Vapour Deposition and Evaluation of Conducting Polymeric Thin Films

by

Scott Ferguson, B.Eng.

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

Master of Applied Science

in

Electrical and Computer Engineering

Ottawa-Carleton Institute for Electrical and Computer Engineering

Department of Electronics

Carleton University

Ottawa, Ontario

April 2016

©2016

Scott Ferguson

Abstract

In this work an apparatus was designed to perform oxidative chemical vapour deposition (oCVD) of polymeric films. The minimization of reactant waste was a major design consideration. This resulted in several key features not common in literature including: a static deposition phase, quick-loading precursor holders, a double wall vacuum, and a hot wall deposition chamber. The base pressure of the system was below 20 mTorr and its upper temperature limit was 200 °C.

Employing the system, poly(3,4-hexyldioxythiophene) (PEDOT) was synthesized via vapour phase polymerization (VPP). These samples, along with an in-situ polymerized (ISP) PEDOT control group, were characterized using SEM, AFM, four-point probe, FTIR, and UV-vis. Results showed that the VPP films were thicker, less rough, and more conductive than their ISP counterparts with values of 380 nm, 2 nm, and 1130 S/cm respectively. Spectroscopic tests indicated high levels of conjugation and minimal polymer damage.

Acknowledgements

First and foremost I would like to thank my thesis supervisor, Dr. Steven McGarry; without whom I would never have been able to get so far. His interest and enthusiasm for the project enabled me to overcome the many challenges it presented. We had many long conversations ranging from the overall direction of the project to the minute details. His knowledge and experience from industry with all types of instrumentation and equipment facilitated my progress and was responsible for several milestones being met. The openness of our meetings drove me to conceive novel creative ideas and workarounds. The scope of this project and Dr. McGarry's passion for continued learning lead to my acquisition of many varied and useful skills in computer, mechanical, and chemical engineering. As a result of this project I consider myself a much more diversified and well-rounded engineer. I could not have asked for a more supportive and knowledgeable supervisor.

I would like to thank the staff of the Carleton University Microfabrication Facility (CUMFF) lab for all their invaluable support. Rob Vandusen and Rick Adams helped me greatly in the design process; providing technical advice and suggestions on vacuum vessels, feedthroughs, gauges, and valves. Their supervision and aid in making complicated connections for gas and liquid lines was vital to the completion of the apparatus. They also educated me in the use of several pieces of equipment necessary to the fabrication exotic structures used in the characterization of the PEDOT films. Angela Burns introduced me to the procedures and policies in the Microfabrication facility. Her concern for safety was fully conveyed, understood and appreciated. I took all necessary precautions when dealing

with chemical reactants, including corrosive substances and strong oxidizing agents, so as to not endanger myself and everyone else in the facility. She supervised and worked alongside me in the solutions-processing of the PEDOT precursors; a task that proved extremely capricious. Long troubleshooting discussions took place leading to the amelioration of the process. Furthermore, she instilled important scientific values of following proper cleaning protocols between processing steps; the merits of which are demonstrable through the improvements in film uniformity and conductivity. I am extremely grateful for their support and extra hours they put in to helping me achieve my goals.

I was fortunate to have the assistance of intern student Evan de Sousa for a summer. Along with aiding in the assembly and construction of the system, he also laid out and populated the PCB for PWM control. The time he spent machining parts and fabricating the circuits greatly accelerated the timeline. His input on the design was deeply valued and I would like to thank him for all his help.

Adam Bottomley, of the Ianoul research group in Carleton's Chemistry Department, was very generous in lending his time for AFM measurements. His expert assistance at short notice was greatly appreciated. The advice given on how to process the AFM data using SPM software was also extremely helpful.

I am also indebted to the team at Carleton's Science and Technology Center (STC) for their services rendered. Steven Tremblay and Ron Roy not only machined complex parts vital to the vapour deposition system but provided a new perspective on vacuum vessels and methods of fabrication. Their input on the structural and mechanical aspects simplified several designs, saving much time and headache.

The team at Carleton's Mechanical and Aerospace Engineering (MAE) Machine Shop were extremely helpful. Alex Proctor, Kevin Sangster, and Ian Lloy took time out of their busy schedules to teach me how to use machining equipment on my own. During my time in the machine shop they showed me the basic principles of machining and several handy tricks. A great joy and sense of accomplishment is to be had from turning raw

materials into functional components and I would like to thank them for introducing me to that. They also provided insightful advice on the system blocks I was crafting and ways in which to assemble them.

Nagui Mikhail, the hidden hero of the Department of Electronics, has been immensely helpful throughout this journey. He has produced many pieces of equipment for testing and characterization in a timely manner. His efforts in maintaining the equipment in the Department and providing extremely useful software tools to the graduate students is much appreciated.

The administrative staff of the Department of Electronics, Blazenka Power, Anna Lee, and Sylvie Beekmans were also very helpful during my tenure as a Master's student. The time and effort they invested in the application and processing of scholarships, grants, teaching assistantships, and project expenses is greatly appreciated. Not to mention the organization of the thesis defence.

I would like to thank my fellow graduate students for their ideas, encouragement, and friendship. Their sincerity made for a warm and welcome atmosphere which motivated me to work harder. The weekly board game nights made for great stress relievers and got me out of my corner to socialize and be merry.

Lastly I would like to thank my parents for providing a positive and supportive atmosphere. My father Derek Ferguson, a mechanical engineer, and I discussed many aspects of the design. His input was welcome and extremely helpful. I would also like to thank them for distracting me from certain challenges at times to keep my stress levels down.

Contents

Abstract	i
Acknowledgements	ii
Table of Contents	viii
List of Tables	ix
List of Figures	xiii
Nomenclature	xiv
1 Introduction	2
1.1 Thesis Objectives	2
1.2 Thesis Overview	2
2 Background	5
2.1 Polymer Films in Electronics	5
2.2 Motivations for Organic Electronics	6
2.3 Fabrication of Polymer Films	10
2.3.1 Solution-Processed Methods	10
2.3.2 Vapour-Processed Methods	12
2.3.2.1 Vapour Deposition Polymerization (VDP)	12
2.3.2.2 Plasma-Enhanced Chemical Vapour Deposition (PECVD)	14

2.3.2.3	Initiated Chemical Vapour Deposition (iCVD)	14
2.3.2.4	Oxidative Chemical Vapour Deposition (oCVD)	16
2.3.2.5	Comparison of Vapour Phase Fabrication Methods	18
2.4	Recent Advancements in oCVD	19
2.4.1	oCVD	19
2.4.2	oMLD	21
2.4.3	VPP	23
2.4.4	Summary of oCVD Advancements	25
3	Apparatus	26
3.1	Design Goals, and Constraints	26
3.2	System Overview	29
3.3	oCVD System Interior	30
3.4	Exterior Vacuum Chamber	33
3.5	Temperature Regulating Systems	39
3.5.1	Temperature Measurement	40
3.5.2	Rope Heater	42
3.5.3	Vial Control	46
3.5.4	Substrate Control	49
3.5.5	Control Station	52
3.6	Completed Apparatus	54
4	Experimental	59
4.1	Foreword	59
4.2	Pre-conditioning	59
4.3	Spin Coating	61
4.3.1	PEDOT:PSS Adhesion Layer	61
4.3.2	In-situ Polymerized (ISP) PEDOT	62

4.3.3	VPP Oxidant Solution	63
4.4	Vapour Phase Polymerization (VPP)	64
4.4.1	Estimation of Required EDOT Volume and Vaporization Temperature	64
4.4.2	VPP Procedure	66
4.5	Post-conditioning	71
4.6	Metallization	73
5	Testing and Results	77
5.1	Sample Pictures	77
5.2	Profilometer Measurements	79
5.3	SEM Pictures	85
5.4	AFM Measurements	90
5.5	Four-Point Probe Measurements	95
5.6	Fourier Transform Infrared (FTIR) Spectroscopy Measurements	98
5.7	UV-Visible (UV-vis) Spectroscopy Measurements	103
6	Conclusion	107
6.1	Thesis Summary	107
6.2	Knowledge Contribution	110
6.3	Future Work and Improvements	110
6.3.1	oCVD	110
6.3.2	Mobility Measurements	112
6.3.3	Possible Design Changes	113
	APPENDICES	129
A	Electronic Theory of Polymers	129
A.1	Organic Semiconductor Band Formation	129
A.2	Free Carriers and Doping in Polymers	132

A.3	Charge Carriers and Transport in Polymers	135
B	Characterization of Conducting Polymer Films	141
B.1	Four Point Probe Measurement	141
B.2	Atomic Force Microscopy	144
B.3	Scanning Electron Microscopy	147
B.4	Fourier Transform Infrared Spectroscopy	148
B.5	UV-Visible Spectroscopy	151
C	Vaporization Theory	154
D	Pressure Vessel Mechanical Design	158
D.1	Stress Calculations	158
D.2	Finite Element Analysis Stress Simulations	159

List of Tables

2.3.1 Comparison of Vapour Phase Fabrication Methods	19
2.4.1 Conductivity of PEDOT Pre- and Post-Rinse for Various Solvents	23
2.4.2 Summary of oCVD Initiatives	25
3.1.1 Design Goals	27
3.6.1 Specifications of Final Apparatus	58
5.2.1 Summary of Profilometer Measurements	85
5.4.1 AFM 1D Profile Measurements	93
5.4.2 Summary of AFM Results	94
5.5.1 Four Point Probe Summary Table	98
6.3.1 Oxidation Potentials	111
C.0.1 Antoine Coefficients for Selenophene	155

List of Figures

2.2.1	Application of Roll-to-Roll Printing to Organic Electronics	9
2.3.1	Fully Screen Printed Polymer Based 13 MHz RFID Chip	11
2.3.2	Diagram of a Standard VDP Reactor	13
2.3.3	Diagram of a Standard PECVD Reactor	14
2.3.4	Diagram of Branching and Cross-linking in Polymers	15
2.3.5	Diagram of a Standard iCVD Reactor	15
2.3.6	Diaz Mechanism for Step-Growth Polymerization of PEDOT	17
2.3.7	Chemical Doping of PEDOT via Oxidation	18
2.4.1	MIT oCVD Reactor	20
2.4.2	Acid-Initiated Coupling of PEDOT	21
2.4.3	NCSU oMLD Reactor	22
3.1.1	Swagelok Joint Sealing Mechanism	28
3.2.1	Diagram of Deposition Apparatus with Inner and Outer Vacuum Chambers	29
3.3.1	Inner Vacuum Chamber Manifold Line (Incomplete)	31
3.3.2	KF Flange Sealing Mechanism	31
3.3.3	Diagram of KF Parts in Reactor Chamber	32
3.3.4	Reactor Chamber Composed of Two KF Flanges	33
3.3.5	Convectron Gauge and Controller	33
3.4.1	Purchased Outer Vacuum Chamber	34
3.4.2	Cross Section of Exterior Pressure Vessel Lid with Panel Mounted Valve .	35
3.4.3	Valve Stem Silicone Gaskets Cut by Water Jet	36

3.4.4	Exterior Pressure Vessel Lid Feedthroughs	37
3.4.5	Prototype Electrical Feedthrough for Exterior Pressure Vessel Lid	38
3.4.6	Side View of Inner Chamber Lid Assembly with T-Slot Support Structure	39
3.4.7	Exterior Pressure Vessel Installed in Fumehood	40
3.5.1	Omega Data Acquisition Module	41
3.5.2	AC Phase Control Circuit Schematic	43
3.5.3	AC Phase Control Example Waveforms	44
3.5.4	Rope Heater PID Temperature Controller and Accompanying SSR	45
3.5.5	Side View of Sliding Stage with Oil Bath Vial Heaters	47
3.5.6	PWM Circuit Schematic	48
3.5.7	PWM PCB for TEC Power Control	49
3.5.8	Water Block for Substrate Temperature Control	50
3.5.9	Graph of Volumetric Flow Rate of Water versus Pressure	51
3.5.10	Diagram of Substrate Temperature Control Assembly	52
3.5.11	Systems Control Rack (Front)	53
3.5.12	Systems Control Rack (Back)	54
3.6.1	Completed Vacuum Chamber Mounted in Fumehood	55
3.6.2	Inner Chamber Pressure Rise Upon Isolation	57
4.2.1	Plasma-Preen-II-862 Oxygen Plasma Treatment Apparatus	60
4.3.1	WS-400-6NPP Spin Coating Apparatus	61
4.3.2	Hotplate with Dried CB40 Film	64
4.4.1	Fitted Vapour Pressure Curve of EDOT	65
4.4.2	Graph of Inner Chamber Pressure vs Time for a VPP Deposition	69
4.4.3	Control Program Screenshot	70
4.5.1	ISP PEDOT Film After Gentle Methanol Rinse	71
4.5.2	ISP PEDOT Film Rinsed on Top Half Only	72
4.6.1	Quadrant of Superposed Shadow Masks	74

4.6.2	Covap Thermal Deposition System	76
5.1.1	CB40 on Glass Octagon Before and After VPP	78
5.1.2	PEDOT on Glass	78
5.2.1	Dektak IIA Profilometer	79
5.2.2	Sample Dektak Profile	80
5.2.3	Dektak Profile of a 2000 Å Thick Silver Contact	81
5.2.4	Tencor P1 PEDOT:PSS Adhesion Layer Measurements	82
5.2.5	Dektak Profile of ISP PEDOT (G5)	83
5.2.6	Dektak Profile of VPP PEDOT (OCT1)	83
5.2.7	Dektak Profile of Annealed Oxidant (OCT1)	84
5.3.1	SEM Apparatus	86
5.3.2	SEM Pictures of a Preliminary VPP-PEDOT Sample	87
5.3.3	SEM Pictures of VPP PEDOT (OCT1)	88
5.3.4	SEM Pictures of ISP PEDOT (G6)	90
5.4.1	AFM of ISP (G5)	91
5.4.2	AFM of VPP (OCT1)	93
5.4.3	Roughness Profiles	95
5.5.1	Four Point Probe Setup	96
5.5.2	Example Four Point Probe Graph of Early Low Conductivity VPP Sample	97
5.5.3	Four Point Probe of ISP vs. VPP PEDOT	97
5.6.1	ATR-FTIR of Final Films - VPP vs. ISP	99
5.6.2	ATR-FTIR on ISP PEDOT Along a Diagonal going from Center to Corner	100
5.6.3	Normalized FTIR of Unrinsed VPP PEDOT and Ferric Tosylate Oxidant	101
5.6.4	Normalized FTIR of Glass, PEDOT:PSS, and VPP PEDOT	103
5.7.1	UV-Vis Spectra of ISP, VPP, and Glass Substrate	104
5.7.2	Energy Band Diagrams of PEDOT and their Allowed Optical Transitions	105
5.7.3	Attenuation Coefficient of ISP, VPP, and ITO Films	106

6.3.1	Proof of Concept oCVD PEDOT Film using Iodine Oxidant	112
6.3.2	Possible Design Changes	113
A.1.1	Orbital Overlap in Covalent Bonds	129
A.1.2	Orbital Overlap in Conjugated versus Non-Conjugated Oligomers	130
A.1.3	Energy Levels of Ethylene	131
A.2.1	Thermal Promotion in Semiconductor Bands	132
A.2.2	Band Gaps and Material Properties	133
A.3.1	Neutral Soliton in Trans-Polyacetylene	136
A.3.3	Non-Degeneracy in Polythiophene	136
A.3.2	Charge Carriers in Trans-Polyacetylene	137
A.3.4	Electronic States Introduced Via Doping in Polypyrrole	138
A.3.5	Propagation of Chain Deformations	139
B.1.1	Four Point Probe Measurement Setup	142
B.1.2	Comparison of Resistances in 2 and 4 Point Probe Measurements	142
B.2.1	Atomic Force Microscopy	145
B.3.1	Schematic Diagram of a SEM	148
B.4.1	Electronic, Vibrational, and Rotational Energy Levels	149
B.4.2	Michelson Interferometer	150
B.5.1	Optical Transitions Between Electronic States	152
B.5.2	Typical UV-Vis Spectrophotometer Setups	153
C.0.1	Graph of Vapour Pressure of Water	156
D.1.1	ASME BPV Code Shell Stress - Graph of Factor A	160
D.1.2	ASME BPV Code Shell Stress - Graph of Factor B	161
D.2.1	COMSOL Finite Element Simulations of Exterior Pressure Vessel	162
D.2.2	COMSOL von Mises Stresses Near Counterbored Holes	163

Nomenclature

- Organic Molecules: a molecule predominantly composed of carbon and hydrogen atoms. Can present itself in aromatic (ring) or chain arrangements with carbon atoms serving as the backbone. Substitutions of carbon atoms with other chemical species such as nitrogen or sulfur are frequent. Some exceptions to this classification are carbides and carbonates.
- Monomer: A single unit of a polymer chain; unbonded organic molecule.
- Polymer: A long organic molecule with repeating units of one or several smaller organic molecules. A chain consisting of an extremely high, uncountable number of monomers.
- Oligomer: A shorter chain consisting of finite, countable number of monomers.
- Band: Continuum of overlapping energy levels of differing magnitude.
- LUMO: The lowest unoccupied molecular orbital. Analogous to the valence band edge in inorganic semiconductor theory.
- HOMO: The highest occupied molecular orbital. Analogous to the conduction band edge in inorganic semiconductor theory.
- Band gap: the energy difference between the valence band and conduction band edges. A forbidden energy range in a solid where no electron states can exist. In organic chemistry the band gap exists between the HOMO and LUMO levels.

- Conjugation: alternating of single and double bonds in organic molecules as a result of pi-bonds. It is the overlap of one p-orbital with another across an intervening sigma bond. Can result in formation of pseudo 1D bands in organic compounds.
- Work Function Φ : the energy difference between the vacuum level and the Fermi level of a material.
- Electron Affinity χ : The energy difference between the vacuum level and LUMO or conduction band edge in a material.
- Ionization Energy I_E : the energy difference between the vacuum level and the HOMO or valence band edge in a material.
- Charge Carrier: particle free to move, carrying an electric charge, especially the particles that carry electric currents in electrical conductors.
- Carrier Mobility: characterizes how quickly a charge carrier can move through a metal or semiconductor under the influence of an electric field.
- Transistor: a semiconductor device used to amplify and switch electronic signals and electrical power
- Organic Transistors: transistors in which the material required for operation is organic in nature.
- Precursor/Reactant: A starting chemical species which reacts with another substance to produce an intermediate or final compound. It is often consumed during the reaction.
- CVD: Chemical vapour deposition is a process used to create high quality solid films. Volatile precursors are introduced in vapour form to the surface of a substrate upon which they adsorb and react yielding a new species whose thickness increases with exposure time.

Chapter 1

Introduction

1.1 Thesis Objectives

The primary objective of this project was to design a system capable of synthesizing polymeric thin films - especially poly(3,4-hexyldioxythiophene) (PEDOT) - via oxidative chemical vapour deposition (oCVD). The secondary objective of this work was to verify operation of the system. This was to be achieved by synthesizing several high quality films using the apparatus. Insight as to the effects of process variables was to be gained from the characterization of the oCVD films alongside a control group of In-Situ Polymerized (ISP) films. Small scale research initiatives which raise the quality of producible polymers can be immeasurably helpful in understanding the intricacies involved. The knowledge can be applied and reworked in the future for mass production.

1.2 Thesis Overview

Since the scope of this thesis is quite ambitious - covering the design of a vapour deposition apparatus, fabrication of polymer films, and characterization of said films - sufficient background information is presented to establish context. Chapter 2 first summarizes the motivation and history of polymers in electronics. Subsequently, the various fabrication

methods of polymer films are introduced, accompanied by a literature review of the more pertinent methods. Additional background information can be found in the appendices. Appendix A features a brief discussion of organic semiconductor physics including band formation, carrier generation via doping, and charge transport. Appendix B provides an explanation of the operating principles of the equipment used for film characterization and the information that can be extracted.

Chapter 3 covers the design of the system. First, the design goals and desired system specifications are established. The construction of the inner chamber is outlined, including the components that were incorporated and their justification. Next, the design methodology for the outer pressure vessel is introduced. A review of the various heating and cooling sub-systems is also provided. Following a discussion of the control systems, sub-system test results are analyzed and compared against the specifications.

Chapter 4 details the experimental procedures to achieve both the ISP and Vapour-Phase Polymerized (VPP) PEDOT films. Pre-conditioning, spin coating, ethyldioxythiophene (EDOT) monomer vapour exposure, and post-process rinsing are all summarized. Corresponding spin-speeds, reactant quantities, and exposure times are included for maximum reproducibility.

