resistance of a layer, the resistance of a site and the number of conduction paths between the two electrodes, respectively.

\( r_{i-1,i} \) is the resistivity between layers \( i \) and \( i - 1 \). By defining the ratio of occupied sites as \( \theta \), the resistance of the active site as \( r_1 \) and finally the

![Figure 2-4: The equivalent circuit of conductive film based on the works of Hwang et al. [58]](image-url)
resistance of the vacant site as \( r_0 \), one can obtain:

\[
R = m \theta r_1 + m (1 - \theta) r_0
\]  

(2-5)

Furthermore, the value of \( \theta \) can be obtained from Langmuir adsorption equilibrium as [58]:

\[
\theta = \frac{K_mC_0}{1 + K_mC_0}
\]  

(2-6)

where \( K_m \) is the adsorption equilibrium constant and \( C_0 \) is the concentration of the target gas in the ambient. By noting that \( R_{tot} = R/n \) and combining equations (2-5) and (2-6), leads to:

\[
R_{tot} = \frac{(r_1 - r_0)m}{n} \frac{K_mC_0}{1 + K_mC_0} + \frac{mr_0}{n}
\]  

(2-7)

Other than adsorption, another observation widely encountered for conducting polymers is the phenomenon of swelling when the polymer is in contact with certain vapours which can be detected using atomic force microscopy (AFM) or other techniques [59]. The degree to which swelling occurs depends on many factors including the molecular volume of the polymer, the strength of attraction of the solvent for polymer and the physical state of the polymer [48]. The amount of polymer swelling for many gases is negligible for conductive polymers because under room temperature and normal circumstances most of conductive polymers reside at their glassy state. However, for the case of organic vapours, the swelling of the polymer is as a significant interaction mechanism [60]. In general, polymers under the effects of swelling will have their structures configured in a certain style: the distance
between the polymer chains is increased influencing the transition of electrons on the surface and therefore the conductivity. The swelling of composite polymers is more complicated as each layer can render a different value of swelling resulting in unpredictable changes of the overall conductivity [61].

Another important interaction mechanism between the polymer and target molecules can be attributed to hydrogen bonding as well as dipole-dipole interactions. This effect has been confirmed by infrared spectroscopy of PPy film exposed to acetone [56].

X-ray diffraction tests on conducting polymers after being exposed to organic vapour have revealed the change in crystallinity of the conducting polymer as another alternative interaction mechanism [56]. It was observed that small alcohols such as methanol and ethanol diffuse more rapidly through polymer crystals and give rise to higher changes in the structure compared to larger molecules.

Another way that analytes contribute to changes in conductivity of the conductive polymers is the dissolution of the negative counter ions of the doped polymer when they are exposed to organic analytes [62].

2.2.4 Metal-oxide semiconductor devices

Among different types of gas sensing devices, metal-oxide semiconductor (MOS) based sensors are one of the most widely used devices. These devices operate on the principle of change of the DC conductivity of the MOS layer as it is
exposed to a target gas. The amount of conductivity change can be related to the gas concentration [63].

Based on the type of intrinsic doping, these devices can be categorized into two groups: $n$-type MOS devices are usually formed with metals such as zinc, tin, titanium or iron, and $p$-type devices whose cation part usually comprises of metals such as nickel and cobalt [64]. The type of doping is determined by the characteristics and possible oxidation levels of the metals. For example, in the case of iron, some of the iron(III) ions can be replaced with lower oxidation level ions, namely, iron(II) possessing an extra electron that can render MOS devices an $n$-doped characteristic.

The $n$-type MOS devices are usually exploited in detection of reducing gases, while $p$-type MOS sensors are incorporated for detection of oxidizing gases. The mechanism of operation of $n$-type MOS devices can be paraphrased as follows: oxygen in the air serves as an oxidizing agent with an affinity to attract an electron from the MOS surface. Consequently, the conductivity of the MOS layer drops sharply in the presence of oxygen. Nevertheless, when the MOS device is treated with a reducing gas such as hydrocarbons, hydrogen, or hydrogen sulphide, these gases react with the highly reactive oxygen anion on the surface of MOS layer, leaving behind an electron on the surface of the oxide. Therefore, a sharp increase in the conductivity of MOS is expected depending on the concentration of the target gas. In other words, the metal oxide serves as a catalyst or intermediate in the oxidation reaction of the reducing gas with oxygen. These reactions can be paraphrased as:
\[ O_2 + 2e^- \rightarrow 2O^- (MOS) \]
\[ O^- (MOS) + X \rightarrow XO + e^- \]  \hspace{1cm} (2-8)

where \( X \) represents the reducing gas and \( O^- (MOS) \) means the oxygen anion trapped on the surface of MOS [65].

\( P \)-type sensors, on the other hand, have an affinity for oxidizing gases such as oxygen and chlorine. These gases absorb electrons from the surface of MOS in order to reduce their oxidation states. As a result, more holes are generated that give rise to a higher conductivity proportional to the concentration of the oxidizing gas [66].

Many fabrication methods, including both thin and thick film processes can be used to prepare MOS sensors. Some of the methods used for deposition of MOS films are [66]: screen-printing, spin-coating, RF sputtering, and chemical vapour deposition. The substrates, either in flat or tube format can be made from alumina, glass, silicon, and ceramics. Similar to chemiresistors with conductive polymers, the interdigitated configuration is the most desirable one among many different alternative electrode designs. Subsequently the chosen types of electrodes (\( e.g. \) gold, aluminium, \( etc. \)) are deposited using a similar method. Moreover, since MOS sensors operate in the elevated temperatures of 200°C-500°C, a heating element is incorporated on the back side of the substrate to provide the desirable temperatures. In some special cases, a catalytic species might be added to expedite the reaction and refine the sensitivity of the sensor [65].
The sensitivity of the MOS sensors depends on many factors such as the thickness of the MOS film, temperature of operation, and ambient conditions such as humidity. Thin films usually show better sensitivity compared to thick films [67]. It was shown by Galdikas et al. [68] that by using certain catalytic species, such as addition of copper, one can remarkably increase the sensitivity of $SnO_2$, but over-doping degrades the performance of the device. Among all the parameters that influence the performance of the device, the grain size of oxides is of special significance due to the fact that they serve as scattering centres for the electrons.

One of the attractive features of MOS devices is their short response time and swift recovery of their response whenever the device is no longer exposed to the target species. Response and recovery times both depend highly on temperature [69]. The fabrication processes for MOS devices are readily available and they can be easily incorporated inside standard circuits. However, the high temperature of operation is not desirable as it leads to more power consumption and makes these sensors not easily applicable in the areas that high temperatures could trigger an explosion. Another disadvantage of these devices is their poor selectivity as each one of them is sensitive to a wide range of gases. Sulphur poisoning is yet another downfall of these devices, since sulphur irreversibly binds to the active sites of the oxides and prevent further proper bonding of other gases to the surface and thus degenerates the performance of the sensing device.
2.2.5  Conductive polymer and MOS based devices

Chemiresistors

Chemiresistors are one possible sensing configuration of conductance based sensors, with widespread applications. A chemiresistor can be simply defined as a resistor whose electric resistance is modulated in response to chemical changes in the environment. Some of the most desirable features of chemiresistors include easy and affordable fabrication process and very simple and low-cost electronics for their measurement (e.g., a simple ohmmeter and a differential configuration are sufficient to measure the changes of resistivity for most applications [48]). Moreover, chemiresistors can incorporate thin films, fibres, polymers and bulk materials as sensitive layer to modulate their conductivity profiles. Chemiresistors can operate at different temperature ranges based on the sensing behaviour of their active layers. All these features have made chemiresistors ubiquitous in industrial applications. However, chemiresistors suffer from variations in their sensitivity to many other factors such as temperature fluctuations and humidity. Additionally, the contact resistances to electrodes lead to non-linear change of response of the device to analyte characteristics. Moreover, though simple electronics is economically desirable, it provides insufficient information and hence results in poor selectivity in distinguishing between different gases with varying concentrations.
Chemiresistors, in the simplest form, comprise of a pair of electrodes that are in contact with a layer of conductive material (Figure 2-5.a). In order to improve the sensitivity of chemiresistors, the electrodes are usually fabricated in interdigitated form with a deposited polymeric film (Figure 2-5.b). The equivalent circuit model is illustrated in Figure 2-6 [70]. The total conductivity of the polymer (\( \sigma \)) can be calculated as parallel combination of three conductivities: \( \sigma_h \) as the intramolecular conductivity of the polymer, \( \sigma_c \) as the intermolecular conductivity and \( \sigma_i \) as the ionic conductivity. The intermolecular conductivity (\( \sigma_c \)) is primarily determined by the doping level and is affected when a redox reaction happens on the surface. However, \( \sigma_h \) is mostly determined by the properties of the polymer such as its glassy state and the distance between with the chains. The main parameter affecting \( \sigma_i \) is the mobility of the counter ions as a result of the interactions between the ions and target molecules [70].

![Figure 2-5: structure of chemiresistors](image-url)
Thin film transistors and diode sensors

Thin film transistors (TFTs) are typically composed of two electrodes (drain and source) positioned on two sides of an active semiconducting region and a third electrode (gate) which is separated from the active semiconducting layer by an insulating region. The potential of gate electrode can be used to modulate the current in the drain-source channel when a source drain voltage is applied. Two configurations are used widely to incorporate a conductive sensing layer within the transistor to obtain chemical sensors (Figure 2-7).

The conductive layer can either be used to fabricate the gate of field effect transistors (Figure 2-7.a) or can be exploited as the active layer of the transistors (Figure 2-7.b). The former configuration is usually referred as insulated gate filed-effect transistor (IGFET) for which a capacitor is formed between the conductive sensitive gate layer and the channel [70].

![Figure 2-6: The equivalent circuit of associated with a chemiresistor [70]](image-url)
At this type of arrangement, the sensing layer does not directly affect the drain-source current ($I_{DS}$) and hence the only change in the behaviour of device is caused by the modulation of the work functions. The electric field generated between two chemically different materials connected through an insulator is proportional to the difference of the work functions of the two layers [71]. These changes in work function in turn modify $I_{DS}$ and the value of threshold voltage, $V_t$ of the transistor. This configuration has been widely used for sensing purposes [72].

On the other hand, for the other arrangement shown in Figure 2-7.b, $I_{DS}$ varies with both changes in the work function and also based on the conductivity of the material [48]. As a result, these sensors are recognized to have less sensitivity and show lower robustness of the response.

![Schematics of FET transistors for gas sensing applications](image)

Figure 2-7: Schematics of FET transistors for gas sensing applications
Application of diodes for gas sensing

Another electronic device that has been modified to be used as gas sensor is the diode. When conductive polymers that usually undertake $p$-doping after a redox doping reaction are contacted with a metal or $n$-doped semiconducting region, a hetero-junction diode is formed which in the metal case is one type of Schottky barrier diode (Figure 2-8) [71].

The built-in potential of a pn junction is sensitive to the doping levels of on the two sides of the junction which can be modulated by exposure of the sensitive layer to an analyte that can act as the dopant [73].

Transistors and diodes provide more detailed information and more

![Figure 2-8: Schematic of a diode chemical gas sensor](image-url)
parameters to be measured compared with chemiresistors [48]. Additionally, transistor-based sensors provide better detection limits as a result of the amplification of the signal by the transistor. One of the most favourable features of these devices is that they can be more easily incorporated in CMOS microfabrication processes.

### 2.3 Electrochemical gas sensors

The central key to the operation of electrochemical sensors is based on solid electrolytes. Due to the low value of conductivity of solid electrolytes at room temperatures, electrochemical sensors are usually operating at elevated temperatures. This makes their applications especially appealing for high temperature demanding areas such as determination of exhaust gases [74]. Electrochemical gas sensors are compact, robust and cost effective for large scale production [75]. However, their applications to combustible gases such as methane are complicated by their high temperatures of operation.

One of the electrochemical sensors types is referred as potentiometric sensing where the electromotive force (emf) of a reaction is exploited to determine the concentration of a target species. Another common configuration that electrochemical sensors are applied is amperometric sensing where current is the measured quantity.
2.3.1 Potentiometric sensing

The potentiometric sensor is usually comprised of a Galvanic cell with two electrodes usually referred as reference and working electrodes. The change of the electrochemical potential at the oxidation and reduction half reactions at anode and cathode of this Galvanic cell leads to a net electromotive force (emf). The produced emf is dependent on the concentrations of species participating in the half reactions based on Nernst equation [12]:

\[
\xi = \xi_0 - \frac{2.303 \times RT}{nF} \log(Q(P,T))
\]

where \( \xi \) is the emf, \( \xi_0 \) is the standard emf, \( T \) is the temperature, \( R \) is the universal gas constant, \( F \) is the Faraday's constant, \( n \) is the number of electrons exchanges in the electrochemical reaction and \( Q(P,T) \) is the value of the reaction quotient (equal to pressure of the gas in the case of gas sensing).

The main requirement for reference electrode is that its potential should be independent of the target gas. Therefore, its potential is usually controlled with respect to a reference gas at a fixed concentration. The reference gas is usually incorporated inside a chamber containing the reference electrode and the other electrode is in contact with the target gas [76]. Another important requirement for maintaining a constant potential at the reference electrode is to prevent its reaction with any other gases. Therefore, sealing is a critical issue regarding electrochemical potentiometric sensors. However, because of the different
temperature expansion coefficients of the sealant and solid material, and different operating temperatures, sealing may lead to some complications [77].

One of the most ubiquitous potentiometric sensors are Lambda sensors used for controlling the air fuel mixture in the engines [78]. The sensor has a thimble shape and comprises of doped zirconium oxide. Air is served as the reference gas to the reference electrode of this sensor positioned on the interior part of the thimble while the exterior part is in contact with the gas in the engine. Oxygen gas in the air or the engine is reduced by reacting with the extra electrons on the doped zirconium oxide.

### 2.3.2 Amperometric sensors

Amperometric detection of gases is based on an electrolytic cell in contrast to the galvanic cell employed in potentiometric analysis. One of the main applications of amperometric cells is at measurement of oxygen concentration in lean-burn engines [79]. When an external voltage is applied to the electrolytic cell, oxygen is reduced at the cathode of these cells and the hydroxide anion is oxidized at the anode. Therefore, the whole reaction can be paraphrased as reduction of oxygen and its transportation to anode where it gets re-oxidized. The current between the anode and cathode is related to geometrical parameters of the cell as well as the concentration of the gas (oxygen in this case) and the rate of diffusion inside the electrolyte. By combining Faraday's law and Fick's first law of diffusion, the current $I$, is measured as [80]:

$$I = nFADC_lD_{O_2}$$

where $n$ is the number of electrons, $F$ is the Faraday constant, $A$ is the area of the electrode, $D_{O_2}$ is the diffusion coefficient of oxygen, and $C_l$ is the concentration of oxygen at the electrode.
where $A$ and $L$ are respectively the area and length that diffusion takes place, $\chi$ is the mole fraction of the target gas, and $D$ is the diffusion constant. At lower concentrations, the logarithmic term equals to 1 and $I$ can be linearly related to the gas concentration.

Compared to the potentiometric sensors, amperometric devices do not require a reference electrode, which significantly simplifies their packaging and application. Moreover, these devices exhibit linear dependence on the analyte gas concentrations and small temperature sensitivity [81].

One of the main issues regarding amperometric detection of gases is the need of application of a solid electrolyte capable of transporting the anions of the analyte gas. Since the numbers of solid electrolytes that feature such transportations are limited, the numbers of gases determined by this method are restricted [81]. However, this downfall can be circumvented by using an indirect amperometric mechanism. In this technique, a sufficiently high voltage is applied to the cathode of the amperometric cell to electro-dissociate the gas to the anion that the solid electrolyte can transfer. For instance, at 800°C and 1.2 $V$, water molecule can be reduced at the cathode producing hydrogen gas and hydroxide anions which can be transported through the sensor [82]. The other benefit of using the method is that, each gas is reduced at a certain potential, which can be used to identify the gas. Therefore, this method opens the possibility of multi-gas detection using the same structure by simply varying the voltage [81].
2.4 Acoustic wave sensors

Piezoelectric acoustic wave devices are another very common family of gas sensors. Adsorption of target particles on the surface of these sensors leads to perturbations in piezoelectric acoustic wave that can be measured. Acoustic wave devices possess many desirable features that they offer. Acoustic wave devices are small, inexpensive, and can be designed to respond to many gases. Their properties are going to be studied in more detail in Chapter 3. Table 2-1 provides the summary of the properties of commons gas sensors.

2.5 Signal processing methods for multi-gas sensors

For multi-gas sensing applications, an array of sensors is typically used to provide information about the presence and concentration of several gas species. However, in many cases, each gas sensor exhibits a signature response to a variety of gases. For this reason, pattern recognition methods are utilized to produce a relationship between the output signal of multiple sensors and the concentration/presence of the analyte gases. In order to do so, the pattern of interest is at first separated from the background noise and subsequently normalized (signal conditioning and feature extraction). In the next step, referred as feature reduction, informative features are extracted to improve the accuracy of the measurement system. Finally, the classification process distinguishes the unknown gas from a range of possibilities [83].
### Table 2-1: Summary of the properties of the common gas sensors [65]

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Typical Measuring Range</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Typical Target Gases</th>
<th>Min. &amp; Max. ppm Range</th>
<th>Response Time</th>
<th>Recovery Time</th>
<th>Sensing Mechanism</th>
<th>Power</th>
<th>Complex Packaging</th>
<th>Optimal Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100-1000 ppm</td>
<td>10 s ppm-50 ppm</td>
<td>2 s ppm</td>
<td>Sound waves</td>
<td>Low</td>
<td>Easy</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>Electrochemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Iodine and Carbon Dioxide</td>
<td>Low</td>
<td>Complex Packaging</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>Optical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Spectrum</td>
<td>High</td>
<td>High Temperature</td>
<td>Expensive</td>
</tr>
<tr>
<td>MOS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conductance</td>
<td>Expensive</td>
<td>Room-temperature</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conductance</td>
<td>Expensive</td>
<td>Room-temperature</td>
<td>Inexpensive</td>
</tr>
</tbody>
</table>
2.5.1 Signal conditioning

In this step, the raw data is converted into a characteristics feature vector. For example, in the case of sensors operating based on changes of frequency, each gas is successively led inside the chamber and the frequency changes data versus time are recorded. The experiment is repeated for several concentrations of the target gases. At this stage, the data are usually collected based on a normalization method (e.g. vector normalization or vector auto-scaling) in order to reduce the distortion of the pattern induced by concentration changes [84]. The most convenient methods employ the steady state portion of the sensor response to extract the data while discarding the transient response [85].

