Integration of Conventional Lithography and Printing Processes as a Key Enabling Technology for Printed and Flexible Sensing Systems

Binu Baby Narakathu
Western Michigan University, binubabyn@gmail.com

Follow this and additional works at: https://scholarworks.wmich.edu/dissertations

Part of the Chemical Engineering Commons, and the Computer Engineering Commons

Recommended Citation
Narakathu, Binu Baby, "Integration of Conventional Lithography and Printing Processes as a Key Enabling Technology for Printed and Flexible Sensing Systems" (2014). Dissertations. 386.
https://scholarworks.wmich.edu/dissertations/386

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.
INTEGRATION OF CONVENTIONAL LITHOGRAPHY AND PRINTING PROCESSES AS A KEY ENABLING TECHNOLOGY FOR PRINTED AND FLEXIBLE SENSING SYSTEMS

by

Binu Baby Narakathu

A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy
Department of Electrical and Computer Engineering
Western Michigan University
December 2014

Doctoral Committee:

Massood Z. Atashbar, Ph.D., Chair
Bradley J. Bazuin, Ph.D.
Margaret Joyce, Ph.D.
Paul D. Fleming, Ph.D.
Sensors, which are used ubiquitously in a wide variety of applications, are revolutionizing the already ever-changing world we live in by providing real-time information about our surroundings. This dissertation focuses on the integration of conventional photolithography and printing processes as a key enabling technology for printed and flexible sensing systems.

Initially, an efficient opto-electrochemical sensing system, for the dual detection of heavy metal compounds was successfully developed. A novel microfluidic flow cell, with a reservoir volume of 25 µl, was designed and fabricated using acrylic. An electrochemical sensor with gold (Au) interdigitated electrodes (IDE) on a glass substrate was photolithographically fabricated. Electrical impedance spectroscopy (EIS) performed on cadmium sulfide (CdS) and mercury sulfide (HgS) yielded picomolar concentration detection levels. Selective detection of CdS and HgS was made possible based on optical signals produced in the Raman emission spectra.

Then, conventional printed circuit board (PCB) and traditional printing technologies were employed to develop an electrochemical microfluidic sensing
platform (MSP) for the detection of bio/chemicals. IDEs were fabricated by inkjet printing silver (Ag) ink on a flexible polyethylene terephthalate (PET) substrate. PCB technology was used to create master molds for polydimethylsiloxane (PDMS) based microfluidic channels. The printed PET substrate and PDMS microfluidic channels were bonded to form the MSP. The EIS based response of the system towards CdS and HgS revealed picomolar detection levels as well as the feasibility of integrating PCB and printing technologies to create flexible MSPs for various bio/chemical sensing applications.

Finally, a novel fully printed flexible pressure sensor was also fabricated using traditional screen and gravure printing techniques. The sensor was printed on a flexible PET substrate with Ag nanoparticle (NP) ink as metallization layer and PDMS as dielectric layer. The capacitive response of the sensor demonstrated a percentage change of 5% and 40% for the minimum and maximum detectable compressive forces of 800 kPa and 18 MPa, respectively when compared to the base capacitance of 26±0.007 pF. The response of the sensor demonstrated the feasibility of employing printing techniques for the fabrication of flexible pressure sensing devices.
ACKNOWLEDGMENTS

Education, the long and arduous path to wisdom, is seldom achieved alone. It is a journey that is often accomplished through the selfless and invaluable support from your teachers, friends and family. I would like to express my sincere and heartfelt thanks to each and every individual who has supported me throughout the course of my dissertation.

First and foremost, I want to express my deepest gratitude and sincere thanks to my advisor, Dr. Massood Z. Atashbar, who has been a constant source of guidance and encouragement. This work would not have been possible without his expertise and persistently generous advice. His confidence and trust in my knowledge and abilities has helped me to progressively explore novel ideas. I also want to thank all the members on my committee: Dr. Margaret Joyce, Dr. Bradley J. Bazuin and Dr. Paul D. Fleming for their esteemed comments and support of my dissertation.

I would like to express my sincere appreciation and profound gratitude to Sai Guruva Avuthu Reddy, Ali Eshkeiti, Sepehr Emamian and Zeinab Ramshani for their great friendship and help in the Sensors Technology Laboratory (STL), the Center for Advanced Smart Sensors and Structures (CASSS) and the Center for the Advancement of Printed Electronics (CAPE). I want to thank everyone in the Electrical and Computer Engineering (ECE) Department, Chemical and Paper Engineering (ChP) Department for the support and all resources provided to me during the course of this dissertation work. Moreover, many thanks go to Dr. Sandrine
Acknowledgments—continued

Martin, Dr. Pilar Herrera-Fierro and Dr. Katharine Beach for providing access to the Lurie Nanofabrication Facility (LNF) at the University of Michigan. I also want to thank Mr. Thomas Vaalburg for his technical support.

I am grateful to my entire family for supporting me throughout this endeavor. I would like to thank my wife, Simi Kothanath, whose constant love and encouragement has kept me motivated throughout these tireless years. I am eternally grateful to her for the endless emotional support and tolerance of my insensitivity, while I was busy with my education and research. It is with the warmest respect and love that I acknowledge my parents, Baby Narakathu Poulouse and Jancy Baby Narakathu, who have raised and nurtured me with unconditional love. I am also grateful to my in-laws, Dr. T.P. Ramachandran and Shoba Kothanath, for their understanding of my absentmindedness during the course of this work. I would also like to thank my siblings, Nibu Baby Narakathu and Niju Baby Narakathu, as well as my brother-in-law, Sekher Kothanath, and my sisters-in-law, Megha Ramesh and Katherine Saju, who have all been an unwavering wall of support. I would have never achieved my goals without all of my family being an integral part of my life and thus I dedicate this degree to all of them.

Binu Baby Narakathu

iii
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................... ii  
TABLE OF CONTENTS ......................................................................................................... iv  
LIST OF TABLES ................................................................................................................... ix  
LIST OF FIGURES .................................................................................................................. x  

## CHAPTER

### I. INTRODUCTION .............................................................................................................. 1  
1.1. Motivation ........................................................................................................................... 1  
1.2. Author’s Contributions ...................................................................................................... 4  
1.3. Organization of the Dissertation ......................................................................................... 5  
1.4. References .......................................................................................................................... 7  

### II. LITERATURE REVIEW ................................................................................................ 13  
2.1. Introduction ....................................................................................................................... 13  
2.2. Sensors ............................................................................................................................. 14  
2.2.1. Introduction to Sensors ................................................................................................. 14  
2.2.2. Sensor Science ............................................................................................................. 15  
2.2.3. Sensor Characteristics ................................................................................................. 18  
2.2.3.1. Sensitivity ................................................................................................................. 19  
2.2.3.2. Selectivity ................................................................................................................ 20  
2.2.3.3. Dynamic Range ....................................................................................................... 21  
2.2.3.4. Accuracy ................................................................................................................ 21  
2.2.3.5. Resolution .............................................................................................................. 22  

iv
| CHAPTER |
|------------------|------------------|
| 2.2.3.6. Noise .......................................................... | 22 |
| 2.2.3.7. Calibration .................................................. | 23 |
| 2.2.3.8. Hysteresis .................................................... | 24 |
| 2.2.3.9. Non-Linearity .............................................. | 24 |
| 2.2.3.10. Saturation .................................................. | 26 |
| 2.2.3.11. Repeatability ............................................... | 26 |
| 2.2.3.12. Dead-Band .................................................. | 27 |
| 2.2.4. Types of Sensors ................................................ | 27 |
| 2.2.4.1. Acoustic Sensors ............................................ | 29 |
| 2.2.4.2. Thermal Sensors ............................................. | 30 |
| 2.2.4.3. Chemical and Biological Sensors ........................ | 32 |
| 2.2.4.4. Optical Sensors ............................................... | 34 |
| 2.2.4.5. Mechanical Sensors .......................................... | 35 |
| 2.3. Electrochemical Sensors .......................................... | 37 |
| 2.3.1. Electrochemical Sensor Configurations ..................... | 39 |
| 2.3.1.1. Voltammetric and Amperometric Sensors .................. | 39 |
| 2.3.1.2. Potentiometric Sensors ...................................... | 40 |
| 2.3.1.3. Conductometric Sensors ...................................... | 41 |
| 2.3.1.4. Capacitance and Impedance Sensors ....................... | 41 |
| 2.4. Raman Sensors .................................................... | 42 |
| 2.5. Pressure Sensors .................................................. | 44 |
Table of Contents—continued

CHAPTER

2.5.1. Detection Techniques ................................................................. 45

2.6. Printed Electronics ........................................................................... 46

2.6.1. Why Printed Electronics? ............................................................. 47

2.6.2. Challenges in Printed Electronics ................................................. 48

2.6.3. Types of Printing ........................................................................... 49

2.2.3.1. Flexographic Printing ............................................................. 50

2.2.3.2. Gravure Printing ...................................................................... 51

2.2.3.3. Screen Printing ........................................................................ 52

2.2.3.4. Inkjet Printing .......................................................................... 53

2.7. Summary ........................................................................................... 54

2.8. References ........................................................................................ 56

III. OPTO-ELECTROCHEMICAL BASED DUAL DETECTION OF
HEAVY METAL COMPOUNDS USING A NOVEL FLOW CELL .......... 70

3.1. Introduction ....................................................................................... 70

3.2. Background ....................................................................................... 72

3.2.1. Design of the Electrochemical Sensor ......................................... 72

3.2.2. Fabrication of the Electrochemical Sensor .................................... 76

3.2.3. Fabrication of the First Generation Flow Cell .............................. 79

3.2.4. Results .......................................................................................... 81

3.3. Experimental .................................................................................... 83

3.3.1. Chemicals, Materials and Sample Preparation ............................ 83

3.3.2. Sensor Fabrication ....................................................................... 83
# Table of Contents—continued

## CHAPTER

3.3.3. Second Generation Flow Cell Fabrication ........................................ 83

3.3.4. Experimental Setup ........................................................................ 88

3.4. Results ................................................................................................. 89

3.5. Summary .............................................................................................. 95

3.6. References ........................................................................................... 97

## IV. A NOVEL FLEXIBLE MICROFLUIDIC PLATFORM:
INTEGRATION OF CONVENTIONAL PRINTED CIRCUIT BOARD
TECHNOLOGY AND INKJET PRINTING METHOD ................................. 103

4.1. Introduction ......................................................................................... 103

4.2. Experimental ....................................................................................... 104

4.2.1. Chemicals, Materials and Sample Preparation .............................. 104

4.2.2. Design of PDMS Based Microfluidic Flow Channels ................... 105

4.2.3. Fabrication of PCB as Master Mold for PDMS Based
Microfluidic Channels ........................................................................... 109

4.2.4. Machining of Delrin ...................................................................... 110

4.2.5. Preparation of PDMS ..................................................................... 110

4.2.6. Fabrication of Microfluidic Channels ............................................. 110

4.2.7. Microfluidic Channel Characterization .......................................... 112

4.2.8. Inkjet Printing of Electrodes ............................................................ 114

4.2.9. Integrating Microfluidic Flow Channels and Electrodes for Final
Flexible Microfluidic Sensing Device ...................................................... 115

4.2.10. Experiment Setup ......................................................................... 116

4.3. Results ................................................................................................. 117
Table of Contents—continued

CHAPTER

4.4. Summary ........................................................................................................... 123
4.5. References ....................................................................................................... 125

V. A NOVEL FULLY PRINTED AND FLEXIBLE CAPACITIVE PRESSURE SENSOR ................................................................................................................................. 131

5.1. Introduction ..................................................................................................... 131
5.2. Experimental .................................................................................................. 133
  5.2.1. Chemicals, Materials and Sample Preparation ........................................ 133
  5.2.2. Fabrication of Fully Printed Pressure Sensor ........................................... 133
  5.2.3. Experiment Setup .................................................................................... 136
5.3. Results ............................................................................................................ 137
5.4. Summary ....................................................................................................... 140
5.5. References ..................................................................................................... 141

VI. CONCLUSION AND FUTURE WORK ............................................................... 145

6.1. Conclusion .................................................................................................... 145
6.2. Future Work .................................................................................................. 147
6.3. References .................................................................................................... 150

APPENDIX ............................................................................................................. 151

A. LIST OF PUBLICATIONS ............................................................................... 151
LIST OF TABLES

2.1. Types of sensors and corresponding stimulus ........................................ 28
2.2. History of chemical and biological sensors ............................................ 33
2.3. Specifications of four major printing techniques used in printed electronics ........................................................................................................ 50
4.1. Assembly blocks for Microfluidic Channel Design ............................... 107
LIST OF FIGURES

2.1. Market growth in sensor technology .......................................................... 15
2.2. The five human senses ................................................................................. 17
2.3. Different roles of sensors in a data acquisition and sensing system. Sensor A is noncontact, sensors B and D are passive, sensor C is active, and sensor E is internal to the data acquisition system ........................................ 19
2.4. Sensitivity measurement from slope of transfer function of a sensor ............ 20
2.5. Hysteresis of a sensor .................................................................................. 25
2.6. Non-linearity of a sensor ............................................................................. 25
2.7. Output characteristics of a sensor with saturation region ......................... 26
2.8. Deadband regions in a sensor output ............................................................ 28
2.9. Schematic of a bulk acoustic piezoelectric sensor ........................................ 30
2.10. Schematic of a thermistor based thermal gas sensor .................................. 31
2.11. Schematic of a chemical or biological sensor ............................................ 32
2.12. Schematic of an optical fiber guide .............................................................. 34
2.13. Schematic of mechanical pressure sensor .................................................. 36
2.14. Typical Rayleigh and Raman (Stokes and Anti-Stokes) scattering processes ...................................................................................................................... 44
2.15. Classification of printing technologies ........................................................ 49
2.16. Schematic of flexography printing technique .............................................. 51
2.17. Schematic of the basic structure of gravure printing technique .................. 52
2.18. Schematic of screen printing process .......................................................... 53
List of Figures — continued

2.19. Schematic of (a) continuous, (b) thermal and (c) piezo inkjet printing processes .......................................................... 54

3.1. Current comprisement curves of interdigitated electrodes. A curve of 80% means that 80% of the current flows beneath the curve ................. 73

3.2. Typical interdigitated electrode geometry .................................................. 74

3.3. Calculated capacitance for varying number of interdigitated electrodes (N) and interdigitated electrode length (L) ........................................... 75

3.4. Schematic of the electrochemical sensor ................................................... 75

3.5. Mask Layout .......................................................................................... 76

3.6. Electrochemical fabrication process steps .................................................. 77

3.7. (a) Diced wafer with photolithographically fabricated sensors and (b) an individual electrochemical sensor ........................................... 78

3.8. (a) 3D Profilometry scan of the gold interdigitated electrodes illustrating an (b) average thickness (ΔZ) of 0.2 µm and (b) average width (ΔX) of 5.5 µm ................................................................. 79

3.9. Flow cell with electrochemical sensor placed in sensor groove and showing inlet and outlet ports along with O-Ring and SOIC test clip ........ 80

3.10. Sensor response to (a) mouse monoclonal IgG and (b) D-Proline, at applied potential of 1 mV ................................................................. 82

3.11. Schematic of the opto-electrochemical dual detection flow cell ............. 84

3.12. Schematic of the inlet and outlet ports of the (a) first and (b) second generation flow cells. Photographs of the of the inlet and outlet ports of the (a) first and (b) second generation flow cells ........................................... 85

3.13. Schematic of the inlet and outlet ports, within the O-ring reservoir, of the (a) first and (b) and (c) second generation flow cells. Photographs of the of the inlet and outlet ports, within the O-ring reservoir, of the (a) first and (b) second generation flow cells ........................................... 86

3.14. Opto-electrochemical dual detection flow cell ......................................... 87
3.15. Experiment Setup. ........................................................................................................... 88

3.16. (a) Dynamic impedance based electrochemical response of sensor towards CdS at 1 kHz and applied potential of 1 mV; (b) Raman spectra of CdS with an integration time of 3 seconds at 300 mW and excitation of 785 nm ......................................................................................................................... 90

3.17. (a) Dynamic impedance based electrochemical response of sensor towards HgS at 1 kHz and applied potential of 1 mV; (b) Raman spectra of CdS with an integration time of 3 seconds at 300 mW and excitation of 785 nm ......................................................................................................................... 91

3.18. (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of CdS at 1 kHz and applied potential of 1 mV ......................................................................................................................... 93

3.19. (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of HgS at 1 kHz and applied potential of 1 mV ......................................................................................................................... 94

4.1. Rules of PDMS design process. (a) Schematic of a PDMS structure showing design rule parameters. Two possible problems that may arise from the softness of PDMS: (b) Sagging of recessed structures with aspect ratios T/W < 0.5; and (c) Pairing or lateral collapse of relief structures with aspect ratios T/W > 5 ......................................................................................................................... 106

4.2. Examples of complete microfluidic flow channels assembled using designed microfluidic assembly blocks ................................................................................................................................. 109

4.3. (a) Schematic of microfluidic flow channel designed in ExpressPCB™ software and (b) fabricated PCB board ................................................................................................................................. 111

4.4. (a) Dimensions of Delrin block and machined area (b) Photograph of Delrin block after machining ................................................................................................................................. 111

4.5. (a) PCB master mold and (b) Fabricated PDMS microfluidic flow channel ................................................................................................................................. 112

4.6. 3D output of the vertical scanning interferometry of the microfluidic channel ................................................................................................................................. 112

4.7. Flow velocity distribution of liquid in (a) laminar, (b) transitional and (c) turbulent flow conditions ................................................................................................................................. 114
4.8. Contact angle measurement of water on PDMS; (Inset) contact angle measurement of water on PDMS versus time ........................................ 114