Chapter 5 examines the characterization test results. ISP and VPP films are compared to each other and literature using a number of techniques. The chapter begins with several sample pictures, then introduces profilometer measurements of thicknesses for poly(3,4-hexyldioxythiophene):polystyrene sulfonate (PEDOT:PSS), ISP, VPP, and metal layers. Scanning Electron Microscopy (SEM) pictures present more detail on film roughnesses and cross sections whilst Atomic Force Microscopy (AFM) provides actual quantitative data. With the AFM film thicknesses in hand, four point probe sweeps are executed and conductivities are calculated. Lastly, Fourier Transform Infrared (FTIR) and Ultraviolet-Visible (UV-vis) spectroscopy are performed and the respective peaks of the films are scrutinized and compared to each other and published data.

Chapter 6 provides conclusions, contributions to knowledge, and a list of possible future work. Priorities for publications are mentioned, including the use of Iodine as an oxidant in oCVD and extraction of PEDOT film mobility values using an emerging technique known as Charge Extraction by Linearly Increasing Voltage (CELIV). Possible changes or improvements to the apparatus design are also suggested and elucidated.

Chapter 2

Background

2.1 Polymer Films in Electronics

The history of polymer research is surprisingly old, dating back to early 1900s [1]. Beginning with Pocchettino's interest in the dark and light conductivities of anthracene crystals, there was a short period of interest culminating in a prototype organic photovoltaic cell by Vollmer in 1913 [2]. After a brief lull in activity, molecular crystals garnered much attention following the discovery of electroluminescence in the 1960s [1]. This led to the development of early models for the processes involved in optical excitation and charge carrier transport by Pope, Kallman, and other scientists at the forefront. Research continued as Heilmeyer and Zanoni [3] reported the first field-effect measurements of organic films with α -Copper Phthalocyanine in 1964 and McGinness et al. [4] created the first organic semiconductor switch from melanin in 1974. Shortly thereafter, interest exploded yet again with the demonstration by Shirakawa et al. [5] that the polymer, polyacetylene, could be doped post-formation at room temperature to significantly increase its conductivity. Afterwards, development of conductive polymers became a main focus of many chemists, physicists, and material scientists. The field of research expanded even further when the first organic

transistor was created by Koezuka et al. [6] in 1987. Once more, the concept was validated - that polymers could indeed be a viable alternative to the traditional inorganic materials.

Moving forward into the present, there has been extensive research into the use of solution-processed polymers in Field Effect Transistors (FETs), gaining substantial momentum in the mid-1990s [7]. Commercial applications were realized with Organic Field Effect Transistor (OFET) addressed Organic Light Emitting Diode (OLED) displays, organic complementary circuits, and organic photovoltaic cells [8, 9, 10].

2.2 Motivations for Organic Electronics

With the strict conditions necessary to fabricate microscale Integrated Circuits (ICs), it is widely known that the setup costs for an IC fabrication facility or foundry are enormous [11]. Since the performance of silicon devices is extremely susceptible to the presence of impurities such as sodium atoms, cleanliness of the environment is absolutely essential [12]. The temperature and humidity of the facilities must be accurately maintained within a specified range for fabrication processes and to minimize static charge build-up. Additionally, some rooms must be damped against vibrations to prevent the jarring of precise mechanical equipment.

The capital costs required to set up a large scale in-house fabrication facility or external foundry have well exceeded \$1B [11]. The Taiwan Semiconductor Manufacturing Corporation (TSMC) foundry, Fab15 established in 2012, is estimated to have cost roughly \$9.3B - not including the costs for lifetime maintenance and operation of equipment [13]. These expenses are in large part due to the precise photolithographic, ion implantation, etching, cleaning, and dicing equipment. As such, it is difficult for smaller companies to fully enter and compete in the industry. With the rising costs of manufacturing in the semiconductor device industry, an exceptional amount of money and effort has gone into exploring cheaper alternatives. One promising solution is the use of organic materials,

specifically conjugated polymers and or organic small molecule semiconductors, in creating cheap low performance electronics and solar cells.

Although the inclusion of impurities in organic devices can sometimes lead to leakage currents and worst case, render them inoperative, the effects seem to be much less pronounced than in silicon technologies [14]. For this reason, the exorbitant fabrication facilities and precise environmental controls are not entirely necessary. Mass-producing organic devices without ultra-clean rooms (of class 100 / ISO4 or lower) can lead to a substantial reduction in start-up costs [15]. Furthermore, some organic materials - such as poly(trivinyltrimethylcyclotrisiloxane) or PV_3D_3 - have a much higher biocompatibility when compared with silicon devices [16]. Currently, materials are being studied for use inside the human body as low-cost wireless sensors to monitor in vivo life functions [17, 18, 19]. These emerging technologies have the possibility to revolutionize the health care system - in particular geriatric and diagnostic medicine. Another advantage of organic films is their flexibility. Molecules in the disordered film are not held together by rigid covalent bonds like silicon, but instead by weak Van Der Waals forces; this allows for the semi-crystalline shape to be morphed or distorted relatively easily without extensively degrading the film's electrical properties [20, pp. 139-143]. It has already been shown that this aspect of organic materials has allowed industry to cover "high area morphologies" and produce pliable, rollable screens and solar cells [21, 22].

The issues of sustainability and waste management also arise in the electronics industry. In terms of energy use, semiconductor manufacturing can be extremely intensive [23]. Calculating the required energy per unit of material processed, semiconductor manufacturing methods - especially oxidation, sputtering, and dry etching - are up to six orders of magnitude more demanding than for metal or plastic processing. "Typical hazardous waste streams generated by the semiconductor industry include waste rinsing water, spent process baths, waste acids and bases used for cleaning, and metal salts" [23]. These wastes cannot be disposed of in standard landfill sites unless they have been treated beforehand to

meet the stringent requirements. As a result, billions of dollars are spent in the semiconductor industry every year to minimize waste production, recycle waste water, and dispose of the remnants. Disposal of electronic products termed e-waste also leads to problems. Through organic electronics it is possible - though still extremely challenging - to fabricate biodegradable devices with processes that require much less energy, generate no toxic waste, and still remain economically feasible [24]. In the long term, organic electronics can provide avenues that are much more sustainable.

In several applications including capacitive touch screens and solar cells it is extremely important to have a top conducting layer with low broadband absorbance. The more light that is absorbed by the top layer for solar cells, the less light that is absorbed by the active region lowering the efficiency. Similarly, for touch screens, to achieve the same visible brightness through the top layer with a higher absorbance, a more luminous backlight or LED is required leading to increased power consumption and shorter device lifetimes. Current technology uses Indium Tin Oxide (ITO) as the top conducting layer; however, it is becoming more and more scarce as a global resource, driving up the price [22]. Conversely, some conducting polymers have extremely plentiful precursors and exhibit the required transparency and sheet resistance to compete with ITO, further motivating research in the field. A great deal of effort has gone into synthesizing highly conducting transparent PEDOT as a viable replacement with some success [25, 26].

Ultimately, the dream that many researchers share for this emerging field is ultra-rapid production via solutions-processed roll-to-roll printing. The invention of the Gutenberg printing press and subsequent evolution into the modern printing press, such as the one shown in Figure 2.2.1a, revolutionized mass communication in speed of information dissemination by rapid production. The advent of this technique created a boom for the newspaper industry and could likely do so for the electronics industry. If a similar technique is applied with dispensation of specifically formulated viscous organic solutions, patterned layers can be built up at high speeds with fair accuracy. Again, solar cells are one

(a) Newspaper Printing Press [28]

(b) A3 Sized Printed Organic Solar Cells [27]

Figure 2.2.1: Application of Roll-to-Roll Printing to Organic Electronics

such technological application where the constraints for accurate locational layer deposition are less demanding. Figure 2.2.1b shows an Australian roll-to-roll solar cell printing process that generates sheets the size of A3 paper [27].

However, there are several disadvantages to this method and the use of polymers in integrated circuits in general. Firstly, the mobility of charge carriers in polymers is significantly lower compared with silicon [29]. This leads to slower switching speeds and overall lower performance. Furthermore, modern high-speed lithographic processing tends to have a much larger minimum feature size ($\sim 20\mu\text{m}$) compared with the latest silicon processes ($< 30\text{ nm}$). As a result, each device on chip consumes much more space than its silicon equivalent. For the reasons detailed above, it seems unlikely that organic electronics will usurp silicon technology in markets requiring compact high speed operations such as computer CPUs and DRAM. Still, in other less intensive applications there is a lot of space for low-cost low-performance organic components. One such area gaining attention is flexible printed polymer Radio-Frequency Identification (RFID) tags as discussed below.

Note that organics materials, while extremely promising, are not the only alternatives to single crystalline silicon (c-Si) being researched. One other notable contender is amorphous silicon (a-Si), which compared to c-Si also provides more economical, less resource intensive manufacturing of lower performance devices [30]. Having a less rigid

structure, much thinner layers of a-Si for substrates can be obtained; thus reducing raw material usage [31]. Furthermore, with deposition temperatures as low as 150 °C, plastic substrates can be employed making a-Si another candidate for roll-to-roll processing [32].

2.3 Fabrication of Polymer Films

There are a plethora of methods being researched and developed for fabricating high quality conducting polymer films. These methods can be divided into two main classes: solution-processed and vapour-processed. Each have their own merits. Furthermore, the polymers can be formed before or during deposition. Monomers and other reactants may exhibit differing processing properties from final polymers; some examples would be vaporization temperature and solubility in various solvents. Polymerization during deposition may yield advantages over deposition of pre-formed polymers [33].

2.3.1 Solution-Processed Methods

One of the simplest deposition methods is spin coating. A solution is drop-cast onto a substrate and distributed over the surface using centripetal acceleration while excess material is simultaneously removed; after which the remaining solvent is evaporated leaving behind the intended organic material. This method covers the entire substrate area but sometimes lacks in uniformity. Alternatively, solutions can be formulated into viscous inks allowing various printing methods to be employed. Printing can merge patterning and deposition steps, thus increasing production speed and conserving materials. Screen printing, gravure printing and ink-jet printing are just a few examples. If roll-to-roll printing process are implemented - similar to those used in the newspaper industry as shown in Figure 2.2.1a - then the production speed can be increased significantly [29]. This technology is not just limited to solar cells as there have been several recent significant advances. In 2007, Fix [34] reported the production of a functioning polymer based 13 MHz RFID chip that was

Figure 2.3.1: Fully Screen Printed Polymer Based 13 MHz RFID Chip [34]

fully roll-to-roll printed except for the antenna. Figure 2.3.1 is a picture of the chip; it is approximately 2 cm by 3 cm.

There are several inherent problems with the conventional thin film polymer deposition techniques based in solutions chemistry [21, 16]. Many polymers are insoluble making processing difficult to impossible; other polymers only have high solubility in highly corrosive and harmful solvents. The use of such solvents leads to possible damage or degradation of human tissue or the substrate - respectively lowering device biocompatibility and affecting device performance/lifetime. Additionally, highly conformal layers are hard to obtain as the liquid coating's surface tension causes beading. Similarly, with roll-to-roll printing, fast-moving substrate material can blur edges limiting the minimum feature size.

One last category of solution-based deposition methods is electrochemical polymerization. It involves placing a monomer in an electrolytic solution and pulsing a periodic voltage across a set of electrodes [35, 36]. Monomer molecules are radicalized through anodic oxidation and react with each other forming continuously growing oligomers [37]. The dopant anions sourced from an acidic or aqueous electrolyte, migrate towards the anode and balance the oligomers. Its restrictions lie in the fact that the polymer is deposited only on the electrodes. To coat a substrate with this method the substrate must be conductive. Furthermore, the shape of the electrode becomes important when considering field strength as resultant film thickness will vary with field strength along the electrode.

2.3.2 Vapour-Processed Methods

Vapour processing methods allow the circumvention of the aforementioned problems. Since reactants are introduced in vapour form, recent organic vapour deposition techniques can also avoid time consuming pre and post-treatment steps. Additionally, the surface conformity of the film and underlying crystallinity can be greatly improved over solution-processed methods. Many papers have been published concerning vapour-processed polymer deposition; each with a slightly different name or title and minor to major changes in experimental setup. Sreenivasan and Gleason [33] have appropriately categorized them into four main methods - mostly based on their respective reaction schemes. They are: Vapour Deposition Polymerization (VDP), Plasma-Enhanced Chemical Vapour Deposition (PECVD), Initiated Chemical Vapour Deposition (iCVD), and Oxidative Chemical Vapour Deposition (oCVD). Note that VDP and PECVD are well-established techniques whilst iCVD and oCVD are just over a decade old. Each category has its own nuances concerning precursor material, environmental conditions, and resulting polymer films. These will be highlighted in the following sections along with some applications and recent progress.

All four categories of reactions take place under vacuum to varying degrees. The vacuum itself is important for several reasons. It provides a more pure environment that is easier to control, whether it be introducing molecules at a certain concentration or flow, keeping out contaminants, or generating a plasma. Furthermore, by reducing the number of molecules inside the chamber, the average distance between them increases and the chances for collision drop significantly [38].

2.3.2.1 Vapour Deposition Polymerization (VDP)

VDP can be considered the simplest of all categories. The only precursors used in the reaction are monomers; often two different sources which intermingle to form chains with alternating units. Figure 2.3.2 portrays a simple VDP reactor. The reaction takes place in a single deposition chamber at Ultra-High Vacuum (UHV). The monomers are held in

ceramic crucibles which are heated, often resistively, to increase the vapour pressure and hence the rate at which the gases evolve. In UHV, the interaction between molecules is greatly reduced, leading to a directed initial flow. A cooled substrate is placed in the path of the vapour resulting in preferential condensation onto the substrate.

Figure 2.3.2: Diagram of a Standard VDP Reactor

The temperature of the substrate, as with all the other categories, plays an important role in determining the orientation and conjugation length of polymer chains in the film. Having a higher substrate temperature increases the average energy of oligomers and allows them to more readily rearrange into the energetically favourable states of long chains. Having long conjugation length and a consistent orientation among polymer chains improves the overall conductivity in that direction. Therefore, increasing the temperature leads to a more uniform film with higher conductivity. However, there is a tradeoff involved; with increasing temperature, the rate at which the monomer molecules adsorb onto the substrate decreases - resulting in longer deposition times for target thicknesses. Furthermore, a cooler surface leads to less degassing off the substrate.

This technology has been used for a wide range of applications in fields such as biotechnology and photonics. In 2003, Lee and Frank [39] fabricated films of polypeptides from a range of alpha-amino acids for use as protein-based biosensors. Through VDP, Chen et al. [40] enhanced the Young's modulus of various polymer fibres including polybenzoxazole (PBO or Zylon) over the standard solution-cast fabrication method.

2.3.2.2 Plasma-Enhanced Chemical Vapour Deposition (PECVD)

In PECVD, monomer vapours are exposed to a plasma full of free radical ions and electrons [41]. The monomer molecules become radicalized and polymerize on a cooled substrate through one of several possible chemical reactions. The electrodes are placed such that the plasma field surrounds the substrate with a linear flow of monomer from one port over the substrate and out to the vacuum exhaust as shown in Figure 2.3.3.

Figure 2.3.3: Diagram of a Standard PECVD Reactor (Modified from [41])

The chaotic reactions of free radical oligomers in PECVD produce atypical films; “the chains are branched and are randomly terminated with a high degree of crosslinking”, as depicted in Figure 2.3.4 [41]. Standard operating pressures fall within the medium vacuum regime around 300 mTorr, with the majority of setups using a 13 MHz alternating electric field to generate nitrogen and oxygen plasmas. As the molecules in the plasma are very energetic, the destruction of pendant groups lining the backbone of the polymer occurs frequently - which in turn allows for non-selective cross-linking. While PECVD is relatively common in both organic and inorganic processing, one interesting application of late has been the fabrication of a transparent semiconducting film using Lavender oil as a monomer [33].

2.3.2.3 Initiated Chemical Vapour Deposition (iCVD)

Similar to PECVD, iCVD makes use of free radical species to achieve a one-step polymerization of the monomer vapour [33]. Differentiation lies in the way the free radicals

Figure 2.3.4: Diagram of Branching and Cross-linking in Polymers (Modified from [42])

are generated. In iCVD an ‘initiator’ vapour, denoted as I_2 in Figure 2.3.5, is introduced concurrently with the monomer vapour. As shown in Figure 2.3.5, the path of flow is lined with resistively heated elements maintained in the range of 200-700 °C [43]. The thermal energy provided by the filaments can decompose the initiator molecules into free radicals, I^+ . The pyrolysis of the initiator takes place inside the main vacuum chamber usually just above the cooled substrate. Employing Mass Flow Controllers (MFCs), with precise control of the flow rates of precursor gases, facilitates tuning for desired growth rate. With a lower reaction energy, iCVD avoids the unintentional reactions with secondary groups that take place in PECVD. Accordingly, iCVD does not balance functional group retention with growth rate as is required in PECVD.

Figure 2.3.5: Diagram of a Standard iCVD Reactor [43]

With exceptional control over the functional groups and stoichiometry, iCVD proves to be an excellent method for obtaining polymer films with specific properties such as hydrophilicity and phobicity, chemical resistance, pH sensitivity, antimicrobial activity, adhesiveness, etc. [43]. One such example is the coating of a tissue with PTFE by Martin et al. [44]. The conformity over the high morphology woven fibres is quite impressive

yielding superior hydrophobicity. Another interesting application has been in Microelectromechanical Sensors (MEMS). Integrated with standard silicon based MEMS technologies, iCVD polymers have been used to provide “chemical specificity and reactivity” [33]. One such sensing device was constructed by Arora et al. [45] from a silicon nitride cantilever coated with poly(maleicanhydride-diethyleneglycoldivenyether). In response to the presence of nucleophiles such as amines and alcohols, the mechanical stress results in the cantilever deflecting and closing a circuit.

An ubiquitous application which can be grouped into this category is Parylene coating. The CVD process for Parylene dates back to 1947 but has gained popularity in recent years. As a twist on iCVD, pyrolysis of the dimer acts as a source for both the initiator and monomer. Furthermore, deposition occurs at room temperature allowing for even thermally sensitive devices to be coated. Processing has reached a point where extremely precise and conformal pinhole-free films are guaranteed. In electronics and other industries, parylene is frequently used as an encapsulating material for its many exceptional properties. Among those, it functions as an excellent barrier for humidity and other vapours, has a strong chemical resistance, and is highly electrically insulating.

2.3.2.4 Oxidative Chemical Vapour Deposition (oCVD)

Oxidative chemical vapour deposition (oCVD) differs slightly from iCVD. It instead employs an oxidant to radicalize monomers for ensuing polymerization [21]. The substrate is introduced to both oxidant and monomer in vapour phase. The substrate can be exposed to the oxidant and monomer vapours concurrently or one after the other. As with the other processes, a cooled stage is used to promote condensation. Sources, especially less-volatile oxidants, are often thermally vaporized and transported in a carrier gas over the substrate and into the exhaust [46]. Precise flow control of the vapour streams is possible enabling fine tuning of reactant ratios.

Figure 2.3.6: Diaz Mechanism for Step-Growth Polymerization of PEDOT [21]

Figure 2.3.6 shows the Diaz reaction mechanism to generate PEDOT from an unspecified oxidant and EDOT monomer. First, the oxidant removes electrons from the monomer units creating radical cations; next, pairs of charged monomers covalently bond to form dimer units. Subsequently, oxidant ions deprotonate the charged dimers leaving them neutral. “Substitution of the EDOT thiophene ring at the 3,4-positions blocks β -coupling, allowing new bonds only at the 2,5-positions” [21]. The step-growth polymerization reaction can continue with the oxidation of dimers, further bonding between radicalized units, and deprotonation of the fast-growing oligomer chains. As the chain length increases, the electrons in the conjugated backbone become increasingly delocalized. The attractive force exerted on the electrons by the chain core is lessened, effectively reducing the oxidation potential and facilitating further chain growth. These reactions can become somewhat violent, as the reaction rate increases until all precursors are consumed or displaced.

The oxidant serves a secondary purpose; oligomers can be further oxidized resulting in a charge imbalance at the Sulfur in the Thiophene ring. This effectively dopes the chain generating mobile charge carriers in the form of positive polarons and bipolarons. As shown in Figure 2.3.7, part or all of the oxidant becomes a balancing counter-ion along the

Figure 2.3.7: Chemical Doping of PEDOT via Oxidation (Modified from [46])

backbone of the chain until otherwise removed. As this occurs, the polymer undergoes a transition from its intrinsic benzoid state to a doped quinoid state. There is however, an observed upper limit to the amount in which the chain can be doped.

In an investigation of pyrrole polymerized in-solution using ferric chloride, micro-analysis of resulting films was performed varying the initial molar ratio of precursors. [47]. The analysis revealed that the maximum molar ratio of chlorine to pyrrole was 1/3, indicating that every third pyrrole molecule in the chain was doped with a chloride counter-ion. This maximum doping level was later extrapolated for PEDOT to be every three or four units as the polymers are quite similar. The physical reasoning for this maximum level was only ever speculated to be based in lowest favourable energetic states with the doped quinoid form of the polymer occupying a higher state than the undoped benzoid chain [35, 48].