In order to avoid the difficulties of dealing with high dimensionality and redundancy, the initial vectors are transformed into low dimensional spaces. For the cases that the number of training sets (individual experiments done on single sensors) is very large, the value of error in classification is negligibly increased by increasing the number of species (features). However, for the case of low number of training sets compared to the number of features, a low dimensional transformation should be performed in order to provide a reasonable range of accuracy [83]. The aim of mapping methods is to reduce the dimensionality of the vectors while preserving as much information in the initial set as possible.

The most common extraction methods used for multi-gas sensing applications are principle component analysis (PCA) and linear discriminant analysis (LDA). Other methods such as Independent Component Analysis (ICA)
[90] and blind source separation (BSS) or neuroscale [86] have also been employed in electronic noses.

*Principle component analysis*: this method is based on preservation of the variance of the feature vector data as much as possible. Therefore, the transformation matrix is chosen in a way to minimize the mean squared distance between the original data and the reduced data [87].

*Linear discriminant analysis (LDA)*: this method considers the scattering of the data within each class [88] and also the scattering between different classes. The projection method incorporated in LDA, maximizes the intra scattering of classes in the data [61].
3: ACOUSTIC WAVE DEVICES

The origin of using acoustic devices for sensing applications can be traced back to the work of Sauerbrey [89] in 1959 as a method for correlating changes in the oscillation frequency of a piezoelectric crystal with the amount of deposited mass on its surface. Simultaneously, he proposed a method for measuring the frequency changes by incorporating the crystal within the loop of an oscillator circuit. This method was later used by King [90] to sense organic vapours. The principle of mass loading has been extended to surface acoustic wave (SAW) devices [91] and later to other configurations of acoustic devices. It was pointed out that if the acoustic device is coated with a layer that is sensitive to a certain gas, the sensitivity and selectivity of the sensor increases significantly. Moreover, if the layer is sufficiently selective, the sensor can be used to determine the composition and concentration of the target species in a gas mixture.

The reason for the upsurge of interest in the use of acoustic wave devices for gas sensing applications in the recent decades can be associated with many desirable features that they offer. Acoustic wave devices are small, inexpensive, and can be designed to respond to many gases. They are particularly useful for detection of low concentrations of gases [92]. Acoustic wave devices can be employed in one or two port configurations. In the former, a single port serves as both input and output. The input signal excites an acoustic mode resulting in
changes in impedance or other characteristics. This change is simultaneously measured from the same port. On the other hand, for two port devices, the two ports are interchangeable and can be used as either input or output. The input signal generates an acoustic wave that propagates through the device and generates a signal on the receiving transducer where it is finally detected.

With this introduction, the most common acoustic wave devices, their advantages, disadvantage, and their applicability as sensors are studied in this chapter.

3.1 Families of acoustic wave sensors

3.1.1 Thickness shear mode Devices

Thickness shear mode (TSM) acoustic wave devices are usually fabricated from thin disks of AT-cut quartz with circular electrodes patterned on their both sides (Figure 3-1). The name commonly used to refer to such TSM sensors is quartz crystal microbalance (QCM). QCMs work in the frequency range of 5-10 MHz and have very high quality factors [93]. Therefore, oscillator circuits employing QCMs as their frequency determining block have high stability and can be easily used to measure a few Hz of frequency change in a base frequency on the order of MHz. TSM devices with resonant frequencies as high as 1.6 GHz have been fabricated using ZnO as the piezoelectric material [94]. Some of the other promising features of TSM devices are their low cost and the relatively low cost of measurement instruments. Since most QCMs operate frequencies of 1-
20MHz, the complications arising from high frequency electronics (a few hundred MHz) can be evaded. Moreover, due to properties of the AT-cut quartz, QCMs are not too sensitive to temperature fluctuations. Additionally, since these devices are associated with shear modes, normal components of displacement do not exist, making them suitable for liquid applications. However, many complications arise in the liquid and many damping mechanisms have to be taken into account [95].

Due to Piezoelectric effect and orientation of the crystal, application of a voltage results in shear deformation in this device. The value of maximum displacement occurs on the surface of the crystals. Therefore, TSM devices are extremely sensitive to surface perturbations [93]. When an alternating voltage is applied on the electrodes, bulk waves of opposing polarities are generated. By considering the coordination system defined in Figure 3-1, the value of displacement wave along $x$-direction, $(u_x)$ can be written as [96]:

\[
\text{Figure 3-1: Structure and packaging of a QCM.}
\]
\[ u_x(z, t) = (A e^{jkz} + B e^{-jkz})e^{i\omega t} \]  \hspace{1cm} (3-1)

where \( A \) and \( B \) are constants, \( \omega \) is the angular frequency, \( k \) is the wavenumber determined by: \( k = \frac{2\pi}{\lambda} = \frac{\omega}{v_s} \) and \( v_s \) is the shear wave velocity: \( v_s = \sqrt{\mu_q / \rho_q} \) where \( \rho_q \) is the mass density of the substrate (2.648 \( \frac{g}{cm^3} \) for quartz) and \( \mu_q \) is the shear modulus of quartz (for AT-cut crystal \( \mu_q \) is \( 2.947 \times 10^{11} \frac{g}{cm^2 s^2} \)).

The boundary conditions on the external surfaces can be obtained by considering that no external force acts on them, therefore these surfaces are stress free. Considering that the maximum displacement occurs on the surfaces, we have \( \frac{\partial u_x}{\partial z} = 0 \), giving rise to:

\[ u_x(z, t) = u_{x0} \cos(kz)e^{i\omega t} \]  \hspace{1cm} (3-2)

where \( u_{x0} \) is the maximum displacement at the surface. For constructive interference of the waves, the thickness of the device, \( h_q \) should be an integer multiple of half the wavelength of the acoustic wave \( (\lambda = N \left( \frac{h_q}{2} \right) ) \). A more rigorous mathematical analysis shows that only odd harmonics can be excited \( N = 1, 3, 5, ... \) [97].

### 3.1.1.1 Mass sensitivity of QCMs

The mass sensitivity of QCMs can be evaluated using Rayleigh’s method [96]. This method is based on the principle that resonance takes place at the frequency for which the maximum of potential energy \( (U_p) \) is equal to the maximum of kinetic energy \( (U_k) \). This simple principle provides invaluable insight
on the operation of the acoustic wave devices. When a mass is accumulated on
the surface of QCM, the kinetic energy is increased while potential energy
remains essentially the same. Therefore, Rayleigh’s hypothesis predicts that the
frequency of oscillation should be modified to rebalance the kinetic and potential
energies. It should be noted that the maximum kinetic energy happens at
maximum velocity. By assuming a negligible thickness for the film on quartz
surface and therefore uniform displacement on the film we have:

$$U_k = U_{kq} + U_{ks}$$  \hspace{1cm} (3-3)

where $U_{kq}$ and $U_{ks}$ are the kinetic energies of the quartz and film, respectively.

By differentiating equation (3-2), we have:

$$\dot{u}_x(z,t) = u_{x0} j \omega \cos(kz)e^{j\omega t}$$ \hspace{1cm} (3-4)

Assuming that the velocity along the film thickness is constant and equal
to the velocity of crystal surface results in:

$$U_k = \frac{\omega^2}{2} \left( \rho_s \ u_{x0}^2 + \rho_q \int_0^{h_q} |u_x(z)|^2 \, dz \right)$$ \hspace{1cm} (3-5)

where $\rho_s$ is the areal mass density of the film. Therefore:

$$U_k = \frac{\omega^2}{2} u_{x0}^2 \left( \rho_s + \frac{\rho_q}{2} h_q \right)$$ \hspace{1cm} (3-6)

The potential energy is found from the equation of potential energy for a
spring $U_p = \frac{1}{2} k_s x^2$ where $k_s$ in here is the stiffness ($\mu_q$):

$$U_p = \frac{\mu_q k^2 u_{x0}^2}{2} \int_0^{h_q} \sin(kz)^2 \, dz = \frac{\mu_q k^2 h_q u_{x0}^2}{4}$$ \hspace{1cm} (3-7)
Equating (3-6) and (3-6) and noting that \( \omega_0 = k \nu_s = \left( \frac{N \pi}{h_q} \right) \left( \sqrt{\frac{\mu_q}{\rho_q}} \right) \), results in:

\[
\left( \frac{\omega}{\omega_0} \right)^2 = 1 + \frac{2 \rho_s}{h_q \rho_q}
\]  
(3-8)

Differentiation of both sides and the assumption that \( \rho_s \ll \rho_q h_q \) (i.e. the deposited mass is negligible compared with the mass of the crystal) and substitution of \( h_q \) by \( \lambda/2 \) leads to Sauerbrey’s equation:

\[
\frac{\Delta f}{f_0} = -\frac{\rho_s}{h_q \rho_q} = -\frac{2f_0 \rho_s}{\sqrt{\mu_q \rho_q}}
\]  
(3-9)

Sensitivity can be calculated from (3-8) or (3-9) as:

\[
S = \frac{df}{d\rho_s} = -\frac{f_0}{\rho_q h_q}
\]  
(3-10)

Therefore, sensitivity is proportional to frequency and inversely proportional to the thickness of the deposited film.

Since Sauerbrey equation is the basis of mass loading effect on QCMs and the experimental results of this project mainly focus on QCMs, it is beneficial to shed more light on its nature by deriving the Sauerbrey equation in a more direct way to have more insight on the performance of QCMs [98]. Notice that \( f = \nu/\lambda \) where \( \nu \) is the velocity of the wave and \( \lambda \) the wavelength whose value is equal to half the length of the quartz resonator for the first excited TSM mode. Therefore, \( f_0 = 2 \frac{\nu_s}{h_q} \). The value of velocity \( \nu_s \) is considered constant and thus it is possible to say that: \( f_0 \propto \frac{1}{l} \) where \( l \) is the length of the quartz
resonator (initially equal to \( h_q \)). Consequently by differentiation of both sides, we have: \( \frac{\Delta f}{f_0} = -\frac{\Delta l}{l_0} \) and the value of length change can be formulated as: \( \Delta l = \frac{\Delta V}{\Delta A} \), where \( V \) and \( A \) are the volume and area of the resonator. If the mass and thickness of the deposited layer are negligible with respect to that of quartz substrate, and considering that the surface area is constant, we have: \( \Delta l = \frac{\Delta m/A}{\rho_q} = \frac{\rho_s}{\rho_q} \). Now, by substitution of \( l = h_q = v_s/f_0 \) in these equations Sauerbrey’s equation can be derived.

### 3.1.1.2 Electrical models for QCMs

Because of the piezoelectric nature of quartz in QCMs, the electric field generated by the AC input signal leads to propagation of an acoustic wave in the device. This acoustic wave leads to mechanical displacement and the resonant frequency of oscillation is changed in the presence of an analyte. The electrical behaviour of QCM circuits can be described using transmission line equivalent circuit. In the transmission line model [99], QCM is modeled as a device with two acoustic and one electrical ports. The stress and velocity are coupled via a transformer to the electrical port. The properties of the resonator are represented by mechanical impedance. For the unperturbed device, stress is zero on two ports and they can be shorted, giving rise to a more simplified lumped-element circuit, known as Butterworth-Van Dyke model [100].
In this model, a capacitance $C_s$ represents the feedthrough between the input and output. The motional impedance arising from electromechanical coupling is represented by an RLC circuit (with resistance $R_m$, capacitance $C_m$, and inductance $L_m$). The bonding pads and signal routes give rise to two often similar capacitors ($C_p$) in the circuit (Figure 3-2). These parameters can be formulated as [96]:

$$C_s = \frac{\varepsilon_{22} A}{h_s}$$

$$C_m = \frac{8K^2 C_s}{(N \pi)^2}$$

$$L_m = \frac{1}{\omega_s^2 C_m}$$

$$R_m = \frac{\eta_q}{\mu_q C_m}$$

(3-11)

where $A$ is the active piezoelectric area of the resonator, $\omega_s$ is the series resonant frequency, $K^2$ is the electromechanical coupling coefficient, $\varepsilon_{22}$ is the dielectric

Figure 3-2: Simplified equivalent circuit of a QCM.
permittivity of quartz and $\eta_q$ is the effective viscosity in the crystal.

The value of the series resonant frequency ($\omega_s$) is found by solving for the frequency for which the imaginary part of the motional impedance becomes equal to zero:

$$j\omega_s L_m + \frac{1}{j\omega_s C_m} = 0$$

resulting in $\omega_s = \frac{1}{\sqrt{L_mC_m}}$. At $f_s = \frac{\omega_s}{2\pi}$, the inductive and capacitive parts of motional impedance have the same magnitude. At frequencies higher than this series resonance, the inductive term on the left hand side of equation (3-12) takes over. Consequently, at frequencies higher than $f_s$ the inductive type motional branch can couple with $C_s$ to bring about another resonance called parallel resonance, $f_p$. This frequency is obtained from:

$$\omega_p = \frac{1}{\sqrt{(L_mC_{eq})}}$$

where, $C_{eq}$ is the parallel combination of $C_m$ and $C_s$ (i.e., $C_{eq} = (C_m^{-1} + C_s^{-1})^{-1}$).

### 3.1.2 Surface acoustic wave devices

The stress free boundary condition on the surface of crystals brings about a unique acoustic wave which is confined very near to the surface of the substrate [95]. This wave is termed as a surface acoustic wave (SAW) and was first discovered by Lord Rayleigh. These waves are of particular interest in seismological studies due to the fact that the some of the waves activated during
earthquakes belong to the SAW family, but with much greater amplitude [96]. Since SAWs are almost exclusively confined to the surface, they are very sensitive to surface perturbations and can be incorporated in the design of gas sensors [101]. The sensitivity of SAW devices increases with frequency, and therefore, they are used in high frequency circuits, which leads to moderate complexities in the electric circuits required for their operation [96]. SAW sensors can be easily employed in differential mode in order to reduce their dependence on temperature and noise fluctuations. Because of the possibility of fabrication of several SAW devices on the same piezoelectric wafer, they are perfect candidates for multi-gas sensing applications [95]. Compared with QCMs, SAW devices have lower quality factors and are more susceptible to temperature variations [101].

A general SAW propagating along $x$-axis, in a solid with depth across the $z$-axis, has the displacement profile given by [96]:

$$u(x, y, z, t) = (u_x(z) e^{j\phi_1} \hat{i} + u_y(z) e^{j\phi_2} \hat{j} + u_z(z) e^{j\phi_3} \hat{k}) e^{j\omega t} e^{-\gamma x}$$ (3-14)

where $\gamma$ is the complex propagation factor, $u_x$, $u_y$ and $u_z$ are the displacement components, $\hat{i}$, $\hat{j}$ and $\hat{k}$ are the unit orthogonal vectors along $x$, $y$ and $z$ axes, respectively. $\phi_i$'s are the phases of components with respect to $u_x$. Regarding equation (3-14) a few important features of SAWs can be pointed out:

I. The term $e^{-\gamma x}$ indicates that the wave is propagating along the $x$-axis.
II. Each one of $u_i(z)$ functions, approximately have the exponential form of $e^{-\frac{2\pi z}{\lambda}}$, where $\lambda$ is the SAW wavelength [102]. This shows that the wave decays rapidly along the thickness, and therefore, it is reasonable to assume that the energy of SAWs is confined within one wavelength below the surface. Furthermore, this exponential relation implies that at higher frequencies (shorter wavelengths), the acoustic energy is confined more effectively along the surface, giving rise to an improved sensitivity with respect to surface perturbations.

III. For isotropic materials, or for excitations along an axis of symmetry of the crystal, the transverse component $u_y(z)$ vanishes and the particle on the surface travels in an elliptical orbit [103].

Because of the presence of the displacement component normal to the surface ($u_x(z)$), the SAW device functions poorly for applications that require sensing in liquid media [96]. The normal displacement component leads to extra power dissipation when in contact with liquid. The compressional waves introduced in the liquid by SAW leads to excessive attenuation in the device. However, it should be noted that SAW devices, still operate more efficiently in liquids than bulk acoustic wave resonators with the primary mechanism for propagation of the wave is confined to normal component displacement along the thickness of the substrate.

SAW devices can be excited and detected by patterning interdigitated transducers (IDTs) on the surface of piezoelectric materials [104]. Application of a voltage between alternately connected electrodes leads to formation of a
periodic electric field. Furthermore, when an alternating current (AC) voltage is applied, a periodic strain field is generated that results in formation of standing surface acoustic waves. When the wave potential is incident on receiving transducers, a current is induced inside that transducer. Subsequently, the currents on receiving transducers are summed up to produce an external current flow in the detection circuit. For maximum efficiency, the wavelength, $\lambda$ must match periodicity of the electrodes, $d$. In other words, the periodicity of the electrodes should be $d = \nu_0/f_0$, where $\nu_0$ is the velocity of propagation of the SAW and $f_0$ is the frequency of activation of the device [101].

3.1.2.1 Perturbation mechanisms of SAW devices

The sensing applications of SAW devices are usually based on perturbations in wave propagation characteristics, especially the wave velocity and attenuation [102]. Due to the fact that propagation of SAW in piezoelectric medium generates both an electrical potential and mechanical deformation, two types of couplings can happen between the SAW and the active film. The electrical coupling between the wave and charge carriers in the over-laid film leads to acoustoelectric affect, while the mechanical coupling results in mass loading, elastic, and viscoelastic deformations in the film.