4.9. 3D Profilometry scan of the inkjet printed silver electrodes illustrating an average thickness (ΔZ) of 0.3 µm. ........................................ 115

4.10. PDMS based printed and flexible microfluidic sensing device; (Inset) printed interdigitated electrodes ........................................ 116

4.11. Experiment Setup ........................................................................ 117

4.12. (a) Simulation results for flow velocity of liquid through microfluidic channel, (b) simulation results for pressure distribution of liquid in the microfluidic flow channel .................................................. 119

4.13. Dynamic electrochemical impedance response of the flexible microfluidic sensing device towards varying concentrations of KCl, at a frequency of 1 kHz with a 100 mV voltage excitation .......................... 120

4.14. (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of CdS at 1 kHz and applied potential of 100 mV ................ 121

4.15. (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of HgS at 1 kHz and applied potential of 100 mV .......... 122

5.1. Schematic for the fabrication of the fully printed flexible pressure sensor (a) Bottom conductive electrodes on PET substrate, (b) Dielectric PDMS layer, (c) Top conductive electrode layer, (d) PDMS passivation layer ................................................................. 134

5.2. Photograph of fully printed pressure sensor ........................................ 135

5.3. (a) 3D output of the vertical scanning interferometry and (b) AFM image of printed Ag NP ink on PET .................................................. 135

5.4. Experiment Setup ........................................................................ 136

5.5. Percentage change in the capacitive response of the fully printed pressure sensor towards varying compressive forces when compared to base capacitance ................................................................. 137
List of Figures — continued

5.6. Capacitive response of the fully printed pressure sensor towards varying compressive forces.......................................................................................................................... 138

5.7. Dynamic capacitive response of the pressure sensor towards the lowest detectable force of 800 kPa for 1000 cycles at 16.6 mHz................................................. 139
CHAPTER I

INTRODUCTION

1.1 Motivation

Sensors, which represent the “ears”, “noses” or “eyes” for information processing systems, are being widely used in numerous industrial applications as well as in our day-to-day lives. Sensors are typically employed to provide real-time information, which has helped in advancing the electronic industry by simplifying modern technical systems and making many technical applications more cost effective, reliable and safer. The need for sensing technologies has seen a dramatic increase in sensor R&D and applications over the past 25 years [1]. The remarkable advances, in sensing technology, which have already been made possible along with the potential range of applications that are yet to be developed has placed sensors on the threshold of a revolution similar to that experienced by silicon technology in the computing industry during the 1980s [1]. An increasing demand for miniaturized, cost effective and reliable sensors capable of monitoring multiple environmental, physical, chemical and biological parameters thus requires the development of novel sensing devices with advanced capabilities. In order to realize this, an interdisciplinary study that involves the realms of electrical, mechanical, chemical, biological and manufacturing engineering is required.

The development of lab-on-a-chip (LOC) devices with the capabilities of performing laboratory based micro-analytical operations on a small scale has been very appealing [2,3]. LOCs help to shrink and integrate typical laboratory functions, such as separation and analysis of various bio/chemicals, using micro or nano
volumes of analytes. Moreover LOCs, with rapid and highly sensitive detection capabilities, are of great demand in the field of life sciences. A steady effort has been made on the development of efficient and easy-use electrochemical sensors that can be used in LOC devices. More recently, optical sensors have been utilized in LOC devices as an analytical tool for the detection of bio/chemicals [4-6]. Furthermore, sensing systems that incorporate simultaneous electrochemical and optical techniques allows for versatile detection of analytes, thereby reducing the possibilities of false positives [7-9]. The author believes that the development of sensing systems that integrate dual detection techniques and are capable of quantitatively detecting various bio/chemicals is thus paramount towards the development of the sensor technology and engineering fields.

In this era of industrial modernization, heavy metal detection has been receiving growing interest due to the toxic effects of heavy metals on both flora and fauna, even at the micro or nano molar concentration levels, in the biomedical, food and environmental industries. Heavy metals, a major source of environmental pollution, enter the environment by run-off and ground water from mining, pharmaceutical and chemical industries [10]. Mercury (Hg) and cadmium (Cd) are heavy metals that are typically found as mercury sulfide (HgS) and cadmium sulfide (CdS) in nature. The metals have been classified as global heavy metal pollutants and are the most frequently observed heavy metal compounds [11]. Hg and Cd are known to attack the nervous, gastrointestinal and renal systems with adverse health effects such as neurotoxicity and nephrotoxicity [12-15]. Moreover, prolonged exposure to Hg and Cd causes a significant incidence of cancers due to the strong bonds that these heavy metals create with sulfur molecules of the human body [16]. The problems associated with heavy metal compounds has motivated the author to explore the
development of cost effective, highly sensitive and rapid sensing systems that can be deployed as LOCs for the detection of heavy metals.

The rapid change and evolution of sensors has led the author to investigate the potential of new electronic manufacturing technologies based on the current market product trends. Printed electronics (PE) is a rapidly emerging technology with significant commercial potential that is driving investments in research and development within the semiconductor industry [17,18]. The new PE technology is set to revolutionize the fabrication of electronic devices on flexible substrate materials, such as plastic, paper, and textiles using electrically functional inks in combination with standard printing processes, such as screen, gravure, flexo and inkjet printing [19-21]. PE uses solution-processable electronic materials to develop printed devices such as organic thin film transistors (OTFT) [22], organic light emitting diodes (OLED) [23], photovoltaics (PV) [24], radio frequency identification tags (RFID) [25], and biochemical sensors [26]. PE technology is an additive process where electronic materials are deposited selectively, eliminating the need for masking and etching; and this results in a cleaner process that produces less waste than traditional methods. PE also has low production costs when compared to traditional CMOS fabrication processes. The advantages of PE thus create a very promising opportunity that could lay the foundation for a variety of PE applications ranging from fully printed wearable to implantable electronic devices.

Over the last decade, a steady and considerable effort has been directed towards the development of cost effective microfluidic devices for applications in the biomedical and environmental industries [27-30]. Typically, master molds for microfluidic channels have been fabricated using silicon based technology, which is significantly more expensive and time consuming. However, the capability to use
conventional printing techniques along with traditional lithography processes, to create flexible microfluidic sensing systems, is very promising. In addition, a major focus of research has been aimed at the development of pressure sensors on flexible substrates for applications in aerospace engineering [31], automotive engineering [32], robot tactility [33], environmental monitoring [34] and the biomedical field [35]. Pressure sensors are typically manufactured using conventional CMOS processes, which are often expensive and fabricated on rigid substrates [36-39]. Almost all pressure sensing systems built to date utilize hanging structures or cavity based sensor design configurations [40-44]. However, none of these configurations offer the high flexibility and conformability, required for various pressure sensing applications. With the remarkable interest that PE has been gaining in recent years, the author has been inspired to explore the potential of using printing technologies to manufacture pressure sensors and thus further enhance the fundamental knowledge of developing PE devices.

1.2 Author’s Contributions

The author’s research work has resulted in forty five conference publications, five intellectual property (IP) disclosures, two patent applications and ten high-quality peer-reviewed journal publications as given in the list of publications in Appendix A. The publications directly related to the research performed for this dissertation have been marked with “*”, in the Appendix A. The results of the projects have been published in prestigious journals such as Biosensors and Bioelectronics; Sensors and Actuators: B Chemical; Nanoscale and the Journal of Sensor Letters. The author has also presented the research work at several international conferences which have been published in the proceedings of the IEEE Sensors Conference (2009, 2010, 2011, 2012, 2013, 2014); International Meeting for
Chemical Sensors (IMCS) (2010, 2012, 2014); Annual Flexible Electronics and Displays Conference (2011, 2013, 2014); Euroensors Conference (2011); International Conference on Sensing Technology (ICST) (2012); and IEEE International Conference on Electro/Information Technology (EIT) (2013). The author was also awarded the All-University Graduate Research and Creative Scholar Award for 2012-13 and the prestigious Gwen Frostic Award for 2014-15 by Western Michigan University as well as an IEEE Bioelectronics Travel Grant by the National Science Foundation (NSF) to attend the IEEE Sensors Conference in Baltimore, Maryland in September 2013.

1.3 Organization of the Dissertation

This dissertation brings together details of the research projects that the author performed during the course of his Doctoral studies. This includes developing a microfluidic sensing system that employs a photolithographically fabricated electrochemical sensor and a CNC machined novel flow cell. In addition, the fabrication of printed and flexible sensing systems by integrating conventional printing technologies such as screen, gravure and inkjet along with traditional printed circuit board (PCB) manufacturing processes is also presented. The rest of the dissertation consists of five chapters.

The author presents a comprehensive literature review in Chapter 2. This chapter will present a detailed introduction to sensors and PE. A discussion covering the science behind the basic working of sensors, the sensor characteristics and the various types of sensors is included. Out of the different types of sensors presented, the author provides an introduction and review of the three specific sensors (electrochemical, Raman and pressure) which will be designed, fabricated and tested in the rest of this dissertation. This is followed by an introductory discussion about
PE, a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associates with PE and the different types of printing.

In Chapter 3, a project on the development of an opto-electrochemical based dual detection system for the sensing of heavy metal compounds, using a novel flow cell, is presented. This includes the design, fabrication and characterization of an electrochemical sensor and flow cell. The measurement set-up, testing and results obtained are also presented. This work will demonstrate the capability of the developed system to detect heavy metal compounds at pM concentration levels.

In Chapter 4, a research project for developing a novel microfluidic sensing platform (MSP) for the detection of various bio/chemicals is presented. This includes the design, fabrication and characterization of the flexible microfluidic sensor. The measurement set-up, testing and results obtained are also presented. The response of the system will demonstrate the feasibility of integrating conventional PCB and printing technology to create flexible microfluidic sensing systems for various applications in the biomedical and environmental industries.

In Chapter 5, a project on the development of a fully printed pressure sensor using gravure and screen printing is presented. This includes the design, fabrication and characterization of the printed pressure sensor. The measurement set-up, testing and results obtained are also presented. The results obtained will show the potential use of fully printed flexible sensors in various pressure sensing applications.

Finally in Chapter 6, the author concludes with a summary of the dissertation along with suggestions for future work.
1.4 References


detection based on a dipyridophenazine ligand,” Tetrahedron Lett., vol. 49,
of the solubility and bioaccessibility of arsenic in realgar wine using a simulated
gastrointestinal system,” Science of the Total Environment, vol. 409, no. 12,
R. Rezzani, “Different role of Schisandrin B on mercury-induced renal damage
and applications for large area electronics: solution-based approaches”, Chem.


CHAPTER II

LITERATURE REVIEW

2.1 Introduction

In this chapter, the author provides a comprehensive literature review on sensors and PE. The background review on sensors will provide a deep insight into the science behind the basic working of sensors, the sensor characteristics and the various types of sensors. The author then presents an introduction and review of the three specific sensors (electrochemical, Raman and pressure) which will provide the reader an understanding of the sensors that have been investigated during the course of this dissertation work. An introductory discussion about PE, which is a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associated with PE and the different types of printing are also presented to provide the reader with an opportunity to understand the evolution of the manufacturing of electronics. It is the author’s hope that those who are just developing an interest in sensing systems, and printed electronic sensing systems, will gain a practical understanding of the interdisciplinary field of study, from this chapter. With this background knowledge, the reader should be exposed to the more detailed real world applications of sensors and PE sensing systems Furthermore, the author expects that they will be inspired by the information provided to delve further into the rest of the dissertation and utilize the vast potential of PE based sensing systems for new research and possibly new applications, in the future.
2.2 Sensors

2.2.1 Introduction to Sensors

The development of sensor technology has been constantly driven by advancements in materials science and engineering with sensors for various applications being in existence before the beginning of the 1900’s. As examples, a copper resistor based temperature sensor was first developed by Wilhelm von Siemens in 1860 [1] and the surface acoustic wave sensor (SAW) was first discovered by Lord Rayleigh in 1885 [2]. During the period up to 1950, the field of sensor technology experienced a slow but gradual advancement in the development of sensors. However, with the advent of the semiconductor technology in the 1960’s, a modern era of sensor technology was ushered in along with the ongoing development of material technology [3-14]. These changes, which include the use of silicon technology, thus enabled the development of sensors with advanced features and increased reliability.

The penetration of sensors in modern day human life is all the more evident from the market analysis data. According to the Business Communications Company, Inc. (BCC) Research, the global market for sensors was valued at $79.5 billion in 2013 and is expected to increase to $86.3 billion, $95.3 billion and to nearly $154.4 billion in 2014, 2015 and 2020, respectively at a compound annual growth rate (CAGR) of 10.1 % over this five-year period [15]. Even though, sensor technology had been typically associated with military and industrial applications in the past, sensors are now being increasingly and ubiquitously deployed in almost all markets. The consumer market has been the most revolutionized by this emerging trend which has enabled sensors to be used in more intelligent and versatile means. There has been an unprecedented growth in the number of products implementing sensor technology, as
shown in Fig. 2.1 [16]. It is estimated that the number of products using sensor technology will increase from 10 billion units in 2012 to almost 30 billion units in 2017, at a CAGR rate of 22.3%.

2.2.2 Sensor Science

The word “sensor” has been derived from “sentire”, in Latin, which means “to perceive” [17]. A sensor, in a very broad sense, can be defined as a device that responds to external signals or stimuli. However, there are both natural and man-made sensors in the world. Natural sensors, like those found in living organisms, usually respond with signals having an electrochemical character based on ion transport whereas in man-made sensors information is transmitted and processed in electrical form through the transport of electrons. Sensors, especially those used in artificial systems, must communicate the same language as the devices with which they are interfaced.

Figure 2.1: Market growth in sensor technology.
A somewhat narrower definition of sensors can now be phrased as, “A sensor is a device that receives a stimulus and responds with an electrical signal” [18]. The stimulus can be any input physical property that is detected by a sensor. This input is typically a non-electrical entity. The sensor then converts this entity into an electrical signal that is compatible with electronic circuits. Thus, the function of a sensor can said to be a convertor of a non-electrical value into an electrical value. The sensor’s output signal, which could be in the form of a current or voltage, is generally analyzed based on the amplitude, frequency or phase.

Sensors are classified into two kinds: active and passive [19]. An active sensor is one that requires an excitation signal for its operation and this signal is converted by the sensor to produce the output electrical signal. Thermistors are one of the best examples of an active sensor because the variations in the resistance, due to an excitation potential applied, can be directly related to temperature through a known function. On the other hand, a passive sensor does not require any additional energy source and, in response to an external stimulus, directly generates an electric signal. A photodiode sensor, a thermocouple and a piezoelectric are examples of passive sensors.

The most common and one of the best examples of a sensing system is the human body. It consists of various sensors that are capable of sensitively and selectively detecting different measurands. These sensors can be considered to be real-time control systems. The five main sensors in the human body are related to sound, smell, taste, vision and touch (Fig. 2.2) [20].
The human ear is an example of a very sensitive sound sensor with a dynamic frequency range from 20 Hz to 20 kHz [21]. It is capable of detecting sound levels from $10^{-12}$ Watts/m$^2$ (0 dB) to 1 W/m$^2$ (120 dB) [21]. The human nose, capable of detecting and differentiating very subtle differences in odor, is one of the most sensitive and selective sensors in the human body. The sensitivity of the human nose is in the range of low parts per billion (ppb) to the low parts per million (ppm) levels [21]. The human tongue is one of the best examples of a taste sensor. It is capable of detecting the differences in sweetness, saltiness and sourness of food. The human eye can detect both mobile and non-mobile objects of various sizes, within a finite dynamic range defined by the visible part of the electromagnetic spectrum (from 4,100 Å to 6,600 Å) [21]. Moreover, the ability of human eyes to differentiate between different colors as well as selectively identify familiar faces in a large group is also amazing. The whole human body can be considered to be a touch sensor because it can feel and respond to any physical contact applied on the skin. The most common touch sensitive part associated with the human body is the hand because it is capable of feeling the physical characteristics of an object such as shape, size,
smoothness, etc. The sensors in the human body can be considered to be real-time control systems. It is crucial that they communicate with each other reliably, rapidly and accurately for the proper functioning of the whole human body.

Similarly in industrial applications, sensors are always a part of a larger ecosystem that may include signal conditioners, detectors, signal processors, data recorders, memory devices, and actuators. Figure 2.3 shows a block diagram of a data acquisition and control device, which illustrates the use of sensors in such a system. The “subject” could be any object that is prone to measurements of some kind. The total number of sensors in a system could vary depending on the application and need. In this example, there are five sensors (sensor A, B, C, D and E). Sensor A measures the subject without any physical contact and, therefore is known as a non-contact sensor. Sensors B, C and D are positioned directly on or inside the subject and are therefore contact sensors. Sensors A, B, D and E are passive sensors, whereas sensor C is active as the former set of sensors does not require any excitation signal. Sensor E serves a completely different purpose by monitoring the internal conditions of the data acquisition system itself. Moreover, some sensors require the use of interface devices like signal conditioners (sensors A and B) and thus cannot be directly connected to standard electronic circuits because of inappropriate output signal formats.