With the same reaction mechanism as oCVD, Vapour Phase Polymerization (VPP) mimics most of the benefits. It is a partial vapour reaction; the oxidant which tends to be less volatile is applied to the substrate in solution form; whether by spin-coating or dip-coating for textiles, a semi-uniform layer is applied. This layer is dried to remove all of the solvent and then exposed to the monomer vapour, proceeding down the same reaction path.

2.3.2.5 Comparison of Vapour Phase Fabrication Methods

Table 2.3.1 summarizes the four sub-classes of vapour phase fabrication outlined above noting their respective advantages, disadvantages, and peculiarities.

Table 2.3.1: Comparison of Vapour Phase Fabrication Methods

Method / Properties	VDP	PECVD	iCVD	oCVD
Principle	Thermal evaporation of one or more co-polymers	Free radical polymerization via plasma ionization	Free radical polymerization via pyrolyzed initiator	Step-growth polymerization via oxidizing agent
Vacuum Level	UHV	MV	MV	MV
Nuances	Condensation reaction	Electric field: RF (~13.56MHz), DC or pulsed	Heated filaments	Use of separate delivery mechanisms common
Advantages	<ul style="list-style-type: none"> Improved hygroscopic resistance Improved stiffness 	<ul style="list-style-type: none"> Better process control Faster deposition rate 	<ul style="list-style-type: none"> Lower substrate temperature leads to less side reactions and higher deposition rates 100% retention of functional groups possible with no growth rate tradeoff 	<ul style="list-style-type: none"> Highly conductive films can be produced in-situ Highest deposition rate possible (unstable)
Disadvantages	<ul style="list-style-type: none"> Metering of flow rates difficult Lower degree of anisotropy Low growth rates Chain length vs growth rate tradeoff 	<ul style="list-style-type: none"> Branching chains, random terminations and cross-linking Functional group retention vs growth rate tradeoff 	<ul style="list-style-type: none"> Poor adhesion Monomers must be stable at initiator decomposition conditions 	<ul style="list-style-type: none"> Oxidant strength and volatility must be carefully selected Moderation of polymerization rate may be required Crystallization of polymer film in presence of water

2.4 Recent Advancements in oCVD

This dissertation will focus on the vapour-processing methods of VPP and oCVD. Several notable groups have put forth series of papers outlining their advancements and discoveries in the fields of VPP and oCVD over the past years. These papers not only discuss methods of improvement for depositions but speculate as to the finer details of the reactions taking place.

2.4.1 oCVD

The Gleason group at MIT has specifically studied the effects of substrate temperature on PEDOT deposited via oCVD [21, 48]. Figure 2.4.1 shows the apparatus that was employed. They used a vacuum chamber held on the order of 100 mTorr with MFCs regulating the flow of EDOT monomer and pyridine to several sccm [21]. The oxidant, ferric chloride, was introduced by sublimation at 240 °C with a 2 sccm flow of argon as a carrier gas. The substrate temperature was controlled by a closed water loop with both orientations of

Figure 2.4.1: MIT oCVD Reactor [48]

substrate, upright and inverted, being used. Typical spacing between substrate and oxidant source is approximately 20 cm to prevent any proximity heating [48]. It was reported that by varying the substrate temperature from 15 °C to 100 °C the conductivity of resulting films increased from approximately 10 S/cm to 400 S/cm. A shift in doping levels of the films was observed through the translation in positions of the C=C peak and polaronic energy peak in Raman/FTIR and UV-VIS spectroscopy respectively. The ability to tune the conductivity of a thin film just through substrate temperature is highly desirable.

The inclusion of weak bases such as pyridine - as above - or imidazole to control the potentially explosive reaction rate has been well documented [49, 50]. The mild bases moderate the potential of the strong oxidants but also neutralize acidic byproducts such as hydrochloric acid. As shown in Figure 2.4.2, acid initiated-coupling does cause polymerization to some extent but generates oligomers with unconjugated backbones reducing the number of paths for current flow and overall conductivity [21]. In extremely acidic environments, polymerization may be limited to trimer lengths.

The MIT group has also experimented with several other oxidants besides ferric chloride [52, 53]. With the same deposition conditions, cupric chloride was used and resulted in conductivities an order of magnitude lower [52]. It was theorized that the lower oxidation potential of the cupric ion ($E_0[Cu^{2+}] = 0.161$ eV) compared with that of the ferric

Figure 2.4.2: Acid-Initiated Coupling of PEDOT [51]

ion ($E_0[Fe^{3+}] = 0.771$ eV) drove the reaction to a lesser extent - though the possibility of thermal decomposition existed at the crucible temperature. Furthermore, the corresponding density was lower due to increased nano-porosity.

In verification of this theory, a stronger and more volatile oxidant, bromine, was introduced through a side port into the reactor [53]. The resulting film was slightly more dense and smoother - 4.5 nm for bromine and 5 nm for ferric chloride - as measured through AFM. The resulting conductivity was also noticeably higher at 380 S/cm. This work suggests that choice of oxidant is extremely important, affecting film doping level and morphology.

2.4.2 oMLD

Oxidative Molecular Layer Deposition (oMLD) is another variant of oCVD styled after Atomic Layer Deposition (ALD). The Parsons group out of North Carolina State University (NCSU) applied this process to PEDOT. Figure 2.4.3 shows the reactor scheme used by Atanasov et al. [46]. They used the design of Peng et al. [54] with small tweaks and a more volatile oxidant, $MoCl_5$, to obtain highly conformal thin films generated through “self-limiting half reactions [...] in a binary cycle [...] with submonolayer precision”. The linear reactor consists of a 3.5 cm diameter stainless steel tube with heated walls [54]. Short

Figure 2.4.3: NCSU oMLD Reactor [54]

pulses of oxidant and monomer vapours are separately released into the tube by solenoid valves and carried by a viscous flow of argon. The precursor vapour would flow over the samples with a Quartz Crystal Microbalance (QCM) in place to monitor deposition via mass gain. The precursors take separate exhaust paths - also controlled with solenoid valves - with one flowing through a liquid nitrogen trap before rejoining at the vacuum pump.

A purge separates the polymerization stages, resetting the system for the next layer of controlled growth. In the purge, any unreacted precursors and acidic byproducts are removed [46]. As such no additives were needed to stem unwanted side reactions. Using this method, the highest known conductivities for PEDOT films to date have been attained. The process also provides greater conformity for high aspect morphologies. As with the the oCVD group at MIT, the conductivity as a function of substrate temperature was studied. Changing from a deposition temperature of 100 °C to 150 °C resulted in an increase of over ten times, from sub-100 S/cm to 1000 S/cm.

In addition to deposition temperature, the role of post-rinse solvents was studied. The conductivity, as well as elemental composition (using XPS and EDS analysis) were examined pre and post-rinse [46]. Table 2.4.1 shows the effects of various solvent rinses on oMLD PEDOT deposited at two temperatures. It is important to note that a DI water rinse resulted in a drop of 5-10 times in conductivity while exhibiting a decrease in oxygen and molybdenum and total loss of chlorine. The loss of chlorine is synonymous with a loss of dopant molecules. The chlorine atoms with their strong electronegativity pull electrons

away from the conjugated chain generating charge carriers in the form of polarons and bipolarons. As their concentration decreases so does the conductivity of the sample.

Table 2.4.1: Conductivity of PEDOT Pre- and Post-Rinse for Various Solvents [46]

	Conductivity, σ (S/cm)			
Deposition Temperature, T (°C)	100		150	
Solvent	Pre-Rinse	Post-Rinse	Pre-Rinse	Post-Rinse
Methanol	84 ± 12	79 ± 9	995 ± 8	711 ± 6
DI water	75 ± 10	8 ± 7	1000 ± 8	190 ± 5
0.5M Sulfuric Acid	71 ± 4	68 ± 7	1440 ± 9	1810 ± 14
1M Hydrobromic Acid	-	-	1790 ± 10	2250 ± 14

Methanol rinses displayed only small drops in conductivity balancing a decrease in chlorine with increase in oxygen. 0.5M Sulfuric acid replaced chlorine with sulfur leading to mixed results; slightly lower conductivity at 100 °C deposition temperature and a 33% boost at 150 °C.

2.4.3 VPP

The Fabretto Thin Films Coating group at the University of South Australia has been performing VPP under vacuums on the order of 10 Torr [35, 55, 56, 57, 58, 59, 60]. The relative humidity was also reported to play a large role in the conductivity of VPP PEDOT [57]. Sweeping Relative Humidity (RH) in a VPP chamber with all other conditions constant, the formation of crystals was observed above 46% RH. At 59% RH, 43.7% of total sample area was crystallized. This crystallization suggests breaks in the PEDOT chains at the grain boundaries. If the oxidant was already crystallized, the exposure to EDOT would increase local water vapour condensation and exacerbate the issue leading to even more crystallized PEDOT.

To combat this problem, the additive polyethylene glycol-polypropylene glycol-polyethylene glycol (PEG-PPG-PEG) block trimer was incorporated. Varying the percentage mass of PEG-PPG-PEG in the oxidant solution, SEM images revealed a decrease in

crystallization with increasing glycol concentration due to its amphiphilic properties - PPG is hydrophobic and PEG is hydrophilic.

Furthermore, PEG-PPG-PEG served another purpose. In a similar experiment the PEG-PPG-PEG mass percentage in the oxidant solution was varied. The same volume of each solution was spun onto substrates and polymerized under near identical conditions. Interestingly, for mass percentages of 10-25% the resulting PEDOT thickness was fairly constant; this suggested that while the amount of oxidant in the same volume is decreasing with added PEG-PPG-PEG, the PEG-PPG-PEG itself intercalates into the polymer matrix and accounts for some of the volume in the final film. Inside this range the PEG-PPG-PEG acts as a complexing agent with the iron as its coordination centre of the oxidant lowering its “effective reactivity” in a different manner than the weak bases of pyridine and imidazole [60]. At the extremes, 5% and 30% the behaviour is quite different. From 5-10% there is not enough PEG-PPG-PEG to slow the polymerization and protect against crystallization. At 30%, the conductivity drops and the excess of PEG-PPG-PEG that cannot intercalate into the structure must interfere with polymerization before removal with rinse.

To better understand the formation of PEDOT in their reaction, a Time Of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurement was performed. In this procedure gaseous argon atoms were ionized, collimated, and accelerated using a field. The ion beam was directed towards a VPP PEDOT sample, acting as a drill digging down into the depth of the sample. Secondary ions were sputtered off and captured for analysis by a mass spectrometer. Three main masses were marked: iron indicating the presence of oxidant, PEDOT for the film, and silicon suggesting glass (SiO_2) [58]. The counts of each particle were monitored over time as the ion beam drilled deeper into the film with changing composition. The results of their measurement suggested that the PEDOT film was mainly formed at the surface of the spin coated oxidant. The PEDOT concentration decreased into

the depth as the oxidant concentration increased. The point at which the substrate was reached was inferred through the sudden jump in silicon ions.

This revelation brought more questions, including how the PEDOT film could continue to form if the local concentration of oxidant was depleted. A maximum film thickness should be observed versus deposition time if no other mechanisms were at place. Since this was obviously not the case, further investigation was required. The conclusion was the presence of capillary action in the oxidant, transporting itself from the substrate to the surface. It was previously thought that the oxidant was fully solidified and partially crystallized but Evans et al. [58] submit that the oxidant layer maintains liquid-like properties; enabling the acts of self-healing and leeching through the nanoscale voids.

2.4.4 Summary of oCVD Advancements

Table 2.4.2 summarizes the results from the groups mentioned above including notes on deposition temperature, oxidant used, additives, or extra steps involved. Note that oMLD does indeed have the highest reported conductivity to date as expected due to the novel oxidant, high substrate temperature, and precise control over process variables. The oCVD process has made great strides over the years and is slowly approaching its goal of becoming a viable replacement for ITO with a conductivity of ~ 13000 S/cm - whose main constituent, indium, is becoming more rare and costly [61].

Table 2.4.2: Summary of oCVD Initiatives (PEG* $\equiv$ PEG-PPG-PEG)

Method	Oxidant	T_{sub} ($^{\circ}$ C)	Comments	σ (S/cm)	Reference
oCVD	$CuCl_2$	80	-	32	Im et al. [52]
oCVD	$FeCl_3$	85	Pyridine	105	Lock et al. [21]
oCVD	$FeCl_3$	100	-	348	Im and Gleason [48]
oCVD	Br_2	80	-	380	Chelawat et al. [53]
VPP	$FeTos_3$	50	Pyridine	1000	Winther-Jensen et al. [49]
VPP	$FeTos_3$	35	15%wt PEG*	1487	Fabretto et al. [35]
oCVD	$FeCl_3$	150	HBr post-rinse	1620	Howden et al. [62]
VPP	$FeTos_3$	35	20%wt PEG*	2500	Evans et al. [58]
oMLD	$MoCl_5$	150	Acid post-rinse	5300	Atanasov et al. [46]

Chapter 3

Apparatus

3.1 Design Goals, and Constraints

The system for performing oCVD had several difficult conditions to fulfill. Foremost, it had to operate at moderate vacuum (1-1000 mTorr range) and temperature (0-200 °C range). These ranges were chosen based on previous reactor designs and realistic expectations. Precursors, especially less volatile oxidants, require low pressures and high temperatures to achieve appreciable vapour pressures and diffuse unimpeded through the chamber. Since strong oxidant vapours were used as reactants, it was also acknowledged that the housing material should be as resistant as possible to corrosive chemicals; primarily to avoid unwanted vapour releases and minimize oxidant wasted. Accordingly, AISI 316 - a stainless steel alloy - was selected as the body material for all fittings and components in the manifold line. As with most stainless steel alloys, it can handle vacuum pressures and high temperatures. However, AISI 316 was chosen specifically because it has a relatively high concentration of molybdenum when compared to other stainless steel alloys while still being a common option for standard vacuum fittings. Higher concentrations of molybdenum have been shown to increase corrosion resistance [63]. Similarly, any non-metal sealant material applied to gaskets and o-rings required corrosion resistance if exposed to oxidant

Table 3.1.1: Design Goals

Property	Value
Budget	\$3000
Corrosion resistance	High
Ease of operation	Low
Operating pressure	1-1000 mTorr
Operating temperature	0-200 °C
No. of monomer sources	3
No. of oxidant sources	3
Precursor waste	Minimal
Deposition scheme	Static
Volume	Minimal
Walls	Heated
Substrate	Cooled

vapours. Fluoropolymers such as Viton are known to have these properties along with suitable temperature limits [64].

Having multiple monomer and oxidant sources was also designated as an objective. This could enable sequential deposition of multiple polymer films or even co-polymer variants. Three holders of each source type were desired. This presented the challenge of isolated individual temperature control for each precursor.

One of the main design goals in this project was to minimize the amount of precursor waste. The intent was to have nearly 100% of the initial precursor mass preferentially sublime onto the cooled substrate. Other similar oCVD systems use a dynamic flow of monomer and/or oxidant vapour over the substrate which creates a fair amount of waste. For this project, the apparatus was designed with a static layer of vapour hovering over the substrate. Theoretically, stagnation is avoided with continuous deposition and diffusion of the vapour until all is sublimed. Possible sources of mass loss include flow out through the exhaust line, pressure leaks, and unwanted condensation on the walls of the system - which could build up over time and impede gas flow. To avoid the latter, another design goal was established; maintaining the wall of the vacuum chamber at a higher temperature than the vaporizing precursor. Termed the ‘hot wall effect’, the temperature gradient would

Figure 3.1.1: Swagelok Joint Sealing Mechanism [66]

reduce the rate of adsorption of precursor onto the walls. Conversely, the substrate temperature had to be regulated at a lower temperature than the precursor temperature to promote condensation in the correct location.

With a reasonable budget of \$3000, parts were evaluated on a cost-benefit basis. Although welded joints are undoubtedly superior with regards to sealing, they were not opted for due to the high service charge, exorbitant cost of connectors, and risk of component deformation under the extreme heat applied during the welding process. Instead, Swagelok joints comprised of a dual crush ferrule design were selected. Figure 3.1.1 details the sealing mechanism of the joints. As the nut is tightened onto the body of the fitting, the front ferrule is wedged between the body of the fitting and tube forming the first sealing layer. The back ferrule is forced into the tube, deforming or ‘swaging’ it. This creates the second sealing layer but also grips the tube to immobilize the front ferrule. These joints offer straightforward assembly with a helium leak rate below $15 \text{ cm}^3/\text{h}$ at an internal vacuum pressure of 1 mTorr and room temperature [65]. While they are not meant to be re-used, if parts become inoperable due to corrosion or precursor build-up they are relatively easy to disassemble and replace.

3.2 System Overview

Figure 3.2.1 shows a diagram of the overall apparatus. This design features two separate pressure vessels. An inner chamber which is exposed to precursor vapours and an outer chamber which serves several purposes detailed later. Both chambers are pumped down to medium vacuum during operation. The inner chamber is enveloped by a heater to establish the hot wall effect. Mounted onto the lid of the outer chamber, the inner chamber needs to be lowered into a large pressure vessel. Precursors are held in vials which are heated separately to achieve appreciable vapour pressures. There are two rows of precursor holders oriented into the page. Deposition occurs when the valve corresponding to the heated vial is opened and the cooled substrate is exposed to the vapour. At the same time, the inner chamber is isolated from the vacuum pump to prevent exhaust of vapours. Until the vial valve is closed, adsorption of the vapour onto the surface of the substrate continues. In the following sections the purpose, design, and selection of individual components and sub-systems will be discussed.

Figure 3.2.1: Diagram of Deposition Apparatus with Inner and Outer Vacuum Chambers

3.3 oCVD System Interior

Figure 3.3.1 displays the partially completed manifold line of the inner vacuum chamber. It consists of several union crosses connected to Swagelok SS-1RS4 regulating stem needle valves. The valves were selected based on the temperature rating and chemical compatibility of their constituent materials. Unfortunately, most economical actuated valves could not stand the high temperatures so manual needle valves with a high temperature PFA packing were chosen. The needle valves were placed in between the main line and precursor holders to isolate them from each other until needed. The vacuum and nitrogen gas purge lines were also connected via the union crosses with the option to isolate using needle valves. The vacuum line was connected to a GE Motors 1/3 HP rotary vane roughing pump flowing through an oil mist filter and out to the HVAC exhaust system of the FANSSI lab lined with several carbon scrubbers.

The precursor holders were comprised of two parts: a 12 mm diameter glass vial, into which the chemical was loaded, and a Swagelok SS-8-UT-1-6 Ultra-Torr fitting which sealed around the exterior of the vial with an o-ring and ferrule squish design. The standard o-ring which accommodated a 1/2" OD tube was replaced with an o-ring of the same OD but slightly larger cross section of 3/16". Six vial holders were constructed to allow subsequent film depositions. The vial holders were arranged in two rows on either side of the main line; one row was allocated for monomers and the other for oxidants.

The reactor chamber is located at one end of the main line and is comprised of two 'Kwik-Release' (KF) flanges and an o-ring encircling a centering ring. Figure 3.3.2 depicts the sealing mechanism with a cross-sectional diagram. Each flange has a milled groove to accommodate the ridge of the centering ring. The o-ring itself is squished between the flat surfaces of the flanges to form a seal.

Figure 3.3.3 provides isometric views of the specific flanges used in the reactor chamber. A blanking flange was used for the bottom piece which held the substrate. To accommodate a round 2" wafer, the ridge in the middle of the flange was milled down.

Figure 3.3.1: Inner Vacuum Chamber Manifold Line Mounted to Underside of Exterior Vacuum Vessel Lid (Incomplete)

Figure 3.3.2: KF Flange Sealing Mechanism [67]

Figure 3.3.3: Diagram of KF Parts in Reactor Chamber (Modified from [68])

Wafers were placed on the newly flat surface with the centering ring resting overhead on the flange's inner edge. As a result, the ring was elevated from the wafer out of contact, just shadowing the perimeter of the wafer. The top flange was an adapter from KF to NPT to Swagelok fittings. The ridge of the top flange was left as is to provide backup mechanical support to the centering ring. Non-contact between the ring and wafer was verified with the clamp secured.

Figure 3.3.4 shows the reactor chamber in-situ. The top plate has a fitting attached to the main line through a twice-bent solid pipe. Previously, a corrugated flexible stainless steel hose was employed but resulted in deposition inside the folds of the hose lowering overall yield. The o-ring has a 5 mm cross section which creates a very small space between the top and bottom flanges but still results in some thermal isolation, allowing cooling of the bottom flange.