3.1.2.2 Mass loading of SAW resonators

When changes of the mass density occur on the surface (i.e. by adsorption of a gas), the surface waves carries these particles with itself on the surface.
Therefore, the mass related to the mechanical deformation wave is increased while the potential energy remains essentially the same. By considering conservation of energy and neglecting damping mechanisms (if the film is thin enough), the increase in mass leads to a decrease in the wave velocity in order to maintain a constant kinetic energy. The mass-loading mechanism only affects the wave velocity and has no effect on attenuation of the wave [105]. It can be shown that [92]:

\[ \frac{\Delta v}{v_0} = -c_m f_0 \Delta m_s \]  \hspace{1cm} (3-15)

where \( \Delta m_s \) is the mass change on the surface, \( c_m \) is the mass sensitivity coefficient and \( f_0 \) is the operating frequency of the device.

### 3.1.2.3 Acoustoelectric effect

When a SAW is travelling on the surface of a piezoelectric material, it produces a mechanical wave that is accompanied simultaneously by a layer of bound charges on the surface [106]. In presence of an overlaid conductive film, the mobile charge carriers of the film are redistributed in order to compensate for the bound charge layer arising from propagation of SAW in the medium. Compared to mass loading effect, the mechanism gives rise to a peak in acoustic attenuation (\( \alpha \)) and a decrease in wave velocity (\( v_0 \)) as follows [106]:

\[ \frac{\Delta v}{v_0} = -\frac{K^2}{2} \frac{\sigma_s^2}{\sigma_s^2 + (v_0 c_s)^2} \]  \hspace{1cm} (3-16)
\[
\frac{\Delta \alpha}{\alpha} = -\frac{K^2}{2} \frac{\nu_0 c_s \sigma_s}{\sigma_s^2 + (\nu_0 c_s)^2}
\]

where \( K^2 \) is the electromechanical coupling coefficient; \( \sigma_s \) is the sheet conductivity of the film; \( \nu_0 \) is acoustic wave phase velocity and \( c_s \) is the sum of air and substrate dielectric permittivities.

### 3.1.3 Acoustic plate mode devices

Acoustic plate mode (APM) devices utilize shear horizontal acoustic plane mode propagation.
(SH-APM). In this mode, whenever a wave propagating along the x-axis, the particle displacement takes place along the y-axis (z-axis is in the direction of the thickness of the resonator) [107] (Figure 3-3). In contrast to SAW and BAW devices, the lack of normal components permits the SH-APM wave to propagate in contact with liquid without severely attenuating the wave. For this device single-crystalline quartz plate acts as a waveguide and acoustic energy is confined between the upper and lower surface of the plate. Therefore it can be concluded that the sensitivity of SH-APM devices is inversely proportional to the thickness of the plate; i.e., the acoustic energy will be more dissipated in the substrate when the thickness is increased [108]. Additionally, the two surfaces of the resonator can be exploited for sensor application as the wave propagates on both of them. APM devices are of particular importance for liquid applications due to excitation of shear horizontal modes and absence of normal displacement components.

The particle displacement of the \( n^{th} \) order horizontal shear plate mode propagating in x direction can be represented by the equation [107]:

\[
  u_y(x) = u_{x0} \cos \left( \frac{n \pi z}{h_q} \right) e^{j\omega t - \gamma_n x} \tag{3-17}
\]

here, \( u_{x0} \) is the particle displacement on the surface and \( \gamma_n \) is the value of wavenumber for propagation along the x-axis. The sinusoidal term in this equation affirms that maximum transverse displacement occurs on the surfaces of the resonator. In contrast to TSM devices (such as QCM), the electrodes are placed only on one of the faces of SH-APM devices [96].
The non-symmetry property of APM waves allows the wavelengths to undertake any values equal to an integer multiple of half the thickness of the device (unlike TSM devices that only permit odd harmonics) [107]. Similar to SAW devices, IDTs can excite APM-SH devices most effectively when the periodicity of the transducers \(d\), matches the wavelength, \(\lambda\) of propagation of the APM wave along the length of the device giving rise to the frequencies:

\[ f_n = \frac{v_n}{d} \]

where \(v_n\) is the phase velocity of the \(n^{th}\) order horizontal shear plate mode [109].

### 3.1.3.1 Mass sensitivity of the APM devices

Similar to SAW devices, masses bound to the surface of APM devices propagate in tune with the acoustic wave, giving rise to a decrease in the propagation velocity of the wave. It is shown that [105]:

\[
\frac{\Delta v}{v_0} = -c_m \rho_s
\]

(3-18)

where \(c_m\) is the mass sensitivity and \(\rho_s\) is the surface mass density of the film. Another prominent difference between SAW and APM-SH devices can be perceived from comparison of equations (3-18) and (3-15). It turns out that unlike Rayleigh mode devices for which the sensitivity is directly proportional to frequency, the sensitivity of APM-SH mode devices is independent of frequency. The reason for this behaviour can be attributed to the fact that for surface acoustic waves, the energy becomes more trapped on the surface of resonator by increasing the frequency. Consequently, this results in less attenuation and
better sensitivity. However, for the case of TSM and SH-APM resonator, the energy density of each propagating mode is not dependent on the frequency but only on plate thickness [96].

3.1.4 Flexural plate wave devices

Flexural plate waves (FPW) can be excited in a thin membrane. One of the most salient features of FPW devices is that if they operate at sufficiently low frequencies, the phase velocity of the wave would be smaller in the device than inside the liquid [110]. Therefore, the acoustic wave energy is trapped inside the membrane and does not dissipate to the surroundings. This feature makes FPW devices especially useful for liquid sensing applications. Moreover, because of performance of these devices at lower frequencies, the difficulties arising from the high frequency electronics can be avoided. Another interesting feature of these devices is that the electrodes can be positioned on the back of the device and therefore avoid the corrosive analytes in chemical sensing applications. Due to the fact that the plates are very thin (a few μm), mass loading of the absorbed species contributes to a great mass change and subsequently the value of the phase velocity is reduced to a higher level accordingly [111]. Furthermore, for the same amount of power, the magnitudes of displacement of flexural plane waves are relatively higher with respect to other acoustic waves. Consequently, due to their large-amplitude motion, other than sensing applications, FPW devices can be employed to for pumping and mixing of liquids [110].
By writing the constitutive equations that relate stress to strain (Hooke’s law) and successively using Newton’s second law to relate the acceleration of the medium and the spatial variation of the force, one can finally solve the displacement functions that satisfy these conditions and obtain the characteristics of the FPW devices. The solution for the simple case of an isotropic plate exists in the form of an infinite set of waves known as Lamb waves [24]. These modes are normally divided into two groups: symmetric waves, represented as $S_0, S_1, \ldots$, with their particle displacement symmetric with respect to the neutral axis of the plate; and anti-symmetric waves denoted by $A_0, A_1, \ldots$ whose displacement components are asymmetric (odd) with respect to neutral axis of the plate. It can be shown that, if the flexural plate is thin enough, only the first two primary modes ($A_0$ and $S_0$) prevail. These modes are displayed in Figure 3-4.

As can be seen, the propagation of a particle travelling on $A_0$ Lamb wave resembles the waving of a flag in the wind [96]. When the thickness if the plate is negligible compared to the wavelength of $A_0$ wave, the wave velocity, $v_p$, asymptotically reaches zero. As the thickness of the plate increases, $v_p$ increases as well, ultimately reaching the surface wave velocity of the medium.

![Figure 3-4: The symmetric and anti-symmetric Lamb modes in a thin plate.](image)
The reason for the rise of phase velocity can be attributed to elevated effective stiffness as the thickness of the plate is increased. However, for the $S_0$ mode, the phase velocity is maximum for small thicknesses of the plate and decreases gradually as the thickness of the plate is increased to finally meet the velocity of the surface acoustic wave in the medium [105]. The asymptotic approach of the phase velocities of $A_0$ and $S_0$ to that surface acoustic wave is not surprising, as a SAW can be denoted by superposition of symmetric and anti-symmetric plate waves [96]. The more interesting applications of FPWs are associated with very thin films compared to their wavelengths. This leads to lower values of $v_p$ and favors the application of FPW devices for bio-sensing and liquid media. The frequency of the operation of the device is directly proportional to the phase velocity of the associated plane wave ($f = \frac{v_p}{\lambda}$); therefore a low phase velocity implies lower frequency of the operation of the device and thus less complicated electronics. The phase velocity of FPW can be formulated as [112]:

$$v_p = \left( \frac{B + T_x}{M} \right)^{\frac{1}{2}}$$

(3-19)

where $B$ is the bending stiffness of the elastic isotropic plate, $M$ is the mass per unit area of the plate and $T_x$ is the in-plane component of the tensile stress (aligned with the propagation of the wave) developed during fabrication process. This simple equation can be used to calculate the sensitivity of FPW sensors as a mass per unit area, $m$ is deposited on its surface. The new phase velocity and its Taylor expansion are given by:
Therefore, the fractional change in phase is:

\[
\frac{\Delta \nu_p}{\nu_p} \approx -\frac{m}{2M}
\]  

(3-21)

where the 2\textsuperscript{nd} and higher order terms are neglected. It can be seen that sensitivity is inversely proportional to areal mass of the plate as expected.

### 3.1.5 Thin rod or fibre acoustic wave devices

For fibre acoustic wave (FAW) devices, the change in the resonant frequency of the sensor is inversely proportional to the diameter of the rod. Performance of these devices is very similar to FPW devices [113]. The diameter of the fibre is on the order of a few \(\mu m\) leading to high sensitivities. The drawbacks of FAW devices are complexity of their fabrication and integration in microelectronic processes in addition to high insertion losses [114].

### 3.1.6 Tube acoustic wave devices

These devices are very similar to FPW and FAW devices in the way that the change in frequency is inversely proportional to their wall thickness. The interesting feature of these devices is that the tube serves as a natural package,
accommodating the analyte gases inside while the electrodes are positioned on the outside to avoid corrosion of the electronic parts [115].

3.1.7 Micromechanical structures

These devices are micromachined variants of the other acoustic wave devices described earlier [116]. The frequency alterations are very large and there is some level of chemical selectivity in their response [92]. The resolution and sensitivities of these devices are generally lower than traditional piezoelectric sensors such as SAW devices and QCMs. The most noticeable advantage of these devices is their compatibility with microelectronic structures because of the absence of the piezoelectric materials.

3.2 Advantages of QCMs

Now that the different types of mass sensors have been shortly introduced, it would be beneficial to explain the reasons behind using QCMs in this project. QCMs provide fast, reliable responses which are most suitable for in-situ monitoring of analyte species. However, a sensing film is required which sometimes introduces frequency fluctuations. They are cost-effective and eliminate the need for time-consuming sample preparations. Some of their other benefits are high-sensitivity, operation at room temperature and low power consumption which leads to longer battery life for portable sensors. Because of their high quality factors, low temperature sensitivity and low frequency of operation, their oscillator circuits are extremely robust and simple and provide
high precisions for measurements of frequency changes (for the sensors in this project measurements as low \( 0.5 \text{ Hz} \) were possible for a circuit operating on a \( 10 \text{ MHz} \) QCM providing good precisions). Nonetheless, more research has to be done to reduce the amount of drift and reproducibility in order to make them suitable for long-term applications in typical environment conditions. One of the most effective ways to increase their sensitivity and stability is to employ techniques with good control over the uniformity of layers of sensing material with better mechanical and morphological properties at their surface. This uniformity and dominance over the characteristics of the sensing layer such as thickness result in higher quality factors, leading to more stable response from the oscillating circuit that employ QCMs. Therefore, the main purpose of this work has been focused on providing high quality thin films with selectivity towards a special analyte. These films were subsequently coated over the surface of crystals by using efficient methods such as electrospinning, electrospraying, and spin coating to improve their performance.
4: ELECTROSPINNING AND ELECTROSPRAYING

Electrospinning process has attracted lots of attention from researchers and engineers due to its versatile applications as well as its benefits that it offers. Using a relatively simple set-up, electrospinning offers many remarkable characteristics such as capability of fabrication of ultra-thin films of fibres with diameters ranging from a few microns to tens of nanometers [117]. These thin films can be produced from numerous materials and have characteristics such as enhanced surface areas, superior mechanical properties, nano-porosity, and improved surface characteristics such as uniformity and stability of the resulting films [118]. Furthermore, there is a substantial level of control over the parameters determining the characteristics of the resulting fibres which can be engineered to fabricate the thin film with favoured morphological features such as diameter of nanofibres and their patterning as well the thickness and uniformity of the film [119]. The possibility of tailoring a wide range of characteristics makes electrospinning a strong candidate to fulfil the dramatic surge of demands for fabrication of thin films in various applications.

The early work on electrospinning can be traced to the work of Lord Rayleigh about 100 years ago to produce fibres. The term that he used in his report was electrostatic spinning [120]. The parameters and set-up were further developed through the works of many researchers. Formhals developed a viable
experimental set-up that could be exploited for practical fabrication of many fibres using electrostatic force to overcome the surface tension in the solutions and weave the fibres on a surface [121].

After development of the practical set-up, the attention was gradually shifted towards better understanding of the process. In his widely-known work, Taylor closely observed the transformations that the polymer solution undertakes during the electrospinning process [122]. He was particularly interested in the shape that the polymer solution takes when it is placed at the orifice of a blunt needle when high electric field was applied to it. He noticed that when the magnitude of electric field is raised above a certain threshold value, the small solution droplet takes the shape of a cone. These cones were referred as Taylor cone by other researchers since then. When the voltage is increased further, some portions of the solution start erupting onto the collector. It was noticed that this ejection of the polymer occurs from the apex of the cone. He further hypothesized that the reason for formation of this cone is two opposing forces on the solution: the surface tension of the solvent as an attractive force that tends to keep the molecules of the solution together and the electrostatic repulsive force due to the presence of high voltage and electric field. At the time of formation of the cone, these forces are balanced with each other and as the voltage is increased, the repulsive electrostatic forces take over and the liquid erupts towards the collector. Additionally, it was noticed that the diameters of the resulting fibres are much smaller than the diameter of the needle [119]. Much research has concentrated on deriving reliable mathematical formulas that
predict the shape, size, and other properties of Taylor cones. Moreover, the effect of different process parameters (e.g. properties of the solution, feed-rate, etc.) on the configuration of Taylor cones was highly investigated [123] [124].

With the advent of modern testing methods, scientists can now measure the morphological properties of the fibres. Consequently, the centre of attention has steered from better understanding the parameters influencing electrospinning to monitoring the properties of the resulting fibres such as nanoporosity and morphological features (i.e., diameter and configuration of the fibres, their shape, the way that fibres are weaved together and presence and types of beads (non-fibrous parts) in the fibres). Baumgarten reported an electrospinning set-up in 1971 for production of fibres with 500-1000nm diameter range [125]. Moreover, properties of fibres resulting from melts were also investigated at that time by Larrondo and Mandley [126]. They concluded that the fibres resulting from electrospinning of the melts usually had much larger diameters compared with ones prepared from solutions.

Over the last decade, there has been a vivid upsurge of demands for fabrication of thin films in various applications and the research on electrospinning has been rekindled to match these applications [117].
4.1 Electrospinning set-up

The basic electrospinning set-up typically comprises of five major components (Figure 4-1): a High Voltage (HV) source, a syringe pump, a syringe, a needle, and a grounded collector [118].

4.1.1 Mechanism of electrospinning

A small droplet is formed at the tip of the blunt needle when the pump pushes the fluid through the syringe. As a high-voltage is applied with the value of the voltage set above a threshold value, the droplet undertakes the shape of

---

**Figure 4-1:** Schematic of a typical electrospinning set-up.
Taylor cone (Figure 4-2).

As the voltage is increased above this certain value, the electrostatic forces dominate the surface tension of the solvent and liquid jets from the apex of the cone towards the collector [123]. This jet is under the influence of electrostatic force between the two terminals. The force leads to acceleration of the droplets on their way towards the lower potential. The jet is further thinned down along the
way due to evaporation of the solvent. Furthermore, the stretching, whipping and entanglement of large polymer molecules with each other on the way towards the collector give rise to generation of a mat of nanofibres on the collector [127].

The formation of Taylor cones can be theoretically derived based on two assumptions: (1) the surface of the cone generates an equipotential surface and (2) the cone is in steady state conditions. In order to form an ideal cone, a semi-vertical angle of 49.3° is required. The shape of the cone generated at the electrospinning process approaches the theoretical shape just before jet formation. In order to satisfy these conditions, the electric field is required to have azimuthal symmetry in order to balance the attractive force arising from surface tension. The voltage, \( V \) as the solution to this problem is given by [122] [128]:

\[
V = V_0 + A R^{ \frac{1}{2} } P_{ \frac{1}{2} } (\cos \theta_0)
\]  

(4-1)

where \( R \) is the distance from the cone’s apex, \( V_0 \) is the potential of the equipotential surface, \( \theta_0 \) is the semi-vertical angle, \( A \) is an angle and \( P_{ \frac{1}{2} } (\cos \theta_0) \) is the Legendre polynomial of order \( \frac{1}{2} \). From equation (4-1), it can be seen that \( \theta_0 \) is the value for which the Legendre polynomial becomes zero, meaning that the surface condition of equi-potentiality is satisfied.
4.1.2 Parameters controlling the electrospinning process

Many parameters contribute to the material properties and morphological configuration of the final film. In general, we can divide the parameters affecting electrospinning in three groups [123] [118] [127]:

I. Solution properties such as type of the solution, properties of the polymer, the strength and nature of interactions between the solvent and dissolved polymers as well as vapour pressure, surface tension, viscosity/concentration and electrical properties of the solvent (i.e., dielectric constant of the solvent and conductivity of the solution).

II. Control variables including the feed-rate of the syringe pump, the value of voltage adjusted by high-voltage supply, the distance between the needle tip and the collector plate, the gauge of the needle and finally geometry, size and even the motion of the collector.