2.2.3 Sensor Characteristics

The author will now introduce the reader to some important sensor characteristics that are typically analyzed to understand the relationship between the input stimulus applied to a sensor and the output signal obtained.
2.2.3.1 Sensitivity

The sensitivity of a sensor can be defined as the ratio of the smallest change in the output response to the corresponding change in the input measurand [22]. The sensitivity can be determined by plotting a sensor response curve, which is a representation of its output as a function of the measurand applied to its input. For example, consider the case of a strain gauge where it is subjected to increments of elongations from 0 mm to 16 mm, as shown in Fig. 2.4. From the graph, it can be seen that the resistance increases by 2 Ω for a 4 mm change in elongation. Thus, the sensitivity of this strain gauge can be calculated to be equal to 0.5 Ω/mm.
2.2.3.2 Selectivity

The selectivity of a sensor can be defined as the degree to which a sensor responds only to the desired measurands, with little or no interference from non-target measurands [22]. Even though sensors are typically designed to be responsive only to certain measurands, it can sometimes show undesired sensitivities to other stimuli, which could be of physical, chemical, or even biological origins. A sensor can be used to selectively respond to a particular measurand from a group of measurands by utilizing an array of sensors. For example, consider a set of sensors, each sensitive to the same ‘a’ quantities that are measured using ‘b’ sensors with \( b \geq a \). The response of the sensors can be represented by Eq. (1) [22].

\[
\begin{align*}
(r_1 &= f_1(x_1, \ldots, x_a) \\
(r_m &= f_b(x_1, \ldots, x_a) \\
(r_m &= f_b(x_1, \ldots, x_a)
\end{align*}
\]
where $x_1, \ldots, x_a$ are manifolds of measurands. A Jacobian matrix, given by Eq. (2), can be used to define the sensitivities of the sensors toward all the involved quantities.

$$
S = \begin{pmatrix} 
\frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_a} \\
\vdots & \ddots & \vdots \\
\frac{\partial f_b}{\partial x_1} & \cdots & \frac{\partial f_b}{\partial x_a} 
\end{pmatrix} \tag{2}
$$

The maximum selectivity is achieved when the Jacobian matrix is diagonal, which corresponds to the case of an array composed of ‘a’ specific sensors.

### 2.2.3.3 Dynamic Range

The dynamic range of a sensor can be defined as the maximum and minimum range of stimuli over which a sensor works well [18]. In other words, it refers to the highest and lowest possible inputs that can be given to a sensor in order to get an output without causing large inaccuracies. Generally, sensors will not work outside the dynamic range or sometimes the sensor can even be damaged. However, some sensors can be made to work outside this range by using special circuitry and calibration methods. For example, consider a thermometer that has been designed to measure temperatures from 20-80 °F. If it is introduced into an environment that is greater than 80 °F or less than 20 °F, it may either not show an output or saturate at the maximum value of 80 °F or even break depending on the quality of the materials used in the manufacture of the thermometer.

### 2.2.3.4 Accuracy

The accuracy of a sensor is actually defined by the inaccuracy of the sensor. The inaccuracy of a sensor is defined as the deviation of the output value from the
ideal or expected value [18]. For example, consider the case where a sensor is expected to generate a 10 mA per 2 mm elongation. This translates to a standard sensitivity of 5 mA/mm. If the output received was 12 mA per 2 mm elongation, this means that the sensitivity was 6 mA/mm and the output was inaccurate by 1 mA/mm. The outputs of all tests done with a particular sensor are compared to the standard sensitivity of the sensor.

2.2.3.5 Resolution

The resolution of a sensor can be defined as the smallest value of measurand that it is capable of detecting [18]. For example, consider that a thermometer has the capability to measure temperatures in relative steps of 0.001 °F. Then the resolution of that thermometer is 0.001 °F. However, if the same thermometer had an accuracy of only 0.01 °F, then only the values with a relative change that is smaller than 0.01 °F can be acceptable. The resolution of a sensor is often controlled by the quantization in digitizing the output signal during the sampling process. For example, one bit can be equal to 0.001 °F. In some cases, the noise in a system can limit the resolution of a sensor. Certain electronic circuitry such as narrow bandwidth filters can be employed to reduce the noise power.

2.2.3.6 Noise

Noise, in a sensor, can be defined as the extra undesired signal that is seen in addition to the desired output. Sensors, irrespective of their complexity, manifest noise in the output signals. This happens due to the unavoidable fluctuations in any property of the sensor or the system such as chemical, physical, and biological quantities. Even though noise from the sensor is the reason for reduced system
performance, it is not considered as an important factor in some systems because the
tensor’s noise could be much less than the fluctuations of the physical elements and
additive noise from elements in the electronic circuitry. Different kinds of noise may
be present, even if not simultaneously, in a given sensor, such as Johnson (thermal),
shot, generation recombination, contact, and flicker noise [23]. This noise is one of
the reasons that, the resolution in a sensor, cannot approach the zero value and
without the knowledge of the noise level, it is not possible to estimate the resolution.

2.2.3.7 Calibration

In order to use a sensor in the real world, it has to be calibrated. This helps in
increasing the accuracy of the sensor by compensating for any manufacturing or
material defects. Calibration in turn helps to reduce the interfacing circuitry and
manufacturer tolerances. During calibration, a new transfer function is defined with
specific variables for the sensing system and the variables can be mathematically
calculated by Eq. (3) and Eq. (4) for a linear and exponential model, respectively [18].

\[
V = x + ys
\]  \hspace{1cm} (3)

\[
V = ze^{ks}
\]  \hspace{1cm} (4)

where \( V \) is the output electric signal. To calibrate the system, the variables \( x, y, z \) and \( k \) must be determined. For example, consider a simple linear transfer function of
a strain gauge with two variables; where elongation is the input and resistance is the
output, as shown in Eq 5.

\[
R = x + yE
\]  \hspace{1cm} (5)

A two point calibration is required to determine the values of \( x \) and \( y \). The
strain gauge has to be elongated to two different elongations \( (E_1 \) and \( E_2) \), which will
result in two different resistance values ($R_1$ and $R_2$). The corresponding transfer function can be given by Eq. (6) and Eq. (7).

$$R_1 = x + yE_1 \quad (6)$$

$$R_2 = x + yE_2 \quad (7)$$

The constants can be mathematically computed by Eq. (8) and Eq. (9).

$$y = \frac{R_2 - R_1}{E_1 - E_2} \quad (8)$$

$$x = R_1 - bE_1 \quad (9)$$

2.2.3.8 Hysteresis

Hysteresis of a sensor is defined as the change in the sensor’s output at a specified point of the input signal when it is approached from opposite directions [18]. For example, consider the case of a strain gauge where it is subjected to increments of elongations from 0 mm to 16 mm and the output resistance is 9 $\Omega$ at 8 mm (Fig. 2.5). When the elongation is decreased from 20 mm to 0 mm, the output resistance is 6 $\Omega$ at 8 mm. This means that the sensor has a hysteresis of 3 $\Omega$ at 8 mm.

2.2.3.9 Non-Linearity

The non-linearity of a sensor can be defined as the maximum deviations that the transfer function of an output signal has when compared to that of the ideal transfer function, which can be approximated by a straight line over the specified dynamic range. The nonlinearity of a sensor is typically measured by using a straight line (line A) that lies midway between two parallel lines (lines B and C) which encompass the entire transfer function, over the dynamic range (Fig. 2.6). In cases
Figure 2.5: Hysteresis of a sensor.

(Hysteresis of 3 Ω at 8 mm)

Figure 2.6: Non-linearity of a sensor.
where the non-linearity falls outside the range of the transfer function, calibration curves can be used to compensate for this error.

### 2.2.3.10 Saturation

Every sensor has a linear and saturation region. In the linear region, the sensor produces some form of desired output. However, every sensor has its own operating limits and it becomes non-responsive at some threshold input level. There will be no output or the sensor will saturate after this point and the corresponding outputs fall under the saturation region (Fig. 2.7).

### 2.2.3.11 Repeatability

The repeatability of a sensor can be defined as the ability of the sensor to produce similar results for multiple tests, performed under the same experimental conditions.

Figure 2.7: Output characteristics of a sensor with saturation region.
environmental conditions. Usually, the repeatability of a sensor is expressed by calculating the standard deviation and error bars. The standard deviation can be mathematically calculated using Eq. (10).

\[
\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \mu)^2}
\]  \hspace{1cm} (10)

where, \(\sigma\) is the standard deviation, \(N\) is the number of samples, \(x\) is the output value and \(\mu\) is the mean.

For example, consider the case of a strain gauge that is being tested 5 times for an elongation of 3 mm. Let the outputs be 10 \(\Omega\), 8 \(\Omega\), 9 \(\Omega\), 11 \(\Omega\) and 12 \(\Omega\). This sensor thus has a mean value of 10 with standard deviation of 1.6.

### 2.2.3.12 Dead-Band

There are certain regions in the output signal of a sensor that are undesired. This could be because the sensor was unresponsive during this period of time due to damage or any unwanted changes in the input stimuli. These situations could cause the output signal to either go to a certain value (often zero) or produce random noise (Fig. 2.8). The sensor can thus be said to be insensitive during this period of time.

### 2.2.4 Types of Sensors

A sensor generally works by altering its physical property in response to a stimulus, and hence produces an electrical signal. Sensors are typically classified into acoustic, magnetic, thermal, electric, optical and mechanical sensors based on the stimulus (Table 2.1).
Figure 2.8: Deadband regions in a sensor output.

Table 2.1: Types of sensors and corresponding stimulus [18].

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Stimulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic</td>
<td>Wave Amplitude, Phase or Velocity</td>
</tr>
<tr>
<td>Thermal</td>
<td>Temperature, Voltage</td>
</tr>
<tr>
<td>Chemical and Biological</td>
<td>Chemical or biological reaction causing change in: conductivity, mass, density, etc.</td>
</tr>
<tr>
<td>Optical</td>
<td>Refractive Index, Absorption, Transmission, Reflection</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Pressure, Mass, Position, Density, Force, Strain, Stress, Shape</td>
</tr>
</tbody>
</table>
2.2.4.1 Acoustic Sensors

Acoustic wave sensors can be defined as sensors that typically detect the propagation of an acoustic wave through various materials. These sensors are classified into two types based on the mode of wave travelling through the material. When a wave is traveling through the volume of the material, it is known as a bulk acoustic wave sensor. It is referred to as a SAW sensor when the wave travels along the surface of the system. Acoustic wave sensors are also categorized as shear horizontal waves or shear vertical waves based on its mode of propagation. The properties of velocity and amplitude of the propagating wave are affected by changes in the material, which can be monitored by observing the difference in frequency and phase characteristics.

Acoustic wave sensors are used as electrochemical, pressure, force, torque shock and mass detectors [24,25]. The schematic for a typical bulk acoustic piezoelectric sensor, which is capable of detecting acoustic waves, is shown in Fig. 2.9. It consists of a thin piezoelectric material sandwiched between two electrodes. When an acoustic wave is propagated through the bulk of the piezoelectric material, a mechanical motion is produced, and hence a fundamental resonance occurs. This causes a change in the resonant frequency of the piezoelectric material, which can be detected in the impedance based response of the device.

Even though acoustic sensors have been employed for several applications, such as mobile cell phones [26]; tire pressure monitors [27]; gas sensors [28]; vapor, humidity and temperature sensors [29], its inherent disadvantages such as degradation of performance due to the damping associated with liquid loading and the low frequency of operation have limited their applications in liquid media [30,31].
2.2.4.2 Thermal Sensors

Thermal sensors are devices that typically measure the change in temperature. Based on the mode of detecting temperature, these devices are classified as contact and non-contact thermal sensors. A thermistor is an example of a contact mode thermal sensor, whereas infrared (IR) is a non-contact thermal sensor. Figure 2.10 shows a thermistor based sensor that can be used to measure the thermal conductivity of a gas [32]. It consists of two thermistors ($T_1$ and $T_2$) that are supported by thin wires to minimize thermal conductivity loss to the housing. $T_1$ is exposed to the outside gas through small venting holes whereas $T_2$ is hermetically sealed in dry air. Both $T_1$ and $T_2$ are connected to a bridge circuit ($R_1$ and $R_2$), which is powered by an input voltage. The thermistors develop self-heating due to the passage of electric current. Initially, the bridge is balanced by introducing dry air.
through the venting holes, to establish a zero reference point. When a gas is introduced through the vent holes, the difference in thermal conductivity can be measured by the change in the electrical resistance value of the thermistors.

Galileo Galilei has been credited for the discovery of the first instrument for measuring temperature in 1603, even though humans have always been aware of the different degrees of heat, ever since the mind can imagine [33]. Since then, there have been different types and forms of thermal sensors for various applications [34-37]. However, one of the main limitations of thermal sensors is the need for a controlled environment for temperature measurements. The entire measurement setup often
needs to be completely sealed and thermally stable. This requires relatively expensive materials, complex manufacturing steps and time-consuming measurements methods [38].

2.2.4.3 Chemical and Biological Sensors

A chemical or biological sensor works by emitting a signal (typically a voltage or current) in response to an event such as a chemical reaction or binding between two molecules in a sample, known as the “analyte”. It typically consists of a sensitive biological element or material, a transducer and associated electronics or signal processors [39]. A commercial example of a biochemical sensor is the blood glucose sensing system. The schematic and working of a typical chemical or biological sensor is shown in Fig. 2.11. It consists of a sensing layer coated on interdigitated electrodes (IDE). When a test sample is introduced onto the sensor, it comes into contact with the sensing layer and a chemical or biological reaction takes place. This reaction causes a corresponding capacitance or impedance based change in the output signal across the IDEs.

![Figure 2.11: Schematic of a chemical or biological sensor.](image-url)
The history of chemical and biological sensors is shown in Table 2.2. A major evolution of early chemical and biological sensors started to take place in the 1980s [40]. During this period, the first electrode based sensors were developed into commercially available products. Following this, in the 1990s, several next generation bio/chemical sensors were developed with improved performance levels. By the turn of the century, these sensors entered the commercial market with numerous applications in the biomedical, environmental and military industries [41]. Some of the conceivable applications include bio/chemical laboratory tests, food freshness packets, portable pollutant monitors and bioreactors [40]. The wide variety of applications made possible by these sensors has caught the attention of both research scientists and engineers alike.

**Table 2.2: History of chemical and biological sensors [40].**

<table>
<thead>
<tr>
<th>YEAR</th>
<th>CHEMICAL AND BIOLOGICAL SENSOR DEVELOPMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1916</td>
<td>First report on protein immobilization</td>
</tr>
<tr>
<td>1922</td>
<td>First glass pH electrode</td>
</tr>
<tr>
<td>1925</td>
<td>First blood pH electrode</td>
</tr>
<tr>
<td>1954</td>
<td>Invention of oxygen electrode</td>
</tr>
<tr>
<td>1962</td>
<td>First amperometric biosensor</td>
</tr>
<tr>
<td>1964</td>
<td>Coated piezoelectric quartz crystals bio/chemical sensors</td>
</tr>
<tr>
<td>1969</td>
<td>First potentiometric biosensor</td>
</tr>
<tr>
<td>1972-74</td>
<td>First commercial enzyme electrode glucose sensor</td>
</tr>
<tr>
<td>1975</td>
<td>First microbe based biosensor</td>
</tr>
<tr>
<td>1975-76</td>
<td>First immunosensors</td>
</tr>
<tr>
<td>1979</td>
<td>Surface acoustic wave (SAW) gas sensors</td>
</tr>
</tbody>
</table>
2.2.4.4 Optical Sensors

Optical sensors are devices that detect a change in measurand by using light as the stimulus. The most common and simple example of an optical sensor is an optical fiber guide, which generally consists of a circular core with a cylindrical cladding layer as shown in Fig. 2.12. The light inside the guide is conducted like electricity inside a cable, due to total internal reflection, because the refractive index of the circular core ($n_1$) is always higher than that of the cylindrical cladding ($n_2$) [42-45].

Optical sensing techniques have been reported as far back as the 1930s by Kautsky and Hirsch for oxygen sensing [46]. Similar oxygen sensing optical systems have also been reported by Pringsheim et al. [47] and Zakharov et al. as well [48]. A complete optical system, which included a UV light source, oxygen sensitive fluorescent layer and a photodetector was reported by Bergman [49]. Following this,
several papers on different types of optical sensors for several applications have been reported [50-52]. Some of the early optical sensors were actually a subset of the chemical and biological sensors because the measurement was done for visual identification of a color change due to some bio/chemical reaction [53]. For example, a pH indicator strip was used to change the color of a cellulose paper soaked with dyes when exposed to varying pH values. In 1975, Harper reported on the immobilization of pH indicator dyes on glass [54]. With the advent of the semiconductor technology, several modern optical sensors that utilize light emitting diodes (LED) photonic nanowires and Raman spectroscopy (RS) have also been reported [55-58]. Optical sensors are typically non-electric and contactless sensing devices; permits remote sensing; are immune to radio frequency and electromagnetic interference; does not contaminate the environment; and are not subjective to corrosion [59]. These advantages, along with the tremendous growth and advancement in the last few decades, have placed optical sensors in a unique position to revolutionize the sensor technology field.

2.2.4.5 Mechanical Sensors

The principle of operation of mechanical sensors is based on detecting the deformation of a material and translating it as an electrical signal [60]. Some of the basic parameters measured by mechanical sensors are pressure and stress, acceleration, flow rate, position and angle. Piezoelectric sensors and cantilever sensors are a few common examples of mechanical sensors [61]. Figure 2.13 shows the schematic of a capacitive pressure sensor as an example of a mechanical pressure sensor. When a force is applied on the sensor, the structure deforms and the top electrode comes closer to the bottom electrode. This deformation thus causes an increase in the capacitive response of the sensor.
Mechanical sensors, among the oldest measurement devices, have undergone constant evolution throughout the history of mankind. One of the earliest examples of a mechanical sensing device is the use of officially certified bronze nozzles by the Romans to control the rate of water flow to customers [62]. Yet, another use of an early mechanical sensing device is an odometer, which consists of a series of gears in a chariot wheel, for measuring distance traveled [63]. Cantilever based pressure sensors have been reported by Tsobkallo et al. for measuring the elastic modulus of sheet materials [64]. A large number of sensors have been used in automotive plants [65]. A new kind of spinning rotor pressure gauge was reported by Beams et al. [66]. In the medical field, mechanical sensors have been employed as flow sensors to measure the blood flow in tracheal walls by Dobrin and Canfield [67]. The use of mechanical pressure sensors has been reported by Walters for use in car wheel rims to detect over inflated or under inflated tires [68]. Mechanical sensors have also been employed for several applications in the automotive, space and robotics industries [69-71]. Even though the last two decades has seen an explosive growth in the field of mechanical sensing applications, more is yet to come because of the need for more precision and better performance. The most common types of modern mechanical sensors that are of current interest to the engineering world can be
classified into four main groups: accelerometers, gyroscopes, force and pressure sensors.