The pressure of the inner chamber is monitored through a connection to a Granville-Phillips 275 Convectron gauge, located at the other end of the main line. The Convectron gauge is governed by a Terranova 906-A Convection Gauge controller; both of which can be seen in Figure 3.3.5. The operating principle for the gauge is the inference of number density or pressure based on the registered heat loss of a resistor. A Wheatstone bridge

Figure 3.3.4: Reactor Chamber Composed of Two KF Flanges

Figure 3.3.5: Convectron Gauge and Controller for Monitoring Pressure Inside [69]

is employed with one leg acting as the sensor; a temperature compensator across another leg improves the accuracy of measurement in low vacuum from its predecessor the Pirani gauge. With its wide measurement range from μTorr to atmosphere and its millisecond response time, the gauge was well-suited for this application though other options did exist.

3.4 Exterior Vacuum Chamber

During the deposition phase, the main line was isolated from the pump to reduce the amount of material that was lost to the exhaust line. While this decreased the amount of waste material, it presented other issues. The pressure inside the main line would rise at a rate such that unwanted condensation on the walls of the main line was likely. At the same

time, the presence of air molecules would interfere with transport of the reactant material to its destination. As such, a lighter vacuum on the outside of the system was introduced to reduce the leak rate into the system and maintain moderate vacuum during deposition. It also served other purposes, providing another safety layer between the precursors and the user. Furthermore, by removing the air surrounding the inner chamber the thermal load experienced by the heating systems was greatly reduced. Without air, convective losses were negligible and the heaters could operate more efficiently.

The weak outer vacuum was generated using a thin aluminum pressure vessel with a gasketed lid purchased externally. The assembly also featured a glycerine filled vacuum gauge and custom valve manifold; both of which had custom engineered feedthroughs. Figure 3.4.1 shows the original vacuum chamber. Given that the reactants were not present in the outer vacuum, aluminum was selected as the body material.

Figure 3.4.1: Purchased Outer Vacuum Chamber [70]

The concept for combining the inner and outer chambers was to mount the inner chamber to the lid using the panel mount nuts of the needle valves. This way the majority

of connections in the inner chamber would be contained within the outer chamber. Only the stems of the needle valves would be exposed to ambient pressure. The valves themselves allowed for panel thicknesses of up to $1/4$ ". Since the original lid was 1" thick acrylic, a new thinner lid was machined out of stainless steel. This was for several reasons. First, the acrylic was thought to not be able to withstand elevated temperatures. Second, the lid was too thick to allow for panel mounting of standard valves. Third, stainless steel was selected to avoid galvanic corrosion with the fittings and valves.

The diameter of the stainless steel lid was kept the same as the acrylic lid, 15.25". This allowed for the orange silicone gasket to be re-used as the outer vacuum chamber seal. Similarly, the custom valve manifold and glycerine filled vacuum gauge were also recycled for later use. The ball valves on the manifold allowed for isolation from the vacuum and/or nitrogen lines.

To ensure that the new lid did not implode under the load of vacuum, calculations and simulations for the stresses on surfaces were performed for various thicknesses - and are available in Appendix D. Unfortunately, the required thickness of $3/8$ " for the stainless steel lid was still too large to accommodate the needle valve stems. To circumvent this problem, counterbored holes with a 1" diameter and $1/8$ " thick shoulder were machined into the lid; this allowed the jam nuts to sit in the depression squeezing against a gasket. Figure 3.4.2 depicts the method of panel mounting and specifics of the counterbored holes - note that this diagram is not to scale. For safety, simulations considering the additional stress of counterbored holes in the lid geometry were also performed.

Figure 3.4.2: Cross Section of Exterior Pressure Vessel Lid with Panel Mounted Valve

The gaskets, shown in Figure 3.4.3, were fabricated from a $1/8''$ sheet of 60A durometer silicone gasket material purchased from McMaster-Carr. A Computer Numerically-Controlled (CNC) water jet was used to cut gaskets to the exact dimensions of the counterbored holes and panel mount sections of the valves.

Figure 3.4.3: Valve Stem Silicone Gaskets Cut by Water Jet

Aside from the valve stem feedthroughs, many other lid feedthroughs to both the inner and outer vacuum chambers were required; most of which can be seen in Figure 3.4.4. Holes were machined in the lid to fit Swagelok $1/4''$ bulkhead feedthroughs for inner chamber vacuum, nitrogen, and pressure gauge connections. For the outer vacuum chamber, feedthroughs matching those found on the commercial acrylic lid were machined to accommodate the valve manifold (for vacuum and nitrogen) and the glycerine filled vacuum gauge with their custom gaskets. Larger bulkhead feedthroughs were incorporated for the $1/2''$ OD water connection fittings. Note that all feedthroughs into the lid, except for those which already had gaskets, were sealed with the same silicone gasket material as mentioned above. RTV sealant was also applied as a secondary layer to reduce leakage.

Lastly, a port for electrical connections was inserted. Given the sheer number of power and thermocouple connections, commercial electrical vacuum feedthroughs proved quite expensive. Instead, a custom feedthrough was fabricated using fittings intended for fluid connections. A $3/4''$ -14 NPT hole was drilled and tapped in the stainless steel lid. A bored-through $3/4''$ NPT to $5/8''$ OD Swagelok adapter fitting was threaded into place

Figure 3.4.4: Exterior Pressure Vessel Lid Feedthroughs

- allowing the appropriately sized tube to slide freely through unimpeded by the standard shoulder. For electrical connections, heavily insulated 18AWG wires and J-type thermocouples were fed through a $5/8$ " OD tube. The inside of the tube was sealed with Torr Seal vacuum epoxy and a marine epoxy. After drying for a day, the tube was inserted through the fitting and crimped with ferrules to seal along the outside. It was held under vacuum for an extended period of time to outgas any volatile material. Figure 3.4.5 shows the prototype for the feedthrough. As a result of testing the prototype, it was discovered that air paths through the sheathing of the wires were also present; this necessitated the use of RTV at end of the insulation where the wires had been stripped.

Figure 3.4.6 provides a side view of the partially completed inner chamber and lid assembly featuring a structure composed of 1" series T-slot aluminum bars. The structure was constructed to support the lid assembly when not resting on the rim of the exterior

Figure 3.4.5: Prototype Electrical Feedthrough for Exterior Pressure Vessel Lid

pressure vessel. Vertical columns were carefully attached to the lid around the existing framework of pipes that was the inner vacuum chamber. This was accomplished by milling and tapping shallow $1/4''$ -20 holes. Using these threaded holes, corner mounting brackets were anchored to the lid and vertical columns. Cross-struts were put in place for horizontal stability but also served the purpose of providing a footing for a vertically sliding stage. Upon this stage rested the substrate holder and vial heaters. During the unloading phase, the KF clamp would be removed and the stage would be lowered to allow access. The stage consisted of a thin aluminum sheet attached to two floor mounted flanges with $1''$ cylindrical aluminum tubes. These tubes would slide up and down until the tube holders were deformed through a threaded locking mechanism.

The exterior pressure vessel was mounted into a custom fumehood for additional safety against vapour exposure during operation. This was deemed especially important during the precursor loading procedure which involved removing the caps off vials and inserting them into the Ultra-Torr fittings. A horizontally sliding rail structure was also anchored into place on the fumehood counter top. This allowed the T-slot structure of the lid assembly to gently rest over the exterior pressure vessel during the loading phase. When raising or lowering, the rails could be moved out of the way to provide clearance. The aforementioned installation of the rails and exterior pressure vessel can be seen in Figure 3.4.7.

Figure 3.4.6: Side View of Inner Chamber Lid Assembly with T-Slot Support Structure

3.5 Temperature Regulating Systems

Temperature regulation of several components in the apparatus was essential. Different heating elements and control methods were used to achieve this. In the following sections, the subsystems involved in these processes are detailed and their operating principles are explained.

Figure 3.4.7: Exterior Pressure Vessel Installed in Fumehood

3.5.1 Temperature Measurement

The first element needed for a temperature regulation system is a method of measuring and logging temperature values. The simultaneous temperature monitoring of many locations in the apparatus was required. Accordingly, an OM-DAQ-USB-2401 USB 2.0 Data Acquisition (DAQ) module, shown in Figure 3.5.1, was purchased from Omega Engineering Incorporated. Featuring eight differential (or 16 single-ended) channels, the DAQ could measure voltages with up to 24-bit resolution at a maximum of 1000 samples/sec. Accommodating thermocouples as well, it included cold junction compensation and could correlate measured voltages with absolute temperatures for J, K, T, E, R, S, B, and N types.

A MATLAB class was developed to instantiate the DAQ as an object for obtaining temperature values. The programming environment interfaced with the module through a

Figure 3.5.1: Omega Data Acquisition Module [71]

.NET Application Program Interface (API). All eight channels were enabled and configured for J-type thermocouples. The J-type, with a iron-constantan junction, was selected for its narrow operating range of -40°C to 750°C which results in a higher sensitivity of $50\mu\text{V}/^{\circ}\text{C}$. Six channels were allocated for measuring the temperature of each precursor vial, one for substrate temperature, and one for inner chamber wall temperature. A scan rate of 60 samples/sec was set for the DAQ.

For temperature regulation, an interval of 0.5 s was used. While thermal noise is always present, another source of error present in the thermocouples was Electromotive Force (EMF) induced by the time-varying current waveforms flowing to the various heaters. Indeed, spikes in temperature readings up to 10°C were observed with currents

rapidly transitioning from one extreme to another. Worse still, an instantaneous erroneous temperature reading could lead to a major change in output further increasing the induced EMF. Instability from positive feedback is a serious issue in control theory. To combat this issue, averaging of temperature for each channel over the past ten readings was implemented. Additionally, mild shielding was added and thermocouples and power wires were separated further. With the small changes, a noticeable decrease in the oscillation of temperature readings was observed and stability was achieved.

3.5.2 Rope Heater

To maintain the ‘hot wall’ effect, lowering the rate of deposition on the walls of the main line, a flexible rope heater was wrapped around the tubing, valve bodies, and top flange. A 10' rope heater was purchased from Omega Engineering Inc. for operation at 120 VAC with a total wattage of 522 W or approximately 8.6 W/in^2 . The heater itself is made from “fine [36-40] gage stranded resistance wires that are [...] braid[ed] between layers of fiberglass yarn” to make it electrically insulating and resistant up to approximately 480°C [72]. The temperature was measured using J-type thermocouples placed in several different locations. A Proportional Integral Derivative (PID) loop had command over the AC phase control, affecting the flow of the power to the rope heater and resulting temperature.

The AC phase control circuit schematic is shown in Figure 3.5.2. The top half is a zero-cross detection circuit which allows for a microcontroller to synchronize with the phase of the AC input to properly control the power flowing to the load. The principle of operation is as follows: the sinusoidal voltage goes through the diode bridge and is full-wave rectified. When the voltage is above the built-in potential of the light emitting diode in the optoisolator (along with those in the diode bridge), current flows and light is emitted. The photons excite carriers which act as a base injection current for the Bipolar Junction Transistor (BJT) driver output. With transistor action, the collector of the BJT draws current through the resistor lowering the collector voltage. Since the microcontroller has a

Figure 3.5.2: AC Phase Control Circuit Schematic

high input impedance, it draws minimal current having negligible affect on the BJT circuit. Conversely, when the AC rectified voltage is low, no light is emitted and the collector current reduces to 0 A. At this point the voltage on the collector rises to the power supply rail and the microcontroller registers the voltage, above a certain threshold, as a digital 'HIGH' or 1. In effect, whenever the AC signal nears a zero-crossing a 5 V pulse is generated at the BJT collector output.

The bottom half of the diagram controls the shape of the voltage and current waveforms flowing through the load. When the input voltage is zero, the optocoupler remains off. No current flows into the gate of the Triode for Alternating Current (TRIAC) so it remains off and no power goes to the load. If a pulse is sent at some point between zero-crossings the LED turns on, illuminating the TRIAC. After several microseconds the TRIAC registers the gate current, latches, and begins to conduct in the middle of the AC cycle. This gives the appearance of a horizontally clipped waveform as shown in Figure

3.5.3 for 100%, 75%, and 50% duty cycles. Effectively, the TRIAC begins conducting almost immediately after pulse or trigger is applied. Even if the pulse is removed, the TRIAC will continue to conduct as the charge remains on the gate. However, upon the next zero-crossing the voltage difference between the gate and cathode goes to zero and the conduction period ends. In order for the TRIAC to conduct again the optocoupler must be triggered anew. The delay from a zero-crossing to the following pulse affects how long the TRIAC remains off in a half cycle and thus how much power is transferred to the load.

Figure 3.5.3: AC Phase Control Example Waveforms

Initially, this pulse was applied to the circuit by an Arduino microcontroller. Similarly, the zero-cross signal was fed to an analog to digital converter (ADC) on the Arduino, resetting one of its clocks once above a defined threshold value. As aforementioned, temperature measurement was performed by a DAQ and relayed to MATLAB. A PID control loop was implemented in the same programming environment with the corresponding temperature as an input. The error or deviation of the current temperature from the set temper-

ature influenced the percentage output power. Error values were also logged to anticipate how fast the input changes with output. From MATLAB, percentage power values were relayed to the Arduino through a virtual USB-COM (Communication) port. The Arduino converted the percentage RMS power into a time delay. The CPU on the Arduino with a 16 MHz clock ran much faster than the AC signal, counting tens of microseconds waiting for the start time of the pulse and/or the zero-cross to reset the counter. Since the PID loop updated the power output every half second, the Arduino would run independently for 60 cycles then read the new power value from its serial buffer.

In the final prototype, the above circuit for zero-cross detection and AC phase control was replaced with the EIKS REX-C100, a cheap PID controller and Solid State Relay (SSR) bundle shown in Figure 3.5.4. Though the packaging was slightly different, with a custom enclosure, LCD readout and front panel push buttons, the theory of operation remains the same.

Figure 3.5.4: Rope Heater PID Temperature Controller and Accompanying SSR [73]

The PID controller would read in the Seebeck voltage across by the thermocouple, compare the indicated present temperature to the set point and past temperatures and select a power output. To achieve the desired output, the SSR would be triggered a set amount of time after the zero-cross was detected. The controller featured an auto-tuning function to select the optimal P, I, and D values to critically damp the temperature response. This function was initially employed under vacuum to obtain rough estimates but the final values

were manually calibrated. The result was an overdamped system with a longer ramp in temperature to prevent overtemperature and protect thermally sensitive components.

3.5.3 Vial Control

To achieve vaporization temperatures, independent Peltier or Thermoelectric Coolers (TECs) were employed. The principle of operation of these devices is the Peltier effect, a heat flow between two dissimilar conducting materials which create a p-n junction. The TECs are versatile because they allow for a temperature gradient to be developed across the device in either orientation by switching the direction of current flow. Additionally, the combination of vials and TECs was deemed simpler than constructing tightly wound nichrome (resistive) wire heaters. They also offered a deeper vessel (3 cm) with more containment than a standard thermal evaporation boat - especially important when using liquid precursors. Since the vials were divided into two rows, the TECs were also distributed in the same fashion with each row bonded to a large bar of aluminum acting as a heat sink - or cold sink depending on orientation - by thermally conductive epoxy as shown in Figure 3.5.5. The aluminum bars were subsequently mounted to the sliding stage. One bar accommodated three TECs; each bar was either designated for holding monomers or oxidants to reduce cross contamination.

The top of each individual TEC was bonded to a custom machined aluminum block with a cavity in the center and thermocouple hole in the side. During system operation, the cavity was filled with a low vapour pressure (10^{-10} Torr @ RT) Fomblin diffusion pump oil. The oil enveloped the vial offering more surface area for heating. Furthermore, bearing adequate thermal conductivity (~ 0.190 W K/m) and specific heat capacity (~ 1.3 kJ/(kg K)), it provided a facile low power method for uniform heating of the vial and its contents. At this point, each vial temperature could be independently controlled allowing both cooling during storage, to prevent unwanted vaporization, and heating at the appropriate moment.

Figure 3.5.5: Side View of Sliding Stage with Oil Bath Vial Heaters

Each TEC was individually powered by a KEPCO MST series 200 W digitally controlled power module. Instead of modulating power by changing the voltage output on each power supply channel at a quick rate, Pulse Width Modulation (PWM) circuits were employed. Figure 3.5.6 shows the corresponding schematic. An Arduino microcontroller provides a rectangular wave signal which depending on the input, times the ON and OFF switching for the waveform while maintaining a constant period to achieve the specified duty cycle. The Arduino is coupled to an optoisolator to prevent any electrical shorting to the power supply, thus protecting the microcontroller. When the PWM waveform is high, the optoisolator BJT is ON and draws current from the power supply channel. As current flows through the resistor, a voltage drop is generated between the gate and source of an enhancement mode power P-MOSFET. The PMOS, rated for 23 A of continuous current, then forms a channel and sources the current for the connected TEC.

A test circuit was fabricated first, trying various resistors for different LED and BJT current values to obtain optimal rise and fall times which best emulated the original PWM

Figure 3.5.6: PWM Circuit Schematic

waveform. Once satisfactory, a custom Printed Circuit Board (PCB) was laid out in Eagle freeware by another member of the group, Evan De Sousa, and sent out for fabrication. To accommodate the larger than normal current flow in the traces, thicker layers were used. Each board allowed for four separate PWM circuits. To control seven TECs, two PCBs were employed and sealed in the same enclosure. Figure 3.5.7a shows one populated board resting inside the enclosure. Since the PMOS were sourcing so much current continuously they required adequate heatsinking to ensure junction temperature did not exceed the maximum allowed value. Instead of putting discrete heatsinks on each PMOS, the pins were bent and the FETs, now horizontal, were pressed between a layer of Sil pad attached to an aluminum case and the board itself. Hence, in Figure 3.5.7a the PMOS are hidden below the board. For the optoisolators and resistor blocks, they were simply soldered into place free-standing. Cut-outs were machined into the aluminum case to fit bulkhead feedthrough connectors for conductors coming from the KEPCO MST power modules, Arduino microcontroller, and exterior pressure vessel - as can be seen in both images of Figure 3.5.7. Heavy duty TE connectivity couplings with thick gold-plated pins were selected to conduct the large currents flowing to and from the board. Conversely, since the Arduino was sourcing very little current for the optoisolators, a d-sub connector was suitable. Note that in Figure 3.5.7b, the connector going to the pressure vessel is on the other side of the enclosure.

Figure 3.5.7: PWM PCB for TEC Power Control

The duty cycle of the PWM waveform, and hence the percentage power supplied to the TEC, is set by a PID loop implemented in MATLAB. Similar to the initial control scheme detailed in section 3.5.2, MATLAB would read temperature values from the DAQ and compute the input error, storing past values for the PID algorithm. A TEC class was created and separate objects were instantiated for each TEC. The corresponding temperature values were then forwarded to the correct objects. Again, a USB-COM port was established to interface with the Arduino; however, interaction was greatly simplified as microcontroller did not have to synchronize with an AC signal. When fed a new temperature value, the TEC object would send a percentage to the Arduino which using a built-in PWM function would change the pulse length while handling the timing on its own. With multiple PWM channels and internal clocks, a single Arduino microcontroller handled all seven separate TECs.

3.5.4 Substrate Control

Temperature control of the substrate was vital for performing depositions and in-situ polymerization reactions in the oCVD system. The combination of a Peltier cooler and water block were employed to enable the raising and lowering of the substrate temperature at will. Regardless of the direction of heat flow across the Peltier cooler, the water block provides sufficient flow of water to maintain the temperature on the bottom side slightly

Figure 3.5.8: Water Block for Substrate Temperature Control [74]

below room temperature. A Qin Bo Electronics TEC1-12730 Peltier cooler was selected for its 62 mm x 62 mm size and maximum output power of 253 W. It was acquired with the intent to cover more than the area of the wafer and pump sufficient power to heat and cool the wafer by a $\Delta T = 70^\circ\text{C}$. The water block was connected to a closed chilled water loop operating at a nominal pressure of 90 psi, temperature of 14°C , and maximum flow rate of 18 gpm. The 3" square aluminum water block (WBA-3.0-0.85-AL-01), shown above in Figure 3.5.8 was purchased from Custom Thermoelectric and specified to have minimum and maximum flow rates of 0.5 gpm and 4.0 gpm respectively. To achieve the minimum thermal resistance of $0.011^\circ\text{C}/\text{W}$, the tubes flowing into the block had to be sized appropriately to accommodate the 4 gpm flow. The water discharge from a 100' long hose of varying pressure and nominal diameter was examined using the graph shown in Figure 3.5.9. Locating the intersection of the desired water discharge and the operating pressure, a hose with inside diameter of $3/8''$ - corresponding to the highlight curve - was deemed sufficient at 90 psi and lower. Thus, a $3/8''$ ID reinforced Tygon hose was selected to be used in the low vacuum environment to supply the water block.