III. Ambient conditions such as temperature, humidity, pressure, and air velocity.

Among these parameters, solution properties are harder to control and usually modifying each one of them leads to changes in other properties as well. Furthermore, these parameters are usually pre-determined based on the application and changing them may not be desirable (i.e. the researchers are interested in improving the properties of a certain polymer rather that switching to another polymer). Moreover, control over the ambient conditions such as humidity and air velocity can be achieved at the expense of additional cost and
complexity of the set-up. However, the controlled variables are simply controlled by, for example, modifying the voltage, adjusting the distance between the collector and the needle tip, or changing the solution feed-rate of the pump. Therefore, controlled variables are the most easily available variables that can be set to refine the properties of the resulting films.

As simple as the general mechanism of electrospinning seems, there are many parameters that potentially complicated the outcomes and may result in unpredictable properties of the films. The liquid jets erupting from the apex of the Taylor cone are subject to a number of complexities such as Rayleigh, axisymmetric, whipping and bending instabilities [123]. Whipping and bending are born from the interaction of the external electric field with the surface charges on the jet particles and control the elongation, stretching and thinning of the fibres [127].

4.2 Electrospaying

Electrospinning can be considered as a special case of a more general process of electrospraying [129]. Both of these processes take place when a high voltage is applied to a liquid at the tip of a capillary needle pumped from a syringe and the liquid jets toward the lower potential collector. In the electrospraying, the liquid jet droplets collapse into small particles that hit and deposit on the collector while in electrospinning, as explained earlier, the liquid jet takes the form of a fibrous mat. Consequently, in the former case, a solution with low viscosity and surface tension consisting of preferably monomeric dissolved molecules is
desirable while a polymeric substance and high viscosity solution favours electrospinning conditions [130].

Since the droplets ejecting from the cone in electrospraying are usually larger than the elongated fibres in electrospinning, some additional complications creep in which further complicate the process including: dripping from the cone when spherical droplets eject, spindle mode in which the jet is divided into small filaments before breaking into droplets, emission of the drops from a twisted jet and most importantly precession mode is which the jet erupts on the collector leaving large spot without actually spraying [117].

4.3 Applications of electrospun films

Electrospun fibres have been employed in several applications including as biomedical (e.g. drug carriers, wound dressing, tissue engineering and cosmetics), functional materials and devices (e.g. composite material reinforcements), and sensing applications [117].

4.3.1.1 Medical applications

Nanofibres have appealing properties for medical applications due to the fact that many parts of our living tissues such as skin, bones, teeth, and cartilage [117] are comprised of nanofibres. Consequently, synthetic nanofibres have a well-established place in biomedical applications to replace the natural tissues. Additionally, due to increased surface area of the electrospun nanofibres, they are favourable as drug carriers where the efficiency of the delivery is proportional
to its surface area [131] [132]. Moreover, it is possible to generate nanofibres with similar morphological, chemical, and surface functional characteristics as their natural peers. Therefore, nanofibres have been widely used in tissue engineering products [117]. The high porosity of nanofibres has been put to use in production of wound dressing products. By adjustment of the nanoporosity of these materials, it is possible to keep them at a level to allow the air to pass in while avoiding the bacteria penetration [133] [134].

4.3.1.2 Functional materials and devices applications

Many features of nanofibres including superior mechanical performance due to higher surface area lead to their ubiquitous exploitation in functional materials and devices engineering. One of their most common applications in this field is their employment in composite reinforcements to enhance the mechanical properties of composites. Microfibres were traditionally employed for this application. However, ever since the advancements in nanofibres industry, they have substituted their old predecessors in many application by providing remarkable properties such as increasing the interaction between the fibres and matrix, better reinforcements, better transparency and much higher surface to volume ratios [117] [133] [135].

4.3.1.3 Sensing applications

The high surface area and nanoporosity are the primary characteristics that make nanofibres extremely attractive for sensing applications. Replacement
of conventional methods of coating sensors with their active layers by electrospinning has resulted in improved sensitivities and detection limit of numerous chemical sensors [136]. A gas sensing method based on gravimetric detection of ammonia by electrospun nanofibres was proposed by Ding et al. [137]. Moreover, nanowires based on single crystalline molybdenum oxide were prepared by electrospinning and tested for their potential applications for biological sensing probes [138]. Another method for detection of glucose was proposed by Lee [139] by using enzyme-free nanofibrous membranes made from electrospinning of poly(aminophenylboronic acid) (PAPBA). Furthermore, nanofibrous electrospun membranes have been bounded to substrates and widely used in biosensing applications [140].
5: SENSING OF AMMONIA AND HUMIDITY

Poly (acrylic acid), (PAA) was employed to fabricate an ammonia gas sensor. PAA is a polyelectrolyte or in other words exhibits the properties of both a polymer (having a high molecular weight and being a combination of monomers) and an electrolyte (by hydrolysis of weak acidic carboxyl group forms ions in the aqueous solution) [141]. The structure of PAA is shown in Figure 5-1. Due to the presence of the acidic groups in PAA, this molecule shows an interaction for weak basic species such as ammonia gas. This interaction can be used to fabricate ammonia gas sensors [142]. However, the direct electrospinning of PAA over the substrates is tricky because of the very strong hydrogen bonds that carboxylic groups of PAA form with water. This leads to extremely slow evaporation of the water molecules from the surface and thus the quality of the film is reduced. Subsequently, the sensitivity of the sensor will be worsened as a result of lower quality film [143]. Another reason for lower quality films can be attributed to slow evaporation of the water molecules on the jet erupted from the Taylor cone, which prohibits the fibres to be thinned down. Therefore, it has been suggested to mix the PAA solution with the water soluble poly(vinyl alcohol) (or PVA) as the template material [144]. The structure of PVA is shown in Figure 5-1.

We prepared solutions of PAA and mixed them at different ratios with PVA and measured the response of the system to ammonia. It was noticed that
because of the absence of acidic group in PVA, this polymer shows no affinity towards ammonia gas. Nonetheless, we could electrospin PVA films on QCMs and investigate their responses to humidity.

5.1 Preparation of solutions

PAA (molecular weight= 100,000) solution of 35 % m/ν concentration and PVA (molecular weight= 89,000 – 98,000) powder were purchased from Sigma-Aldrich. The PAA solution was further diluted to reach a concentration of 15 % m/ν. PVA was dissolved in water by heating the solution and vigorous stirring for 20 min to obtain a 10 % m/ν solution. The PVA solution was cooled down to room temperature and then mixed with PAA solution with different ratios. The volumetric ratio of 15 % m/ν PAA to 10 % m/ν PVA in some of the resulting solutions were 0%, 20%, 30% and 60%.
5.2 Thin film formation

Films of PAA and PVA mixtures were electrospun on the surface of quartz crystals. The crystals were purchased from International Crystal MFG and had blank diameters of 0.5 inch with a resonant frequency of 10.000 MHz and quality factor of 6,000. Ti/Au electrodes of 0.20 inch diameter were deposited on both sides of the crystals.

5.2.1 Electrospinning set-up

A high voltage power source from Gamma High Voltage Research, Inc. and an NE-300 syringe pump (New Era Pump System, Inc.) were used as well as a 5 ml glass syringe with blunt metal needles of gauge 15, 22 and 25. The electrospaying set-up is represented in Figure 5-2.

By understanding how different parameters affect the properties of the resulting fibres, it is possible to adjust them to match desired characteristics that we are looking in the final films. In order to obtain the desirable recipe for the sensitive thin film in this work, numerous experiments were performed with different polymers and various observations were collected to reach to a final optimized procedure to prepare sensitive thin films for gas sensing applications.

5.2.1.1 Molecular weight and concentration

Molecular weight of a polymer is an important parameter that directly controls the viscosity of solution. In general, a solution prepared from a polymer with higher
molecular weight has greater viscosity compared with a solution containing a polymer with lower molecular weight. During the process of electrospinning, as the liquid jet starts to leave to apex of the Taylor cone, the intermolecular forces in the polymer molecules prevent the resulting jet from collapsing into droplets on its way towards the collector. The intermolecular forces give rise to entanglement of the polymer chains and overcoming of the electrostatic repulsion force caused by the trapped charges [145]. Moreover, the molecular weight of the polymer is usually proportional to the length of chains, and therefore, with a higher molecular weight polymer and longer chains, the probability of entanglement of chains is enhanced leading to formation of fibres on the collector. We observed that the concentration of polymer has a direct effect on the quality and the degree
to which fibres are coated. An increased concentration in turn leads to higher intermolecular forces in the liquid jet and increases the chances of entanglement. For example, from the experiments we noticed that for the same level of voltage (15 kV), 25 % m/v PAA solution showed a higher tendency towards formation of fibres compared with 10% m/v PVA solution. Moreover, the PVA solution had an improved affinity towards fibre formation after it was mixed with PAA solution at different ratios. It was noted that as the concentration of polymer solution is increased, electrospinning rate became slower and ultimately stopped at a certain concentration unless the voltage was increased to much higher values.

The reason can be attributed to the lower amounts of solvent present in high concentrations of polymer. Therefore, pumping of highly viscous solution

Figure 5-3: A crystal coated with a film of 15 % m/v PAA. In this particular case, the electrospinning was run for about 10 minutes. A typical nano-film for gas sensing applications requires about 20 seconds of electrospinning.
becomes very difficult and the Taylor cone does not receive the required amount of solution to make up for the mass loss from its apex, ultimately resulting in its instability and destruction. Figure 5-3 shows the undesired coating of a quartz crystal electrospun with a high dose for 5 min using a 15% m/v PAA solution.

An additional observation was that at low concentrations of polymers, and accordingly lower viscosities, the film formed on the crystals was mainly composed of very small droplets that are observable even by the naked eye. As the concentration of the polymer solution increases, the thin film's morphology spans a wide spectrum. At very low concentrations, the resulting film consists of a combination of small dots and fibre. As the concentration increases the number of small dots is reduced and a more uniform fibrous film is obtained. If the concentration of the solution is increased beyond a limit, the electrospinning process stops altogether. For PAA solution, the limiting concentrations occurred roughly at 35% m/v and 95% m/v, respectively. Another noteworthy observation was that as the concentration of polymer increases, the area of the collectors covered by the fibres becomes smaller. This effect can be probably explained by noticing that higher viscosity leads to higher mass density of the entangled polymers in the jet, and since the amount of kinetic energy is constant, the speed and the radius of propagation of the fibres are reduced.

5.2.1.2 Properties of the solvent

Solvents can affect the morphology and characteristics of the electrospun films in several ways. One of the significant parameters contributing directly to the
properties of the resulting fibres is the surface tension of the solvents. As mentioned earlier, the onset of electrospinning takes place at the time of generation of Taylor cone whose formation is governed by dominance of electrostatic repulsion forces over the surface tension of the solution. Therefore, elevated surface tension of the solution requires higher electric fields. Additionally, surface tension has the influence of decreasing the surface area per unit volume of the liquid, subsequently making the solvent molecules to have affinity to congregate together; this effect causes the injected jet from the Taylor cone to stay together and prohibits further elongation of the polymer and thus formation of fibres on the collector. Therefore, solvents with high surface tensions are not favourable for electrospraying or electrospinning.

However, regarding the properties of the solvent, many parameters have to be considered to come to a favourable conclusion. In one experiment, isopropyl alcohol was added to the 15% m/v solution of PAA. Since the surface tension in water is much larger than the alcohol, it was assumed that the formation of thin fibrous films should occur more smoothly. However, no tangible difference was measured. This observation can be explained in two ways: a) the effect of surface tension is not that important to give rise to measurable differences in here; or (b) other factors such as dielectric constant and conductivity of the solution are neutralizing the impacts of higher surface tension of the water.

The conductivity of the solution increases its ability to carry more charges, and therefore, more efficient stretches and elongations take place, giving rise to
an improved quality of the fibres [146]. On the other hand, a solvent with higher dielectric constant can accommodate charge more easily, letting it stabilize the jet and prevent its collapse through formation of droplets and spots on the collector. Therefore, one of the reasons pointed out for little or no improvement on the electrospinning conditions, by addition of isopropyl alcohol to water, can be attributed to remarkably high dielectric constant of water.

5.2.1.3 Process parameters

Electrospinning voltage

Increasing voltage affects the electrospinning process in different ways. In general, increasing the voltage, and therefore, raising the accompanying electric field tends to further stretch the jet solution from the apex of the Taylor cone. Therefore, one expects to observe films with better quality on the collector. However, the side effect of the larger electric fields is the higher acceleration of the jet towards the collector, and therefore, shorter time for evaporation of the solvent. This effect reduces the time that fibres have on their way to the collector to thin down. Therefore, the quality of the films is reduced. On the other hand, by increasing the voltage, more charge is transferred to the Taylor cone and the electric field and therefore the rate of ejection of the solution from the Taylor cone is increased, and if the feeding rate is not increased proportionally, the Taylor cone becomes unstable. The experiment ran to verify this phenomenon was as follows: when the voltage was increased from $15 \text{ kV}$ to $20 \text{ kV}$ at a constant feeding rate of $0.1 \text{ ml/min}$ for the PAA solution, the Taylor cone would at first
deform and usually become smaller and finally receded inside the orifice of the needle. A further increase of the voltage (to a maximum value of $21kV$), caused a total disappearance of the Taylor cone and small droplets of the polymer were gathered on a collector positioned 7 cm away from the needle tip. In brief, there is a range of voltages for which the electrospinning process provides the most desirable characteristics of the resulting film and this range can conveniently be determined by performing a few simple experiments.

**Feed-rate of the pump**

Adjusting the value of the feed-rate of the syringe pump is of crucial significance to obtain films with desirable characteristics. If the value of feed-rate is set too high, due to the presence of large volumes of solution at the needle tip, proper elongation and stretching of the fibres does not take place, ultimately leading to formation of droplets and spots on the collector. Moreover, when the feed-rate is set too high, polymer solution jet has less time to have the solvent evaporated and therefore gives rise to wet films with much lower quality and crystallinity. On the other hand, if the value of the feed-rate is set too low, the amount of solution exiting the Taylor cone outweighs the feeding-rate that in turn results in the collapse of the Taylor cone.

**Distance between the needle tip and collector**

The time that the liquid jet spends in the air is determined by the distance between the needle tip and the collector among other parameters such as feed-rate and voltage as discussed before. If this distance is too short, the solvent in
the liquid jet has little time to evaporate. Furthermore, elongation of the fibres cannot happen very effectively at short distances. Such an arrangement usually leads to formation of low-quality films stained by spots of different sizes.

The following observation was made at very short distances (less than 3 cm) and at the time of the start of the process: as the voltage increases from zero to the desired value, small amounts of solution present at the needle tip travelled towards the electrode before the formation of the Taylor cone. This gave rise to formation of non-uniform films on the collector. Therefore, short distances are not favourable. On the other hand, at very high distances (20 cm or more), the efficiency of the electrospinning was seen to drop severely due to a low portion of the fibres reaching the surface of the collector. Therefore, an optimized value of distance has to be found from experiments to fulfil the requirements of the thin film that we are looking for.

**Gauge of the needle**

The gauge of the needle can be important depending on the application of the electrospinning process. It was observed that with higher gauges (i.e., smaller orifices), the possibility of evaporation of the solvent is reduced at most due to small surface contact of the liquid with the ambient. However, it was also noticed that electrospinning can become quite burdensome if high gauge blunt needles are used with viscous solution. Therefore, the gauge of the needle should be chosen based on discretion and the particular application. Needles with three different gauges (15, 22, 25) were used in our works and the optimized needle
for each application was found by performing a few experiments and choosing the best one among them.

**Final recipe**

After noting these observations and measuring the response of each sensor, the highest responses were obtained for the crystals whose coated films had fibrous textures without small dots. The chosen parameters for the works in this chapter were as follows:

- Distance between the needle tip and the crystal surface: 10 cm;
- Pump flow rate: 0.5 ml/min for a few seconds before turning on the high voltage source (the first few drops were gathered from the needle tip and transferred to a vial for later use). The flow rate was subsequently set to 0.47 ml/h;
- Electrospinning voltage: 15 kV;
- Gauge of the needle: 22 (0.643 mm).

The electrospinning process was continued until a frequency change of the coated crystal was measured by the frequency counter.

One of the biggest challenges that we came across was the increased amount of damping of the oscillator circuits using the coated crystals. We suspected this effect could be attributed to the deposition of the polymers on the pins and the electrode contacts of the crystals prohibiting a proper electrical connection. This nonconductive layer of the polymer interferes with the electrical
behaviour of the crystals by increasing the damping to a great extent and therefore leading to deteriorated frequency response of the circuit. In order to overcome this issue we examined two methods:

1) A metal mask was prepared by carving sufficient space on the cap of one QCM packaging to allow the nanofibres to be deposited only on the electrode surface but obstruct their access to the pins.

2) The crystal was unmounted from its packaging and positioned on a spare base to be electrospun. After the electrospinning process completed, the crystal was inserted back in its original packaging.

The second method is preferable since it gives rise to more uniform films. However, the replacement of the crystal should be done very carefully in order not to damage the thin crystals.

5.2.2 Gas experiment set-up

An ammonia gas cylinder of 100 ppm concentration and 0.1 LPM regulator were purchased from Praxair, Inc. Gas flow meters were purchased from Dwyer instruments. Gas chambers with good sealing under the conditions of these tests were built in our lab. The affordable and practical set-up capable of controlling humidity and gas concentration in this work is depicted in Figure 5-4.