2.3 Electrochemical Sensors

Electrochemical sensors, which represent a very important group of chemical sensors, are known for their capability to generate electric signals immediately and provide information about the types, concentrations and chemical states of the species present within a test sample. The use of electrochemical sensors dates back to the 1950s, when they were used mainly for oxygen monitoring. Following this, Clark and Lyons first proposed the initial concept of glucose enzyme sensor electrode array in 1962 [72]. Ever since, this electrochemical sensor industry has witnessed tremendous research activity. The 1970s witnessed the exploration of microelectronic chemical sensors as a low-cost alternative to various laboratory sensing techniques. A common example of this is the conductivity-based thin-film sensor, which was introduced into the research community. These sensors consisted of a film of chemically sensitive material, such as tin oxide or polypyrrole, whose conductivity changed in response to chemical changes in the sensing environment.

Several new electrochemical sensors, with better sensitivity and selectivity, started to become available by the mid-1980s. During this period, research was focused on the development of mediator-based “second-generation” glucose biosensors [73,74], the introduction of commercial strips for self-monitoring of blood glucose [75,76], and the use of modified electrodes for enhancing the sensor performance [77]. Since the 1990s, the electrochemical sensor industry has seen intense research activity towards the development of minimally invasive subcutaneously implantable devices [78,79]. A variety of electrochemical sensors has been developed and is being used in many applications. Research has provided the
capability to fabricate electrochemical sensors with varying physical size, geometry, components and construction methods, depending on its intended use. Even though the appearance of most electrochemical sensors may be similar, its functions could be markedly different.

Generally, electrochemical sensors operate by reacting with the sample of interest and produce an electrical signal proportional to the species concentration. Over the decades, the selectivity of the electrochemical sensors to different species of bio/chemicals has been improved by many different approaches. For example, four palladium MOS-based chemical sensors covered by zeolite filters were used, by Muller and Lange, to selectively detect various chemicals [80]. Bott and Jones used passive (SiO₂, Al₂O₃ and zeolite) and active (thin films of catalytically active metals, oxide-supported catalytic metals and metal oxides) filters on sensor surfaces to distinguish among various combustible gases [81]. Similarly, Meyer et al. employed various external membranes to enhance the selectivity of platinum electrodes to urea and ammonia [82]. Catalysts have also been used to alter the selectivity of chemically sensitive materials. Wang et al. used palladium as a catalyst to enhance the discrimination capability of an array of metal-oxide sensors for analyzing mixtures of acetone and methanol [83]. The use of microelectrodes in electrochemical sensors, both for miniaturization and increased sensitivity, has also been receiving interesting and close attention in this field. Pioneering work was done on the IDEs by Sanderson and Anderson [84]. As a result, several applications that employ IDEs have been reported [85-87]. The characteristics of the IDE electrodes and its applications in electrochemistry have been extensively studied by Tabei and co-workers [88-94]. It was proved that the IDE’s offer higher sensitivity than macroelectrodes of conventional size.
Electrochemical sensors are generally classified based on one of three categories of transduction mechanisms:

1. Voltammetric and Amperometric
2. Potentiometric
3. Conductometric

Voltammetry is the process of sensing the potential generated, at a fixed input voltage, when an analyte is selectively oxidized or reduced. In amperometry, the current is measured as a function of the applied potential. Potentiometers are used to measure the accumulation of charge density (voltage) at the sensor surface, where there is no current flow. Conductometric sensors measure conductivity through the analyte between electrodes.

2.3.1 Electrochemical Sensor Configurations

2.3.1.1 Voltammetric and Amperometric Sensors

Voltammetric systems consist of three electrodes immersed in a solution containing the analyte and supporting (non-reactive) electrolyte. The voltage changes linearly with time for the working electrode. The potential remains constant for the second electrode, which is the reference electrode. Saturated Calomel Electrode (SCE) is the most generally available reference electrode for work in aqueous solutions. The Ag/AgCl reference electrode is also quite common. Platinum wire is used as the third electrode, which is the auxiliary or counter electrode. This serves as an electrical conductor from the source through the solution to the microelectrode. The function of the counter electrode is to provide an alternative route for the current to follow, so that only a small current flows through the reference electrode. There is a variety of conductive materials that can be applied as electrodes.
which include inert materials such as platinum or gold, glassy carbon or pyrolytic graphite or a metal coated with a film of Hg.

Amperometry is based on the measurement of the current resulting from the electrochemical oxidation or reduction of an electroactive species. A constant potential is applied to the working electrode or on an array of electrodes with respect to a reference electrode, which may also serve as the auxiliary electrode. Amperometric sensors employ electrodes usually composed of solid materials, such as graphite fibers, glassy carbon, graphite paste, platinum, gold, copper, nickel or some other metals [95].

One of the main disadvantages of voltammetric and amperometric sensors is that the sensor response is dependent on the hydrodynamic conditions and, accordingly, on the reagent flow rate in flow injection [96]. These sensing techniques also may suffer from interactions between the sensor and sample matrix, leading to poor stability and reproducibility of the electrode surface. The presence of a suitable base electrolyte on which the background current is dependent is a normal requirement of electrochemical analysis. These sensors are sensitive to the rate of flow of substance in the sensor, and also to the process of interaction of the sensor with the sample. They are used in high performance liquid chromatography [97].

2.3.1.2 Potentiometric Sensors

One of the oldest but widely used sensors is the potentiometric sensor. The most common potentiometric sensors used are the ion selective electrodes (ISE), which yield information about the concentration of a compound in terms of the potential difference between two electrodes [98]. This method is popular because of its simplicity, selectivity and relatively low cost. Still, problems may originate in some applications due to the slow sensor response, particularly when analyte
concentrations are low, and to the non-linear relationship between the potential and the analyte concentration.

### 2.3.1.3 Conductometric Sensors

Conductometric sensors operate on the basis of the current flow established by migration of ions of opposite charge, when an electric field is established between two electrodes immersed in an electrolyte solution. As conductivity is additive, this transduction is the least sensitive of the electrochemical techniques, as it is impossible to discriminate between two ions. The small differences in ionic limiting equivalent conductance are not enough to discriminate species. Moreover, if the concentration of one ion is very high, it could mask others. These sensors can measure conductance of both gases as well as liquids through measurement at the surface of the sensor and through measurement of the direction normal to the surface [99].

### 2.3.1.4 Capacitance and Impedance Sensors

Other than the previous methods of detection, there is yet another method which in a narrower sense deals with the phenomena at the electrode surface. For the capacitive sensing technique, the sensor detects the change in capacitance due to a change in dielectric permittivity and charge distribution at the interface of the sensor and the complex formed by an interaction of reactants. Capacitance based sensors can be developed depending upon two methods of interaction as listed below:

1. Measuring the change in capacitance when the bio-chemical substance is catalyzed between two metal electrodes that act as capacitor plates.
2. Detecting the capacitance at the interface of the electrode and analyte when the voltage is kept constant.
The impedance based technique, which is often used in electrochemical impedance spectroscopy (EIS), has been employed for studying electrochemical systems [100]. Some of the applications include corrosion, electrodeposition [101], batteries [102] and fuel cells [103]. The impedance of a sensing system is generally determined at just one selected frequency by applying a voltage perturbation with small amplitudes and detecting the current response. However, in some cases, EIS can be used to correlate the overall impedance to a change in concentration. This is done by analyzing the response of the system within a limited frequency window, where the relative changes are largest. Thus, this simplifies the analytical and measurement processes by enabling the user to detect the impedance alone in such cases.

### 2.4 Raman Sensors

RS, one of the most important optical sensors, has been used as an analytical tool to detect real-time vibrational information on chemical structures and physical forms. It has been mainly employed to fingerprint and identify bio/chemical substances from characteristic spectral patterns. The use of RS had been limited to experts in dedicated academic or industrial research laboratories, due to the fact that the equipment used were bulky, expensive and complicated. However, with advances in modern instrument technology, equipment for RS have become more small, portable and thus accessible to the non-specialist individuals and researchers. The main advantage associated with RS is its ability to examine samples in the solid, liquid or vapor states, as well as in bulk or microscopic particles, irrespective of the environment temperature. Moreover, this technique uses minimal sample preparation and requires simple data interpretations.

RS uses inelastic scattering of light to examine the molecular structure of bio/chemicals [104]. This phenomenon was first proposed by Smekal in 1923 [105]
and first observed experimentally in 1928 by Raman and Krishnan [106]. Typically, when light is incident on a material, the photons from the light source are either scattered or absorbed. If the photons are absorbed, then it is used in absorption spectroscopy. However, in the case of scattering, it is employed for molecular identification in RS. The scattering of the photons is dependent on the molecule of the materials and can be observed by collecting the scattered light. In RS, a single frequency of radiation is used to excite the sample and the radiations from the sample are detected. When excited, the incident light interacts with the molecules and alters the electrons around the nuclei. This creates a virtual-state of the nuclei that are not stable and the incident photons are rapidly re-radiated.

The photons are radiated in two different ways depending on how the energy changes during vibrational spectroscopy. The photons will be scattered with very small frequencies if only electron cloud alteration occurs. This process is regarded as elastic scattering and is known Rayleigh scattering. In some cases, energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon. This process is considered to be inelastic, because the energy of the scattered photon will be different from that of the incident photon by one vibrational unit and is called Raman scattering. The basic processes that occur for one vibration are depicted in Fig. 2.14. Most molecules exist in the lowest energy vibrational energy states, at room temperature. The virtual states are created only when a sample is excited by a light source. In the Rayleigh process, no energy change is involved and hence the light returns to the same state. Two different types of scattering have been observed for RS. The first one is known as Stoke scattering where a molecule is promoted to a higher energy state (n) from the ground vibrational state (m). The
Figure 2.14: Typical Rayleigh and Raman (Stokes and Anti-Stokes) scattering processes.

second type, in which a molecule that exists in the higher energy state (n) is transferred to the ground vibrational state (m), is called as anti-Stokes scattering.

2.5 Pressure Sensors

Pressure, which can be defined as the normal force per unit area exerted on any surface, is one of the most significant property that is being measured in our environment [107]. The detection of pressure is very important in many industrial and consumer applications. Most of the time, a variation in pressure causes many materials to break or not work at all. For example, an increase in pressure in a pipe could cause it to burst whereas low pressures in some pipes could cause it to not move the fluid within it to the target location, especially to a relatively higher altitude. Moreover, pressure sensors, which are a subset of mechanical sensors, are also used in touch sensing, impact pattern recognition or tactile applications such as artificial skins in robotics. In all these applications, the primary element in the corresponding sensing system will be a pressure sensor.

Pressure sensors are typically classified into three types based on the mechanism of pressure involved [107]:
A. **Absolute pressure**, which is defined as the pressure difference between the point of measurement and a perfect vacuum where pressure is zero.

B. **Gauge pressure**, which is defined as the pressure difference between the point of measurement and the ambient or atmospheric pressure.

C. **Differential pressure**, which is defined as the pressure difference between two points, one of which is chosen to be the reference.

### 2.5.1 Detection Techniques

In order to measure pressure, a detection technique is required for converting the deformation of a sensing element to a relative pressure change. The most simple and common technique that has been used to mechanically measure pressure is by implementing flexural lever linkages to drive a pointer over a graduated scale, for example, in the moving pointer barometers [107]. Bourdon tubes have also been employed to drive the wiper arms in potentiometric resistance elements [108]. Some of the older linear-variable differential-transformer (LVDT) pressure sensors have used the displacement of a Bourdon tube to move a magnetic core inside a coil assembly to vary its inductance [109,110]. Yet, another type of pressure sensor used is the vibrating-wire pressure sensor in which a metal wire is stretched from the center of a diaphragm to a fixed anchor [111]. When the diaphragm is excited by some pressure change, it causes the resonant frequency of the wire to change and this can be measured by the readout electronics.

In addition, some of the other different technologies that are available for pressure sensing are piezoelectric, pneumatic, hydraulic, resistive and capacitive [112]. Piezoelectric pressure sensors work by converting the strains caused by the deformation of a sensing element, typically a piezoelectric crystal [113]. However, piezoelectricity is generally not a suitable method for static measurements.
because of its leakage current. The piezoelectric response tends to degrade, over time, when a constant load is applied to it. Both the pneumatic and hydraulic methods usually require complicated measurement set-ups and are bulky when compared to their counterpart measurement techniques [114]. Resistive pressure sensors are based on the principle of resistance change of a piezoresistive material, when a force or pressure is applied. Even though these types of pressure sensors utilize relatively simple electronic circuitry, they have a similar tendency as a piezoelectric sensor, to degrade over a relatively faster time period.

The capacitance based pressure sensors works by measuring the change in capacitance between two parallel plates, when a pressure is applied. Typically, two conductors are mounted on a non-conducting elastomer sheet. When pressure is applied, the conductors move closer and the capacitance value increases. This method is known to be more advantageous, since the elastomer layer is encapsulated within the conductor and hence is not affected by temperature or humidity. Moreover, since the capacitive sensors measure the average pressure over the sensing area, it tends to produce a lower output value. This requires that a capacitive pressure sensor be fabricated at a much smaller size in comparison to the other techniques.

2.6 Printed Electronics

With the global interest in PE growing exponentially, almost every branch of our economy could be affected, if not revolutionized, by printed electronic devices. At the same time, the field of printed sensors is still very much in its infancy. Sensors are typically manufactured using conventional CMOS processes, which are often expensive and fabricated on rigid substrates [115-122]. As a result, none of these offer the high flexibility and conformability, required for various sensing applications. A continuous layer-on-layer configuration, associated with PE, is envisioned as a
promising approach that will overcome the drawbacks associated with conventional sensing systems. The successful implementation of the printing techniques for fabricating sensors could lay the foundation for a variety of PE applications ranging from fully printed wearable to implantable electronic devices.

2.6.1 Why Printed Electronics?

The advent of integrated circuits (IC) in the semi-conductor based electronics industry has radically affected human life, especially the way in which we interact with the world. This industry, through various electronic products and functions, has made possible the exploitation of IC computational speeds and memory capacities in consumer products such as smartphones and computers. The second half of the 1970s saw the introduction of a new realm of electronics known as “large-area electronics”, which aimed at decreasing the cost per area for consumer products [119]. This was followed by the introduction of PE, in the 1990s, which uses low-temperature manufacturing with high throughput patterning techniques [123].

The use of printing methods for the fabrication of electronic devices is a relatively new technique for electronic manufacturing companies. Research has shown that integration of printing techniques with conventional fabrication methods is promising for cost efficient and high volume electronic manufacturing. The ability to use conventional printing techniques to deposit functional materials enables the advantages of inexpensive large-area-electronics and additive manufacturing along with a versatile portfolio of novel applications that have been unimaginable before. This technology has the potential to decrease the usage of materials because additive manufacturing uses only functional materials in required design areas, in contrast to the traditional lithography based subtractive approach.
The transition from a high vacuum and high temperature manufacturing of ICs to the use of PE is mainly due to the ability to fabricate structures and devices that are similar to conventional electronics, with much less complexity, greater speed and lower cost [124]. The availability of conductive and semi-conductive inks in conjunction with the technical expertise available in printing allows for the easy integration of this technology with current electronic manufacturing. This has also enabled the ability to develop novel products, which goes beyond the current paradigm of human imagination, and thus opens up new markets. The potential to move from the clean-room based electronic manufacturing to ambient room condition based electronic manufacturing, using printed techniques, for the development of devices with viable functionalities is thus very interesting.

2.6.2 Challenges in Printed Electronics

The strengths of printing are paired with the challenges that this technology faces: it is namely difficult and expensive to develop a new electronic technology using an approach that in a few minutes can generate rolls covered with hundreds of meters of electronics to be characterized and optimized. Uniformity, performance and yield are daunting tasks to be solved for future PE applications. The potential low cost, the compatibility with large flexible substrates and the wealth of devices that characterize organic and PE will make possible applications that go far beyond the well-known displays made with conventional large-area silicon electronics. Organic and PE can enable a true revolution in the applications of electronics.

Like with all other technologies, PE has its own challenges along with its advantages. The main challenge that has been daunting the PE industry is the ability to achieve feature sizes, along with proper device functionality, which are comparable to conventional electronic manufacturing. Printing has always been a microscale
manufacturing process, whereas the electronic industry demands nanoscale production capabilities. Some of the other patterning issues that are crucial include: (a) proper registration for multi-layered devices, (b) adaptation of design rules, (c) standard processing of printed electronic materials with optimum functional properties and (d) attaining admissible yield.

2.6.3 Types of Printing

Printing processes are divided into two main categories: (a) impact printing and (b) non-impact printing [125]. Impact printing is based on an image carrier (screen or cylinder), which is used to transfer the image or design onto a substrate. However, non-impact printing does not require an image carrier and is based on digital control of the image. Figure 2.15 shows the classification of various printing technologies.

Figure 2.15: Classification of printing technologies [126].
The four main printing techniques used in PE are flexography, gravure, screen and inkjet printing. Table 2.3 summarizes the specifications of these individual printing processes [125]. The required printing technique for the manufacture of an electronic device is selected based on the resolution, ink viscosity, layer thickness and roughness.