The flow through the water block was metered using the combination of an Omega flow meter and stop valve. The allowable range was from 0-4 gpm. The plumbing stemming from the cooling loop was sized larger at $1/2''$. In operation, it was verified that a maximum flow of 4 gpm was obtained though a nominal glow of 3.5 gpm was set during

Figure 3.5.9: Graph of Volumetric Flow Rate of Water versus Water Pressure for a 100' Length of Hose (Modified from [75])

depositions. The control scheme for the substrate TEC is the same as that explained in Section 3.5.3; the DAQ provides temperature values to MATLAB which computes a duty cycle that is applied as a waveform to the PWM circuit. The same Arduino microcontroller and PCB board is used for all seven TECs - six for vial control and one for substrate control.

A diagram of the substrate temperature control assembly can be seen in Figure 3.5.10. To ensure good thermal contact between the water block and TEC, Sil pad was once again employed. In order to establish contact between the substrate and TEC, a mounting frame was designed. A rectangular plate and cylindrical spacer were machined with aluminum - rather than stainless steel - as a body material to improve thermal conductivity between the TEC and substrate. The cylindrical spacer is sandwiched between the KF flange and mounting plate and sized to accommodate the KF clamp as it envelops the flanges.

Figure 3.5.10: Diagram of Substrate Temperature Control Assembly

Thermal epoxy was used to bond the plate, spacer, and bottom flange together. To secure the mounting plate to the TEC, countersunk holes were machined into the plate in-line with those in the top face of the water block. Threading and tightening screws from the mounting plate to the water block, the TEC is compressed between them with Sil pad on either side. To monitor the substrate temperature, a small 2 mm hole was drilled in the side of the cylindrical spacer to allow for insertion of a thermocouple directly under the center of the wafer. Thermal compound was also injected into the hole to improve the thermal contact between the aluminum and thermocouple.

3.5.5 Control Station

The TECs were controlled via PID loops on an external PC loaded with MATLAB. Figure 3.5.11 shows a 19-inch rack with all control system components mounted within. At the bottom is a series of KEPCO MST digitally controlled power modules. They are loaded into a KEPCO RA-55 19-inch rack adapter with a MST 488-27 GPIB controller. From the control unit, a Prologix GPIB-USB adapter provides connection to a PC mounted immediately above. Atop the PC, are two panel-mounted instruments: the Terranova 906-A Convection Gauge controller and REX C-100 temperature controller. Above the panel are

the keyboard tray and mounted computer monitor. A custom user interface was designed in MATLAB to facilitate monitoring and control of pressure and temperature variables.

Figure 3.5.11: Systems Control Rack (Front)
19-inch Rack with PC, Power Modules, and PID Controllers Installed

Figure 3.5.12 shows the back side of the systems control rack. The metal box on the top left contains the custom PCB for controlling the TECs. It has three connector bundles: one going down to the back of the power supplies attached via shielded alligator clips, the second goes into the external vacuum chamber through the wall of the fumehood covered with a corrugated PVC sheathing, the last goes to the Arduino for the PWM waveforms. The Arduino in a translucent blue case, is mounted to the left sidewall midway up. Beside the PCB box are some fuseholders, and a large heatsink. The rope heater SSR is located on the other side of the panel, screwed into the heatsink and bridged by thermal paste.

High voltage and current terminal connections on the other side of the panel are safely enclosed within a locked hinged box in compliance with electrical code. Along with the rack-mounted power bar for cable management, the wire bundles in PVC sheathing have been given lots of slack which allows the wheeled rack to be easily moved if required.

Figure 3.5.12: Systems Control Rack (Back)
19-inch Rack with PC, Power Modules, and PID Controllers Installed

3.6 Completed Apparatus

Figure 3.6.1 shows the completed system mounted into the custom fumehood. The completed water, nitrogen, vacuum, power, and thermocouple connections are all visible. The lid assembly can be seen resting on the slide rails in Figure 3.6.1a and resting on the rim of the exterior pressure vessel in Figure 3.6.1b - with the front slide rail fully removed for visibility.

(a) Open State - Raised Lid with Lowered Stage

(b) Closed State - Lowered Lid with Raised Stage

Figure 3.6.1: Completed Vacuum Chamber Mounted in Fumehood

After completion, the performance of each individual system was evaluated. Vacuum tests were executed throughout the apparatus as an insufficient vacuum would render the system inoperative and require a complete overhaul. For the inner vacuum chamber, the base pressure and leak rate were tested with and without the application of the outer vacuum. The inner vacuum alone reached a base pressure of ~ 100 mTorr after pumping for 30 minutes at an elevated temperature of 60°C with a nitrogen backfill to remove water vapour. Upon pump isolation, the inner chamber rose to ~ 5 Torr in two minutes. This leak rate is relatively high and suggests multiple significant leak points. During assembly the inner chamber was tested repeatedly. Positive pressure leak tests were performed by pressurizing the chamber with nitrogen and applying a soapy solution to the joints. If leaks were present the escaping gas would form bubbles in the solution. Interestingly, no bubble formation was observed. Negative pressure tests were also run. Under vacuum isopropyl alcohol was applied to joints one at a time. The IPA would form a temporary seal lowering the leak rate for several seconds. This would result in a noticeable drop in pressure and was confirmed a few times when joints were loose. However, after completion no pressure drops were observed. This does not suggest that there are no leak points but simply that they are not readily accessible for these qualitative visual tests.

The outer vacuum could achieve a base pressure of 10 Torr, as read by the Convec-tron gauge, after pumping down for thirty minutes with a single nitrogen purge. The leak rate of the outer vacuum was not investigated since the outer pump would never be isolated.

For one trial with both pumps active, the base pressure of the inner chamber dropped to just under 50 mTorr after being baked out. Maintaining the chamber at 80°C , upon isolation the inner chamber pressure rose at a slower rate with the outer chamber buffering - Figure 3.6.2 shows the change over time. After ten minutes the pressure rose to slightly below 3 Torr. Note that for an actual deposition run the pressure would jump much faster due to saturation of the environment with the monomer. In several minutes it would approach

an asymptote as the deposition rate would approximately equal the sum of the vaporization and leak rates.

Figure 3.6.2: Inner Chamber Pressure Rise Upon Isolation (Buffered By Outer Vacuum)

For the inner chamber wall heating system, due to the change in thermal mass along the line, varying temperatures and warm up times were recorded. With a heavy valve body at 80 °C the lighter pipes would register 140 °C at steady state. At maximum power, the rope heater could easily raise the pipes to 400 °C and the valve bodies to 300 °C. However, these limits were never tested as the seals for the lid feedthroughs and valve stems break down at 200 °C - though there would be a sizable thermal gradient between the valve bodies and stems due to the massive heatsink of the lid and flowing air of the fumehood.

For the vial heating systems, a temperature of 220 °C was achieved according to the thermocouples. Unfortunately, this limit on temperature still prevents use of some well known oxidants which require temperatures exceeding 300 °C for sublimation. The temperature range for the substrate followed similarly. However, unlike the precursor vial TECs, whose cold side temperatures could also rise through Joule heating, the substrate TEC was kept at a constant temperature by the water block. This led to a lower maximum temperature of 120 °C. Conversely, for cooling mode the TEC fared worse. With such a

large thermal mass attached even with the water block constantly removing waste heat the substrate only registered a temperature minimum of -10°C at full power.

The final substrate holder could accommodate a 2" diameter wafer. It was desired that larger wafers also fit wholly inside without having to cleave them into smaller pieces. However, since the structure was made from a modified KF flange, it was limited by the maximum size of the flange in the series. It would have been possible to increase the size while retaining the design, but that would require custom machined KF flange parts including a large centering ring and specially sized o-ring. Again, minimum volume was desired so a smaller flange was opted for.

The final volume of the inner chamber main line - excluding the segments isolated by needles valves - was estimated at roughly 50 cm^3 . The small inner diameter of the tubes at 0.186" ($\sim 0.47\text{ cm}$) greatly reduces the total volume. Combining the $\sim 20\text{ cm}^3$ estimated as the volume of the pipes with that of the KF flange reactor chamber, also 20 cm^3 , and another 10 cm^3 for the internal volume of the additional pipe fittings, the final total is obtained. The goal of minimal inner vacuum chamber volume was achieved, though improvements can be made. This low volume caused the saturation pressure to be reached quickly and without much monomer mass. The combination of a high saturation pressure and low local vapour pressure further promoted precursor adsorption onto the substrate.

Table 3.6.1 summarizes the results of the sub-system tests.

Table 3.6.1: Specifications of Final Apparatus

Category	Specification	Desired	Obtained	Comments
Pressure (mTorr)	Inner Vacuum Base Pressure Combo	1	20	Leak limited.
	Outer Vacuum Base Pressure	5000	8000	Large volume.
	Pressure 10min after pump isolation	1	2300	Joint leaks; 2300mTorr is tolerable.
Temperature ($^{\circ}\text{C}$)	Maximum Inner Vacuum Temperature	400	200	Limited by thermal breakdown of seals.
	Maximum Source Temperature	400	220	Waste heat proves useful.
	Maximum Substrate Temperature	150	120	Limited by water cooling.
	Minimum Substrate Temperature	0	-10	Limited by phases changes of matter.
Space	Maximum Wafer Diameter (in)	4	2	Limited by maximum size of KF flange.
	Inner Vacuum Chamber Volume (cm^3)	0	50	Successfully small.
	Number of Monomer Sources	3	3	Achieved.
	Number of Oxidant Sources	3	3	Adds possible leak locations.
Miscellaneous	Corrosion Resistance	High	Medium	SS not impervious to strong oxidants.
	Difficulty of Operation	Low	Low	Requires physical strength.

Chapter 4

Experimental

4.1 Foreword

The procedures outlined below detail the processing steps for the synthesis of ISP and VPP PEDOT. Samples were processed side by side on similar wafers using a shared supply of precursors to offer the closest possible comparison between the solution and VPP techniques. Although the goal of this project was to engineer an environment for performing oCVD, the success of VPP was to be first observed as proof of concept or milestone. The oCVD oxidants to be vaporized inside the chamber are strongly corrosive. Without a proper protective coating, a small risk exists for pitting corrosion attacks eventually leading to through holes in the reactor - posing a problem for vacuum leaks and safety. As such, VPP - which did not require the exposure of the vacuum chamber to the oxidant vapour - was first performed with the intent to eventually execute oCVD. This allowed for test runs to be executed and small adjustments to be made without the risk of corrosion.

4.2 Pre-conditioning

Before spin coating the oxidant, substrates were pre-conditioned to remove organic matter and promote adhesion of the PEDOT films. To achieve uniform films, it was imperative

to fully clean the substrate of any aberrations in surface texture, keeping roughness to a minimum. Glass or oxidized silicon substrates first underwent a glassware clean - also known as Step 1 in an RCA (Radio Corporation of America) clean. This consisted of immersing substrates for 10 minutes in a solution of 5 parts DI water to 1 part ammonium hydroxide to 1 part hydrogen peroxide heated to a temperature of 80 °C. Once removed they were thoroughly rinsed in DI water until pH neutral. Even if particles are insoluble in any of the solvents, it is believed that the presence of the alkaline solution induces a negative zeta potential repelling them from the surface of the wafer [76].

Afterwards, the substrates were inserted into a Plasma-Preen-II-862 from Plasmatic Systems Inc. shown in Figure 4.2.1. Substrates were placed on ceramic tiles inside of the bell jar. The chamber was pumped down to a base pressure of 0.03 Torr then a 5 sccm flow of oxygen was introduced and a plasma was generated inside. The plasma was sustained for 5 minutes to raze the surface of the substrates and eliminate all organic matter. Afterwards, the oxygen flow was ceased, base pressure was recovered and the bell jar was vented with nitrogen. The plasma preen also had the effect of functionalizing the surface to have hydrophilic properties. This was ideal for the PEDOT:PSS dispersions in water that were later applied.

Figure 4.2.1: Plasma-Preen-II-862 Oxygen Plasma Treatment Apparatus

4.3 Spin Coating

After pre-conditioning the glass or silicon substrates, film-forming solutions were distributed over the surface into thin semi-uniform films via spin coating. A WS-400-6NPP spinner from Laurell Technologies was employed for this task. Figure 4.3.1 shows the apparatus in its open and closed states. The spinner was located inside of a fumehood to shield users from solvent exposure during evaporation. The spin speed, acceleration, and duration could all be set using the control panel on the right. Multi-stage spin processes were also possible. The minimum substrate size that could be accommodated on the chuck was that of a round 2-inch wafer; any smaller and the vacuum channels would not be fully covered disabling spin operation.

(a) View with Lid Closed

(b) View with Lid Open Showing Spin Chuck

Figure 4.3.1: WS-400-6NPP Spin Coating Apparatus

4.3.1 PEDOT:PSS Adhesion Layer

To further promote adhesion of the final films on the glass or silicon substrates, an adhesion layer of PEDOT:PSS was applied. Commercially available under the name Baytron P (now Clevios), it is a 1.3% by weight dispersion in water with a 1:6 PEDOT:PSS ratio. With the PSS co-polymer backbone, the PEDOT molecules exhibit increased polarity. As a result

the PEDOT:PSS sheets easily and adheres well to hydrophilic surfaces such as an oxygen plasma treated oxide. However, the PSS also acts as a counter-ion doping the PEDOT and generating holes. For this formulation, the associated conductivity is typically between 1-2 S/cm. To reduce the contribution of this adhesion layer to the overall conductivity, the solution was sonicated in an ultrasonic bath for 5 minutes. It was believed that the energy from the bath was transferred into the molecules, breaking the polymer bonds and shortening the average chain length.

The solution was puddled over the entire stationary wafer and spun for 1 minute at 4000 rpm with an initial acceleration of 900 rpm/s. Relative humidity in the range of 35-45% proved favourable for sheeting and drying effects. Subsequently, the films were baked on a hotplate for 15 minutes at 150 °C to ensure evaporation of the water solvent. This was followed by a minimum drying time of 15 minutes in air before any further processing took place.

4.3.2 In-situ Polymerized (ISP) PEDOT

Clevios outlined the standard procedure for ISP of EDOT [77]. For both the ISP and VPP processes the same source of oxidant and monomer were used: CB40 V2 from Baytron, a 40 wt% solution of Iron(III) p-toluene sulfonate (or Ferric Tosylate) in n-butanol. The monomer, sold as Baytron M, is EDOT with trace amounts of waters below 0.5%

A newly coated wafer was cleaned of dust with a nitrogen gas gun then mounted to the chuck. 0.1 g of Imidazole (a weak base), 5 g of CB40, and 0.225 g of Baytron M were mixed together in that exact order before each spin session. Since polymerization begins the instant the EDOT is added to the mixture, the allowable time for processing is short - less than 15 minutes. Regardless, the solution was agitated for two minutes before processing to promote further mixing and polymerization increasing the viscosity. The solution was puddled over the entire wafer, in a stationary state, with a 0.45 µm filtered syringe. Care was taken to avoid the generation of bubbles on the wafer as they could interfere with the

dispersion. The wafer was spun at 3000 rpm for one minute with an initial acceleration of 450 rpm/s.

The wafer was transferred to a hotplate and baked for 5 minutes at 50 °C. As the polymerization progressed, the film became increasingly thick taking on a dark blue hue. This was followed by an hour of drying in air and post-processing steps detailed later.

4.3.3 VPP Oxidant Solution

The oxidant used for VPP was also CB40. It is intended for use in ISP but has a well-established history of use in VPP [57, 78, 79]. To the CB40, a PEG-PPG-PEG trimer was added to create a 15% wt mixture. Once the substrate was centered on the chuck and vacuum was applied, the oxidant solution was generously puddled over the entire surface using an eyedropper. The lid was closed and a 1900 rpm spin was initiated for 30 s. Higher spin speeds would lead to thinner films but often had small voids in the dispersion. The lower spin speeds seemed to reduce this effect. Additionally, thicker films facilitated measurement of sheet resistance and other parameters by being more robust and having higher overall conduction. The use of filtered syringes for application was not investigated at the time.

Immediately after spin coating the CB40, the substrate was moved to a hotplate preheated to 70 °C and left to dry for 2 min. Figure 4.3.2 shows the Cole Parmer 04644 Digital Hot Plate/Stirrer with a dried CB40 film. In the image, a 3 '' glass substrate was coated and subsequently cleaved into smaller pieces - for insertion into the reactor. Additionally, an off-center low volume dispersion was executed with this sample to investigate selectivity of the VPP reaction. The solution started with a translucent yellow-brown hue and shifted to an opaque yellow as the evaporation of the butanol solvent progressed. What remained was the iron(III)tosylate and PEG complex. To minimize the crystallization of the oxidant film, the sample was inserted into the oCVD apparatus and pumped down shortly after.

Figure 4.3.2: Hotplate with Dried CB40 Film

4.4 Vapour Phase Polymerization (VPP)

4.4.1 Estimation of Required EDOT Volume and Vaporization Temperature

For the volume of EDOT needed assuming 100% deposition, an arbitrary film thickness of $1\text{ }\mu\text{m}$ was chosen to react with the already deposited several microns of oxidant. This yielded a volume of approximately $2\text{ }\mu\text{L}$.

$$V_{EDOT} = A_{wafer} * t_{Film} = \pi r_{wafer}^2 t_{film} = \pi (2.54\text{cm})^2 (1\text{um}) = 2.026 * 10^{-3} \text{cm}^3 = 2.026 \text{uL}$$

Considering the difficulty of measuring such a minuscule volume (meniscus from surface tension), a larger volume was selected. Scaling by a factor of 10 gave a volume of $20\text{ }\mu\text{L}$, little more than a droplet, though it ensured an ample supply of EDOT for the reaction. It was important to maintain the same precursor volume for reproducibility between deposition runs and their resulting films. Therefore, an Eppendorf syringe system was employed to meter out this precise amount. It allowed for volumes down to $10\text{ }\mu\text{L}$ to be dispensed accurately.

To select the correct vaporization temperature given the environmental conditions, a vapour pressure curve following the Antoine Equation (Equation C.0.2) was fitted to three data points taken from literature [43, 80]. Figure 4.4.1 is the result of that fit. The original experimental data points are represented by the red circles. Initially, a vaporization temperature of 60 °C was chosen; corresponding to a vapour pressure of 2.11 Torr. Assuming an inner chamber pressure of 1 Torr or less, this temperature would result in the boiling of the EDOT quickly saturating the chamber for a uniform reaction. Later, the substrate temperature was increased to 50 °C to facilitate the polymerization. While this lowered the deposition rate, it improved chain yield and thus overall conductivity. To offset the decrease in the thermal gradient, the source and chamber temperature were raised to 80 °C. This corresponded to a vapour pressure of 6 Torr which was still below the base pressure of the outer chamber.

Figure 4.4.1: Fitted Vapour Pressure Curve of EDOT

4.4.2 VPP Procedure

When the system is in an idle state at atmospheric pressure, the outer vacuum chamber is open with the inner chamber lid structure resting on two cross struts. All of the valves, including needle and ball valves on the top as well as nitrogen and water line valves, are firmly closed. The clamp of the KF flange is off and the stage is in its lowered position. This gives roughly 2" of clearance for the loading and unloading of vials, along with the extraction or insertion of the wafer. The following outlines the standard physical steps necessary for system setup prior to initial pump-down. First, a vial is filled with EDOT, capped and transported to the system. Upon uncapping, it is inserted and sealed in an Ultra-Torr fitting. The corresponding aluminum bath block is filled with thermally conductive low vapour pressure oil. Next, the wafer is inserted into the milled depression of the bottom KF flange of the reactor chamber. Afterwards, the stage locks are removed and the stage is raised - guided by the tube rails - to make contact with the top KF flange. With the locks re-engaged, the KF clamp is applied and tightened. Lastly, the lid is lifted up and the two cross struts are moved out of the way. The lid assembly is slowly lowered into the exterior pressure vessel, resting it centered on the rim.

The pump-down and deposition procedure is as follows:

1. Inner vacuum chamber is pumped down to base pressure (100 mTorr).
2. Nitrogen is back-filled into the inner chamber up to 0.5 atm (-15 inHg).
3. Inner chamber is pumped back down.
4. Outer vacuum chamber is pumped down to base pressure (~ 10 Torr).
5. Nitrogen is back-filled into the outer chamber up to 0.5 atm.
6. Outer chamber is pumped back down.
7. Valve corresponding to the vial full of EDOT is opened for 5 s.