A nitrogen tank connected to chamber A (1 L) through a gas valve was the starting point for our set-up. Chamber A was connected to three flowmeters: FM1, FM2 and FM3, which in turn where connected as the following:
The gas line out of flowmeter FM3 was driven into a water bubbling system (chamber C, 1 L) to generate a nitrogen/water vapour mixture, which was directed to chamber D (1 L) where it was mixed with nitrogen from flowmeter FM2. This part of the set-up allowed for a tight control of the relative humidity of the final gas through the control of the ratio of the flow of FM2 and FM3 flowmeters. The gas line out of flowmeter FM1 was connected to chamber B (1 L), which was also connected to the ammonia tank. This part of the set-up allowed for ammonia to be diluted with nitrogen in chamber B, and the tight control of this dilution using flowmeter FM1. Finally, outlets from chambers D and B were mixed in chamber E (1 L), which was connected to the test chamber containing the operating QCM in an oscillator circuit.

5.3 Measurement of ammonia concentration

The resulting quartz crystals were put in an oscillator circuit and the frequency was read by an Agilent 53132A frequency counter. The frequency counter was connected via GPIB cable to a PC to save the data by labview software.

The frequency response of the crystals after electrospinning of the thin films was measured using a Rhode and Schwarz ZVB4 vector network analyzer (VNA). The quality factor of a crystal that was directly drop-casted with 33 % ratio of PAA to PVA solution was measured to be 132. Based on this magnitude of quality factor for the same amount of frequency change, we concluded that by drop-casting of the PAA/PVA solution on the crystals, it is not possible to generate a
uniform layer of the polymer which is essential for proper operation of the sensor. Furthermore, we speculated that rather than forming a uniform layer, the polymer molecules have gathered as nanocrystal clusters. This crystal was inserted inside an oscillator circuit and it was observed that due to low quality factor of the crystal, the circuit’s performance was poor and subject to noises and ambient fluctuations. This sensor only showed a small response of 10 Hz to ammonia of 100 ppm concentration.

The frequency response of the crystal electrospun with PAA /PVA (ratio of 30 % ) is shown in Figure 5-5 and the measured value of quality factor was 1180 (the value of the peak divided by 3-dB bandwidth). This value indicates the formation of a higher quality film layer that results in superior performance in the oscillator circuit and provides better sensitivity and detection limit to NH₃ sensing. The SEM images of this film at two different magnitudes are shown in Figure 5-6.
Figure 5-4: Block diagram of the gas experiment set-up
Figure 5-5 shows the diagram of frequency change, $\Delta f$ of the oscillator circuit, as this crystal was subjected to a 100 ppm concentration of ammonia.

At first, nitrogen gas was purged inside the chamber until a stable frequency was obtained. Afterwards, ammonia gas was led inside the chamber.

Figure 5-6: SEM images of PAA/PVA film at two magnitudes.
and the frequency response was observed until no further changes occurred. At that point, the ammonia valve was closed and nitrogen was run into the chamber to remove the ammonia. Due to the reversible interaction between ammonia and PAA the frequency of the oscillator settled back to its baseline.

As ammonia gas was led inside the chamber, the frequency experienced a fast drop at the start followed by a slower drop afterward, before reaching a stable equilibrium value (Figure 5-7). The same pattern is observed when ammonia valve is closed and nitrogen gas is released in the testing chamber: the frequency increases sharply at the start, followed by a slower rate to finally reach a stable value. This behaviour is due to the absorption, diffusion and desorption phenomena taking place at the film interface. When ammonia is in contact with the film, because of the adsorption effect and the interaction between the lone electron pair on ammonia and the acidic proton of the carboxyl group on PAA, the ammonia molecules are trapped inside the film which gives rise to a sharp drop in the frequency response. This change in frequency is slowed down, as bulk diffusion effect takes over. By considering that the host/guest supra-molecular relationship, is dynamic by nature, it is implied that the adsorption and desorption phenomena are happening simultaneously.

The rate of adsorption is constant and proportional to concentration of ammonia molecules in the gas phase. On the other hand, the rate of desorption is zero at the start and increases with time proportional to the concentration of ammonia trapped in the polymer film. As a result, the rate of desorption reaches
the value of adsorption after a while and the process reaches equilibrium, hence stabilizing the frequency response.

The response of the crystal with PAA/PVA ratio of 30% films was investigated to two other concentrations of ammonia at room temperature, and the results are plotted in Figure 5-8.

Figure 5-9 shows the change in oscillator frequency, when PAA/PVA films of various compositions are treated with 100 ppm ammonia. As it is expected, as the concentration of PAA increases there will be more acidic sites on the polymer that can interact with ammonia gas. However, if the ratio of PAA is raised further, a reverse effect is observed and the response is degenerated, which can be
related to strong hydrogen bonding of water molecule and PAA as explained earlier.

Similar to any other sensors based on adsorption/desorption phenomena, a saturation effect is expected. However, the highest concentration of ammonia available in our work was 100 \textit{ppm} which is evidently below the saturation level of the film.

The lowest detectable value of ammonia concentration was also found theoretically by letting the QCM circuit run for one hour in order to reach a stable value. Afterwards, the frequency response of the QCM operating in the oscillator circuit was monitored for 10 \textit{min}. It was observed that the frequency readings was stable within a range of 1Hz for the PAA/PVA with 30\% ratio film. Using Sauerbrey’s equation and considering a signal to noise ratio of 3: 1, this value of frequency change corresponds to 1 \textit{ppm} of ammonia concentration.

![Figure 5-8: Change in frequency vs. ratio of PAA in a PAA/PVA solution](image)

Measurement of humidity

The effect of humidity and potential use of these films for humidity sensing was investigated. Figure 5-10 represents the response of crystal with PAA/PVA with 50% to humidity. The PAA molecules interact strongly through strong hydrogen bonds with water molecules, and therefore, the response of this film to water molecules is barely reversible. On the other hand, the response of the film fabricated from electrospinning of only PVA exhibits better reversibility with respect to water molecules, letting the film be used for a humidity sensor (Figure 5-11). The response of PVA film to different relative humidity levels is represented in Figure 5-11.

We carried out another experiment for humidity sensing to offer better insight on the interaction of the water molecules and the active layer of the sensors. In this experiment, the crystal in the oscillator was not coated with any material and the response of this crystal to different relative humidity levels was measured. The interesting observation was that the response to all humidity levels ranges from 0 to 200 Hz.

![Graph showing frequency change of PAA/PVA film vs. concentrations of ammonia (ppm)](image)

Figure 5-9: Frequency change of PAA/PVA film vs. concentrations of ammonia (ppm)
levels was almost zero. We then heated the water in bubbling system in our set-up (Figure 5-4) to 50°C, and interestingly observed a 120 Hz of frequency change. The reason for this behaviour is due to the physical equilibrium between liquid and gaseous water: \( H_2O(l) \leftrightarrow H_2O(g) \), the value of the thermodynamic equilibrium constant is equal to partial pressure of water vapour and is only a function of temperature.

Consequently, at relative humidity levels of less than 100 %, the physical equilibrium does not occur (because liquid water cannot exist) and equilibrium is always shifted to the right side of the reaction. In other words, there will no water droplet can be condensed on the surface of crystals under these circumstances. Due to the fact that the surface of uncoated quartz crystal does not have strong bond with water molecules, the measured frequency change would be zero. However, when water is heated, the thermodynamic equilibrium constant increases, giving rise to a higher water pressure inside the bubbler. This pressure is in fact higher than the water vapour pressure at room temperature.
Consequently, when this stream is flowed to the sensing chamber, the reaction is shifted to the left side and water molecules can condense on the surface. This gives rise to a response in the oscillator circuit.

This experiment and considering that PVA shows response to humidity at room temperature confirm the actual physical interaction (in the form of hydrogen bonds) that takes place between the water molecules and the polymer.

Figure 5-11: The response of PVA film to 50 % humidity
Sensing and detection of methane is important in several applications. When accumulated in a closed area, such as mines, methane causes life-threatening explosions. Methane is the main constituent of natural gas which is ubiquitously used in industry and house residences for heating purposes. Furthermore, methane is abundantly produced by oxidation of organic compounds in nature. It also contributes greatly to the greenhouse phenomena [3].

One of the methods used for quantification of methane is gas chromatography (GC). However, this method is expensive and is not properly fitted for in-situ monitoring which is essential in most cases [147].

Electrochemical sensing of methane faces many challenges due to the inertness of methane molecule. The anodic potential necessary for direct oxidation of methane is higher than the value of oxidation potential for water [148] making the direct amperometric sensing of methane troublesome. In order to circumvent this problem, Otagawa et al. used an organic solvent and Pt-Teflon electrode which allowed application of high anodic potentials which were not compatible with aqueous solutions [149] [150]. Notwithstanding permission of high voltages, this method suffers from the fact that water is necessary in the electrochemical half oxidation reaction of methane and thus humidity has to be
induced in the gas stream. This humidity produces a great amount of background noise which can be partially overcome with differential sensing on two streams of gas, one containing methane and humidity and the other only humidity.

Optical systems possess some advantages, such as increased safety, possibility of remote access to monitoring places, and the feasibility of in-situ measurements [151] [152] [153] [154]. On the other hand, their disadvantage is that the main absorption band for most gases occurs at the infrared (IR) region which is not in the transmission window of silica fibres, or laser diode sources. However, most gases, such as methane, carbon monoxide and carbon dioxide have overtones and combination absorption bands in near infrared (NIR) region which can be scanned by the mentioned light sources. Once more, the fact that the amplitude of these overtones is typically 200 times smaller than the value of fundamental bands implies that sensitive and thus more expensive sources, fibres and detectors are necessary [155]. Because of the convenience of distributed feedback (DFB) lasers, they are frequently used in gas sensors as they can be accurately tuned to the absorption peak of a particular gas which leads to higher spectral power densities within the absorption linewidth of the gas. Nevertheless, DFB lasers are expensive and gas specific [156]. Jaffrezic et al. covered the optical fibre core with a transparent polymer containing a methane sensitive substance in order to measure the methane concentration in the environment. As methane is absorbed, the effective refraction index of the polymer changes which is detected using evanescent wave (EW) optical fibre sensor. In this method, intensity modulation and a laser diode (\(\lambda = 670\,nm\)) are
used as light source. The best detection limit for methane in this method is about 2% (157).

Semiconducting oxides have been traditionally used to measure methane concentration. The key to their operation is the change in surface conductivity of the semiconducting oxide as the ambient gas is absorbed on the surface (158) [159] [160]. By taking advantage of the fact that Pd and Pt catalyze the oxidation reaction of methane at elevated temperatures (about 400°C), it is possible to make the surface of semiconducting oxides selective to methane with a minimum detection limit of about 0.5% (161). Another class of catalytic gas sensors uses narrow Pt wire coils coated with a catalyst mounted on an inert porous material which can detect methane concentrations as low as 0.1% (162).

Gallium Oxide (Ga2O3) films working in the temperature ranges of 300-1000°C can be used to oxidize reducing gases such as methane at their surface and can be potentially developed as sensors for them (163). The wide range of operating temperatures makes different types of interactions and mechanisms between the reducing gas and gallium oxide possible which consequently leads to different levels of sensitivity upon change of temperature (164). However, these high temperatures are not suitable for sensing of methane in mines or in places where explosions could happen.

Zinc Oxide (ZnO), an n-type semiconductor with hexagonal structure, can be used for methane detection at relatively lower temperatures (100-200°C) (165). This semiconductor can be coated on different substrates by convenient methods such as sputtering or chemical vapour deposition (CVD), while the conductivity of
the final film is usually controlled by the amount of doping. Furthermore, ZnO lattice is compatible with silicon for standard CMOS technology [166] [167]. A report on dynamic response of ZnO films to methane is presented in [168] where it is shown that the optimum working condition using $Pd-Ag$ catalytic metal contact to ZnO is obtained at $250^\circ C$ which is still above the safe temperatures for detection of methane.

The elevated temperatures that metal oxide methane sensors operate, generally makes their employment difficult for environments where high temperatures can cause explosions. Moreover, high operation temperatures translate into higher power consumption which leads to shorter battery life for portable or remote sensing applications [169]. Furthermore, the response time of these sensors can take up to a few minutes [170] [162].

6.1 Supra-molecular detection of methane

Supramolecular interaction is related to an assembly where the molecules are held together by non-covalent bonds. Detection of methane molecules at room temperature is possible by incorporating supra-molecular interaction between a host molecule and methane. Employment of supra-molecular compounds has given rise to an exciting family of gas sensors. These host molecules and the analyte molecules undergo a key-lock mechanism, by analogy to antibody/antigen coupling in biological systems. These supra-molecular interactions between the host molecules and solvent have been studied on quartz crystal microbalance (QCM) and surface acoustic wave (SAW) devices.
It was shown by means of nuclear magnetic resonance (NMR) spectroscopy that members of the cryptophane family can selectively and reversibly capture neutral compounds through a host-guest mechanism, where the cavity inside the cryptophanes can be tailored to match the size of the guest molecule. Among all the results, the first and smallest member of the family, Cryptophane A (CrypA) demonstrates a strong affinity towards methane molecules. The sensitivity of CrypA towards methane is largely due to the fact that the methane size is complementary and well-fitted with the cavity of CrypA and thus strong Van der Waals interactions will keep methane inside the cavity of Cryptophane A.

In the work of Nicolas et al. [173], the behaviour of cryptophane molecules as new chemical receptors for methane gas sensing was investigated. Their results showed that the deposition technique used to make the cryptophane film was of great importance. They concluded that the main difficulty was the immobilization of host molecules without loss of their properties for the supramolecular interaction with methane molecules. A method for the measurement of dissolved methane in aqueous solutions was presented by Mowlem [174] as well, where a minimum concentration of 0.2\(\mu\)M of methane and a dynamic range of 1-300\(\mu\)M were observed. This method is based on detection of modulation of effective refraction coefficient of CrypA molecules dissolved in polydimethylsiloxane (PDMS) when the layer is exposed to methane.

Cryptophane molecules (I) comprise of two cyclotrimeratrylene units connected together by three O-Z-O bridges as shown in Figure 3-1. The Z group
determines the size of the cavity of the host molecule which in turn regulates the size of the analyte species. X and Y determine the exterior properties of the cryptophane molecule, such as hydrogen bonding and dipole-dipole interactions. Group Z in in the form of \((CH_2)_n\) where \(n\) can be in the range of 2-10 [173]. When \(n\) is equal to 2, the smallest member, CrypA (II) is obtained (Figure 3-1).

Other than methane, cryptophanes form stable non-covalent complexes with other neutral molecules, such as halomethanes both in aqueous and non-aqueous solvents, e.g. tetrachloromethane [175]. Smaller family members of cryptophanes can also maintain stable complexes with charged ions such as quaternary ammonium salts [176]. The value of equilibrium constant for complex bonding of methane to CrypA in tetrachloromethane was estimated to be \(130M^{-1}\) at 27°C [177]. CrypA is shown to have an affinity for interaction with xenon as well [178].

![Diagram of cryptophanes](image)

**Figure 6-1:** General structure of cryptophanes (I) and the structure of CrypA (II).
6.2 Synthesis of Cryptophane A

In 1981, Gabard and Collet, [179] proposed a method for the synthesis of cryptophanes starting with a substituted meta-methoxy benzyl alcohol derivative. A perchloric acid mediated trimerization afforded a $C_3$-trimer, which was subsequently converted into an iodo derivative, which in turn was reacted with a phenol to yield a $C_3$-phenol derivative. The resulting phenolic compound was then dimerized in hot formic acid, yielding a cyclotrimeratrylene-like crown: CrypA in a 3.8% overall yield (Figure 6-2). The main disadvantages of this method were the use of low concentrations of the phenol derivative to favor the intramolecular

![Chemical structure](image)

Figure 6-2: Three step method for synthesis of CrypA
reaction and the isolation of the compound by preparative thin layer chromatography (TLC), which limit the scale-up potential of this synthesis.

Canceill and Collet improved this method by first synthesizing a dimer of vanillinyl alcohol using a dialkyl halide which was then trimerized in hot formic acid to yield CrypA [180] (Figure 6-3).

In our work, CrypA was prepared from vanillin following Benounis et al. method [157], in three steps with 3.7% overall yield (with an improvement over the reported 3.2%).

6.2.1 Synthesis procedure

Vanillin, 1,2-dibromoethane, sodium hydroxide, sodium borohydride and all of the other solvents were purchased from Sigma-Aldrich and were used without further purification. $^1$H-NMR spectra were recorded on a Bruker 400 MHz spectrometer.

![Diagram of synthesis process](image)

**Figure 6-3: Two step method for synthesis of CrypA**
and were referenced to the residual solvent peak. The TLC plates (Macherey-Nagel MN818333, Alugram Xtra SIL60, UV254, 0.2 mm) and the silica gel (Silica Gel 60, 230 - 400 Mesh) were purchased from Canadian Life Sciences. The reactions of this synthesis are depicted in Figure 6-4.

1,2-Bis(4-formyl-2-methoxyphenoxy)ethane (VIII). To a solution of vanillin (VII) (30 g, 200 mmol) in ethanol (100 mL) was added a solution NaOH (10M, 20 mL) and 1,2-dibromoethane (9 mL, 100 mmol). The mixture was subsequently refluxed for 24 h. After cooling to room temperature, the vanillin dimer was

![Chemical Structures](image)

**Figure 6-4:** Procedure used for synthesis of CrypA in this work, starting with vanillin

((i): BrCH₂CH₂Br, NaOH/EtOH, (ii): NaBH₄, EtOH (iii): HCOOH)
recovered by filtration to yield the desired compound as a solid (24 g, 73.2 % yield). $^1$H-NMR (DMSO-d$_6$, 400 MHz) $\delta$ = 9.85 (s, 2H), 7.58 (dd, $J = 8.2$, 1.8 Hz, 2H), 7.42 (d, $J = 1.8$ 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 4.47 (s, 4H), 3.82 (s, 6H) ppm (Figure 6-5).