### 2.6.3.1 Flexographic Printing

A flexographic press consists of a plate cylinder, anilox roller, inking unit and impression cylinder (Fig. 2.16). The plate cylinder is typically made of either rubber or photopolymer. With respect to the surface of the cylinder, the image areas on the plate cylinder are raised and non-image areas are not raised. The ink is transferred from the inking unit to the image areas of the plate cylinder by the anilox roller, which has an inbuilt doctor blade. Finally, the impression cylinder transfers the ink from the image areas onto the substrate [125].

**Table 2.3. Specifications of four major printing techniques used in printed electronics [126].**

<table>
<thead>
<tr>
<th></th>
<th>Lateral Resolution (µm)</th>
<th>Ink Film Thickness (µm)</th>
<th>Viscosity (Pa.s)</th>
<th>Printing speeds (ft/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexography</td>
<td>15</td>
<td>0.5-2</td>
<td>0.05-0.05</td>
<td>300-1000</td>
</tr>
<tr>
<td>Gravure</td>
<td>15</td>
<td>0.5-8</td>
<td>0.05-0.2</td>
<td>1500-3000</td>
</tr>
<tr>
<td>Screen</td>
<td>15</td>
<td>3-60</td>
<td>0.5-50</td>
<td>300-500</td>
</tr>
<tr>
<td>Inkjet</td>
<td>20</td>
<td>0.05-0.50</td>
<td>0.001-0.04</td>
<td>500 (for 600x600 dpi)</td>
</tr>
</tbody>
</table>
2.6.3.2 Gravure Printing

The “roll-to-roll” gravure printing is known for its high speed, high quality printing, use of low viscosity inks and robustness of the process. The typical gravure system comprises of an engraved gravure cylinder (image carrier), doctor blade, impression roller and ink pan. The basic structure of a gravure printing technique is shown in Fig. 2.17. The surface of the gravure cylinder is engraved to form gravure cells, which are responsible for transferring the ink onto the substrate. The cells are filled with ink when the gravure cylinder is rotated in the ink pan. The excessive ink on the surface of the engraved cylinder is wiped off using the doctor blade. Transferring the ink from the cells onto the substrate is assisted by the impression roller [125].
2.6.3.3 Screen Printing

Screen printing is a push through process in which the substrate is not in direct contact with the mask or image carrier (as shown in Fig. 2.18). The main components of the screen printer are a squeegee and a screen printing plate. Typically, the squeegee is made of rubber or polymeric material and the screen printing plate consists of a steel or aluminum frame, screen fabric and stencil (image). The materials used for the screen fabric and stencil vary, depending upon the use of solvents and cleaning agents. The ink is applied on top of the screen and the rubber squeegee sweeps over the top of the screen with optimum pressure, thus causing the ink to pass through the screen and transfer onto the substrate [127].
2.6.3.4 Inkjet Printing

Inkjet printing, a commonly used non-impact printing (NIP) technology in digital printing, does not require any image carrier or mask. This NIP process is subdivided into two main categories: continuous inkjet and drop-on-demand inkjet.

The working principle of a continuous inkjet printing system is based on an electronically controlled continuous stream of ink (Fig. 2.19(a)). The stream of ink is typically deflected by a voltage source in the non-image areas and hence the deflected ink is recycled back to the printing system.

In contrast to the continuous inkjet system, the drop-on-demand inkjet printing system generates ink only in image areas (Fig. 2.19(b) and (c)). This inkjet printing system usually employs two types of techniques to generate drop-on-demand ink drops: thermal or piezoelectric. A vapor bubble, created due to the vaporization of the ink, is used to push the ink out of the nozzle in the thermal inkjet system. In the piezoelectric inkjet printing systems, electric potentials are used to vibrate or deform...
Figure 2.19: Schematic of (a) continuous, (b) thermal and (c) piezo inkjet printing processes.

the piezoelectric material which in turn changes the volume of the nozzle and the ink drops are pushed out [125].

2.7 Summary

In this chapter, the author provided a comprehensive literature review that includes a detailed introduction to sensors and PE. A discussion covering the science behind the basic working of sensors, the sensor characteristics and the various types of sensors was presented. An introduction and review of the three specific sensors (electrochemical, Raman and pressure) which will be designed, fabricated and tested
in the rest of this dissertation were also presented. This was followed by an introductory discussion about PE, a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associates with PE and the different types of printing. The following chapter discusses a project that involved the development of an opto-electrochemical based dual detection system for the sensing of heavy metal compounds, using a novel flow cell. The author presents the design, fabrication and characterization of an electrochemical sensor and flow cell, as well as the measurement set-up, testing and results obtained.
2.8 References


[52] M.C. Moreno-Bondi, G. Orellana, C. Camara and O.S. Wolfbeis, “New luminescent metal complex for pH transduction in optical fiber sensing:


CHAPTER III

OPTO-ELECTROCHEMICAL BASED DUAL DETECTION OF HEAVY METAL COMPOUNDS USING A NOVEL FLOW CELL

3.1 Introduction

Heavy metals, which are ubiquitous in nature and a major cause of environmental pollution, are a growing concern in the biomedical, food and environmental industries. The main sources of heavy metal contamination are from the discharge of industrial wastes into natural waterways, run-off from various metallurgical industries, accidental spills, agriculture and mining activities [1]. It has been shown that heavy metal contamination can cause adverse health issues even at the micro or nano molar concentration levels and hence has been a major focus of research in the development of different sensing systems [2-5]. Some heavy metals such as iron (Fe), manganese (Mn) and zinc (Zn) are nutritionally essential for a healthy life [6]. However, certain other heavy metals such as copper (Cu), nickel (Ni), Hg, lead (Pb), Cd and chromium (Cr) are known to have toxicological and carcinogenic effects on both flora and fauna [7,8]. Research has shown that some of the heavy metals bond with sulfur and form cancerous sulfide compounds in the human body [9]. This has led the author to further investigate the development of a sensing system that efficiently detects heavy metal compounds that can provide a substantial benefit for many applications in the biomedical, food and environmental industries.

Several analytical methods such as UV-vis spectroscopy [10], plasma mass spectrometry [11], colorimetric analysis [12], liquid chromatography and mass spectrometry [13] as well as some biosensing detection techniques based on enzyme
activation [14] have been reported for the sensitive detection of heavy metals. However, these methods have limitations such as being time consuming, complex, requiring skilled technicians and lacking portability. RS, an analytical method capable of providing highly sensitive and selective real-time molecular level information, has been utilized for the detection and identification of heavy metal compounds [15-17]. The use of EIS has also been receiving remarkable attention in the field of sensor development [18-20]. Research on miniaturization and integration of electrochemical sensors for the detection of heavy metal compounds is highly applicable to the biomedical, food and environmental industries [21]. The rapid response of RS, on label free samples, and the high sensitivity of electrochemical sensors along with pM detection levels are promising for heavy metal detection applications [22,23]. Moreover, the possibility of false positives can be reduced by employing sensing systems that integrate simultaneous optical and electrochemical detection techniques [24-26]. The author thus believes that the innovation and development of miniaturized, rapid, portable, easy-to-use, highly sensitive and low volume sensing systems that integrate simultaneous opto-electrochemical detection capabilities is thus paramount towards the development of hand-held devices for detection of heavy metal compounds.

In this work, the author has developed an efficient microfluidic flow cell based sensing system for simultaneous opto-electrochemical detection of heavy metal compounds. A microfluidic flow cell consisting of an inlet and outlet port was designed and fabricated using acrylic material. The flow cell, with a reservoir volume of 25 µl, was designed with both laser probe and sensor grooves for simultaneous optical and electrochemical measurements. A highly sensitive electrochemical sensor device that incorporates gold (Au) IDEs, fabricated using photolithography
techniques, is employed for the electrochemical detection of various heavy metal compounds such as HgS and CdS based on EIS. Simultaneous optical detection based on RS is used for the selective detection of the heavy metal compounds. The author demonstrates the capability of the fabricated device by investigating the opto-electrochemical response of the microfluidic flow cell based sensing system towards varying concentrations of HgS and CdS.

3.2 Background

This project builds on one of the author’s previous works, which demonstrated the rapid and sensitive detection of various bio/chemicals [27]. In this work, the author developed an efficient impedance based electrochemical biosensor and a first generation flow cell for the detection of various bio/chemicals. A brief description of the design, fabrication steps, measurement steps, testing and results is presented in the following section.

3.2.1 Design of the Electrochemical Sensor

Research in the field of electrochemical sensors has reported on the development of several different electrode geometries [28-31]. This has been possible due to the advancements made in microfabrication methods. Lithographically fabricated microelectrodes have demonstrated higher sensitivity than conventional macroelectrodes. This is because the macroelectrodes have a semi-finite linear diffusion layer and thus causes a larger depletion of reactants, when compared to the microelectrodes [32]. An IDE array, which is one of the most prominent examples of microelectrodes, has been reported to have several advantages such as low ohmic drop of the potential, increased signal-to-noise ratio and fast establishment of a steady-state signal. This has led to the use of two-electrode circuits, rather than the conventional three-electrode potentiostatic circuits [32]. Research by Min and
Baeummer, for the optimization of IDEs has shown that some of the key parameters associated with the IDE geometry are the number of electrodes \((N)\), electrode finger width \((w)\), electrode finger spacing \((s)\) and electrode height \((h)\). This study also proved that lower number of electrodes \((200)\) was better than larger number of electrodes \((400)\), for analyte concentrations in the range of 50-100 \(\mu\)M. In addition, better results were obtained with electrodes of 1-5 \(\mu\)m width, 70-140 nm thickness and 5 \(\mu\)m spacing. Yet another study by Gerwan et al. demonstrated the effect of current comprisement curves in IDEs [33]. A schematic of a current comprisement curve, which shows the region just above the IDEs with the maximum electric field potential, is shown in Fig. 3.1. For example, consider the case of IDEs with widths \((w)\) and spacing \((s)\) of 200 nm. This means that 80\% of the current flows in a region not higher than 200 nm above the surface of the IDEs.

Figure 3.2 shows the typical geometry of IDEs which helps in providing a large sensing area. The capacitance for a parallel plate system is given by Eq. (11).
\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \]  

where \( C \) is capacitance in farads (F), \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the dielectric constant of the medium between the parallel plates, \( A \) is the effective overlapping area of the parallel plates, \( d \) is the distance between parallel plates. This expression denotes that a linear difference in capacitance can be obtained by increasing or decreasing the length of the plates, whereas, adjusting the spacing between the two plates would result an inverse response. Some initial values for capacitance were calculated based on this relationship, as shown in Fig. 3.3.

Taking all the above factors into consideration and with an aim of trying to lower the detection limits as well as miniaturization of the electrochemical sensor, overall device dimensions of 2 cm × 1 cm × 0.05 cm, with IDEs that had a spatial periodicity (\( \lambda \)) of 20 µm, interdigitated space of 5 µm, length of 4995 µm and IDE layer thickness of 0.1 µm was chosen by the author. The sensor was designed with twenty five pairs of electrodes and an active sensing area of 1.25 mm\(^2\). Based on these

![Figure 3.2: Typical interdigitated electrode geometry.](image_url)
Figure 3.3: Calculated capacitance for varying number of interdigitated electrodes (N) and interdigitated electrode length (L) [27].

features, the initial capacitance of the sensor was calculated to be 0.5 pF. Glass, which is an insulating material, was chosen as the substrate for the electrochemical sensor. Au was selected as the electrode material due to its inertness and because of its known affinity and binding ability towards bio/chemicals [34]. A schematic of the electrochemical sensor is shown in Fig. 3.4.

Figure 3.4: Schematic of the electrochemical sensor [27].
3.2.2 Fabrication of the Electrochemical Sensor

The photomask layout for the electrochemical sensor was designed using the CoventorWare™ 2008 software platform (Fig. 3.5). The different layers and steps to be followed at the time of fabrication were designed in the process editor section of CoventorWare™. This file was then imported to the layout editor to design the geometry of shapes for each layer and a finally a .gds format file was created. The photomask was created on a 5” × 5” square soda-lime plate with chrome coating at Advanced Reproductions Corporation, Massachusetts. The fabricated photomask consisted of a second sensor design with similar device dimension and electrode width and spacing which may be studied as part of future work.

The electrochemical sensor fabrication was performed on 4” round glass wafers at the Lurie Nanofabrication Facility (LNF) of University of Michigan. As shown in Fig. 3.6; (A) initially, a positive photoresist (SPR220 3.0) was spin-coated on a glass substrate using Suss Micro Tec ACS200 automatic resist coater-developer; (B) then

![Figure 3.5: Mask Layout [27]](image-url)
the resist film was exposed to UV light through the photomask using a Suss Micro Tec MA/BA-6 contact aligner; (C) evaporation of 10 nm of Chromium (Cr) was followed by evaporation of the 100 nm of Au on Enerjet e-beam evaporator from Denton/Lesker; and finally (D) lift off was done in a heated Shipley Microposit 1112A device, with sonication. The wafers were then diced on Micro Automation MA6 Dicing Saw. A photograph of the fabricated wafer with sensor devices and an individual sensor is shown in Fig. 3.7. The average thickness and width of the Au IDEs was measured to be 0.2 µm and 5.5 µm, respectively using a Bruker GTL-EN-61010 profilometer (Fig. 3.8).

Figure 3.6: Electrochemical fabrication process steps [27].
Figure 3.7: (a) Diced wafer with photolithographically fabricated sensors and (b) an individual electrochemical sensor [27].
Figure 3.8: (a) 3D Profilometry scan of the gold interdigitated electrodes illustrating an (b) average thickness (ΔZ) of 0.2 µm and (b) average width (ΔX) of 5.5 µm.

3.2.3 Fabrication of the First Generation Flow Cell

The first generation flow cell was designed in AutoCAD™ and fabricated using acrylic material. An O-Ring was used in the flow cell with an outer diameter of
7/16 inch and inner diameter of 5/16 inch, resulting in a reservoir volume of 25 µl. The O-Ring was placed in a groove designed with a depth of 1050 µm so that the O-ring exposure would be 537.5 µm high from the electrode surface thereby providing more than 100 times the required height for an optimal 80 % current comprisement curve. The inlet port was designed at an angle of 50º with the outlet port for a complete flow of the sample solution through the microfluidic chamber. An axially magnetized set of Neodymium magnets (Diameter - 0.25 inch; Thickness - 0.375 inch; Magnetic strength – 13,200 Gauss) purchased from K & J Magnets, Inc. was incorporated for the efficient closing of the flow cell, which results in the tight sealing of the O-Ring around the sensing area of the sensor. A photograph of the fabricated flow cell is shown in Fig. 3.9.

Figure 3.9: Flow cell with electrochemical sensor placed in sensor groove and showing inlet and outlet ports along with O-Ring and SOIC test clip [27].
3.2.4 Results

The author demonstrated the capability of the sensor through the quantitative detection of various bio/chemicals like mouse monoclonal IgG and D-Proline. Mouse IgG was chosen as a test sample due to its extensive use as an antibody in various biosensing applications [35-37]. D-Proline was used due to its structural similarity to domoic acid, which is a main cause of seafood poisoning and according to the US Food and Drug Administration (USFDA), the approved domoic acid limit is 20 µM [38].

Figure 3.10(a) shows the measured impedance response of the electrochemical sensor towards various concentrations of mouse monoclonal IgG at an operating frequency range of 20 Hz to 2 kHz, with an applied potential of 1 mV. A distinguishable and better signal to noise ratio was achieved from 400 Hz to 500 Hz, as shown in the inset. As an example, for measurements at 450 Hz frequency, the impedance value decreased from 5542 Ω to 5047 Ω to 4212 Ω to 3929 Ω to 3656 Ω to 3358 Ω as concentrations of mouse monoclonal IgG increased from 1 pM to 10 pM to 1 nM to 5 nM to 50 nM to 100 µM, respectively. These impedance responses displayed a detection level as low as 1 pM and the ability of the sensor to distinguish among a wide range (micro, nano and pico level) of sample concentrations.

Figure 3.10(b) shows the impedance percentage change at the D-Proline biosensor interface when compared to a phosphate buffer solution (PBS). Experiments were conducted at various concentration levels of 1 pM, 100 pM, 100 nM, 100 µM and 100 mM of D–Proline and a distinguishable and better signal to noise ratio was achieved from 20 Hz to 50 Hz. The impedance percentage changes at 20 Hz for D-Proline were 18 %, 25 %, 26 %, 27 % and 29 %, when compared to
PBS levels. At 50 Hz, D-Proline exhibited a 14\%, 21\%, 22\%, 23\% and 24\% change in impedance response with respect to PBS levels.

Figure 3.10: Sensor response to (a) mouse monoclonal IgG and (b) D-Proline, at applied potential of 1 mV.
3.3 Experimental

3.3.1 Chemicals, Materials and Sample Preparation

CdS and HgS in crystalline form were purchased from Sigma-Aldrich Chemical Company. Spring loaded small outline integrated chip (SOIC) test clips (14 pin) were purchased from Pomona Electronics. Tubing (Inner diameter - 0.01 inch; Outer diameter – 0.0625 inch) and tube connection accessories for sample transfer were purchased from Upchurch Scientific. CdS was suspended in deionized (DI) water to form solutions of 100 pM, 100 nM, 100 µM and 100 mM concentrations. 1 pM, 100 pM, 1 nM and 100 nM concentration solutions of HgS was also prepared in DI. All solutions were stored at 40 °F in 10 ml aliquots before use.

3.3.2 Sensor Fabrication

The design and fabrication process of the electrochemical sensor device used in this study has been reported previously [27]. In brief, the electrochemical sensor was photolithographically fabricated, at the LNF of University of Michigan, on a glass substrate with overall dimensions of 2 cm × 1cm × 0.05 cm and Au IDEs. The sensor has twenty five pairs of IDEs with an active sensing area of 1.25 mm². The IDEs have a spatial periodicity (λ) of 20 µm, interdigitated space of 5 µm, length of 4995 µm and Au layer thickness of 0.1 µm.