8. Vacuum is maintained and a minute is given before the next step.
9. Rope heater is turned on and set to 80 °C.
10. Water flow is established for the water block.
11. Once at temperature, steps 2 and 3 are repeated two more times.
12. The substrate TEC for the substrate is set to 50 °C.
13. Five minutes are allowed for substrate to reach steady-state temperature.
14. The EDOT vial TEC is set to 80 °C for 10 min.
15. Two minutes are allowed for the the vial to heat up.
16. EDOT vial valve is opened.
17. Inner vacuum valve is immediately shut.
18. Deposition ensues.
19. TEC shuts off after specified time has elapsed.
20. EDOT vial valve is closed.
21. Substrate TEC is set to 10 °C.
22. Inner chamber is pumped down to base pressure.
23. Pressure release for EDOT vial to vacuum is performed.
24. Step 22 is repeated.
25. Continuous flow of nitrogen is passed through the inner chamber for 30 s.
26. Steps 1-3 are repeated.
27. Rope heater is turned off.

28. After 10 min, the inner and outer chambers are vented together.
29. Pressure release on EDOT vial to atmosphere is performed.
30. Lid is lifted and secured.
31. KF clamp is removed, stage is lowered, and sample is extracted.

Elaborating on the above, a large portion of the procedure concerns the conditioning of the vacuum chamber. Several cycles of pumping down and nitrogen back-filling along with the ‘baking’ of the chamber - using the rope heater - are performed to reduce the the oxygen and water vapour concentrations within. Unfortunately, water vapour tends to outgas undesirably under vacuum, increasing the internal pressure. This necessitates the strict protocols for chamber conditioning. ‘Baking’ of the chamber refers to heating the walls and maintaining them at elevated temperatures to accelerate the desorption of water [38].

During the cycling period, a pressure release is performed on the EDOT vial by opening the vial for a very short period of time. Since the vial is inserted at ambient pressure, the excess air must be removed before deposition. Given the length of the release and temperature of the EDOT, the composition of gas evacuated from the vial is mostly air. Further pumping and pressure cycling is performed to extract the additional newly introduced oxygen and water vapour - along with any EDOT that may have vaporized.

When the chamber is finally conditioned, regulation of the substrate temperature is initiated. Once at temperature, the deposition process is activated and the vial TEC begins to heat. With a much smaller thermal load, the aluminum block and pool of oil heat much more quickly reaching steady state in 30 s. Two full minutes are allowed for the EDOT to partially vaporize before the vial valve is opened. The inner vacuum is immediately isolated and actual deposition proceeds. At first, the pressure inside the chamber rises quickly with the initial rush of vapour, but as the system nears equilibrium the pressure rise becomes more gradual. The rivalling processes of the vaporization, ongoing diffusion, condensation,

and leaking of nitrogen control the pressure. With the rate of surface reaction increasing, condensing EDOT out of the gas mixture, the pressure asymptotically approaches 2-5 Torr.

Figure 4.4.2 plots the inner chamber pressure against deposition time for a standard run at 80 °C. Note that the vial valve was opened after 120 s allowing for the source to reach and stabilize at temperature. On the graph, this corresponds to a sudden jump in pressure to 600 mTorr followed by a slow rise. After completion of the deposition, the EDOT source vial was isolated and the chamber pressure fell back down to ~1600 mTorr before being pumped down again. The monomer was still vaporizing and condensing at the end of the run; but once the supply was cut, the condensation became dominant and lowered the chamber pressure.

Figure 4.4.2: Graph of Inner Chamber Pressure vs Time for a VPP Deposition

After the deposition time has elapsed, the vial TEC shuts off and the EDOT valve is isolated once again. The polarity of the substrate TEC is reversed, enabling cooling of the wafer. As the TEC pumps heat from the substrate into the water block, the desorption of the EDOT from the wafer surface is reduced. At the same time, the inner chamber is pumped out to remove the EDOT. Nitrogen is continuously passed through to scrub the walls of the chamber for any condensed EDOT. With the deposition complete, the vent

phase is initiated. Another pressure cycle is performed and the rope-heater is shut off. Subsequently, a simultaneous venting of inner and outer chamber is performed. A pressure release of the EDOT vial must be completed so the vial itself can be removed and reloaded for the next deposition. Finally, the lid is lifted up from the outer chamber and rested on the struts for extraction of the wafer. Lastly, the KF flanges are cleaned with acetone.

Figure 4.4.3 shows the user interface for the control program coded in MATLAB which regulates all the heaters and tracks pressure. Extensive log files are automatically generated and saved so separate runs can be compared in terms of dependent variables.

Figure 4.4.3: Control Program Screenshot

4.5 Post-conditioning

After the polymerization reaction the extra ferric salts, acidic byproducts, and unreacted monomer needed to be removed from the sample. Several papers call for a rigorous rinse in DI water; however, an investigation into the effects of the post-process rinse by Atanasov et al. [46] provides evidence that the DI water de-dopes the sample removing anions weakly held in place.

Initially, post-process rinses were carried out in a beaker of DI water for a three minute period, immersing the sample and agitating. Afterwards, a gentle spray from a DI water gun was applied for ten seconds with the angle of incidence being extremely acute. Subsequently, the samples were dried with a nitrogen gun and left in air for 60 min to further dry. The conductivity of these films was indeed lower than expected and could possibly be attributed to the DI rinse.

In the midst of process runs, the use of DI water as a solvent was ceased. In its stead, methanol was employed. However, almost immediately it was observed that methanol would affect the morphology and adhesion of PEDOT films. They would begin to wash off, folding in and on top of themselves. Figure 4.5.1 shows a picture of a film post-rinse.

Figure 4.5.1: ISP PEDOT Film After Gentle Methanol Rinse

The above result was consistent between many samples and proved disastrous in attempts to obtain fully coated surfaces of high conductivity uniform films. At this point, the effects of abstaining from rinsing were investigated. A single sample of ISP PEDOT was rinsed with 15 s of methanol very gently on one-half of the substrate. Figure 4.5.2 shows the result after being left for one day to dry. The top half, being the side that was rinsed, displays signs of poor adhesion once again with the film substantially curling up in the top right corner. More interestingly, there is a distinct difference in colour between the two halves. After rinsing, the top half became a much clearer and a deeper blue whilst the bottom half turned to a pale green - suggesting that the acidic byproducts may be affecting the polymer structure. Fabretto et al. [59] have indeed reported that poor quality PEDOT films with dioxane ring cleavage or those with short chains take on a greenish tinge represented by an optical peak around 350 nm. Furthermore, the bottom half shows signs of crystallization; this is most likely due to the oxidant taking on water over time. Overall, the film quality degrades significantly in a few days if the film is not rinsed.

Figure 4.5.2: ISP PEDOT Film Rinsed on Top Half Only

With the need for a post-rinse verified, other adhesion layers were explored. Note that prior to the application of adhesion layers, oxygen plasma treatments were always performed. First, hexamethyldisilazane (HMDS) was explored. HMDS is an organosilane commonly used to promote adhesion of photoresist for lithography steps [81]. It was

vapour deposited to create a film only several nanometres thick. The substrates were loaded into a glass boat and placed inside a conditioned chamber at a temperature of 100 °C. The chamber transitioned through several pump and vent cycles to reduce the oxygen and hydrogen content as well as overall pressure. Once satisfactory, a small amount of HMDS was released into the chamber, preferentially condensing onto the less warm substrate. Interestingly, it has the effect of reversing the functionalization of the plasma-preened surface from hydrophilic to hydrophobic. The HMDS proved to be useless. The solutions still sheeted well on top but lift-off was observed almost immediately during methanol rinse.

Subsequently, PEDOT:PSS adhesion layers were tested. This was not the first choice because it could contribute to film conductivity which would inevitably skew results. However, upon rinsing no visible cracking or lift-off was observed. With the new PEDOT:PSS adhesion layer, a standard of post-rinsing was developed. A 30 s second continuous stream from a methanol squeeze bottle was applied to PEDOT samples. The waste methanol solution visibly changed colour from clear to light yellow indicating the successful removal of ferric salts. This rinsing method was chosen over full immersion so surplus precursors would not migrate back into the PEDOT film.

4.6 Metallization

Surface roughness and softness posed a problem when trying to extract conductivity using the standard four point probe setup. To circumvent this issue, metal contacts were deposited through a shadow mask using an Angstrom Engineering Covap II Thermal Deposition System. Figure 4.6.1 shows a quadrant of the shadow mask designed in L-Edit. An Ottawa-based company, PELA Technologies Incorporated, utilized a 0.5 mil spot size laser cutter to carve out holes in a 3 mil thick stainless steel sheet. The sheet was 2" x 2" to accommodate the contacts for a full 2" round wafer. It should be noted that Figure 4.6.1 is the superposition of two separate masks. The light green patterns represent the mask

for film deposition. While this mask was not employed in this thesis, vapour deposition through the mask in the form of oCVD or ALD might later be attempted. The light green regions outline the structures generated for Hall mobility measurements including the standard cloverleaf pattern. Capacitance squares are also present at the top for extracting work function values.

Figure 4.6.1: Quadrant of Superposed Shadow Masks for Metal Contact Deposition (White - Metal, Dark Green - Wafer) [Scale in mil]

The metal contacts are displayed in white. Positioned at the corners of the Hall structures, they also serve as contacts for square and collinear four point probing. There are three different spacings between similarly sized contacts: 100 mil, 80 mil, and 50 mil. This is to ensure that size and geometry of the structures do not play a role in measurement readings. The structures do however, adhere to certain layout rules. For Hall structures, the thickness of the film and diameter of the contacts must be much less than the spacing [82]. Similarly, for collinear four point probe, the contact spacing must be at least 2.5x greater than the film thickness and structures must be 4x the spacing from the edge of the film to use the geometry approximation.

Other structures include: alignment crosses in each quadrant of the two superposed masks; and in the center of the circle spanning horizontally, a series of large metal contacts for extracting mobility via Charge Extraction by Linearly Increasing Voltage (CELIV) measurements. As current density can be very small, large area CELIV structures were allocated to obtain measurable values above the noise floor. Only the collinear four point probe structures were used for this thesis. Measurements utilizing the other structures are expected in the future.

Figure 4.6.2 shows the Covap inside of a nitrogen glovebox. The Covap has an inverted rotating substrate, substrate shields, a turbomolecular pump port, and several resistively heated crucibles and boats. The wafer and shadow mask were mounted to a ferromagnetic plates using rare earth magnets. Magnet placement was important as any flex or lifting of the mask would result in blurred contacts. A small chunk of elemental aluminum was placed in an S38 style boat. The chamber was pumped down below 10^{-6} Torr before deposition, at which point the power to the aluminum boat was slowly ramped. At around 30% power a non-zero deposition rate was measured by the QCM sensor. The rate was controlled at $5 \text{ \AA/s}$ for a total thickness of $1000 \text{ \AA}$. Once settled, the substrate shields would open, measured thickness would be zeroed, and deposition would proceed. After the

(a) Closed

(b) Open - Resistively Heated Boats

(c) Open - Mounted Sample

Figure 4.6.2: Covap Thermal Deposition System

shields closed, the power would ramp down and the system would be allowed to cool for 10 min before venting to ambient.

Chapter 5

Testing and Results

The following chapter contains the results of characterization tests performed on the VPP and ISP PEDOT films. For application as a transparent conductor, both conductivity and transparency are important attributes. In this work, UV-vis spectroscopy was used to evaluate the transmissivity of various films across the visible spectra. Similarly, four point probe measurements were taken to assess film conductivity. In both measurement techniques, film thickness is a quantity of the utmost importance. Calculations for the above characteristics depend on thickness and are extremely sensitive to small percentage changes. As such multiple methods were employed for determining film thickness including profilometry and AFM. Lastly, FTIR allowed for the qualitative investigation of the presence of conjugation, functional groups, and excess leftover oxidant in the resultant films. Appendix B provides further information on some of the characterization techniques including standard experimental setup, the theory involved in how measurements are made and evaluated, and what information can be ascertained from the results.

5.1 Sample Pictures

Figure 5.1.1a shows a glass octagon which was spin-coated with the CB40 solution at a higher speed resulting in a thin patchy film. Figure 5.1.1b shows the same sample after

VPP. Figure 5.1.1c is of a more recent, thicker, uniform VPP sample that has been aged for two weeks, cleaved, metallized, and tested extensively.

Figure 5.1.1: CB40 on Glass Octagon Before and After VPP

Figure 5.1.2a shows a PEDOT:PSS coated glass. Note that the spin speed required to make it noticeable on glass was 1000 rpm and lower. Figure 5.1.2b is an image of ISP PEDOT atop the adhesion layer on a 3"x3" glass substrate. The colour is quite uniform throughout the entire substrate. The thread at the bottom right is a small piece of rolled-up PEDOT on the back side of the glass, likely originating from the large scratch on the left.

Figure 5.1.2: PEDOT on Glass

5.2 Profilometer Measurements

Thickness and surface roughness measurements were taken with Tencor P1 and Dektak IIA Stylus Profilometers. Each profilometer applies a light downwards force on a $12.5\text{ }\mu\text{m}$ radius diamond-tipped stylus, pressing it into contact with the sample. The stylus is dragged very slowly across a short range (max. 30 mm) moving up and down reacting to the topology of the sample. For the Dektak, shown in Figure 5.2.1 the sample is placed on the stage and first levelled using coarse control. After which a scan of at least $1\text{ }\mu\text{m}$ is taken of the sample and the software auto-level is implemented along that range. A video camera allows for real-time viewing of the stylus on the sample; the coordinate location of where the stylus encounters a step is marked and a cursor is placed beforehand for auto-levelling. As no HP-IB printer was available, profiles were saved by taking individual photographs.

Figure 5.2.1: Dektak IIA Profilometer

Figure 5.2.2 is a sample screen from the Dektak after measuring the thickness of a preliminary PEDOT sample on a glass slide. The distribution of the spin coated layer is quite poor resulting in spotty coverage and extremely rough areas. The average height of the area next to the step is consistently higher than the area further away from the step suggesting beading near the film edge. The average thickness of this flat region is taken

as the value for a small area surrounding that particular spot. For this screen the indicated thickness is near $t_{ave} \cong 140000 \text{ \AA} = 14 \mu\text{m}$.

Figure 5.2.2: Sample Dektak Profile

To check the accuracy of the Dektak, profiles of the silver contacts of a known thickness were taken. Figure 5.2.3a shows a screen capture of the video camera feed. From the image and Figure 5.2.3b four distinct regions can be discerned; the white material is a silver contact, gray is glass, and the dark material is VPP PEDOT. The stylus started on bare glass, scanned over one leg of a silver cross contact at a $\sim 20^\circ$ angle, dropped back onto glass, and finally stepped up onto a very thick VPP PEDOT film - indicated by the vertical line near 2500 μm on the x-axis.

The profile of Figure 5.2.3b also shows several different slopes for the deposited silver contact; having a sharp rise then a gradual climb to the middle where it plateaus. It is interesting to note how long each of the slopes are for the contact. Considering the fact that this scan was taken at a non-orthogonal angle to the contact, all distances will be stretched to some extent. The first steep slope spans slightly under 200 μm while the second flatter slope is closer to 300 μm . Taken in scale, the edges of the contact in Figure 5.2.3b are not very well defined. This may be due to space between the mask and film allowing

Figure 5.2.3: Dektak Profile of a 2000 Å Thick Silver Contact

diffraction of incoming metal particles. This contact height should be roughly 2000 Å on average which instils doubt when the plateau height of 3000 Å is extracted from the profile.

Note that an oddity in the Dektak profiles began to arise. Including Figure 5.2.3b, every profile from this point forward would display the same behaviour. During the first hundred microns of a scan, even if on a completely flat surface, the profilometer would register a curve up to the actual height. Henceforth, the beginning of all measured profiles was disregarded.

Since the PEDOT film thickness measurements made no distinction between PEDOT and the PEDOT:PSS adhesion layer, it was absolutely necessary to acquire thickness estimates for the adhesion layer beforehand. However, this proved difficult since the adhesion layer was so soft and thin that the profilometer would often scrape some or all of the PEDOT from the substrate surface. To circumvent this problem, hard metal contacts were deposited with the Covap on top of PEDOT:PSS. The cross structures were then scratched down to the substrate and cleaned thoroughly with a nitrogen gun. The Tencor P1 profilometer was used to measure the step down into this scratch. The metal thickness was measured from a bare silicon witness wafer that was in the same Covap run near the cross. Therefore the PEDOT:PSS thickness could be inferred with suitable accuracy. Figure 5.2.4 displays the profiles for the two scans.

(a) Profile of Scratched Metal Contact on Witness Wafer

(b) Profile of Scratched Metal Contact on PEDOT:PSS Covered Wafer

Figure 5.2.4: Tencor P1 Measurements to Estimate PEDOT:PSS Adhesion Layer Thickness

Figure 5.2.4a shows the witness wafer with the height of the scratch in the metal as 1111 Å. With the PEDOT:PSS underneath the metal, the scratch height in Figure 5.2.4b reads as 1601 Å. Therefore the PEDOT:PSS adhesion layer thickness is approximately $490 \text{ Å} = 49 \text{ nm}$. This is a relatively thick adhesion layer given that a monolayer of HMDS is typically applied for the promotion of photoresist adhesion [81]. However, it is difficult to achieve thinner layers as increasingly high spin speeds yield diminishing returns in terms of thickness reduction. Furthermore, higher spin speeds would result in streaking effects and other non-uniformities. Given the conductivity and uniformity of this layer, the thickness was acceptable.

Figure 5.2.5a shows a large scratch in the ISP PEDOT sample, G5. The corresponding Dektak profile is presented in Figure 5.2.5b. The scan swept from the left side to right side of the scratch; starting on PEDOT, stepping down onto bare glass, and ending on the PEDOT film. Again, the first several hundred microns in the profile are ignored. The profile, imperfectly levelled, shows a somewhat rough plateau on PEDOT dropping down to glass then back up to PEDOT. The average roughness computed by the Dektak was 85 Å. This measurement was taken from the first plateau between the points designated by red lines and labelled ‘1’ after re-levelling. The height of the right step is approximately

240 nm while the left step height is 210 nm. Taking the difference in the averages of the left plateau and the glass yields ~250 nm.

Figure 5.2.5: Dektak Profile of ISP PEDOT (G5)

Figure 5.2.6: Dektak Profile of VPP PEDOT (OCT1)

A similar set of measurements was performed for the VPP sample, OCT1, shown in Figure 5.2.6a. Figure 5.2.6b displays the corresponding Dektak scan taken from the VPP

PEDOT film onto bare glass at the edge. The two cursors placed slightly back from the transition indicate a film thickness of 467.3 nm whilst the difference in plateau averages yields 435.0 nm. The average roughness in range 1 was reported as 62 Å.

To obtain an estimate of the thickness of the initial oxidant layer in VPP, a piece of OCT1 was cleaved off prior to the VPP reaction. Half the area of this sample was subsequently swabbed clean with DI water, acetone, IPA, and again DI water. The result can be seen in Figure 5.2.7a. The edge of the remaining CB40 was definitely compromised as is evident in the discolouration and massive peak in the profile of Figure 5.2.7b. Accordingly, the average height was taken further back from this edge yielding 2.74 µm. If the background of the profile is closely examined, the surface texture of the film can be seen. Periodic lines rising diagonally to the left can be perceived. These lines are the streaks left behind after spin coating which are sometimes visible to the naked eye. The ripples in section 1 of the profile show the stylus moving through the crests and troughs between streaks. Interestingly, this phenomenon cannot be seen in the profile of the final reacted and rinsed PEDOT film, Figure 5.2.6b.

Figure 5.2.7: Dektak Profile of Annealed Oxidant (OCT1)

The Dektak scan of the oxidant reveals an average thickness of 2734.8 nm and roughness of 334.1 nm. Given the thickness of the VPP PEDOT, it is clear that only a small portion of the oxidant reacts with the EDOT monomer in the given deposition time. Significant volume loss occurs during post-rinse resulting in the much lower VPP PEDOT film thickness for the OCT1 sample.

Table 5.2.1 summarizes the measurements presented in this section.

Table 5.2.1: Summary of Profilometer Measurements

Film	Thickness (nm)	Roughness (nm)
PEDOT:PSS	49	5.3
ISP PEDOT	210-250	8.5
VPP PEDOT	435-470	6.2
Oxidant	2734.8	334.1

5.3 SEM Pictures

The resulting PEDOT samples were observed with a JEOL JSM-840 scanning electron microscope, shown in Figure 5.3.1a, at several different magnifications. To achieve optimal resolution and contrast, the accelerating electric field was varied from 10-25 kV. Over time it was noticed that the PEDOT films would build-up charge since their conductivity was not extremely high and the substrates - glass or silicon with an oxide layer - were insulating. To mitigate these effects and prevent any obscuring of images, it was necessary to coat the entire sample with a thin layer of gold using a DC Argon plasma sputtering tool. A Polaron Instrument SEM Coating Unit E5100, shown in Figure 5.3.1b, was used to accomplish this task.