1,2-Bis(4-hydroxymethyl-2-methoxyphenoxy)ethane (IX). To a mixture of (VIII) (13.07 g, 40 mmol) in methanol (200 mL) was slowly added NaBH$_4$ (5.32 g, 140 mmol). The mixture is stirred for 24 h. After filtration, the resulting solid was washed with a mixture of methanol/water (2/1, 200 mL) to yield compound (IX) in 12.5 g as a white powder (97 % yield). $^1$H-NMR (DMSO-d$_6$, 400 MHz) $\delta = 7.00-6.92$ (m, 2H), 6.83 (dd, $J = 8.1$, 1.7 Hz, 1H), 5.09 (broad s, 1H), 4.42 (s, 2H), 4.24 (s, 2H), 3.74 (s, 3H) ppm (Figure 6-6).

Cryptophane A (II).
In a round bottom flask (2 L) equipped with a magnetic stir bar and a reflux condenser, compound (IX) (9 g, 27 mmol) was added to formic acid (1.5 L), and the resulting solution was stirred under reflux for 4 h. After 4 h, the reaction was allowed to cool down and the formic acid was removed under vacuum, yielding a brown solid, which was purified by column chromatography on silica gel (volume = 1 L and diameter = 4 cm) using DCM/Et2O : 9/1 as eluent. The fractions with an $R_f = 0.9$ were collected and the solvent was removed under vacuum to yield the desired compound as a white solid (0.8 g, 5.37 % yield). $^1$H-NMR (CDCl₃, 400 MHz) $\delta = 6.74$ (s, 6H), 6.65 (s, 6H), 4.58 (d, $J = 13.7$ Hz, 6H), 4.14 (m, 12H), 3.77 (s, 18H), 3.39 (d, $J = 13.8$ Hz, 6H) ppm (Figure 6-7).
6.3 Methods used for fabrication of thin films:

Five different methods explained below were tested for deposition of CrypA on the surface of the sensors.

6.3.1 Direct deposition using a solvent

A solution of CrypA (0.15ml) in THF (0.1601 % m/v) was drop-casted on the surface of a crystal and the sensor was left overnight under a fumehood until THF was completely evaporated from the CrypA film.
6.3.2 Direct deposition using K11 and K1000 polymers

A polysiloxane type polymer, siloprene K1000 (Sigma-Aldrich), was used with siloprene cross-linking agent, K11 (Sigma-Aldrich) for this method. K11 and K1000 were mixed at a volume ratio of 1 to 5. To each unit volume of the polymeric mixture, 30 volumes of 0.1601 % m/v of CrypA in THF was added and the resulting mixture (0.15ml) was drop-casted on the surface of a QCM. The resulting QCM was heated at 50 °C for 5 hours before the gas sensing experiments.

6.3.3 Electrospraying of CrypA/THF solution on QCMs

In this experiment, 0.1601 % m/v of CrypA in tetrahydrofuran (THF) was used. The experimental set-up of electrospraying process is presented in chapter 4. A high voltage power supply from Gamma High Voltage Research, Inc. and a NE-300 syringe pump (New Era Pump Systems, Inc.) were used as well as a 5 ml glass syringe and blunt metal needles of gauge 25. The optimal conditions required for this method were determined to be as follows: the distance between the needle tip and the crystal surface was set at 7cm, the value of the voltage of the voltage source was adjusted to 13 kV, and the flow-rate of the syringe pump was fixed at 1 ml/min until the first drops of THF were seen and gathered. Subsequently the value of feed-rate was decreased to 0.5 ml/h.

Due to the mass of the film, the resonant frequency of the quartz crystals was reduced by about 50 kHz. The mass of the deposited film can be related to
the frequency change, using Sauerbrey’s equation for an AT-cut quartz crystal [181]:

$$\Delta f = -2.26 \times 10^{-6} f_0^2 \rho_s$$  \hspace{1cm} (5-1)

where $\Delta f$ is the change in frequency and $f_0$ is the resonant frequency of crystal both measured in Hz, $\Delta m$ is the mass of the film (in grams), which is deposited on the crystal and $A$ is the surface area of the circular electrode in $cm^2$. The calculated mass of the deposited layer was 220 $\mu g$.

6.3.4 Electrospinning of polymeric mixture of CrypA

K11 and K1000 were mixed at the same volume ratio of 1 to 5. To each unit volume of the polymeric mixture, 30 unit volumes of 0.1601 % m/v of CrypA in THF were added. CrypA was completely dissolved in THF before being mixed with the polymers due to the low solubility of CrypA in the polymeric mixture. A uniform CrypA/polymer film was obtained by following this procedure: a blunt needle with gauge 22 was used with the distance between the needle tip and the crystal surface set to 5 $cm$. The flow rate was set to 1 $ml/h$ with an applied voltage of 15 $kV$. The electrospinning was continued until a frequency change of 50 $kHz$ was obtained.

6.3.5 Spin-coating of a CrypA and THF/SU8 3000 film

SU-8 is a negative photoresist originally developed by IBM [182] and is sensitive to wavelengths shorter than 360 nm [183]. When this photoresist is exposed to ultraviolet (UV) sources, a strong acidic group is formed. This step is followed by
epoxy cross-linking which is acid-catalyzed and thermally driven during the post exposure bake (PEB). Microchem produces different formulations of SU-8, specified by a number \( x \) ranging from 2-100 indicating the thickness of SU-8 film in \( \mu m \) at a spinning speed of 3000 \( rpm \) [183]. Thicknesses as high as 200\( \mu m \) can be obtained in one single run of the spin-coating and exposure process [184]. For this work, SU8-3005 was used in the following process [183]:

1. **RCA cleaning of crystals**: to obtain a good yield and reliability in the process, substrates should be as clean and dry as possible. For this purpose a basic RCA-1 clean (\( NH_4OH-H_2O_2-H_2O, 1:1:5 \)) was performed.

2. **Spin coating**: 3 \( ml \) of 1.601 \% \( m/v \) of CrypA in THF was mixed with 3 \( ml \) of SU8 3005. A few drops of this mixture were added to the crystal centre and the quartz resonator was spun at 5000 \( rpm \) for 20 \( sec \).

3. **Pre-exposure bake**: a level hotplate with control and uniformity of temperature was used for 1 \( min \), at 95\( ^\circ C \) for soft-bake step. In order to ensure that the baking temperature and time were optimized, the crystal was removed from the surface of the hotplate after 1\( min \) and was put aside until it reached the room temperature. The crystal was then put back on the hotplate and since no wrinkles were observed on the film, it ensured that the chosen conditions were ideal [183].

4. **Exposure**: an exposure energy dose of around \( 100 \frac{mJ}{cm^2} \) was radiated on samples using a standard lithography system.
(5) **Post-exposure bake**: this step was performed immediately after exposure and the QCM was put on the hot plate at 95°C for 1 min.

(6) **Developing**: Microchem’s developer was used to immerse the post-baked QCM for about 1 min, with moderate agitation.

(7) **Rinse and dry**: the sample was rinsed with fresh developer solution for approximately 10 sec followed by another 10 sec dipped in isopropylalcohol bath. The sample was subsequently dried using nitrogen gun.

(8) **Hard bake**: the sample was finally hard-baked (cured) at 150°C for 3 min on a hotplate.

### 6.4 Data and discussion

Methane gas bottles of 2.5 %, 1000 ppm, and 100 ppm concentrations were purchased with 0.25 LPM and 0.1 LPM regulators from Praxair and Cross Instrumentation, respectively. The experimental set-up used here was the same as the one employed for ammonia gas sensing. This set-up allowed us to control the concentration of methane and humidity.

After the deposition of the host CrypA molecules, the frequency response of the crystals was measured using the VNA. The quality factor, $Q$ of the crystal coated with film prepared by direct drop casting of CrypA solution in THF (Crystal A) was degraded substantially (from 9700 to 79) and the resulting system showed no measurable response to methane. At the same time, because of the low quality factor of the resulting QCM, the frequency behaviour of the circuit was sporadic
and subject to noises in the circuit and changes in the ambient conditions such as temperature and humidity fluctuations. Therefore, we speculated that a uniform layer of CrypA was not formed on the surface of the crystal. In other words, the film was composed of nanocrystal clusters rather than forming a homogenous layer on the substrate.

The quality factor of the crystal that was coated by drop-casting of CrypA in K1000/K11 polymeric film (Crystal B) was measured to be 210, which represents an improvement over the response of Crystal A. The resulting coated crystal, showed an approximate frequency change of 6 Hz after being tested with a methane concentration of 2.5%. The low sensitivity of this film was an indication of formation of nanocrystal clusters instead of a uniform film. The same result was obtained with or without a polymer. The only difference using the polymer technique is a slight improvement on the sensor behaviour, which is still far from being efficient enough to be used in practical applications.

The frequency response of the sensor, obtained by direct electrospraying of CrypA/THF on a crystal (Crystal C) was measured. The value of quality factor was found to be 712 which is better than Crystals A and B, but still much lower than the next two methods proposed here. On the other hand, since CrypA is not in a polymeric form, controlling the properties of the solution to be electrosprayed is particularly problematic. It was found that there is little control over the properties of the final film such as uniformity and thickness. Electrospraying avoids clustering of CrypA and helps to form a more uniform layer while leading to higher quality factor sensor. Since CrypA is not in a polymeric form, controlling
the proper ties of the solution to be electrosprayed is challenging, as there is little control over the properties of the final film.

The quality factor of the crystal coated by CrypA/ (K1000, K11) film via electrospraying method (Crystal D) was measured to be 3100. It can be seen that the quality factor is increased from 712 (Crystal C), to 3100 (Crystal D), for roughly the same amount of CrypA. This observation thus ensures more stability of the frequency response of the oscillator circuit and uniformity of the film on Crystal D. The scanning electron microscope SEM images of this film are provided in Figure 6-8. This figure shows that on Crystal D, fibres have been formed leading to higher surface area and uniformity of the resulting film as explained earlier.

Figure 6-8: SEM images of Crystal D at two different magnitudes
The reason for better quality of the films that are prepared by electrospinning of CrypA in polymer rather than electrospraying cryptophane alone can be attributed to the properties of polymer solution. The polymer solution has a higher viscosity and as high voltage is applied to the solution, a Taylor cone is formed at the needle tip and the solution is ejected from the apex of the cone towards the substrate. The high viscosity of the polymer solution prevents formation of small droplets. Furthermore, on the path towards the substrate, the polymer chains are entangled with each other and give rise to a uniform nanofibrous thin film with high surface area and better uniformity [185].

The frequency response of the crystal deposited by CrypA/SU-8 film (Crystal E), via spin coating and exposure method had a quality factor of 1580. SEM images of this film at two different magnitudes were obtained (Figure 6-9).
This sensor shows a quality factor of 1580 which is much greater than the traditional method of electrospraying CrypA film (Crystal C) solution without any polymer matrices but still lower than electrospinning technique used for Crystal D.

In order to compare the sharpness and stability of the sensors, the frequency responses of the crystals C, D and E were normalized and used to plot Figure 6-10. After the frequency response measurements of these crystals were performed, their response to methane gas was investigated at room temperature (25°C).

Figure 6-11 shows the diagram of frequency change, $\Delta f$ of the oscillator circuit, when Crystal D was subjected to a 2.5% concentration of methane. At first, nitrogen gas was driven inside the chamber until a stable frequency line was obtained. Afterwards, methane gas was led inside the chamber and the frequency response was observed until no further changes happen. At that point, the methane valve was closed and nitrogen was run into the chamber to remove the methane.
The methane trapped by the host CrypA molecules was released and the frequency of the oscillator went back to the baseline. The observed response for this QCM is much higher than those QCMs electrosprayed by CrypA/THF solution directly, which have been traditionally used to make methane gas sensors (200Hz for the saturation concentration with methane [186]).

As methane gas was led inside the chamber, the frequency experiences a fast drop at the start followed by a slower drop afterward, before reaching a stable equilibrium value (Figure 6-10). The same pattern is observed when methane valve is closed and nitrogen gas is released in the testing chamber: the frequency increases sharply at the start, followed by a slower rate to finally reach a stable value. The adoption/desorption principle was behind the observation which was explained previously in Chapter 5.

Figure 6-11: Response of Crystal D to 2.5 % methane concentration.
The response of the Crystal E to the same concentration of methane (2.5 %) was obtained (Figure 6-12). This response is obviously improved with respect to Crystals A, B and C.

The response of Crystals D and E were investigated to several other concentrations of methane and the results of frequency change were used to plot Figure 6-13 for zero humidity. It is evident that the sensor response is proportional to methane concentration. Furthermore, the slope of frequency with respect to concentration is lower at higher concentrations and is already approaching saturation at concentrations higher than 0.5 %. By comparing the responses of these sensors in Figure 6-13, it is worth mentioning that although both sensors exhibit the same pattern, the saturation value of the Crystal D coated with CrypA/ (K1000, K11) film, is lower than Crystal E. This shows that a methane sensor made by Crystal D would be a better candidate for the
monitoring of high concentrations of methane in places such as in mines and in applications with high levels of noise.

While, the response of the Crystal D, is better at lower concentration levels (the response of this film to 100 ppm methane is 5 Hz which is almost twice as much as the response of Crystal E (2 Hz) which shows better minimum detectable concentration (MDC) of methane with respect to other reported works.

The MDC of the sensors with respect to methane concentration was also found empirically by letting the QCM circuit run for one hour in order to reach a stable value. Afterwards, the frequency response of the QCM operating in the oscillator circuit was monitored for 10 min. It was observed that the frequency readings change within a range of 0.2 Hz for the Crystal D and 0.5 Hz for Crystal E. Using Sauerbrey’s equation and considering a signal to noise ratio of 3:1, these values of frequency change correspond to 5 and 7 ppm of methane.
concentration, respectively. The reason for this superior performance may be associated with better uniformity and surface contact of the film and improvements on quality factors of the resonators.

Since these sensors are supposed to operate under ambient conditions, the effect of humidity on these QCM was studied as well. Figure 6-14 shows the frequency change of Crystal D’s response when it is subjected to different levels of humidity. It is clear that the frequency of oscillation of the circuit is reduced as humidity level increases inside the gas chamber. At relative humidity levels of higher than 90%, the frequency change is as high as the saturation value of supra-molecular interaction of methane and CrypA for this film. In order to improve the performance of the sensor amid humidity, another substrate was electrospun by the same ratio of siloprene (K1000, K11) solution with no CrypA present this time. The electrospinning was continued until a 50 KHz drop in resonant frequency was obtained (the same frequency change as that of Crystal D used as the sensor).
Table 6-1 summarized the properties of the crystals coated for methane sensing.

Table 6-1: Summary of the properties of the crystals coated for methane sensing

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Film preparation method</th>
<th>Final Q</th>
<th>Response to 2.5% methane (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Drop-casting</td>
<td>79</td>
<td>Undetectable</td>
</tr>
<tr>
<td>B</td>
<td>Drop-casting (polymer)</td>
<td>210</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>Electrospraying</td>
<td>712</td>
<td>200</td>
</tr>
<tr>
<td>D</td>
<td>Electrospinning</td>
<td>3100</td>
<td>620</td>
</tr>
<tr>
<td>E</td>
<td>Spin-coating</td>
<td>1580</td>
<td>450</td>
</tr>
</tbody>
</table>

The response of this crystal to different levels of humidity was obtained (Figure 6-14). It is observed that these two QCMs show nearly identical response to the same amount of humidity. By using these two QCMs and considering that the one with siloprene, shows no response to methane, subtraction of their response in a differential fashion is a good measure of the concentration of methane in the presence of unknown amounts of humidity.
7: SENSING OF VOLATILE ORGANIC GAS COMPOUNDS USING THIN FILMS OF METAL ORGANIC FRAMEWORKS

One of the most dangerous groups of gases that constantly and pervasively jeopardize our well-being and resources are volatile organic compounds (VOCs). We are consistently at the risk of being exposed to VOCs in different ways. VOCs are commonly found in our ambient environment, soil, groundwater [4], atmosphere and workplaces including research labs and industries [5] [7].

Sources that contribute to production of VOCs are agriculture, energy, food and production industries, solvents, perfumes and landfill [187]. One of the main features of VOCs that makes them threatening to humans, particularly in closed areas, is their swift rate of evaporation, which quickly raises their concentrations to dangerous levels. We can be exposed to these vapours through our skin or by breathing the polluted air or by eating/drinking the contaminated food /drink.

In addition to humans, VOCs serve detrimental to the lives of animals and plants causing them to exhibit signs of chronic and acute toxicity, genotoxicity and volatile halogenated organic compounds (VHOCs) contribute to climate changes and destruction of the ozone layer [188] [189]. VOCs are known to
cause long-term health threats to human beings. Many of VOCs are carcinogens that could incur diversiform cancers such as lymphatic and hematopoietic types. They make liver and kidney liable to damages and spawn disorders and damages to immune, nervous and reproductive systems [190] [187].

There is an increasing demand for development of methods regarding quality control of water supplies. Water sources can be polluted by both manufactured and natural contaminations. Due to abundance of VOCs in industrial process and their wide and varying level of toxicity and physical and chemical properties, numerous researches have been carried out in water quality control area in order to develop reliable methods to quantify the materials [191].

A study on the profiles of the gases emitted during spoilage of meet showed that the gas comprises mainly of VOCs such as acetone and gases like carbon dioxide. Therefore, designs of fast, reliable, stable, robust, and affordable VOC sensors are highly desired in these areas as well [192].

Because of the very different properties that pollutants and toxic gases exhibit such as, different levels of toxicity and dipole polarity, and because of their occurrences at many varying aspects that affect us, in order to monitor and control their impacts, proper measurements have to be taken at several levels. At the first level, environmental monitoring can be carried out to detect greenhouse gases and other pollutants that can impair ozone layer. Moreover, proper actions should be undertaken on the local, indoor and outdoor levels for quality monitoring and detection of toxic, explosive and malodorous compounds [193].
Accordingly, a proper environmental monitoring procedure could start as identification of the polluted sites at first and then proceed to running fast, effective, simple, economically affordable and robust tests on the samples that can be taken from the allegedly polluted soils, air, food, plants or human and animal samples.