3.3.3 Second Generation Flow Cell Fabrication

The schematic of the flow cell is shown in Fig. 3.11. The author has designed the second generation flow cell with an aim of overcoming two major problems that were observed based on studies performed with the first generation flow cell (shown in Fig. 3.8). A detailed analysis revealed the need for a better designed flow cell. The second generation flow cell was then fabricated and tested to overcome the limitations
Figure 3.11: Schematic of the opto-electrochemical dual detection flow cell.

of the first generation flow cell. The problems faced and how they were addressed is given below.

**Bubble formation:** In the first generation flow cell, formation of bubbles within the reservoir was observed. Further investigation revealed that relocating the position of the inlet and outlet ports as well as modifying the design of the flow channels would solve this problem. This was because the length of the flow channels required a higher pressure, in the initial design, to push the test sample out of the chamber. The schematic of the first and second generation flow cells is shown in Fig. 3.12(a) and Fig. 3.12(b), respectively. In the second generation flow cell, the inlet and outlet ports were relocated to the side of the flow cell and the shape of the flow channels were modified. The location of the inlet and outlet ports for the first and second generation flow cells is shown in Fig. 3.12(c) and Fig. 3.12(d), respectively.
This modification enabled for lower analyte flow rates, thereby eliminating the possibility of creation of bubbles. Tests performed on the modified flow cell demonstrated the absence of bubbles.

**Test sample not covering sensing area:** In the first generation flow cell, it was observed that the test samples did not cover the entire sensing area. This was because the inlet and outlet ports within the O-ring reservoir were located close to each other and were also at a greater distance from the reservoir wall. This caused the test sample to start exiting the reservoir even before the entire volume was filled. The schematic of the first and second generation flow cells is shown in Fig. 3.13(a) and
In the second generation flow cell fabricated, these ports were relocated much closer to the wall of the reservoir, thus increasing the distance between them. In addition, the outlet port was positioned at a comparatively higher height when compared to the inlet port (Fig. 3.13(c)). The location of the inlet and outlet ports, within the O-ring reservoir, for the first and second generation flow cells is shown in Fig. 3.13(d) and Fig. 3.13(e), respectively. These two design changes facilitated the complete filling of the reservoir volume, before the sample started to flow out through the outlet port. Tests performed on the modified flow cell demonstrated proper coverage of the sensing area by the test sample.

Figure 3.13: Schematic of the inlet and outlet ports, within the O-ring reservoir, of the (a) first and (b) and (c) second generation flow cells. Photographs of the of the inlet and outlet ports, within the O-ring reservoir, of the (a) first and (b) second generation flow cells.
The second generation flow cell, with sensor and laser probe grooves for simultaneous opto-electrochemical measurements was designed in AutoCAD™ and fabricated using acrylic material. An O-Ring, with an outer diameter of 7/16 inches and inner diameter of 5/16 inches, was used in the flow cell, resulting in a reservoir volume of 25 µl. It also consists of an inlet and outlet port for a complete flow of the sample solution through the microfluidic chamber. The efficient closing of the flow cell was made possible by the use of an axially magnetized set of neodymium magnets (diameter - 0.25 in.; thickness - 0.375 in.; magnetic strength - 13,200 G) purchased from K & J Magnets Inc. which resulted in the tight sealing of the O-Ring around the sensing area of the electrochemical sensor. A photograph of the opto-electrochemical dual detection flow cell is shown in Fig. 3.14.

![Opto-electrochemical dual detection flow cell](image)

**Figure 3.14:** Opto-electrochemical dual detection flow cell.
3.3.4 Experiment Setup

The experiment setup is shown in Fig. 3.15. Before use, the electrochemical sensor was cleaned with acetone and then blow dried with pressurized air. A programmable syringe pump (KD Scientific KDS210) was connected to the inlet port of the microfluidic flow cell chamber for loading the sample onto the sensing area of the electrochemical sensor. A reference signal was initially established with DI water for 5 minutes. Then, varying concentrations of CdS (100 pM, 100 nM, 100 µM and 100 mM) and HgS (1 pM, 100 pM, 1 nM and 100 nM) were injected into the flow cell, at the flow rate of 50 µl/min for 5 minutes each, with intermediate flushing of DI water. A custom built LabVIEW™ program was used for controlling an LCR meter (Agilent E4980A) to acquire EIS measurements, at 1 kHz frequency and 1 mV applied potential. Simultaneously, a 785 nm laser source (Innovative Photonics) was employed to excite the sample using a Raman probe (Inphotonics Inc.), with an integration time of 3 seconds at 300 mW. A spectrometer (QE 65000 Ocean Optics) was used to obtain the RS, which was then analyzed using Spectra Suite software (Ocean Optics).

Figure 3.15: Experiment Setup.
3.4 Results

The response of the opto-electrochemical system was first tested towards CdS, at an operating frequency of 1 kHz and 1 mV applied potential. Figure 3.16(a) shows the dynamic impedance response of the electrochemical sensor to different concentrations of CdS. It was observed that the average impedance decreased from 4.5 kΩ to 4.2 kΩ to 3.8 kΩ to 3.2 kΩ as the concentration of CdS was increased from 100 pM to 100 nM to 100 µM to 100 mM, respectively. This resulted in an impedance percentage change, \((Z_{DI} - Z_{measured})/Z_{DI}\), of 57 %, 60 %, 63 % and 69 % for the 100 pM, 100 nM, 100 µM and 100 mM concentrations of CdS, respectively when compared to DI water. It is worth noting that the approved level of CdS by the USFDA is 3 µM [39]. Figure 3.16(b) shows the simultaneous RS response of the electrochemical sensor towards CdS, with an integration time of 3 seconds at 300 mW and 785 nM excitation. The RS spectrum yielded peaks for CdS at 244 cm\(^{-1}\), 261 cm\(^{-1}\), 291 cm\(^{-1}\), 358 cm\(^{-1}\), 553 cm\(^{-1}\) and 595 cm\(^{-1}\) which are related to the Raman active branches [40].

The opto-electrochemical response of the system was also tested towards HgS, which has been classified as a global heavy metal pollutant and the most frequently observed heavy metal compound [41]. An average impedance of 21.9 kΩ, 22.1 kΩ, 22.5 kΩ and 23.2 kΩ was observed for the 1 pM, 100 pM, 1 nM and 100 nM concentrations of HgS, respectively at an operating frequency of 1 kHz and 1 mV applied potential. The EIS response showed that the impedance percentage change when compared to DI water increased from 20.9 % to 22 % to 24.3 % to 28.2 % as the concentration of HgS was increased from 1 pM to 100 pM to 1 nM to 100 nM, respectively (Fig. 3.17(a)). According to USFDA, the toxicity limit for HgS is 1 µM [42]. Raman peaks (shown in Fig. 3.17(b)) were observed for the Raman active
branches for HgS at 256 cm\(^{-1}\), 292 cm\(^{-1}\) and 353 cm\(^{-1}\) in the RS response [43]. Through these results, the author was able to demonstrate detection levels as low as 1 pM and the ability of the opto-electrochemical system to distinguish among a wider range (milli, micro, nano and pico level) of sample concentrations.

Figure 3.16: (a) Dynamic impedance based electrochemical response of sensor towards CdS at 1 kHz and applied potential of 1 mV; (b) Raman spectra of CdS with an integration time of 3 seconds at 300 mW and excitation of 785 nm.
The author also performed a statistical analysis for the reproducibility or repeatability of the electrochemical sensor. In order to do this, the author investigated the electrochemical response of three different sensors for five times and calculated the mean and standard deviations of the electrochemical sensor, towards varying concentrations of CdS and HgS. Figure 3.18 shows the response of the sensor towards
varying concentrations (100 pM, 100 nM, 100 µM and 100 mM) of CdS. An average impedance value of 19.7 kΩ, 17.5 kΩ, 15.5 kΩ, 12.5 kΩ and 5 kΩ, with an average standard deviation of 520.5 Ω, 684.7 Ω, 588.2 Ω, 696.8 Ω and 299.6 Ω was observed for the DI, 100 pM, 100 nM, 100 µM and 100 mM concentrations, respectively (Fig. 3.18(a)). This corresponds to an average impedance percentage change of 11.2 %, 21.6 %, 36.6 % and 74.3 % with an average standard deviation of 6.1 %, 5.6 %, 6.2 % and 4.2 % for the 100 pM, 100 nM, 100 µM and 100 mM concentrations, respectively (Fig. 3.18(b)), when compared to the base impedance of DI. Using the results obtained, the author showed that that electrochemical response of the sensor could be used to quantify the different concentrations of CdS as there was no cross-over in the overall impedance values, among all three sensors tested.

Similarly, for HgS, an average impedance value of 17.9 kΩ, 20 kΩ, 21.8 kΩ, 23.2 kΩ and 24.9 kΩ, with an average standard deviation of 564.9 Ω, 451.5 Ω, 615.2 Ω, 450.3 Ω and 398.4 Ω was observed for the DI, 1 pM, 100 pM, 1 nM and 100 nM concentrations, respectively (Fig. 3.19(a)). This corresponds to an average impedance percentage change of 12.1 %, 21.8 %, 29.7 % and 39.4 % with an average standard deviation of 5.7 %, 6.6 %, 5.7 % and 5.4 % for the 1 pM, 100 pM, 1 nM and 100 nM concentrations, respectively (Fig. 3.19(b)), when compared to the base impedance of DI. These results demonstrated that there was a crossover in the impedance values of 100 pM and 1 nM concentrations of HgS, among the three sensors tested. However, this crossover was not observed when the impedance values of each individual sensor were compared to each other. Therefore the author concluded that the electrochemical sensor could be used to quantify different concentrations of HgS.
Figure 3.18: (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of CdS at 1 kHz and applied potential of 1 mV.
Figure 3.19: (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of HgS at 1 kHz and applied potential of 1 mV.
3.5 Summary

In this chapter, the author presented an introduction that discusses the need for an opto-electrochemical based dual detection system. The author then presented details of the background work that has led to the current project. This includes the fabrication of an electrochemical sensor and a first generation flow cell as well as the response of the system to different bio/chemicals. This was followed by a detailed account of the experimental tasks involved in this project including the chemicals, materials and sample preparation; sensor fabrication; flow cell fabrication; the experiment setup; and results are presented.

To summarize, an efficient opto-electrochemical sensing system, for the dual detection of heavy metal compounds was successfully developed. A novel microfluidic flow cell, capable of simultaneous opto-electrochemical measurements and with a reservoir volume of 25 µl, was designed and fabricated using acrylic. An electrochemical sensor with Au IDEs on a glass substrate was photolithographically fabricated. EIS performed on CdS and HgS yielded picomolar (pM) concentration detection levels. Selective detection of CdS and HgS was made possible based on optical signals produced in the Raman emission spectra. In addition, a statistical analysis for the reproducibility of the sensor response was also performed by investigating the electrochemical response of three different sensors for five times, towards varying concentrations of CdS and HgS. The response obtained demonstrated that the impedance based electrochemical response of the sensor could be used to quantify different concentrations of CdS and HgS since there was no crossover in the overall impedance values, among all three sensors tested.

In the following chapter, the author presents a project that involved the development of a novel next generation of electrochemical MSP, by integrating
conventional photolithography and printing processes, for the detection of various bio/chemicals. The author discusses the design, fabrication and characterization of the flexible microfluidic sensor. The measurement set-up, testing and results obtained are also presented.
3.6 References


CHAPTER IV

A NOVEL FLEXIBLE MICROFLUIDIC PLATFORM: INTEGRATION OF CONVENTIONAL PRINTED CIRCUIT BOARD TECHNOLOGY AND INKJET PRINTING METHOD

4.1 Introduction

Over the last decade, a steady and considerable effort has been directed towards the development and integration of microfluidic devices for applications in the biomedical field [1-4]. Microfluidic systems, capable of handling very low volumes of analytes at a significantly lower cost per assay is the most promising way to realize an efficient, rapid response, portable and cost effective detection platform. Typically, master molds for microfluidic channels have been fabricated using expensive silicon based technology, which is significantly time consuming and requires expertise [5-11]. These drawbacks deter time-bound and budget-constricted experimenters, especially researchers in academia, from exploiting the advantages of microfluidic structures in their applications. The author thus intends to utilize the promising potential of microfluidics by employing conventional, cost-effective PCB technology to fabricate microfluidic structures.

In recent years, the field of PE has also been gaining remarkable interest due to its ability to mass produce cost efficient and flexible electronic devices [12-18]. PE uses traditional printing techniques for fabrication of electronic devices, which provides several advantages, when compared to conventional lithography techniques, such as reduction of material wastage during fabrication, less complex fabrication and low manufacturing temperatures which ultimately leads to cost efficiency. PE has become an enabling technology for numerous applications in electronic devices such
as solar cells, sensors, RFID tags and displays [19-32]. However, there are little or no reports on the use of printing technologies for the fabrication of microfluidic sensing devices. This has led the author to investigate the possibility of developing flexible microfluidic sensing devices by combining PCB technology along with conventional printing methods such as gravure, screen and inkjet printing.

In this work, the author uses both conventional PCB and printing technology to fabricate an efficient MSP. Polydimethylsiloxane (PDMS) based microfluidic channels were fabricated using master molds created with PCB technology. Silver (Ag) based ink was employed to inkjet print IDEs on flexible polyethylene terephthalate (PET) substrate. The printed PET substrate and PDMS were bonded to form the MSP. The author demonstrates the capability of the fabricated device by investigating the EIS based response of the MSP towards varying concentrations of CdS, HgS and potassium chloride (KCl).

4.2 Experimental

4.2.1 Chemicals, Materials and Sample Preparation

A transparent PET (Melinex® ST 506) film from DuPont Teijin Films was used as the substrate. A conductive Ag ink (TEC-IJ-010 InkTec Inc.) was used for metallization of the IDEs. PDMS, which was used to fabricate the microfluidic channels, was purchased as a two-part heat curable silicone elastomer kit (Sylgard® 184) from Dow Corning. Spring loaded SOIC test clips (14 pin) were purchased from Pomona Electronics. Tubing (Inner diameter - 0.01 inch; Outer diameter – 0.0625 inch) and tube connection accessories for sample transfer were purchased from Upchurch Scientific. Delrin® Acetal Resin block was purchased from McMASTEr-CARR® and used as the base for the master mold. KCl, CdS and HgS (in crystalline form) were purchased from Sigma–Aldrich® Chemical Company. KCl
was mixed with DI water to form solutions of 1 pM and 1 nM concentrations. CdS and HgS were suspended in DI water to form solutions of 1 pM, 1 nM, 1 µM and 1 mM concentrations. All solutions were stored at 40 °F in 10 ml aliquots before use.

4.2.2 Design of PDMS Based Microfluidic Flow Channels

PDMS, an elastomeric polymer has been a strong candidate for the fabrication of microfluidic flow channels due to some of its advantageous features such as: (a) a Young’s modulus and shear modulus of roughly 0.5 MP and of 0.25 MPa, respectively, which are characteristics of a moderately stiff elastomeric polymer; (b) being optically transparent at 300 nm wavelength; (c) being fundamentally hydrophobic with a water contact angle of ~110°; and (d) being a non-toxic and biocompatible material [33-35]. Moreover, the elastomeric property of PDMS enables it to conform to almost any surface, with proper atomic-level contact, which is very crucial for proper sealing in microfluidic applications.

The design of PDMS, or any elastomeric material, requires careful attention. This is because these materials are prone to: (a) lateral collapse causing pairing of narrowly spaced features; or (b) sagging of the region between two widely separated features (Fig. 4.1). It is required that the aspect ratios of PDMS follow the design rules as given in Eq. (12) and Eq. (13) to avoid the problem of sagging and pairing [36].

\[
\left( \frac{T}{S} \right) > 0.05 \quad (12)
\]

\[
0.5 < \left( \frac{T}{W} \right) < 5 \quad (13)
\]

where \( T \) is the height of the microfluidic channel, \( S \) is the spacing between two channels and \( W \) is the width of the PDMS. Calculation of these aspect ratios is
important for the proper designing of the master mold that will be used to create the PDMS structure for the microfluidic channels [37].

The author has designed the microfluidic channels based on an assembly based approach, reported by M. Rhee and M.A. Burns [38]. This approach, which makes use of microfluidic assembly blocks (MAB) as basic building blocks, enables microfabrication experimenters to design microfluidic flow channels in a rapid and standardized manner. Each MAB was designed with a specific function that it will serve in the microfluidic application, as given in Table 4.1. Figure 4.2 shows examples of two designs that were made using the MABs.

Figure 4.1: PDMS design and fabrication potential issues. (a) Schematic of a PDMS structure with microfluidic channel width, spacing and height of S, W and T, respectively; (b) Sagging of recessed structures with aspect ratios T/W < 0.5; and (c) Pairing or lateral collapse of relief structures with aspect ratios T/W > 5.
Table 4.1: Assembly blocks for Microfluidic Channel Design [38].