Note that since the SEM could only accommodate certain sized samples, the glass and gate oxide silicon wafers were cleaved into smaller pieces; only select pieces were coated with gold. One at a time, these pieces were set in a metal clamp and secured at a 45° angle with an edge protruding for cross-sectional images. The chuck was then attached to a rod with a thick acrylic disk located along the shaft. The rod was slowly inserted into

Figure 5.3.1: SEM Apparatus

the SEM load-lock (airlock for loading) with the acrylic disk forming a vacuum seal and acting as a viewport. Once pumped down, the main chamber door was opened and the rod was further inserted. Unscrewing the rod, the sample holder was left on the stage of the SEM for imaging.

Figure 5.3.2 presents a series of SEM pictures taken of the sample shown alongside. This sample was a preliminary attempt at VPP not having undergone a post-rinse. Oxidant coverage was patchy due to a non-centered dispensation of solution during rotation. PE-DOT films were only formed in places with oxidant coverage thus exhibiting the selectivity of the reaction. As a result, voids in the film and bare patches of silicon are visible.

Figure 5.3.2b displays a large void found in the film. Note that the bar scale at the bottom represents one micron. Additionally, both the magnification and tilt of each image are included in each caption. Based on the scale, the void measures over a micron in diameter the step down to the oxide appears gradual. At this point rigorous cleaning protocols were not employed leading to the belief that the void was generated during the spin-coating process by a particle on the wafer surface.

Figure 5.3.2: SEM Pictures of a Preliminary VPP-PEDOT Sample

Figure 5.3.2c shows a cross section of the sample. The silicon can be seen at the bottom whilst a rough carpet-like film sits on top. The ridge at the edge of this sample is quite thick compared to the bulk film which suggests oxidant beading around the perimeter during spin-coating. Using the Dektak, the film was measured to be approximately $3\text{ }\mu\text{m}$ and extremely rough. While difficult to get an exact value from the SEM image using the scale, Figure 5.3.2c does not contradict the Dektak measured thickness. Lastly, Figure 5.3.2d shows the sample from a smaller angle with a lower magnification. As such, a larger portion of the film can be seen in focus. The film itself rises and falls, rippling like waves confirming a high surface roughness. This presents a starting point with which to show the progress made in achieving high quality PEDOT films.

Figure 5.3.3a shows a more recent VPP PEDOT sample on glass, cleaved to fit in the SEM. Along the bottom left edge is a section of bare glass void of PEDOT. In the following SEM image the cleavage edge of the glass is facing the electron probe. To achieve a cross-sectional image it was absolutely necessary to coat the glass in gold. Figure 5.3.3b shows the edge of the glass but captures a large field of PEDOT in focus. Compared to the preliminary field from Figure 5.3.2d, the film seems much more uniform and smooth.

Figure 5.3.3: SEM Pictures of VPP PEDOT (OCT1)

Examining the cross-section again, two layers can be distinguished on top of the glass in Figure 5.3.3c. The first layer on glass is the PEDOT:PSS. The thickness is roughly estimated as $<0.05 \mu\text{m}$ based on the bottom scale. The second layer is the VPP PEDOT. The recession may have been caused during cleavage. Its thickness is estimated between

300-400 nm. Note that the non-orthogonal tilt distorts the sense of height in the layers; therefore, more accurate measurement techniques are employed later. Figure 5.3.3d shows an atypical field of PEDOT. On the right side of the image is a trench created from a scoring line. Flakes of the PEDOT can be seen sticking up from the trench and scattered about; however, adhesion appears to have noticeably improved. The film itself appears extremely smooth outside the trench and along the rippled left edge. Overall, significant progress has been made in achieving highly uniform VPP PEDOT films.

Figure 5.3.4 consists of SEM images taken of a fragment of glass coated with ISP PEDOT. Figure 5.3.4a shows the triangular piece that was imaged by the SEM. The fragment features two straight edges and a cleaved edge. An effort was made to have the tilt and magnification of the ISP PEDOT SEM images be similar to those found in the VPP SEM images of Figure 5.3.3, thus allowing for more direct comparison. Figure 5.3.4b shows a random field on the sample. While fairly smooth it contains several spots seemingly growing up from the film. These may be due to particles lying underneath or microscopic bubbles beneath the surface of the spun oxidant. Given the strict protocols for cleaning and storage, the latter is more likely.

Figure 5.3.4c shows another cross-section; however, this image provides much less detail. Even at the same magnification as Figure 5.3.3c, the start of the PEDOT:PSS and PEDOT layers can hardly be discerned. The layers begin much closer to the edge and each other. Additionally, a build-up of ISP PEDOT which can easily be mistaken for a third layer sits a little further back from the edge. It is suspected that this results from further edge and surface tension effects during the spin coating process. Figure 5.3.4d is of another growth on top of a uniform field, though more substantial. It is believed that the PEDOT in this area took on water and crystallized to an extent. Comparing the methods of PEDOT synthesis, the roughness of both is comparable with VPP appearing slightly better.

Figure 5.3.4: SEM Pictures of ISP PEDOT (G6)

5.4 AFM Measurements

AFM measurements were taken using an NT-MDT NTEGRA Solaris in the Department of Chemistry Ianoul Lab with the help of PhD student Adam Bottomley. The samples used were fixed to a moveable stage with double-sided tape to dampen vibrations. An inverted optical microscope was used to locate areas of interest on the sample, viewing them from the bottom side. The sweeping of the cantilever arm back and forth over the scan area allowed for visual confirmation of what area in particular was being mapped. An aluminum reflex coated crystalline silicon cantilever with 6 nm probe tip was used in tapping mode for all scans.

Figure 5.4.1 shows an AFM and accompanying 1D profiles of a ISP PEDOT film generated with the Scanning Probe Microscopy (SPM) software Gwyddion [83]. To provide an estimate of film thickness a narrow scratch was made through the film and an adjacent metal contact.

(a) Image of Horizontal Scratch with Vertical Metal Interface

(b) Profiles (Black - 1, Red - 2, Green - 3, Blue - 4)

Figure 5.4.1: AFM of ISP (G5)

While the metal contact is not apparent in the image itself, it was visible through the AFM's optical microscope. The contact begins slightly to the left of the middle as confirmed visually during the scanning process. The scratch is situated in the top half of the image as indicated by the darker colour corresponding to a low spot. The edge of the scratch shows extensive damage with several bits, marked in white, bent upwards. With each row being an individual scan, occasional entire scans recorded erroneous values; this appears in what is known as scars. An attempt was made to repair these imaging defects through software interpolation. Furthermore, as most AFM setups are not extremely precise in self-levelling, users are expected to correct or calibrate numerically after the fact. Indeed, the original PEDOT AFM scans were accompanied by major tilt offsets which have since been corrected in software. Figure 5.4.1a was taken after all corrections were made.

Table 5.4.1 contains the results of the 1D profiles taken. Note that the profiles themselves are shown as numerically labelled white lines on the AFM images. Profile 1 in Figure 5.4.1a is of most interest as it traces from the nearly-bare glass in the scratched region onto the PEDOT:PSS ISP-PEDOT stack. According to the grey cursors placed on the profile, the film thickness is approximately 233.4 nm. Note that this does include the adhesion layer which makes the ISP-PEDOT approximately 184.4 nm. Profile 3, tracing over the film and onto the metal contact, shows a fairly gradual slope rising roughly 60 nm then rising even more slowly. Recalling Figure 5.2.3b, this was also the case. The rise to the metal plateau spans hundreds of microns. Given that only 25 μm of the metal was scanned in Figure 5.4.1b, it is probable that the maximum contact height or plateau was never reached.

Figure 5.4.1a also reveals a curious behaviour in the ISP film. In a slightly brighter hue, white cracks or tendrils spread throughout the film. Profile 3 crosses over one of these cracks near 10 μm and is reflected in a 50 nm localized peak. This cracking might be from stress during the rinsing process.

Table 5.4.1: AFM 1D Profile Measurements

Scan	Profile	X1 (um)	Y1 (nm)	X2 (um)	Y2 (nm)	ΔX (um)	ΔY (nm)
ISP	1	6.41	34.3	27.28	267.7	20.87	233.4
	2		37.8		319.2		281.5
	3		264.2		326.2		62
	4		39.5		38.7		-0.8
VPP	1	7.04	228	26.51	659	19.47	431
	2		230		699		468
	3		626		657		31
	4		226		223		-3

(a) Image of Horizontal Scratch with Vertical Metal Interface

(b) Profiles (Black - 1, Red - 2, Green - 3, Blue - 4)

Figure 5.4.2: AFM of VPP (OCT1)

Figure 5.4.2 displays similar measurements for the VPP PEDOT sample, OCT1. As seen here, large discontinuities from displaced pieces of polymer produce shadowing in the image, the result of a temporary shift in cantilever frequency. Profile 1 records a difference of 431.0 nm between bare glass and polymer film. Again, subtracting the adhesion layer thickness, the film thickness is calculated as 382.0 nm. Starting slightly further away from the metal interface, profile 3 only shows a rise of 31 nm from bare polymer to metal. The difference in rises between profiles 1 and 2 also agrees with this value. The polymer to metal transition appears to be gradual due to lateral particle movement in the space between the shadow mask and surface. The VPP film does not show the stress cracking that was previously apparent in the ISP film. This illustrates yet another advantage of the vapour process over solution methods.

Figure 5.4.3a and b examine the roughness along profile 3 for ISP and VPP respectively. For both films, the roughness increases considerably as it enters into the metal region. As the AFM discerned no distinct transition to metal, it is possible that the metal may have partially diffused into the PEDOT layers below. The vertical red lines indicate estimates for the start of the metal transitions based on perceived increases in roughness.

To get a real estimate of Root Mean Square (RMS) film roughness, ignoring that of the deposited metal, a shorter segment of profile 1 along the PEDOT film (Figure 5.4.3c and d) was taken. The results can be seen in Table 5.4.2. The VPP film has a lower RMS roughness even though it is much thicker. This adds to the growing evidence that the vapour method in this application yields higher quality films over the solution method.

Table 5.4.2: Summary of AFM Results

Film	ISP	VPP
Thickness (nm)	184.4	382.0
RMS Roughness (nm)	6.5	2.3

Figure 5.4.3: Roughness Profiles

5.5 Four-Point Probe Measurements

The conductivity of PEDOT films synthesized via ISP and VPP methods was extracted using the four-point probe measurement technique. An attempt was made to use a Resistivity Test Rig from A&M Fell Ltd but proved too noisy to obtain usable data. The rig itself consisted of a spring loaded arm with four probe tips spaced 50 mil apart. The probes were connected to a current source and Keithley digital multimeter to measure voltage. However, when the probes were lowered into contact with the sample, the readings on the multimeter would jump orders of magnitude with the thermal noise floor being very close to the expected values. This was attributed to poor physical contact between the probe tips and the PEDOT, given its soft nature and roughness.

As such, a makeshift four point probe was implemented. Silver contacts were deposited through a shadow mask. Some of these contacts were in groups of four equally

spaced squares ranging from 50-100 mil apart. Using a Wentworth Probe Station individual probes were landed on each of the four contacts as shown in Figure 5.5.1.

Figure 5.5.1: Four Point Probe Setup

An HP4145 Semiconductor Parameter Analyzer was connected with the following setup: the first channel was set to a sweeping current source. The second and third were set to constant current sources with zero output to measure voltage. Lastly, the fourth channel was set to ground to sink the current. Channel 1 was swept from 0 to 1 mA in steps of 10 μ A. The voltage at each channel was measured and the difference between channels 2 and 3 was computed for each point. The data was saved and analyzed in Microsoft Excel. Least squares regression was performed to get an estimate for slope. Figure 5.5.2 shows an example graph of an early VPP film. For this film in particular, the current was swept over a smaller range since the film conductivity was much lower.

Using Equation B.1.3 and the corresponding Dektak measured thickness of 14 μ m the conductivity for the early VPP film was calculated as:

$$\sigma = \frac{1}{4.5324t(V/I)} = \frac{1}{4.5324(14\mu m)(115.23)} \approx 1.3684 S/cm$$

Figure 5.5.2: Example Four Point Probe Graph of Early Low Conductivity VPP Sample

Multiple sweeps were performed at each contact cluster on a sample to verify the accuracy of the measurements. For the final ISP and VPP PEDOT film on glass, G5 and OCT1 respectively, Figure 5.5.3 displays one current sweep for each sample.

Figure 5.5.3: Four Point Probe of ISP vs. VPP PEDOT

Interestingly, the sweeps for every OCT1 placement were much cleaner with less overall noise. This may be attributed to the thicker VPP film or perhaps a lower surface roughness which improves overall electrical contact. The thicknesses of the above sweep locations were extracted from AFM measurements taken near the corresponding middle contacts. AFM thickness measurements were taken after the fact as it required partial destruction of the contact group.

Table 5.5.1 summarizes the slope and thickness values used to calculate the film conductivities. The resulting conductivity for the ISP film agrees with the range of 400-600 S/cm as found in the procedure from Clevios [77]. The VPP film conductivity is more than twice that of the in-situ method. This was confirmed over several samples cementing the idea that the introduction of the monomer in vapour form at temperature allows for more favourable arrangement and growth of polymer chains. Furthermore, this conductivity is on the same order of magnitude as leading research groups in the field. Additionally, it has often been noted that there is an optimal thickness for peak conductivity which tends to be below 100 nm. This presents the possibility of further optimization of film conductivity via thickness management through deposition time.

Table 5.5.1: Four Point Probe Summary Table

Method	ISP	VPP
Thickness, t (nm)	184.4	382.0
Slope, V/I (Ω)	22.478	5.1052
Conductivity, σ (S/cm)	532.3	1131.3

5.6 Fourier Transform Infrared (FTIR) Spectroscopy Measurements

In standard FTIR, a superposition of two broadband IR spectrum rays is passed through the sample and the output interferogram is recorded. If there is no transmission, the resulting

interferogram is null. This is the case for the glass and silicon substrates upon which the PEDOT was deposited. The silicon substrate reflects most of beam whilst the glass is thick enough to severely attenuate it. To achieve a non-trivial interferogram, a non-standard accessory was employed. Attenuated total reflectance (ATR) FTIR works through shining the IR beam towards the sample and capturing the reflected beam. Rays which are received by the apparatus are most often reflected at a depth of $2\text{ }\mu\text{m}$ or less into the sample.

Figure 5.6.1 shows the ATR-FTIR of the most recent PEDOT films that were produced. The blue line represents a PEDOT film synthesized via ISP of EDOT with a Ferric Tosylate solution controlled by an Imidazole inhibitor. The black line represents a PEDOT film synthesized via vapour phase polymerization of EDOT using a spun-on film of Ferric Tosylate mixed with the PEG-PPG-PEG trimer. Some of the main peaks are labelled. As can be seen, the peaks of both spectra are consistent.

Figure 5.6.1: ATR-FTIR of Final Films - VPP vs. ISP

Starting from left and moving towards the right, the peaks at 1555 cm^{-1} and 1430 cm^{-1} fall within the range for C=C stretch in aromatic molecules [46, 84]. The peak at 1375 cm^{-1} shows C-C stretch. These three peaks further verify that oxidant-initiated coupling dominates over acid-initiated coupling in the overall reaction - as little to no conjugation is expected in the latter. For the C-O-C moieties in the dioxane ring, peaks in the

range of $1300\text{--}1000\text{ cm}^{-1}$ are representative of asymmetric and symmetric stretch - towards the high and low limits respectively [85, 46]. Lastly, the peak at 990 cm^{-1} corresponds to the C-S stretch in the thiophene ring [85]. This closely follows many other spectra found in literature [48, 21, 86, 46]. There are slight deviations which are easily accounted for through difference in doping levels, type of dopants, and deposition temperatures.

Since ATR-FTIR employs reflection from the film rather than full depth penetration, the thickness of films may affect relative absorbance values. Loss of signal via transmission through the transparent stage was expected and likely resulted in higher absorbance values for the thinner films; as is the case with the thinner ISP film having higher absorbance compared to the thicker ISP film. This concept was further observed through a series of measurements. Figure 5.6.2 shows FTIR spectra for an earlier ISP PEDOT film mapped across the substrate. The measurements were taken starting in the center of the substrate where the film is thickest - and darkest- and radiating outwards along a diagonal. Note that the blue 'Middle' line refers to the middle thickness, lying between the center and corner of the substrate.

Figure 5.6.2: ATR-FTIR on ISP PEDOT Along a Diagonal going from Center to Corner

The film presented in Figure 5.6.2 did not have a proper adhesion layer and thus presented some stress cracking and film removal after a short 15 s methanol rinse. Compared with the above ISP spectra in Figure 5.6.1, the positions of the main peaks are consistent; however, the C=C stretch peaks at 1550 cm^{-1} and 1430 cm^{-1} are much less pronounced. This suggests less conjugation throughout the polymer chain and indeed conductivities measurements concurred - with values several orders of magnitude lower than the recent ISP film.

To further identify peaks present in the PEDOT spectra, FTIR of the oxidant Ferric Tosylate was also performed. The oxidant solution, CB40, was vacuum dried in a flask to remove the solvent. This yielded a reddish-brown paste which was subsequently smeared onto and sandwiched between KBr plates - transparent in the IR spectrum - and inserted into the standard FTIR setup. Figure 5.6.3 shows the resulting spectrum paired with that of an unrinsed VPP PEDOT film. As the Tosylate spectrum's absorbance was much higher, the two spectra were normalized to their respective maximum values.

Figure 5.6.3: Normalized FTIR of Unrinsed VPP PEDOT and Ferric Tosylate Oxidant

Immediately, it can be seen that both spectra share peaks towards the lower end of the spectrum such as 1122 cm^{-1} , 1035 cm^{-1} , 1007 cm^{-1} and 812 cm^{-1} . Since these peaks dwarf the others in the VPP spectra, the presence of the Ferric Tosylate must dominate the FTIR spectrum of the polymer in the unrinsed film. Re-examining Figure 5.6.1, upon rinsing the relative height of the aforementioned peaks drops considerably suggesting the removal of the substance to an extent. The fact that they are still non-zero after rinsing may indicate the inclusion of Tosylate as a doping counter-ion. This seems likely given the measured conductivities of the rinsed PEG-VPP film.

Analyzing the higher end of the spectrum in Figure 5.6.3, the Ferric Tosylate sample shows a massive peak around 3200 cm^{-1} . This can be attributed to the O-H bonds implying that the Butanol solvent is still very present. The unrinsed PEDOT also has a large peak in the vicinity characteristic of O-H bonds. As there are none in the monomer or rinsed PEDOT, it may provide evidence that the dioxane ring is being attacked by the acidic byproducts. Another unwanted side reaction resulting in deterioration of the dioxane ring and conjugated backbone is marked by the peak at 1666 cm^{-1} corresponding to a carbonyl (C=O) group.

Since ATR-FTIR can probe up to $2\text{ }\mu\text{m}$ into the sample, the substrate might contribute to the resulting IR spectrum of thinner films. FTIR was performed on the glass substrates used as well as a vacuum dried PEDOT:PSS sample, representing the adhesion layer, to determine whether any contributions were present. Figure 5.6.4 couples the normalized spectra of glass alone, PEDOT:PSS on glass, and VPP PEDOT on a PEDOT:PSS coated glass slide. A scan of the glass alone yielded a large peak at 900 cm^{-1} and smaller peak at 770 cm^{-1} ; neither of which seemed to greatly contribute to the resulting PEDOT spectra. The PEDOT:PSS displayed a large peak at 3400 cm^{-1} indicating remaining water in the sample as well as C=C and C-C peaks at 1700 cm^{-1} and 1260 cm^{-1} respectively. The latter perfectly lines up with the VPP PEDOT with a much broader peak indicating a higher level of doping in the VPP PEDOT. Additionally, a shoulder in the VPP PEDOT

near 1650 cm^{-1} is somewhat visible which may be generated by an absorbance peak in the PEDOT:PSS beneath. Overall, there is little evidence that the materials below the VPP PEDOT film are significantly influencing the measured ATR-FTIR spectrum.

Figure 5.6.4: Normalized FTIR of Glass, PEDOT:PSS, and VPP PEDOT

5.7 UV-Visible (UV-vis) Spectroscopy Measurements

Measurements were taken on an Agilent Technologies Cary 300 UV-Vis Spectrophotometer. First, a blank glass slide was scanned to observe its effects in the UV spectrum. The initial glass spectrum is shown in Figure 5.7.1 in black. Note that the absorbance jumps up suddenly at $\sim 330\text{ nm}$. This verifies that glass absorbs a large portion of the UV spectrum. The peak grows even larger towards 200 nm . In that range, the absorbance of glass is so high that the transmitted signal became extremely small and susceptible to noise. For this reason, none of samples were scanned below 300 nm as the recorded values are too noisy and inaccurate. Conversely, the top end of the spectra were limited by the range of the machine into the near-IR. For the ISP and VPP films, a reference spectrum of PEDOT:PSS

on glass was taken. Subsequent subtraction from the new spectra yielded the absorbance contribution of only those particular films.