Presently, the most reliable and common method of quantification of VOCs is gas chromatography/mass spectroscopy (GC/MS) [194]. Although this is a precise method, it is time consuming and needs expensive chemicals and apparatus. Moreover, GC/MS is not usually suitable for online monitoring and requires troublesome liquid handling and sample collection. Unfortunately the results can even be sample specific. All these factors in the end limit the quality, quantity, and frequency of the testing [195]. As a result, development of fast, reliable, robust, non-destructive, economic, and stable sensors for detection of VOCs is highly demanded. Consequently, there is an increasing interest in the development of such sensors [196] [197] [198] and many researchers have been investigating new methods to design sensors with proper characteristics. Mitsubayashi et al. reported fabrication of a formaldehyde sensor using electrochemical detection based on enzymes [199]. In the work of Mascini et al. [200], piezoelectric sensors were employed to produce a dioxine biosensor. Tatsuri et al. reported a colloidal-based VOC sensor [201]. Colloidal crystals are three-dimensional periodic lattices that diffract light according to Bragg’s equation in a similar way as regular crystals. The lattice constant of the colloidal crystal determines the wavelength of the diffracted light. If the lattice constant is in
submicron range, the refracted beam’s wavelength will be in the visible region. This wavelength is referred as the structural color of the sensor. In their work, Polydimethylsiloxane (PDMS) was used to produce the sensors that operate at room temperature.

Measurement of the change in DC resistance of a semi-conductive layer exposed to an analyte gas has been used ubiquitously for detection of VOCs. Metal oxide semiconductor (MOS) sensors are probably the most widespread sensors of this class. Additionally, conductive polymers have recently attracted lots of attention on the way of development of VOC sensors. These sensors have been used for sensing of a wide spectrum of organic compounds including volatile halogenated organic compounds (VHOCs) [202] [203] [204] [205]. Conductive polymers have also been incorporated in electronic nose (E-nose) systems for detection of VOCs [206] [207].

Applications of E-nose systems to environmental monitoring, hazardous material detection, and water and food quality and safety evaluation have been previously reported [208] [209]. In many of E-nose systems, each individual sensor in the array is not sensitive to a single gas but each shows overlapping partial sensitivities to different analytes [210]. Therefore, pattern recognition (PARC) techniques are incorporated in the signal processing unit of the E-nose set-up. The most encouraging PARC method currently employed in gas sensing systems is based on artificial neural network (ANNs) [211]. The reason for this terminology is that they imitate the behaviour of human olfactory system to a
limited extent. Usage of E-nose systems for VOC monitoring can be affordable, reliable, and fast [212].

As it was mentioned earlier, monitoring quality of the vulnerable water sources is of crucial importance for safety and health of human beings. Conductive polymers and MOS-based sensors have been used for detection of pollutants in water supplies. For example, in [213] an effective chemiresistor is suggested for on-line, in-situ monitoring of VOCs in water supplies. Also, in [214] commercial tin-oxide is used to fabricate a MOS sensor for identification of VOCs. However, in both of these methods, the active part of the sensor is packaged inside a waterproof chamber with permeable membranes that allows vapour to pass through. This leads to only passive transportation of the gas and higher levels of integration for contact with water is not possible [195]. Furthermore, the system is also susceptible to temperature fluctuations. This shortcoming can be overcome by using microheaters [214], which could lead to more power consumption and complication of the system. Use of microfluidic sensors has the benefit of providing the required fluidic routings and large surface contact, in addition to more efficient delivery of the solvent. In [215] silicon-in-plastic microfabrication technology was used to produce a microfluidic-based VOC gas sensor operating in water supplies.

7.1 Metal Organic Frameworks

Metal-organic frameworks (MOFs) are made from metal ions connected with organic ligands acting as bridges. These materials are in the group of
coordination polymers which can possess one, two or three dimensional structures based on the structure of the organic linkers, how it joins the metal ions with each other and also the availability and characteristics of the vacancies on the metal ion sites [216].

Tomic [217] described materials made from bi- or tri-valent carboxylic acids and metals such as zinc, nickel, iron, aluminium, thorium, and uranium in an article in 1965. In the same year, Biondi et al. [218] reported on polymeric compounds made from copper (II) and tricyanomethanide ion. These materials were termed as metal-organic frameworks (MOFs) almost three decades later. Hoskin et al. reported on synthesis of copper (I) centres and tetracyanotetraphenylmethane in 1990 [219]. Significance of research on MOFs was revived by the works of Yaghi reporting the structure of MOF-5 and introducing the concept of reticular design in synthesis of MOF compounds [220]. So far, several hundreds of MOFs have been identified [221].

MOFs offer many interesting features that make them particularly appealing to the researchers. These materials are nanoporous and often have high mechanical, thermal, and chemical stabilities. Regularity and uniformity of their pore size and other properties make them exhibit elevated rates of molecular transport in addition to high surface areas. Furthermore, due to high modularity of their synthesis and wide range of inorganic-organic compositions, many of chemical, mechanical, and morphological properties of MOFs can be precisely adjusted [222].
Though other solid compounds such as zeolites, activated carbons, and oxides also show nanoporosity and high surface area of interaction, there is rather limited control over variations of chemical formula and functionality of the groups composed of these materials. Tailoring the pore sizes of these materials is challenging due to the absence of versatility of available chemical and morphological alterations. MOFs surpass this limitation by being equipped with both organic and inorganic sites, making engineering their pore sizes and properties more controllable [223]. The most important difference of MOFs and their inorganic counterparts such as zeolites is the typical absence of dead-volume in MOF structures [221]. This feature is the most desirable characteristic of MOFs that gives them the highest values of surface area and porosities [224]. Another difference between MOFs and other solid compounds such as zeolites is the absence of organic groups in zeolites, which makes them exhibit higher thermal stability. Therefore, zeolites are more suited for high temperature applications.

### 7.2 Synthesis of MOFs

MOFs can be synthesized in the general theme of providing the necessary organic linkers and inorganic sites in a proper form and allowing them to react under controlled conditions to favour, from a chemical equilibrium point of view, the formation of the products. This process is normally done through using soluble salts of the metal ion (nitrates, acetates, or sulphates), carboxylic acids of different valences as the organic linkers (mono, di, tri and tetra), and a polar
solvent such as an amine. The reactants are stirred for a few hours in a reaction chamber at temperatures ranging from room temperature to 200°C, followed by continuously recycling the solvent [225]. After the MOFs are gathered, drying and activation of the final product is highly significant, as due to high surface area and lack of dead volume, MOFs can carry large amounts of solvent within themselves. This activation process is usually done under mild pressure and temperature conditions at first followed by a harsher treatment under higher pressures and temperatures prior to their use. In large-scale production of MOFs, using of high concentrations of nitrates can be catastrophic and lead to explosions. Thus, an alternative method based on electrochemical reactions has been developed [226]. In this procedure, a metal ion is applied as the anode of an electrochemical cell with carboxylate solution. This method is particularly useful for MOFs with open metal sites.

Different characterization methods can be applied to MOFs to check their properties. For example, their crystallinity can be readily characterized by X-ray diffraction (XRD) and their porosity can be studied using an adsorption experiment [227].

7.3 Applications of MOFs

Having high porosities, large surface areas, total absence of hidden volumes and existence of modular methods to tailor the physical, chemical, and morphological properties of MOFs make them perfect candidates for many applications such as adsorption, separation, purification, catalysis and sensing.
7.3.1 Adsorption and purification of gases

MOFs with accessible metal sites can be used to adsorb small traces of electron-rich gases such as sulphur compounds, phosphines, and amines from other gases (e.g. natural gas supplies [221]).

7.3.2 Gas separation

MOFs have been investigated to replace the traditional methods such as distillation that are used for separation of gases like nitrogen-oxygen mixtures in air [228]. Specifically, adsorption of carbon dioxide is important because of the global warming awareness and due to its blatant greenhouse effect. Currently, separation of carbon dioxide emanated from fuel cells is adsorbed by reversible chemisorption reaction with an amine in an aqueous solution [221]. MOFs as substitutes for these aqueous amine solutions have been investigated [229]. When carbon dioxide is adsorbed on the surface of an MOF, it is bonded by physical dipole-dipole and Van der Waals forces. However, in the case of adsorption in amines, a stronger chemical bond is formed (chemisorption) which is more favourable thermodynamically. Presently, however, MOFs are not as efficient as aqueous solutions of amines for separation of carbon dioxide.

7.3.3 Gas storage

One of the most attractive applications of MOFs is their employment in gas storage industries. Because of the absence of dead volumes, MOFs can store large amounts of gas. The achievable level of storage is even higher than what is
possible in traditional methods such as gas cylinders. The reason for such behaviour can be explained by considering that inside a cylinder, the behaviour of the gas is governed by the equation of state of the gas, \( P = f(V, T) \) where \( P \) is the pressure, \( V \) the volume and \( T \) the temperature in the cylinder. In an MOF gas cylinder comprising of MOF and the free volume above the MOF, the gas is stored by two mechanisms. The first one is the storage of gas based on its equation of state, the same as the case for no MOF present in the cylinder. This mechanism is overlaid by the adsorption of the gas inside the MOF. The very attractive feature of MOFs to show almost no dead volume, makes up for the volume loss that has happened based on space blockings of the MOF structure. These two mechanisms together will contribute to higher storage capacities of MOFs over gas pressure cylinders. The limit on the density of storage of gas in MOF cylinders is set by the density of liquid state of the gas. In other words, MOFs cannot compress the gas more than its liquid density [221]. Some research for storage of acetylene, hydrogen, and other gases over MOFs has been conducted [230]. Furthermore, MOFs are shown to have more desirable adsorption properties compared with classical sorption materials such as zeolites. For instance, the adsorption of carbon dioxide and hydrogen on MOFs were found out to be almost twice higher than the zeolites [231].

### 7.3.4 Catalysis

Morphological and size selectivity are two of the main features of chemical catalysts employed in the processes. For solid materials, in order to exhibit these
properties, they should bear pores of uniform density leading to a highly ordered structure. Due to crystallinity of MOFs, pores are intrinsically incorporated within their structures, producing highly ordered structures. Moreover, lack of dead volume, as well as remarkable high surface areas of these structures, increases the density of active sites and the probability of their exposures. Interestingly, besides providing the highly porous and regular structure (due to preserving an extremely open structure) MOFs have quite reasonable diffusion rates and hinder the transport of the reactive ingredients, only to a little extent compared to pure solvents [232]. Therefore, considering all of these favourable features, MOFs are perfect candidates for heterogeneous catalysis. MOFs are currently applied for catalysis using three different approaches [221]: (1) their use as a carrier for the active mass; (2) insertion of the catalytically active groups inside the framework by altering the structure of known catalysts to make them form MOFs; and (3) creation of the coordination species and stabilizing it with the aid of the frameworks. This technique is specifically intriguing in the case that coordination species is unstable by itself under the conditions of the chemical reaction and the framework's function is to stabilize it. A review on application of MOFs in several famous instances including Ziegler-Natta polymerization, Diels-Alder reaction, and photoreactions is provided in [233].

7.3.5 Sensing applications

Since MOFs provide high surface areas and extraordinary regularity of porosity in addition to reversible sorption characteristics, they are encouraging candidates to
be used as sensitive materials for gas sensing technology. Even though MOFs have been extensively studied for a wide range of industrial applications including molecular sieves, desiccants, ion exchangers, gas storage cylinders and catalysts, little research has been done on their implementation as sensitive layers integrated in gas sensors. When an MOF layer is exposed to an analyte gas, changes in properties of the MOF can be measured and used to detect and quantify the gas. The alterations may include the dielectric properties of MOF layer giving rise to change in impedance of the material. However, adsorption/desorption of the analyte gas on MOF can also induce mass changes that can be detected using gravimetric sensing methods, e.g., the change in the resonant frequency of a QCM coated by MOF film. Due to possibility of synthesis of MOFs with a wide and versatile range of morphological, chemical, and physical characteristics as well as the possibility of engineering of the sizes on the highly ordered pores in MOFs, they are promising candidates for gas sensing applications. Furthermore, proper MOFs can be designed and utilized to detect a wide spectrum of analytes under varying conditions of temperature and concentration of the gas. Achmann et al. [234] studied the capability of MOFs to detect different levels of humidity in gas atmosphere. It was reported that adsorption/desorption of gas species can result in notable changes of the structures of MOFs, e.g., a crystal transformation between two tetragonal structures was observed for hydration/dehydration of MIL-53 MOF [235] [236].
7.4 Experiment setup

In our work, HKUST-1 MOF is used to fabricate gravimetric mass sensors for detection of VOCs including acetone, isopropyl alcohol (IPA) and tetrahydrofuran (THF). HKUST-1 has the structural formula $Cu_3(BTC)_2(H_2O)$ [237]. Single-crystal studies on this MOF have shown that this material is comprised of face-centred-cubic crystals containing an intersecting three-dimensional system of large square-shaped pores. Copper (II) centres produce dimers having each copper atom coordinated by four oxygen groups coming from benzene-1,3,5-tricarboxilate ligands and by one water molecule [238]. The copper (II) centres are joined together by weak bonds and the coordination site occupied by water molecule can be readily made available by heating the MOF to $110^\circ C$. The availability of this coordination site makes HKUST-1 a perfect candidate for catalysis and detection of electron-rich compounds such as VOCs [239]. HKUST-1 structure comprises of two cages and two windows, each one on either sides of the cages. The large cages (13.2 and 11.1 Å in diameter) are interlinked by square windows ($9 \times 9$ Å) and tetrahedral shaped side pockets (6 Å) through triangular shaped windows ($4.6 \times 4.6$ Å) [39].

7.4.1 Thin film fabrication

Two methods were investigated to fabricate an MOF layer on the surface of quartz crystals (QCMs had the same specifications as explained in earlier chapters):
7.4.1.1 Drop-casting

HKUST-1 MOF in the form of crystalline blue powder was purchased from Sigma-Aldrich. 10 mg of the MOF was mixed vigorously with 5 ml of THF to make a suspension (0.2 % m/v). This suspension was successively drop-casted at the centre of the electrode of a crystal using a 1 ml syringe. The crystal was then removed from its packaging and baked inside an oven at 150 °C for 3 hr. It was noticed that the adhesion of the resulting film on QCM was not sufficient and the film would loosen and fall during further processing. Therefore, another approach was investigated. After taking the crystal out of the oven, a few drops of THF were added to the film and the film was put back inside the oven for another hour. After repetition of this procedure for 3 times, the resulting film showed good adhesion to the surface of the crystal. The frequency change of the crystal was about 40 kHz.

7.4.1.2 Electrospraying

The same suspension (0.2 % m/v) of MOF in THF was used for this purpose. Since MOF molecules cannot be dissolved in THF, electrospraying of the suspension in a traditional set-up did not succeed. The reason can be attributed to the precipitation of the MOF molecules on the lower part of the syringe. It was noticed that the liquid exiting the needle tip was transparent. So it was assumed that a successful electrospraying has not taken place. This assumption was further verified by the following observation. The suspension was electrosprayed on one crystal. The voltage and the feed-rate were set at 15 kV and 1 ml/h,
respectively, with the distance between the needle tip and the collector set to 5 cm. After the electrospraying of the suspension for 10 min, the resonant frequency of the crystal was measured immediately. It was noticed that the frequency had dropped by 10 kHz. However, the frequency would drift back to its original value in a few minutes. Therefore, it was speculated that only solvent molecules have been deposited on the surface of crystal and then evaporated.

In order to circumvent this issue, two methods were investigated. In the first method, liquid soap was added to the solution as a surfactant. This surfactant reduced the surface tension of the solvent and extended the time that MOF molecules are floating in the solvent. The resulting solution was successfully electrosprayed on the surface of a crystal (at 15 kV, 1 ml/h of feed-rate and 5 cm distance).

However, the resulting film exhibited no reversible affinity towards VOCs. The reason for deterioration of sensor characteristics can be attributed to the presence of surfactants on the MOF film over the crystal. We assumed that these surfactant molecules have occupied the available cavities inside the MOF. Therefore, the MOF shows no response to VOCs.

In the other method, the syringe was put vertically above the surface of crystal (Figure 3-1). This time the precipitation of the MOFs from the suspension were done on the surface of the syringe that contained the orifice. It was noticed that MOFs can be electrosprayed on the samples using this method. The voltage and the feed-rate were set at 15 kV and 0.6 ml/h, respectively. The distance between
the needle tip and the collector was set at 20 cm. A higher distance of separation between the collector and the needle tip was chosen compared with the other films. The reason was to ensure that most of the THF would evaporate on its route towards the collector. All of these electrospraying experiments were performed with a gauge 15 needle. The electrospraying was continued until 40 kHz of change in the frequency was observed.

Figure 7-1: Schematic of vertical electrospraying used for generation of thin MOF films
7.4.2 Gas experiment set-up

An altered version of the set-up that was used for methane and ammonia sensing was employed. The set-up allows relative changes of the concentration of the organic vapour (Figure 7-2). A nitrogen tank connected to chamber A (1 L) through a gas valve was the starting point for our set-up. Nitrogen was lead to Chamber A which was connected to two flowmeters FM1 and FM2, which in turn were connected as described here. The gas line out of flowmeter FM1 was driven into a bubbling system containing the organic solvent to generate a nitrogen/organic vapour mixture, which was directed to another chamber where it was mixed with nitrogen from flowmeter FM2. This part of the set-up allowed for a tight control of the relative concentration of the gases through the control of the ratio of the flow of FM1 and FM2 flowmeters. The flow out of this chamber was directed to the gas sensing chamber containing the operating QCM in an oscillator circuit.

Using this setup, the responses of these sensors to three widely used organic vapours of acetone, THF and isopropyl alcohol (IPA) were investigated.