<table>
<thead>
<tr>
<th>Assembly Block</th>
<th>Schematic</th>
<th>Dimension (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet/Outlet Port</td>
<td><img src="image" alt="Inlet/Outlet Port" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>Straight Channel (Short)</td>
<td><img src="image" alt="Straight Channel" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>Cross Channel</td>
<td><img src="image" alt="Cross Channel" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>T-Channel</td>
<td><img src="image" alt="T-Channel" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>Variable Size Connector</td>
<td><img src="image" alt="Variable Size Connector" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>3-Way Fusion Channel</td>
<td><img src="image" alt="3-Way Fusion Channel" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>Y-Channel</td>
<td><img src="image" alt="Y-Channel" /></td>
<td>0.6 × 0.6</td>
</tr>
<tr>
<td>Component</td>
<td>Diagram</td>
<td>Dimensions</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------</td>
<td>--------------</td>
</tr>
<tr>
<td>90° Bend Channel</td>
<td><img src="image1" alt="Diagram" /></td>
<td>0.6 x 0.6</td>
</tr>
<tr>
<td>Spacer/Stopper</td>
<td><img src="image2" alt="Diagram" /></td>
<td>0.6 x 0.6</td>
</tr>
<tr>
<td>Reaction Chamber (Small)</td>
<td><img src="image3" alt="Diagram" /></td>
<td>0.6 x 0.6</td>
</tr>
<tr>
<td>Reaction Chamber (Large)</td>
<td><img src="image4" alt="Diagram" /></td>
<td>1.2 x 1.2</td>
</tr>
<tr>
<td>Culture Bed</td>
<td><img src="image5" alt="Diagram" /></td>
<td>1.2 x 1.8</td>
</tr>
<tr>
<td>Straight Channel (Long)</td>
<td><img src="image6" alt="Diagram" /></td>
<td>0.6 x 1.8</td>
</tr>
<tr>
<td>Mixing Meander Chamber</td>
<td><img src="image7" alt="Diagram" /></td>
<td>0.6 x 1.8</td>
</tr>
</tbody>
</table>
4.2.3 Fabrication of PCB as Master Mold for PDMS Based Microfluidic Channels

The master mold for the microfluidic channels was designed in ExpressPCB™ software (Fig. 4.3(a)) and fabricated using conventional PCB technology (Fig. 4.1(b)). It had overall dimensions of 3.8” × 2.5” × 0.062” (96520 µm × 63500 µm × 1575 µm). The copper line thickness of 0.0017” (43 µm), which is typically used in the PCB manufacturing process, was selected and this
thickness corresponds to the height of the microfluidic channel. The width of the microfluidic channels was chosen to be 500 µm. These dimensions relate to a designed aspect ratio of \((T/S) = (43/500) = 0.086\), which ensures that there is no sagging of the PDMS in the microfluidic channels, as per Eq. (13).

4.2.4 Machining of Delrin

A 4” × 3” × 0.5” (43 µm × 43 µm × 43 µm) Delrin® Acetal Resin block with overall dimensions of 3.8” × 2.5” × 0.2” (96520 µm × 63500 µm × 5000 µm) was machined, as shown in Fig. 4.4.

4.2.5 Preparation of PDMS

PDMS, a soft polymer, which is widely used to make cheap, disposable microfluidic devices, was purchased as a two-part heat curable silicone elastomer kit. The Sylgard 184 pre-polymer was mixed in a 10:1 (w/w) ratio with the included curing agent and stirred vigorously until well mixed. The mixing introduces bubbles which were removed by setting the mixture aside at room temperature for 30 minutes.

4.2.6 Fabrication of Microfluidic Channels

The fabricated PCB was then placed in the machined area of the Delrin (Fig. 4.5(a)) to form the master mold. The prepared liquid PDMS was then poured into this master mold and the whole setup was cured at 90 °C for 30 minutes in a VWR oven. The PDMS was finally peeled off from the PCB master mold (Fig. 4.5(b)). The inlet and outlet ports, with a diameter of 1 mm, were cored out using a biopsy puncher (33-31AA) from Miltex®.
Figure 4.3: (a) Schematic of microfluidic flow channel designed in ExpressPCB™ software and (b) fabricated PCB board.

Figure 4.4: (a) Dimensions of Delrin block and machined area (b) Photograph of Delrin block after machining.
4.2.7 Microfluidic Channel Characterization

The average width and thickness of the microfluidic channels were measured to be 500 µm and 54 µm using a Bruker GTL-EN-61010 profilometer (Fig. 4.6). This relates to a practical aspect ratio of \( \frac{T}{S} = \frac{54}{513} = 0.105 \), which ensures that there is no sagging of the PDMS in the microfluidic channels, as per Eq. (12).

Figure 4.6: 3D Profilometry scan of the microfluidic channel illustrating an average height of 54 µm.
The flow of a fluid through the microfluidic channel was characterized by the Reynolds number [39], defined as

\[ R_e = \frac{Lv\rho}{\mu} \]  

(14)

where \( v \) is the velocity of the fluid (m/s), \( L \) is the characteristic length (m), \( \rho \) is the density of the fluid (for water, 1000 kg/m\(^3\)), and \( \mu \) is the viscosity of the fluid (for water, 10\(^{-3}\) kg/(m.s)). For aqueous solutions, \( \rho \) and \( \mu \) are fixed parameters (characteristics of the fluid), and the rate of fluid flow \( (v) \) and channel dimension \( (L) \) are controllable. The flow of liquids is classified into three different types based on the Reynolds number. They are: (a) laminar, (b) transitional and (c) turbulent flow (Fig. 4.7). Laminar flow typically occurs for small channels and low flow velocities, whereas turbulent flow happens at relatively higher flow rates and larger flow channels. Transitional flow, which is an intermediate level of laminar and turbulent flows, occurs with laminar flow near the edge of the flow channel and turbulence towards the center of the flow channel. Under typical microfluidic conditions of small sized channels and a low rate of fluid flow, \( R_e \) is almost always low, a value that correlates with laminar flow behavior. Moreover, laminar flow provides a means by which molecules can be transported in a relatively predictable manner through microchannels. With the designed dimensions and a 50 \( \mu \)l/min flow rate, the Reynolds number was calculated to be \( R_e = 3 \), which correlate to laminar flow behavior.

A contact angle of 92.9° for water on PDMS was measured using a goniometer (First Ten Angstroms FTA-2000) (Fig. 4.8). The inset shows the plot of contact angle versus time which demonstrated an average value of 92.9° over a period of 60 seconds. The results obtained show that there was no absorption of the sample on the PDMS surface.
4.2.8 Inkjet Printing of Electrodes

Ag based ink, as IDEs, was printed using a Dimatix 2831 inkjet printer with a 10 pL cartridge and 20 µm drop spacing, on flexible PET. Each sensing chamber had two pairs of IDEs that were 5400 µm long with width and spacing of 200 µm and 600 µm, respectively. The average thickness of the printed electrode was measured to be 0.3 µm using a Bruker GTL-EN-61010 profilometer (Fig. 4.9).
4.2.9 Integrating Microfluidic Flow Channels and Electrodes for Final Flexible Microfluidic Sensing Device

The printed PET substrate and PDMS were cleaned with isopropyl alcohol (IPA) and placed on a non-conducting surface, with the bonding side up. A corona discharge treatment was performed by passing back and forth a laboratory corona treater (Model BD-20AC, Electro-Technic Products Inc.), approximately ¼ inch above each bonding surface, for approximately 15 seconds. The treated surfaces were then pressed together and left undisturbed overnight for the bonding to take effect; and thus form the flexible microfluidic sensing device (Fig. 4.10).
Figure 4.10: PDMS based printed and flexible microfluidic sensing device; (Inset) printed interdigitated electrodes.

4.2.10 Experiment Setup

The experiment setup is shown in Fig. 4.11. Calibration for the wires and probes was done before taking measurements. All measurements were conducted at room temperature. A programmable syringe pump (KDS210P) from KD Scientific was connected to the inlet port of the microfluidic flow channel for loading the test sample. An Agilent E4980A precision LCR meter was connected to the printed electrodes via a SOIC test clip, for impedance measurements. DI water was first loaded into the MSP in order to set the reference signal. Then, sample solutions with different concentrations of KCl (1 pM and 1 nM); CdS (1 pM, 1 nM, 1 µM and 1 mM) and HgS (1 pM, 1 nM, 1 µM and 1 mM) were loaded into the sensing device, with intermediate flushing of DI water. The impedance magnitude of the device was measured at a frequency of 1 kHz with a 100 mV applied potential. The response of the MSP was observed and analyzed using a custom built LabVIEW program.
4.3 Results

The author simulated the fluid flow regime of the microfluidic channel by using the software for multiphysics simulations of microfluidic devices in COMSOL Multiphysics® 4.2a (Fig. 4.12). The model was simulated with a single phase, stationary laminar fluid flow physics interface. This physics interface was chosen to simulate the fluidic conditions in the non-turbulent or laminar regime with a single phase. Moreover, this physical interface is typically considered to model slow-moving fluid flow in environments without sudden changes in geometry, material distribution, or temperature. The equations, boundary conditions, and volume forces were selected for modeling freely moving fluids.

The Navier-Stokes equations, which are primarily used for solving non-turbulent models, were chosen to model the velocity field and the pressure mapping which can be mathematically expressed using Eq. (15) and Eq. (16).

\[
\rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -p I + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) I \right] + \mathbf{F} \tag{15}
\]

\[
\nabla \cdot (\rho \mathbf{u}) = 0 \tag{16}
\]

where \(\rho\) is the fluid density, \(\mathbf{u}\) is the velocity field, \(\mu\) is the fluid viscosity, \(\nabla\) is the de operator, \(p\) is the pressure, \(I\) is the 3×3 identity matrix, \(T\) is the component of
the total stress tensor (which has order two) and $F$ represents the body forces (per unit volume) acting on the fluid.

The “no slip” condition was selected as the boundary condition for the stationary solid walls of the microfluidic channels and liquid. This condition, which means that the fluid wall is not moving generates the parabolic flow profile, was prescribed using Eq. (17).

$$\mathbf{u} = 0$$ \hspace{1cm} (17)

A “laminar inflow” boundary condition, with a flow rate of 50 $\mu$L/min, was considered for the inlet port, as shown in Eq. (18) and Eq. (19).

$$L_{\text{entr}} \nabla_t \cdot [-p_{\text{entr}} \mathbf{I} + \mu (\nabla_t \mathbf{u} + (\nabla_t \mathbf{u})^T)] = -p_{\text{entr}} \mathbf{n}$$ \hspace{1cm} (18)

$$\nabla_t \cdot \mathbf{u} = 0$$ \hspace{1cm} (19)

where $L_{\text{entr}}$ is a fictitious domain of length that is assumed to be attached to the inlet of the computational domain, $\nabla_t$ is the del operator as a function of time, $p_{\text{entr}}$ is the pressure at the inlet port and $\mathbf{n}$ denotes the normal to the boundary.

A “pressure, no viscous stress” boundary condition, which specifies the vanishing viscous stress along with a Dirichlet condition on the fluid pressure, was considered for the outlet port, as shown in Eq. (20).

$$\left[ \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right] \mathbf{n} = 0$$ \hspace{1cm} (20)

The simulated results demonstrated that the maximum fluid velocity in the microfluidic channel was $6.2 \times 10^{-2}$ m/s (Fig. 4.12(a)). This velocity correlates to a laminar liquid flow with Reynolds number of 5. Fig. 4.8(b) shows that the variation of liquid pressure, across the channel, decreased as it moved from the inlet towards the outlet. A maximum pressure of 6.9 kPa was observed at the inlet, which is two orders of magnitude lower than the rating for PDMS-plastic bonding of 103.4 kPa [40].
Figure 4.12: (a) Simulation results for flow velocity of liquid through microfluidic channel, (b) simulation results for pressure distribution of liquid in the microfluidic flow channel.

Figure 4.13 shows the impedance response of the flexible microfluidic sensing device towards different concentrations of KCl. It was observed that a reference signal for DI water was established around 520±11 kΩ. Average impedance measurements of around 700 kΩ and 1.1 MΩ were measured for the 1 pM and 1 nM concentrations of KCl, respectively. The response showed that the impedance percentage change when compared to DI increased from 28 % to 107 % as the concentration increased from 1 pM to 1 nM for KCl. The sensing device was rendered
Figure 4.13: Dynamic electrochemical impedance response of the flexible microfluidic sensing device towards varying concentrations of KCl, at a frequency of 1 kHz with a 100 mV voltage excitation.

reversible, when DI water was introduced after each concentration of KCl was tested, due to the fact that the impedance always attained its base value of 520±11 kΩ. The impedance change in the measured response of the MSP can be attributed to the change in ion concentrations at the sensor-analyte interface. Through the responses obtained, the author demonstrated a detection level as low as 1 pM and the capability of the flexible MSP to distinguish among a wide range (nano and pico level) of sample concentrations.

A statistical analysis for the reproducibility of the response was also performed by investigating the electrochemical response of three different sensors, towards varying concentrations of CdS and HgS. Figure 4.14 shows the response of the sensor towards varying concentrations (1 pM, 1 nM, 1 µM and 1 mM) of CdS. An average impedance value of 485.3 kΩ, 435.8 kΩ, 416.9 kΩ, 369.8 kΩ and 33.3 kΩ, with an average standard deviation of 5.5 kΩ, 2.3 kΩ, 2.4 kΩ, 2.6 kΩ and 4.8 kΩ was observed for the DI, 1 pM, 1 nM, 1 µM and 1 mM concentrations, respectively (Fig. 4.14(a)). This corresponds to an average impedance percentage change of 10.2 %, 14.1 %, 23.8 % and 93.1 % with an average standard deviation of 16.1 %,
16.3 %, 16.7 % and 21.2 % for the 1 pM, 1 nM, 1 µM and 1 mM concentrations, respectively (Fig. 4.14(b)), when compared to the base impedance of DI. It is worth noting that the approved level of CdS by the USFDA is 3 µM [41]. Using the results obtained, the author showed that the electrochemical response of the sensor could be used to quantify the different concentrations of CdS as there was no cross-over in the overall impedance values, among all three sensors tested.

Figure 4.14: (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of CdS at 1 kHz and applied potential of 100 mV.
Similarly, for HgS, an average impedance value of 51.7 kΩ, 40.7 kΩ, 36.2 kΩ, 34.0 kΩ and 31.6 kΩ, with an average standard deviation of 19.8 kΩ, 16.6 kΩ, 19.1 kΩ, 16.0 kΩ and 15.0 kΩ was observed for the DI, 1 pM, 1 nM, 1 µM and 1 mM concentrations, respectively (Fig. 4.15(a)). This corresponds to an average impedance percentage change of 21.4 %, 30.1 %, 34.2 % and 39.0 % with an average standard deviation of 70.4 %, 75.2 %, 69.2 % and 67.3 % for the 1 pM, 1 µM, 1 nM and 1 mM concentrations, respectively (Fig. 4.15(b)), when compared to the base impedance of

![Electrochemical Impedance Response Towards Mercury Sulfide (HgS)](image)

(a)

![Electrochemical Impedance Response Towards Mercury Sulfide (HgS)](image)

(b)

Figure 4.15: (a) Impedance based electrochemical response and (b) percentage change in impedance of three different sensors towards varying concentrations of HgS at 1 kHz and applied potential of 100 mV.
DI. According to USFDA, the toxicity limit for HgS is 1 µM [42]. Therefore the author concluded that the electrochemical response of the sensor could be used to quantify the different concentrations of HgS as there was no cross-over in the overall impedance values, among all three sensors tested.

4.4 Summary

In this chapter, the author discusses the need for a flexible and printed microfluidic sensing system. A detailed account of the experimental tasks involved in this work was then presented. This includes the chemicals, materials and devices used; design of the PDMS based microfluidic flow channels; fabrication of PCB as master mold for PDMS based microfluidic channels; machining of Delrin; preparation of PDMS; fabrication of microfluidic channels; inkjet printing of electrodes; integration of microfluidic flow channels and electrodes; the experiment setup. Finally, the results obtained are also presented.

To summarize, an MSP was successfully fabricated by integrating conventional PCB technology with traditional printing methods. The capability of the MSP to distinguish between varying concentrations of KCl, CdS and HgS was demonstrated. The EIS based response of the MSP towards KCl displayed a percentage change of 28 % and 107 % for the 1 pM and 1 nM concentrations, respectively when compared to DI water at 100 mV applied potential and 1 kHz operating frequency thus demonstrating the capability of picomolar level detection. In addition, a statistical analysis for the reproducibility of the sensor response was also performed by investigating the electrochemical response of three different sensors, towards varying concentrations of CdS and HgS. The response obtained demonstrated that the impedance based electrochemical response of the sensor could be used to quantify different concentrations of CdS and HgS there was no crossover in the
overall impedance values, among all three sensors tested. The results obtained show the potential of employing conventional PCB technology along with traditional printing techniques for the fabrication of flexible MSPs in bio/chemical sensing applications.

In the following chapter, the author presents a project that involved the development of a novel fully printed and flexible capacitive pressure sensor, by integrating conventional screen and gravure printing processes. The author discusses the design, fabrication and characterization of the flexible microfluidic sensor. The measurement set-up, testing and results obtained are also presented.
4.5 References


A NOVEL FULLY PRINTED AND FLEXIBLE CAPACITIVE PRESSURE SENSOR

5.1 Introduction

Recently, there has been a growing interest in the development of pressure sensors on flexible substrates for applications in the aerospace, automotive, and biomedical engineering fields [1-3]. Pressure sensors are typically manufactured using conventional CMOS processes, which are often expensive and fabricated on rigid substrates [4-7]. Almost all pressure sensing systems built to date utilize hanging structures or cavity based sensor design configurations [8-12]. However, none of these configurations offer the high flexibility, stability and conformability, required for various pressure sensing applications. A continuous layer-on-layer configuration is envisioned as a promising approach that will overcome the drawbacks associated with conventional pressure sensing systems. The development of fully flexible and conformal pressure sensors, due to the availability of diverse manufacturing materials and the rapid development of modern fabrication techniques, is thus poised to have a significant impact on the modern society.

Over the last decade, a steady and considerable effort has been directed towards the development of PE using conventional printing technologies. To name a few, OTFT’s using inkjet printing [13-15], flexible displays by means of screen printing [16-18] and electrochemical sensors by rotogravure printing [19,20]. The use of printing technologies overcomes some of the drawbacks associated with conventional silicon technology, which involves high-vacuum and high-temperature deposition processes along with sophisticated photolithographic patterning.
techniques [21]. The advantages of printing include improved cost efficiency, reduction of material wastage during fabrication, flexibility in the substrate and low manufacturing temperatures. Even though a steady and considerable effort has been directed towards the development of flexible electronics, there have been no reports on fully printed flexible pressure sensors. This has led to the research of traditional printing techniques for the manufacture of flexible pressure sensors.