7.4.2.1 Determination of the concentrations of VOCs

Since the standard bottles of VOC vapor were not available, the relative concentrations of VOCs were obtained by the setup in Figure 7-2. It was assumed that for low flow values of the nitrogen inside the bubbler, the flow out of the chamber is saturated with the organic vapour. The equation of state of ideal gases can be formulated as: \( PV = nRT \) where \( P \) is the pressure, \( V \), the
volume, $n$, the number of moles, $R$, the universal gas constant and $T$ the temperature of the gas. At constant temperature, it is implied that the partial pressure of the gas is proportional to its concentration ($P \propto (n/v)$). The vapour pressures of acetone, THF and IPA (at 25 °C) are 180 mmHg, 143 mmHg and 40 mmHg, respectively [240] [241]. Considering the pressure of the air to be 760 mmHg, the mole fractions of these three vapours are calculated as 23 %, 20 % and 5 %, respectively.

Figure 7-2: Gas-sensing set-up used for VOC measurement
7.5 Results and discussions

7.5.1 Frequency response measurement and film qualities

After thin films were produced on the crystals, their frequency responses were measured using the VNA. The quality factor of sample prepared by electrospraying was measured using a VNA to be 5000 which was improved by a great amount compared to the value of 864 when using drop casting for roughly the same amount of HKUST-1. The normalized frequency responses are shown in Figure 7-3. The SEM images of the electrosprayed crystal are presented in Figure 7-4.

The obvious improvement on the quality factor of the electrosprayed crystal ensures formation of a much more uniform layer that results in superior performance in the oscillator circuit and provides better sensitivity and detection limit. On the other hand, the lower quality factor of the crystal can be pertained to formation of less uniform film as a result of clustering of the MOF crystals on the surface of the substrate.

7.5.2 Response to VOCs
After the frequency response of the crystals was measured, they were transferred to the gas set-up to measure their responses to the organic vapours. The response the film with drop-casting method to saturated IPA vapour is shown in Figure 7-5. As it can be seen, the response of this device is not reversible. At first, nitrogen gas was purged inside the chamber until a stable frequency line was obtained. Afterwards, organic vapour was led inside the chamber. This leads to a fall in the frequency due to the adsorption of the organic vapour on the film. Subsequently, the organic vapour valve was closed and the chamber was purged with nitrogen. This process was repeated for two times. However, as can be seen from Figure 7-5 the frequency did not drift back to the original base-line after $t = 1000$ sec.

![Figure 7-3: normalized frequency response of the crystals](image-url)
On the other hand, the response of electrosprayed film was much improved. The reversibility of the interaction of the electrosprayed films to VOCs nominates them as viable candidate for VOC sensing. The response of the electrosprayed films to vapours of acetone, THF and IPA are shown in Figure 7-6. The reversibility of the response of this crystal can be associated with higher uniformity and surface area due to electrospraying. The adsorption of organic vapours on the MOFs is taking place as a result of Van der Waals and dipole-dipole interactions between the gases and the film. As explained earlier, the frequency response change is due to adsorption and desorption taking place on the film. When the film is not uniform and in the form of crystal clusters, the surface area of contact is reduced and the rates of adsorption and desorption are reduced significantly. This effect makes the response mainly irreversible. Furthermore, it was demonstrated in chapter 3 that the sensitivity of the QCM is reduced as the thickness of the film is increased. Drop-casted films have lower

Figure 7-4: SEM photos of the electrosprayed MOF crystals on the substrate
surface areas compared to electrosprayed films. Therefore, for the same amount of MOF, they have higher effective thickness and therefore lower sensitivity.

Figure 7-7 shows the response of electrosprayed film to different concentrations of acetone, THF and IPA. As can be seen, the amplitude of response is decreased as the concentration of organic vapours is reduced and this response is more linear at lower concentrations. The slope of the frequency change is higher for IPA; the reason can be associated with lower vapour pressure of IPA at room temperature giving rise to lower concentrations in the gas mixtures. The sensor is in the saturated region when it is treated with high concentrations of VOC gases. This means that the response of the sensor is not very sensitive to changes in the concentration of the gases in this level of concentration; however, since IPA has the lowest vapour pressure (and thus lower concentration), we saw the highest slope in its diagram of frequency change versus concentration (Figure 7-7).

![Figure 7-5: The response of the drop-casted film to saturated IPA vapor.](image-url)
Figure 7-6: Response of the electrosprayed film to IPA, acetone and THF.
7.5.3 Minimum detectable range

The lowest detectable value of VOC concentration was also found empirically by letting the QCM circuit run for one hour in order to reach a stable value. Afterwards, the frequency response of the QCM operating in the oscillator circuit was monitored for 10 min. It was observed that the frequency readings change within a range of 1 Hz for the crystal with electrosprayed film (the changes were much smaller before contact with VOCs, but the stability was degraded after the first experiment. Therefore, in order to make our estimations more precise, the value of 1 Hz is chosen).

Using Sauerbrey’s equation and considering a signal to noise ratio of 3:1, this value of frequency change corresponds to detection limits of

![Figure 7-7: Response of the electrosprayed film to different concentrations of VOCS](image)
100 ppm, 50 ppm and 10 ppm for acetone, THF and IPA, respectively. This calculated theoretical value is particularly valid for IPA due to the fact that its measurements were performed at lower concentrations (and hence more linear) compared to the acetone and THF which have higher vapour pressures. The frequency change of the drop-casted crystal was also monitored for 10 min and was found to be 5 Hz. This shows that other than having poorer uniformity, the drop-casted film is also suffering from lower stability of its circuit.

Figure 7-8 shows the response of the electrospayed film when it is exposed to 50% level of humidity. As it can be see, the MOF has a strong attraction for water through hydrogen bonding from its organic sites. Moreover, the metal site (copper ion) has a very strong attraction for the lone pair electrons on the oxygen atom. Therefore, as it is expected, the interaction between the electrospun MOF film and water vapour is not linear or reversible.
8: CONCLUSIONS

In this work, various methods were investigated in order to improve the qualities of the sensing layer to produce higher surface areas, uniformity, control over the thickness, and more robust mechanical properties. We employed supramolecular interactions to selectively detect and sense gases such as ammonia, methane, organic vapours (e.g., acetone, tetrahydrofuran and isopropyl alcohol) and humidity. Some of the methods that were employed in this project include electrospinning and electrospraying with different configurations, spin-coating followed by exposure and drop-casting. However, the main focus was devoted on optimizing electrospinning and electrospraying techniques.

A brief review was given on the existing gas sensing technologies including optical, conductive, electrochemical and piezoelectric gas sensors. Other reviews were provided on properties of metal-organic frameworks and their potential exploitation in gas sensing applications as well as the features and mechanisms of electrospinning processes.

A custom-built electrospinning apparatus was set up in order to fabricate the thin films on the sensors. A homemade gas sensing set-up was developed that allowed us to control the analyte gas concentration and humidity.

Ammonia and humidity sensors were prepared by electrospinning different ratios of PAA and PVA polymers on the surface of the crystals. It was noticed
that the PAA cannot be incorporated directly for detection of ammonia due to its high affinity for water molecules through hydrogen bonds. This strong attraction would hamper the response of the sensor. It was further noticed that PVA can be used as a possible candidate for humidity sensing as it shows reversible response to humidity unlike the sensor incorporating PAA as well. An optimized ratio was determined for best results with ammonia sensing. Furthermore, the effects of different parameters of electrospinning process were investigated on the quality and features of the resulting film. It was seen that a 30% ratio of PAA/PVA could be successfully used for determination of ammonia gas.

Cryptophane A was synthesized by an improved 2-step trimerization method and was used to prepare uniform supra-molecular films on the surface of quartz resonators for methane sensing purposes. The response of these sensors to different concentrations of methane was investigated. Five coating methods were investigated to improve the performance of currently used supra-molecular-based methods for detection of methane. One of the methods for the preparation of these uniform films was based on spin coating of CrypA/SU-8 film over the surface of the crystals followed by exposure, leading to a sensor with much improved quality factor. The oscillator circuit operating on this quartz resonator showed promising stability and low limits of detection for methane compared to the literature precedents. Another method was based on electrospinning of cryptophane A solution in a siloprene polymer. This sensor also exhibited a higher quality factor and improved response over the previously reported sensors. The oscillator circuit employing these crystal displayed more stability.
and low detection limits for methane as well. Based on this observation, this sensor was found to be ideal for the detection of very low methane concentrations. The responses of these crystals to different levels of relative humidity were also investigated as well as the response of a reference crystal without cryptophane A. We observed that the response of this crystal to humidity is identical to the behaviour of the working sensor. Therefore, differential use of the crystal as the reference can be a solution to the problems of humidity for its practical applications.

Finally, a new sensor was developed for detection and determination of organic vapours such as acetone, THF and IPA. A technique based on vertical electrospraying was employed to deposit thin layers of the MOFs on the surface of sensors which were otherwise very difficult to generate. It was demonstrated that our electrospraying technique resulted in maintaining a significantly higher quality factor, and hence, improving the sensor resolution and stability. The response of this sensor to different concentrations of the organic vapours was studied and analyzed. The effect of humidity on their response was investigated as well.

The data collected in this project can be used as the core to produce the characteristics data and the learning methods after application of a reduction method. In some cases of multi-gas sensing applications, where each sensor is showing response to a wide range of analytes, much more advanced learning algorithms are required. Moreover, the precision of the system is lowered in these cases. However, based on the selectivity experiment results, our devices
show response to a limited range of analytes. The following observations were obtained for selectivity measurements in this project: the sensors that were fabricated by use of cryptophane A only showed sensitivity to methane and humidity. These sensor, did not give any measurable changes when they were subjected to carbon dioxide and ammonia. The differential use of two sensors prepared from siloprene and siloprene/ Cryp A respectively can be used to eliminate the effects of humidity. In the case of ammonia sensing, the sensor prepared from PVA showed sensitivity only to humidity. Therefore by incorporation of sensors made from PVA and PAA/PVA the effects of humidity on the sensor response at low humidity levels can be minimized. The PAA/ PVA sensors showed no response to carbon dioxide and methane as well. Moreover, the crystals coated by MOFs showed no response to methane, ammonia and carbon dioxide. Consequently, the sensors developed in this project exhibited the favourable characteristic of low cross-sensitivity to other gases. The data obtained from the transient and steady state responses can be incorporated to extract some information about the presence/ concentration of a gaseous species.

The work presented in this thesis has resulted in following publications:


**8.1 Future work**

The gas experiment set-up in this project does not allow dilution of gases below a certain limit. Using a more advanced gas-sensing set up with tighter control over the concentration and temperature can obviously provide more information about the characteristics of the sensor. For experiments with VOCs, the dilution of their concentrations was done more easily compared to the experiments requiring a standard gas bottle compared to the experiments for methane or ammonia sensing. The reason is due to the higher possible gas flow through the bubbler as opposed to the gas bottles with a fixed flow. However, their relative concentrations at low dilutions could not be determined with certainty. At higher
flow rates, the gas cannot be said to be in equilibrium with the liquid inside the bubbler, and therefore, the real concentration of the gas should be lower than expected. One possible solution to mitigate this problem is the use of a stirrer inside the bubbler to provoke equilibrium conditions faster than usual.

One possible future work can be on application of HKUST-1 MOF for carbon dioxide sensing. This idea has the preliminary backing that when the MOF coated crystals were put inside the vacuum chamber to take SEM images, their colour had changed to very dark blue. We speculated that this effect was due to desorption of carbon dioxide from the film. The concentration of carbon dioxide in air is quite high (0.04 %), and therefore, in order to study the response of MOFs, the prepared films need to be tested under vacuum conditions.

For the case of methane gas sensors, cryptophane A showed a very promising response. Unfortunately, the yield of the synthesis reaction of this molecule is very low and separation of this molecule from the crude product is very time-consuming. All the experiments in this work were performed by using only 0.4 g of cryptophane A. Therefore, if more runs of the synthesis of this compound are carried out, other experiments can be conducted. For example, the spinning rate and concentration of cryptophane A in the spin-coating process can be studied for a few samples and their optimized values can be obtained. More experiments can also be conducted on the response of these sensors to methane in the presence of humidity. Moreover, a more advanced gas sensing setup, would allow bringing the concentration of methane to even lower values
than this work, where we believe our sensors will outperform the alternative devices.

The ultimate purpose of these sensors is their employment in multi-gas sensing applications. The PAA/PVA films showed response only to ammonia and the cryptophane A exclusively responded to methane. MOF’s responses to the three different organic vapours are distinct from each other. Therefore, these films have promising potentials to be used in multi-gas sensing applications.

Application of the prepared thin films in this work to other sensors especially SAW devices is possible as several of these sensors can be fabricated adjacent to each other on the same wafer and coated with different materials. By using reference sensors on the same wafer, the effects of noise and temperature fluctuations can be minimized. However, they give rise to lower quality factor sensors and require more complicated electronics for their corresponding measurements.

One of the devices that can be ultimately used in gas sensing applications, are a new level of resonators referred as pn junction resonators. These devices have recently been developed by Ransley [242] [243], and simulation of their performance was performed during this project.

Depletion region resonators presented in [242] [243] use the attractive force between opposite charges in the carrier depleted regions. Based on this technique the regions of opposite charges can be as close as 10nm for a typical CMOS doping level of $10^{16} cm^{-3}$ and 1nm for a harsher doping level of $10^{20} cm^{-3}$ compared to the best gap sizes in electrostatic gap resonators which amount to a
few hundreds of nanometres [244]. Consequently, pn junctions from the perspective of the distance between the opposing charges are very similar to piezoelectric resonators. However, due to higher crystallinity and lower loss in silicon wafer, fabrication of high quality factor devices is possible. Additionally the microfabrication process in order to make these devices is compatible with integrated circuit technology processing.

The benefit of using pn junction resonators for gas sensing applications is the ease of their integration with microelectronic circuits. Moreover, many of these resonators can be fabricated on one chip and coated with different materials in order to be used for multi-gas sensing applications.
APPENDIX A: OSCILLATOR CIRCUITS

Employment of oscillator circuits can be considered as the most convenient method to monitor the frequency changes of quartz crystal circuit. Because of the substantially high quality factors of quartz crystal, stable oscillation can be excited by quite simple circuits [245].

By ignoring the non-linear effects and pre-oscillation process, the conditions required for oscillation to occur can be summarized as:

\[ |k A| \geq 1 \]
\[ \phi = 0, 2\pi, ... \]

where \( A \) is the open-loop gain, \( k \) is the feedback factor and \( \phi \) is the phase change along the loop. The former condition is referred as the amplitude condition while the later is referred as the phase condition for successful oscillation.

For the optimal performance of the oscillator, the crystal must maximize the oscillator’s gain at the resonant frequency and minimize it at other frequencies. It was shown in chapter 3 that at the series resonant frequency, the imaginary part of the admittance of the crystal is set to zero and hence the value of impedance will have a peak (equal to the series resistance of the crystal). Therefore, use of the crystal as a series resonance element can satisfy the
condition of maximum gain at resonant frequency. A typical oscillator circuit using crystal as a series element is shown in Figure 3-1. Both the source and load resistances should be low compared with the crystal's impedance at series resonance in order to give the crystal the maximum amount of control on the loop-gain.

Another possible approach is to use the crystal as a shunt element. In this configuration, the crystal is the shunt part of a voltage divider whose series element is either a capacitor or an inductor. If the series element is a capacitor, the phase conditions of the oscillation around the loop are not satisfied. Therefore, another 90° phase-lead or phase-lag is required in the circuit. If a phase-lead network is added to the shunt crystal configuration the circuit is usually referred as the Miller circuit (Figure A-3). In the case of employment of a lag network, the circuit is referred to as Colpitts circuit (Figure A-2). In order to satisfy the phase condition, the Colpitts circuit requires an inverting amplifier while the Miller circuit requires a non-inverting amplifier.

In practice, the phase lead and lag networks cannot fulfil their 90° of phase shift and the actual value is slightly less. However, this does not threaten...
the performance of the circuit as the oscillation frequency will shift slightly to right or left in order to compensate for the less-than-90° phase shifts of the lead or lag networks [246]. If the frequency shift of the circuit is not sufficient to provide the required phase shift, other levels of RC networks can be added to the circuit.

The disadvantage of Miller circuit is poor resonance stability, while Colpitts circuit has much better frequency stability [246].
A widely-known example of series-resonant oscillators is the Pierce circuit (Figure A-4). This circuit has many desirable characteristics. It can be tuned to work at any frequency from 1 kHz to 200 MHz. Furthermore, since the crystal’s load and source impedances are capacitive; it gives rise to higher in-circuit Q making the circuit’s response more stable. Pierce circuit has got desirable power characteristics as it provides large output signals and provides high output voltage swing. The low power level makes this circuit particularly useful for higher frequencies, where crystals have low dissipation ratings [247]. Moreover, the large phase shifts provided by the RC networks and large shunt capacitances offer several advantages such as making the resonant frequencies less sensitive to small changes in the series resonance or shunt capacitances. In addition, the RC networks act as filters and minimize the amount of unwanted spikes and noise.

Figure A-4: Pierce oscillator circuit diagram.
According to Figure A-4, at the series resonant frequency the crystal’s impedance is only a resistance and provides $90^\circ$ of phase shift together with $C_2$. Below this frequency, the crystal shows capacitive behaviour and hence forms a voltage divider with $C_2$ with zero phase shift. On the other hand, above the resonant frequency, the crystal is in inductive mode and provides $180^\circ$ of phase shift along with $C_2$. Therefore, by just a slight change in frequency, the phase can be shifted from zero to $180^\circ$ [246]. Figure A-5 shows the schematic of the Pierce oscillator circuit that was used to prepare a printed circuit board (PCB) for our work. Other than this circuit, a 10 MHz lever lab oscillator from International Crystal MFG was used in the experiments.

Figure A-5: Schematic of the oscillator used in this project


and physical sensors based on oxygen pumping with solid-state


[121] A Formhals, 1975504 , 1934.


[126] St. John M R. Larrondo L, "Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties.," *Journal of


[158] V.V. Malyshev and A.V. Pislyakov, "Dynamic properties and sensitivity of semiconductor metal-oxide thick-film sensors to various gases in air


[220] D. Y. Siberio-Pérez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M.