Gravure printing is known for its high quality and high printing speed; use of low viscosity inks and robustness of the process [22,23]. Screen printing has an added advantage of producing a relatively larger wet film thickness that is difficult to attain by other print methods [24]. A typical gravure system is comprised of an engraved gravure cylinder (image carrier), doctor blade, impression roller and ink pan, whereas a screen printer consists of a squeegee and a screen printing mask which consists of a frame (steel or aluminum), screen fabric and stencil. Gravure printing is a direct ink transfer process while screen printing is a push through process in which the substrate is not in direct contact with the mask.

In this work, the author uses conventional screen and gravure printing techniques to fabricate a fully printed flexible capacitive pressure sensor. A laboratory scale gravure press was used to print a highly conductive Ag nanoparticle (NP) based ink as the electrode metallization layer on a flexible PET substrate. A dielectric layer of PDMS was deposited using a screen printer. The author demonstrates the capability of the fabricated device to be used as a pressure sensor by investigating the capacitive response based on varying compressive forces applied.
5.2 Experimental

5.2.1 Chemicals, Materials and Sample Preparation

A 130 µm thick flexible PET film (Melinex ST 506) from DuPont Teijin Films was used as the substrate. A Ag NP ink, with an average particle size of 20-50 nm (Inktec, TEC-PR-020) was used as the metallization ink for the top and bottom electrodes layers. PDMS (Sylgard® 184 Silicone Elastomer) from Dow Corning was used for the fabrication of the dielectric and passivation layers. The liquid PDMS pre-polymer was mixed thoroughly with a curing agent at a ratio of 10:1 and degassed for 1 hour.

5.2.2 Fabrication of Fully Printed Pressure Sensor

The different steps associated with the fabrication of the flexible pressure sensor are shown in Fig. 5.1. The fabrication of the sensor was performed at the Center for the Advancement of Printed Electronics (CAPE) in Western Michigan University using a laboratory gravure press (K-Printing Proofer) from Testing Machines Inc. and a screen printer (AMI MSP 485) from Affiliated Manufacturers Inc. The screens, containing appropriate electrodes designs on stencil were fabricated at Microscreen® with a stainless steel mesh count of 325 and MS-22 emulsion thickness of 12.7 µm. The screen had a wire diameter and angle of 28 µm and 22.5°, respectively. The printing plate used for gravure printing was engraved by Southern Graphics Systems (Battle Creek, MI), using electromechanical engraving, with a resolution of 280 lpi (lines per inch).

Initially, an array of 4 bottom electrodes with dimensions of 4 cm × 0.5 cm and 0.5 cm spacing were gravure printed on PET (Fig. 5.1(a)). A 4 cm × 4 cm PDMS dielectric layer was then screen printed on top of the electrodes (Fig. 5.1(b)). This was followed by the gravure printing of an array of 4 top electrodes, with similar
dimensions to that of the bottom electrode, but at a 90° rotation in angle when compared to the bottom electrodes thereby resulting in a grid structure (Fig. 5.1(c)). Finally, a passivation layer of PDMS was screen printed on top of the electrodes (Fig. 5.1(d)). The Ag NP and PDMS printed layers were cured at 120 °C for 15 minutes and at 100 °C for 45 minutes, respectively after each layer was printed. The average overall thickness of the printed pressure sensor was measured to be 200 μm. A photograph of the fabricated flexible pressure sensor is shown in Fig. 5.2.

Atomic force microscopy (AFM) and WYKO RST-plus optical vertical scanning interferometer were used for the roughness and thickness measurements, respectively, of the gravure printed Ag NP ink. A 10 × 10 μm AFM image and 3D output of the interferometry is shown in Fig. 5.3. An average thickness of 300 nm (Fig. 5.3(a)) and RMS roughness value of 82 nm (Fig. 5.3(b)) was measured.

Figure 5.1: Schematic for the fabrication of the fully printed flexible pressure sensor (a) Bottom conductive electrodes on PET substrate, (b) Dielectric PDMS layer, (c) Top conductive electrode layer, (d) PDMS passivation layer.
Figure 5.2: Photograph of fully printed pressure sensor.

Figure 5.3: (a) 3D output of the vertical scanning interferometry and (b) AFM image of printed Ag NP ink on PET.
5.2.3 Experiment Setup

The experiment setup is shown in Fig. 5.4. The printed pressure sensor was placed between a force gauge (Mark-10 model M5-200) and vertically movable platform (Mark-10 ESM 301 motorized test stand). The capacitive response of the sensor was then be tested by applying varying compressive forces, perpendicular to the sensor. The sensor was connected to an Agilent E4980A precision LCR meter with wires attached using a Ag conductive epoxy paste (Circuit works CW2400). The change in capacitance was measured using a custom built LabVIEW™ program on a PC connected to the LCR meter via a USB cable.

Figure 5.4: Experiment Setup.
5.3 Results

The capacitance of the fully printed pressure sensor, which is similar to a parallel plate capacitor, is inversely proportional to the thickness of the dielectric layer. Figure 5.5 shows the change in capacitance for different compressive forces applied to the printed pressure sensor. The author observed that the smallest detectable pressure was ~800 kPa for which the base capacitance increased from 26 pF to 28 pF. The capacitance increased further for different increasing compressive forces applied on the sensor and a capacitance as high as 37 pF was measured for an applied pressure of 18 MPa. A 5%, 10%, 17%, 24%, 36%, and 40% change in capacitance was observed as the pressure increased from 0.8 MPa to 2.6 MPa to 4.9 MPa to 7.7 MPa to 11.2 MPa to 18 MPa, respectively. The author attributes these responses to the shortening of the distance between the electrodes due to the application of varying compressive forces. A study based on a similar non-printed structure has been reported for the detection of pressure with a dynamic range of up to 1 MPa [25]. The dynamic range made possible by the printed sensor was 18 MPa.

![Percentage Change in Capacitance](image)

Figure 5.5: Percentage change in the capacitive response of the fully printed pressure sensor towards varying compressive forces when compared to base capacitance.
Figure 5.6 shows the dynamic capacitive response of the printed pressure sensor towards varying compressive forces. Initially, the capacitance of the pressure sensor was recorded for 5 minutes with no force applied. Then, the sensor was subjected to the minimum detectable pressure of 800 kPa for 5 minutes, after which the compressive force was released. The response of the sensor was again recorded for another 5 minutes. This cycle was continued for different increasing compressive forces up to the maximum detectable compressive force of 18 MPa. The author observed that the sensor was reversible, after each compressive force was released, due to the fact that the capacitance always attained its base capacitance value of 26±0.007 pF. The printed pressure sensor showed a maximum variation of ± 0.15 %, from the average capacitance value of 28 pf, at the minimum detectable pressure. The sensitivity of the printed pressure sensor was calculated to be 0.002 MPa⁻¹, which is comparable to the sensitivities reported by Mannsfeld et al. [26], for varying ranges of pressure.

![Capacitive Response of Fully Printed Pressure Sensor](image)

Figure 5.6: Capacitive response of the fully printed pressure sensor towards varying compressive forces.
Figure 5.7 shows the dynamic capacitive response of the printed pressure sensor towards the lowest detectable compressive force of 800 kPa for 300 cycles at 10 mHz. The noisy output response of the sensor can be attributed to the visco-elastic creep phenomenon, which is typically observed in thin PDMS films of only a few micrometers when compared to thicker PDMS films of several hundred micrometres to millimeters. This causes an increase in the relaxation times due to the entanglement of polymer chains in the PDMS films [26]. The inset shows the averaged capacitive response of the sensor for three cycles selected at random. It was observed that the overall capacitance decreased by 2.5 % from its initial value, after 300 cycles. From the results obtained, the author demonstrated the stability of the printed sensor.

Figure 5.7: Dynamic capacitive response of the pressure sensor towards the lowest detectable force of 800 kPa for 300 cycles at 10 mHz.
5.4 Summary

In this chapter, the author presented an introduction that discusses the importance of developing a fully printed flexible pressure sensing systems. A detailed account of the experimental tasks involved in this work was then presented. This includes the chemicals, materials and devices used and experiment setup used. Finally, the results obtained are also presented.

To summarize, gravure and screen printing techniques were employed to fabricate a fully printed pressure sensor. The top and bottom electrodes of the sensor were gravure printed on a flexible PET substrate using a Ag ink. A dielectric layer, screen printed using PDMS, was sandwiched between the electrode layers. The average overall thickness of the fully printed pressure sensor was 200 µm, with electrode dimensions of 4 cm × 0.5 cm and 0.5 cm spacing. The capacitive response of the pressure sensor was investigated by varying the compressive forces applied. It was observed that the minimum and maximum detectable pressure was 800 kPa and 18 MPa, respectively. A 5% and 40% change in capacitance was measured for the 800 kPa and 18 MPa, respectively. The stability measurements demonstrated a maximum variation of ± 0.15 %, at the minimum detectable pressure of 800 kPa, from the average capacitance value of 28 pF. In addition, the dynamic capacitive response of the printed pressure sensor towards the lowest detectable compressive force of 800 kPa for 300 cycles at 10 mHz demonstrated a 4.5% decrease in capacitance from its initial value, after 300 cycles. The results obtained show the potential use for fully printed flexible sensors in pressure sensing applications.

In the following chapter, the author concludes this dissertation with a summary of the projects performed and also provides some suggestions for possible future work.
5.5 References


CHAPTER VI

CONCLUSION AND FUTURE WORK

6.1 Conclusion

Through this dissertation work, the author has successfully demonstrated the development of a sensing system that utilizes a photolithographically fabricated electrochemical sensor and a CNC machined novel flow cell. In addition, the capability of integrating conventional printing technologies such as screen, gravure and inkjet along with traditional PCB manufacturing processes to develop printed and flexible sensing systems was also accomplished. The accomplishments of each of the three research projects are listed below:

In the first project, the author successfully developed a microfluidic flow cell based sensing system for simultaneous opto-electrochemical detection of heavy metal compounds. The flow cell, designed with a reservoir volume of 25 µl, was fabricated using acrylic material and consists of an inlet and outlet port. The capability of the sensing system was demonstrated by investigating the opto-electrochemical response of the system towards varying concentrations of CdS and HgS. EIS of the heavy metal compounds was performed using an efficient electrochemical sensor with Au IDEs on a glass substrate. The EIS based response of the system revealed pM concentration detection levels for the heavy metal compounds. Simultaneously, selective detection of the heavy metal compounds was made possible based on optical signals produced in the Raman emission spectra. The author also performed a statistical analysis for the reproducibility of the sensor response by investigating the electrochemical response of three different sensors for five times, towards varying concentrations of CdS and HgS. Based on the results obtained, the author concluded that the impedance based
The electrochemical response of the sensor could be used to quantify different concentrations of CdS and HgS since there was no cross-over in the overall impedance values, among all three sensors tested.

In the second project, the author successfully developed a novel next generation MSP, by integrating conventional PCB and printing processes, for the detection of various bio/chemicals. PDMS based microfluidic channels were fabricated using master molds created with PCB technology. Ag based ink was employed to inkjet print IDEs on flexible PET substrate. The printed PET substrate and PDMS were bonded to form the MSP. The capability of the MSP to distinguish between varying concentrations of KCl, CdS and HgS was demonstrated. The EIS based response of the MSP towards KCl displayed a percentage change of 28 % and 107 % for the 1 pM and 1 nM concentrations, respectively when compared to DI water at 100 mV applied potential and 1 kHz operating frequency thus demonstrating the capability of picomolar level detection. A statistical analysis for the reproducibility of the sensor response was also performed by investigating the electrochemical response of three different sensors, towards varying concentrations of CdS and HgS. The response obtained demonstrated that the impedance based electrochemical response of the sensor could be used to quantify different concentrations of CdS and HgS there was no crossover in the overall impedance values, among all three sensors tested. Through the results obtained, the author showed the potential of employing conventional PCB technology along with traditional printing techniques for the fabrication of flexible MSPs in bio/chemical sensing applications.

In the third project, the author successfully fabricated a novel fully printed flexible capacitive pressure sensor using conventional screen and gravure printing
techniques. The sensor was successfully printed on a flexible PET substrate with Ag NP ink as the metallization layer and PDMS as the dielectric layer. The capacitive response of the sensor demonstrated a percentage change of 5% and 40% for minimum and maximum detectable compressive forces of 800 kPa and 18 MPa, respectively when compared to the base capacitance of 26 pF. At the minimum detectable pressure, the stability measurements resulted in a maximum variation of ±0.15% from the average capacitance value of 28 pF. The dynamic capacitive response of the printed pressure sensor towards the lowest detectable compressive force of 800 kPa for 300 cycles at 10 mHz demonstrated a 4.5% decrease in capacitance from its initial value, after 300 cycles. The author thus demonstrated the feasibility of employing traditional printing techniques for the fabrication of flexible pressure sensing devices.

6.2 Future Work

The author believes that there are several opportunities and possibilities to improve upon the current projects. Some suggestions for future work are now discussed.

- **Opto-Electrochemical Based Dual Detection of Heavy Metal Compounds Using a Novel Flow Cell:** The electrode material could be replaced by other metallic conductors such as platinum, aluminum or silver and tested for better performance. The electrochemical based sensors can further be optimized by using CoventorWare™ or COMSOL™ to design different IDE dimensions and new geometries. This could aid in lowering the detection levels to as low as the femto (10⁻¹⁵) or even the atto (10⁻¹⁸) levels. In addition, the use of sensing layers on the IDEs could render the sensor selective towards certain target molecules. For example, biologically active polymers such as glutaraldehyde (GA),
pyroloquinoline quinine or gluconobacter (PQQ-GDH) could be used for selectively detecting different toxic heavy metals [1].

- **A Novel Flexible Microfluidic Platform:** The printed electrode material could be replaced by using other functional inks such as copper, gold, platinum or nickel and tested for better performance. Different IDE dimensions and new geometries can be designed using CoventorWare™ or COMSOL™ to lower the detection levels to as low as the femto ($10^{-15}$) or even the atto ($10^{-18}$) levels. Screen, gravure and flexo printing techniques could be employed to fabricate the MSP IDEs and the performance of each of the sensing systems can be compared for optimum system performance. In addition, the use of sensing layers such as GA, pyroloquinoline quinine or PQQ-GDH on the IDEs could render the sensor selective towards different toxic heavy metals [1]. Moreover, the master mold for the microfluidic channels could be fabricated using screen, inkjet and gravure printing processes, all of which are relatively cost efficient and rapid methods when compared to the PCB manufacturing technique.

- **Fully Printed and Flexible Capacitive Pressure Sensor:** The dielectric layer could be substituted with a variety of elastomeric polymers such as polyurethanes and fluorosilicones. Functional inks based on carbon nanotubes (CNT), copper, gold, platinum or nickel can be used to as the printed electrode material. Inkjet, gravure and flexo printing techniques could be employed to fabricate the electrodes and the performance of each of the sensing systems can be compared for optimum system performance. The pressure sensor can further be optimized by using CoventorWare™ or COMSOL™ to design different electrode dimensions and new geometries.
• *Measurement Displays for Sensor Measurements:* The development of readout circuits for all the sensing systems can constitute a major and very crucial part of their use and future applications. For example, readout circuits such as impedance-to-voltage (I-V) and capacitance-to-voltage (C-V) convertors along with the necessary conditioning circuitry and displays could be developed to be integrated with the sensing systems. The readouts circuits could be developed for calibrating each individual sensor to compensate for the variations in reference signals. The readout circuits could be fabricated using conventional CMOS processes. An even more interesting possibility would be the fabrication of the readout circuits, on flexible substrates, by using printing processes. Incorporating readout circuits would enable portability and further miniaturizing of the currently developed sensing systems for use as field-deployable hand-held systems.
6.3 References

APPENDIX A

LIST OF PUBLICATIONS

A1. Inventions


Western Michigan University, Intellectual Property Disclosure, WMU CASE# 2014-012.


**A2. Journal Papers**


A3. Conference Papers


13\textsuperscript{th} IEEE Sensors Conference, November 2-5, Valencia, Spain, pp. 1192-1195, 2014.


for humidity sensing”, 15th International Meeting on Chemical Sensors (IMCS),
March 16-19, Beunos Aires, Argentina, pp. 107, 2014.

M.K. Joyce, M.Z. Atashbar, “All screen printed circular electrodes as
electrochemical sensors”, 15th International Meeting on Chemical Sensors
(IMCS), March 16-19, Beunos Aires, Argentina, pp. 98, 2014.

dinitrotoluene (DNT) using gravure printed surface enhanced Raman
spectroscopy (SERS) flexible substrate”, 15th International Meeting on Chemical
Sensors (IMCS), March 16-19, Beunos Aires, Argentina, pp. 86, 2014.

detection using shear horizontal surface acoustic wave (SH-SAW) sensors”, 15th
International Meeting on Chemical Sensors (IMCS), March 16-19, Beunos Aires,
Argentina, pp. 88, 2014.

of heavy metal compounds using a novel inkjet printed surface enhanced Raman
spectroscopy (SERS) substrate based on metallic triangular nano structures”, 15th
International Meeting on Chemical Sensors (IMCS), March 16-19, Beunos Aires,
Argentina, pp. 86, 2014.

(SERS) substrate based on Marangoni effect for the detection of heavy metal
compounds”, 15th International Meeting on Chemical Sensors (IMCS), March
16-19, Beunos Aires, Argentina, pp. 120, 2014.