Figure 5.7.1: UV-Vis Spectra of ISP, VPP, and Glass Substrate

With UV-Vis measurements, the onset of a peak is more indicative of band energies than the actual peak location. In the measurements taken, the spectra are quite broad with a high likelihood of the overlap or shadowing between peaks. The broadness of peaks is normally attributed to the multitude of electronic and vibrational states of varying energy to and from which electrons can transition. From left to right, Figure 5.7.2 shows the allowed transitions for neutral, lightly, and heavily doped PEDOT. With a neutral conjugated polymer no states exist inside the band gap. As the doping level increases, positive polaron states are introduced and are accompanied by newly possible optical transitions. For the highly conducting ISP and VPP films, they are moderately to heavily doped so a predominantly bipolaron population of charge carriers is expected. Limited by quantum selection rules and dipole symmetry, there should only be two allowed transitions: one from the valence to the conduction band ($\pi - \pi^*$) and the other from the valence band to the lower bipolaron level ($\pi - BP1$).

Figure 5.7.2: Energy Band Diagrams of PEDOT and their Allowed Optical Transitions (Increasing p-type Doping from Left to Right) [87]

The spectra taken of the ISP and VPP samples share the same general behaviour; their absorbance increases towards the IR region. With a much higher absorbance at lower energies in the visible range both films accordingly appear blue to the eye. The VPP film has a much darker blue hue compared to the ISP film, coinciding with the increased absorbance in the red region - almost double. This can partially be attributed to the difference in thicknesses, 380 nm and 180 nm respectively. Interestingly, both films seem to have similar absorbance in the blue and UV regions. Upon further inspection, the curvature of the spectra is also distinct. The VPP spectra displays a local maxima or peak around 1.5 eV, whilst the ISP peak seems to be lower in energy - clipped by the scan. The VPP crest is believed to be from the lower bipolaronic state with the onset being somewhere around 0.8 eV as is reported in literature [87, 88]. The band gap of Tosylate doped PEDOT has been reported as 1.8 eV through spectroscopic study yielding a maximum optical absorption peak around 2.4 eV [89, 90]. However, these spectra are still consistent with literature, demonstrating a growth in the polaronic and bipolaronic peaks with increased doping at the expense of the interband transition [87]. At the current doping levels of the films, almost no interband peak should be observed with such a large bipolaron population.

While the above measurements only yield so much information about the electronic transitions, they are also important with regards to their application as transparent conductors. Figure 5.7.3 shows the attenuation coefficient of the above samples as well as an ITO sample for comparison.

Figure 5.7.3: Attenuation Coefficient of ISP, VPP, and ITO Films (Normalized by Thickness)

The conversion from absorbance to attenuation coefficient assumes that absorbance increases linearly with layer thickness. In so doing, the samples become normalized in terms of thickness, permitting comparison based solely on material properties. As is evident, the ITO is much more transmissive. Similar to glass, ITO blocks most of the UV spectrum but is transparent in the visible range. While PEDOT may not have the conductivity or transparency of ITO, it is gradually approaching the benchmark [25]. Also note that the VPP sample is noticeably more transmissive than the ISP sample. Generally, more heavily doped (oxidized) PEDOT tends to be more transparent and that is likely the case here [25, 91].

Chapter 6

Conclusion

6.1 Thesis Summary

The goal of this thesis was to design and build a fully functioning apparatus for oCVD of polymeric films - specifically PEDOT. While the design process incorporated common themes between other systems presented in literature, several key differences were engineered. These include: a static deposition phase, in-situ loading, six precursor sources, a hot wall deposition chamber, and double wall vacuum.

A static deposition phase was opted for to minimize reactant waste. With the standard dynamic systems featured in literature, a significant portion of reactant vapour bypasses the substrate and flows out the exhaust. To combat this issue, the vacuum pump was isolated with the vapour saturating the chamber and slowly condensing onto the substrate. This procedural modification presented other challenges including chamber leakage necessitating the use of the double wall vacuum. The inner chamber was crafted from 1/4" pipes minimizing the volume and thus the mass of reactants required to fill the chamber. The substrate holder design featured KF flanges for ease of access whilst the six reactant holders comprised small glass vials sealed with an o-ring squish ferrule fitting.

The inner chamber hot wall was achieved through an AC phase controlled rope heater which enveloped the pipes and fittings. Pulse width modulated thermoelectric coolers were employed for regulating reactant and substrate temperatures. Precursor vials were suspended in baths of low vapour pressure oil for uniform heating. Feedback loop PID temperature control systems were engineered to reliably regulate the inner chamber walls, reactant holders, and substrate. Detailed data logging was implemented to monitor process variables and allow for comparison between discrete depositions.

Given the design constraints and budget, it was not possible to incorporate all computer controlled components. Thus the system itself is semi-automatic with a degree of human interaction required. The base pressure of the system is roughly 20 mTorr and upon pump isolation, rises to ~2500 mTorr in ten minutes. While these chamber properties fall short of specification, they proved satisfactory for deposition. The temperature range of the system approaches 200 °C but is limited by the upper range of vacuum sealant material used. This temperature maximum allows for experimentation with a wide range of reactants; however, it still excludes several notable low volatility oxidants including Ferric Chloride.

To confirm functionality of the system, it was necessary to conduct extensive trial runs. These tests were executed using a variant of oCVD as concerns of pitting corrosion attacks from oxidant precursors were still present. VPP was performed by first spin coating substrates with an oxidant solution. The substrates were then loaded into the apparatus for monomer exposure with the exact same execution as the second half of a segregated oCVD. Prior to the application of the oxidant solution, substrates were prepared through an oxygen plasma treatment resulting in hydrophilic behaviour immediately followed by spin coating of a PEDOT:PSS adhesion layer. The ten minute EDOT monomer exposure phase was monitored many times and all environmental conditions were sufficient. Between depositions, process variables were slightly refined, though process optimization was not a main objective. A PEG-PPG-PEG trimer compound was later included in oxidant solution serv-

ing the dual purposes of reducing crystallization of the oxidant before vapour exposure and slowing the rate of the volatile polymerization reaction.

Resulting PEDOT films were scrutinized with a number of characterizations alongside the control films - solutions processed in-situ polymerized films using near-identical reactants. With the data from each series of characterization measurements, VPP films and ISP control films were compared to each other and literature. Film conformity/uniformity was evaluated using profilometry and microscopy techniques. Dektak profilometer scans were performed amid the rounds of film synthesis. However, as this technique carried limited confidence, AFM measurements were taken to confirm the final results. Simultaneously, SEM imaging gave a closer look at film morphology from various angles including cross-sections; something not as easily accomplished with the fixed-angle AFM. A general consensus between these methods was that the VPP films were thicker but less rough compared to their ISP counterparts. The ~400 nm VPP films had roughnesses around 2 nm whilst the ~200 nm ISP films were closer to 6 nm. Furthermore, visible stress cracking was present in the ISP films.

Film quality was evaluated using conductivity measurements as well as FTIR and UV-vis spectroscopy. Conductivities of the final films were measured via co-linear four point probe method with patterned metal contacts thermally deposited on the wafer. Once again, VPP films surpassed ISP films with over twice the conductivity at 1130 S/cm to 530 S/cm. The ISP conductivity was within the expected range and the VPP films were consistent with comparable literature. FTIR showed little difference between VPP and ISP films though both had signs of high conjugation and little to no damage. UV-vis echoed the results lacking any peaks in the UV and presented a high degree of doping with the bipolaronic peak eclipsing the $\pi - \pi^*$ transition.

Overall, the high quality of VPP films with very little process optimization validated both the apparatus as a research tool and vapour-processing methods in general.

6.2 Knowledge Contribution

The knowledge contribution for this thesis project has been significant. First and foremost, a versatile and robust research tool has been built. This will allow for the research and development of vapour-processed polymer films at Carleton for years to come. A multitude of options for co-polymerization are also available with the numerous reactant holders. Secondly, the procedure for high quality VPP PEDOT films with the equipment at Carleton has been refined and documented. In doing so, the processes from several other papers have been validated. Furthermore, the accompanying results from the suite of tests and characterizations have been made available to the community and future publications are expected.

6.3 Future Work and Improvements

6.3.1 oCVD

While the system has been designed for oCVD of up to three films in a single run, it has not yet been employed for such purposes. The first step would be to achieve conformal single layers through oCVD. However, there still exists a concern for pitting corrosion on the walls of the chamber. The concept of coating the inside of the chamber with another inert polymer, Parylene, has been thoroughly discussed. Parylene in its many varieties offers pinhole-free conformal coatings several nanometres thick. Furthermore, it provides extremely high chemical resistance against oxidizing agents. This makes it an ideal solution for the corrosion issue.

The coating can either be applied commercially for a nominal fee or attempted in-house. The process itself consists of subliming the dimer at 150 °C, pyrolyzing the dimer at 650 °C or higher, and then depositing on the surface at room temperature. Standard setups

employ three separate chambers each under progressively higher vacuum than the previous - starting from 1 Torr down to 0.1 Torr for deposition.

Regardless of whether the coating is applied, oCVD with more volatile oxidants would be attempted; the possible precursors include Bromine, Molybdenum Pentachloride, and Iodine. They are listed in order of decreasing vapour pressure at room temperature with 160 Torr, 1.75 Torr, and 0.31 Torr respectively. Utilization of the first two has been noted and studied which makes them ideal for comparison. However, their vapour pressures - especially Bromine - make handling and loading much more involved. The latter, Iodine, while still a volatile substance is somewhat safer and no mention of its use in oCVD has been found. As shown in Table 6.3.1, Iodine has a lower oxidation potential than Bromine and Iron but greater than Copper. This may lead to more controlled reactions resulting in higher quality films without the need for reaction inhibiting additives.

Table 6.3.1: Oxidation Potentials [92]

Reaction	Oxidation Potential (eV)
$Br_2 + 2e^- \Rightarrow 2Br^-$	1.094
$Fe^{3+} + e^- \Rightarrow Fe^{2+}$	0.771
$I_2 + 2e^- \Rightarrow 2I^-$	0.535
$Cu^{2+} + e^- \Rightarrow Cu^+$	0.161

A non-rigorous proof of concept for iodine oCVD was attempted and Figure 6.3.1 shows the results. Small puddles of the EDOT monomer and an iodine solution were placed on a slide and heated to 80 °C. This was capped with a low volume Petri dish to slow the vaporization by maintaining a closed environment. Inadvertently, the vapour phase reaction primarily took place on the underside of the Petri dish as it was cooler than the hotplate. Since there was very little control of process variables including chamber pressure and deposition temperature, the colour uniformity of the film was lacking. Nonetheless, this overly simple test demonstrates the validity of the reaction. Knowing that Iodine is widely used as a secondary dopant leads to the belief that relatively high conductivities may be achieved with a properly optimized deposition scheme.

Figure 6.3.1: Proof of Concept oCVD PEDOT Film using Iodine Oxidant

6.3.2 Mobility Measurements

Alongside the other measurements, another test was being performed. Charge extraction by linearly increasing voltage (CELIV) is an emerging technique for measuring mobility values and has garnered much interest as a research topic. It offers several advantages over the traditional Time-Of-Flight (TOF) mobility measurement [93, 94]. These include: a much simpler test setup requiring only a function generator and oscilloscope, the ability to extract mobility of more conductive samples rather than just low mobility materials, and the option of using films of sub-micron scale in the experiments.

Unfortunately, sufficient results could not be acquired in the time provided. This work will likely be continued in hopes of achieving positive results while at the same time a large magnet is being readied for Hall mobility measurements. CELIV for PEDOT films has not yet been observed in literature, therefore a good probability exists for publishing a paper comparing the extracted mobility values against the better known Hall method.

6.3.3 Possible Design Changes

There are several possible design changes, other than parylene coating, which might be implemented. The option for dynamic flow of reactants over the substrate can be added with a vacuum port on a new custom blank KF flange. For improved vacuum, another overhaul would likely be required. Figure 6.3.2 details a new reactor design that takes elements found in literature and combines them with the best and most convenient from the current design. Of course, the cost would increase substantially to accommodate these features in a higher quality design. The narrow tubing would be immediately swapped out for a thin, wide rectangular tube. This would accommodate large substrates while still attempting to minimize total volume.

Figure 6.3.2: Possible Design Changes

Nitrogen port and vacuum ports throttled by Mass Flow Controllers (MFCs) would be placed at either end of the rectangular tube. Static or dynamic reaction schemes could be selected simply by turning the vacuum valve on or off during vaporization. This option would allow for further investigation of reaction rates and transport mechanisms. Computer-controlled, high-temperature, pneumatic valves would be employed instead of needle valves to more precisely meter reactant flow - with binary states, open or closed.

To improve film uniformity, a rotating substrate would be included to combat the one-directional flow of precursor over the substrate.

The entire reactant vaporization system would be kept almost the same. The ultra-torr fittings, thermoelectric coolers, oil baths, etc. are practical and function extremely well. Therefore, they would be incorporated into the chamber with welded joints as opposed to the economical but leaky Swagelok joints. Similarly, a CF flange may form a tighter seal for the substrate load chamber. A vertically sliding stage would once again be employed with the TEC and stage assemblies mounted securely and water cooled - though the old stage sliding/locking mechanism would have to be upgraded. To better monitor deposition, a QCM would be placed near the substrate while trying to minimize affect on vapour flow over the wafer.

The entire assembly would be mounted floating inside a heated enclosure with the possibility of external vacuum. The heated enclosure would provide the hot wall effect with much more uniform heating than the previously used heater tape. However, with this change reactants should be cooled below the chamber temperature for storage.

Bibliography

- [1] W. Brutting, “Organic semiconductors,” *Semiconductors*, vol. 6, pp. 1–11, 2005.
- [2] N. Karl *et al.*, *Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Electronic Solids*, R. Farchioni and G. Grosso, Eds. Springer Science and Business Media, 2001.
- [3] G. Heilmeyer and L. Zanoni, “Surface studies of alpha-copper phthalocyanine films,” *Journal of Physics and Chemistry of Solids*, vol. 25, no. 6, pp. 603–611, 1964.
- [4] J. McGinness, P. Corry, and P. Proctor, “Amorphous semiconductor switching in melanins,” *Science*, vol. 183, no. 4127, pp. 853–855, March 1974.
- [5] H. Shirakawa, E. Louis, A. MacDiarmid, C. Chiang, and A. Heeger, “Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (ch)_x,” *J. Chem. Soc., Chem. Commun.*, pp. 578–580, 1977.
- [6] H. Koezuka, A. Tsumura, and T. Ando, “Field-effect transistor with polythiophene thin film,” *Synthetic Metals*, vol. 18, pp. 699–704, 1987.
- [7] C. Dimitrakopoulos and P. Malenfant, “Organic thin film transistors for large area electronics,” *Advanced Materials*, vol. 14, p. 99, 2002.
- [8] L. Zhou, S. Park, B. Bai *et al.*, “Pentacene tft driven am oled displays,” *IEEE Electron Device Letters*, vol. 26, no. 9, pp. 640–642, September 2005.

- [9] M. Kane, J. Campi, M. Hammond *et al.*, “Analog and digital circuits using organic thin film transistors on polyester substrates,” *IEEE Electron Device Letters*, vol. 21, no. 11, p. 534, November 2000.
- [10] K. Walzer, B. Maennig, M. Pfeiffer, and K. Leo, “Highly efficient organic devices based on electrically doped transport layers,” *Chemical Reviews*, vol. 107, no. 4, pp. 1233–1271, April 2007.
- [11] D. Schroder, B. Schuele *et al.*, *Handbook of Semiconductor Manufacturing Technology*, 2nd ed. CRC Press, 2008, ch. 28 - Electrical, Physical and Chemical Characterization, pp. 28–1 – 28–76.
- [12] A. Shepard. Semiconductor technology at tsmc, 2011. Accessed December 2014. [Online]. Available: http://www.youtube.com/watch?v=4Q_n4vdyZzc
- [13] Inside tsmc - a fab tour (n.d.). VLSI Encyclopedia. Accessed December 2014. [Online]. Available: <http://www.vlsiencyclopedia.com/2012/08/inside-tsmc-fab-tour.html>
- [14] F. Li *et al.*, *Organic Thin Film Transistor Integration: A Hybrid Approach*. Wiley-VCH, 2011.
- [15] M. Chason, P. Brazis, J. Zhang *et al.*, “Printed organic semiconducting devices,” *Proceedings of the IEEE*, vol. 93, no. 7, pp. 1348–1356, July 2005.
- [16] S. Baxamusa *et al.*, “Initiated and oxidative chemical vapor deposition: A scalable method for conformal and functional polymer films on real substrates,” *Physical Chemistry Chemical Physics*, vol. 11, no. 26, pp. 5205–5520, July 2009.
- [17] N. Guimard, N. Gomez, and C. Schmidt, “Conducting polymers in biomedical engineering,” *Progress in Polymer Science*, vol. 32, no. 8-9, pp. 876–921, 2007.

- [18] H. Peng, L. Zhang, C. Soeller *et al.*, “Conducting polymers for electrochemical dna sensing,” *Biomaterials*, vol. 30, no. 11, pp. 2132–2148, April 2009.
- [19] M. Singh, P. Kathuroju, and N. Jampana, “Polypyrrole based amperometric glucose biosensors,” *Sensors and Actuators B*, vol. 143, no. 1, pp. 430–443, December 2009.
- [20] P. Bahadur and N. Sastry, *Principles of Polymer Science*. Alpha Science, 2002.
- [21] J. Lock *et al.*, “Oxidative chemical vapor deposition of electrically conducting poly(3,4-ethylenedioxythiophene) films,” *Macromolecules*, no. 39, pp. 5326–5329, 2006.
- [22] Q. Dong *et al.*, “All-spin-coating vacuum-free processed semi-transparent inverted polymer solar cells with pedot:pss anode and pah-d interfacial layer,” *Organic Electronics*, vol. 11, pp. 1327–1331, 2010.
- [23] D. Gilles and R. Loehr, “Waste generation and minimization in semiconductor industry,” *Journal of Environmental Engineering*, vol. 120, no. 1, pp. 72–86, 1994.
- [24] M. Irimia-Vladu, ““green” electronics: biodegradable and biocompatible materials and devices for sustainable future,” *Chemical Society Reviews*, vol. 43, p. 588, 2014.
- [25] A. Elschner, S. Kirchmeyer, W. Lovenich *et al.*, *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*. Taylor and Francis Group, 2011.
- [26] H. Crichton. Flexible ito-free polymer solar cells. Materials Views. Accessed April 2014. [Online]. Available: <http://www.materialsviews.com/flexible-ito-free-polymer-solar-cells/>
- [27] D. Jones, A. Holmes, and S. Watkins. Printing australia’s largest solar cells. [Online]. Available: <http://www.csiro.au/Portals/Media/Printing-Australias-largest-solar-cells.aspx>

- [28] E. Ralston. Fairchild cheney free press bring back newspaper. Fairchild Airforce Base. Accessed December 2014. [Online]. Available: <http://www.fairchild.af.mil/shared/media/photodb/photos/090504-F-0693C-003.jpg>
- [29] W. Fix, A. Ullman, and R. o. Blache, *Organic Electronics. Structural and Electronic Properties of OFETs*, C. Woll, Ed. Wiley, 2009.
- [30] R. Street, Ed., *Technology and Applications of Amorphous Silicon*, ser. Springer Series in Materials Science. Springer Berlin Heidelberg, 2000.
- [31] D. Carlson and C. Wronski, “Amorphous silicon solar cell,” *Applied Physics Letters*, vol. 28, no. 11, pp. 671–673, 1976.
- [32] R. Schropp and M. Zeman, “New developments in amorphous thin-film silicon solar cells,” *IEEE Transactions on Electron Devices*, vol. 46, no. 10, pp. 2086–2092, 1999.
- [33] R. Sreenivasan and K. K. Gleason, “Overview of strategies for the cvd of organic films and functional polymer layers,” *Chemical Vapor Deposition*, no. 15, pp. 77–90, 2009.
- [34] W. Fix, “Polymer based 13mhz rfid transponders,” in *The Fifth Organic Electronics Conference and Exhibition Europe 2007*. The address of the publisher: Organic Electronics Association, 2007.
- [35] M. Fabretto, C. Jariego-Moncunill, J. Autere *et al.*, “High conductivity pedot resulting from glycol/oxidant complex and glycol/polymer intercalation during vacuum vapor phase polymerisation,” *Polymer*, vol. 52, pp. 1725–1730, 2011.
- [36] R. Xiao, S. Cho, and S. Lee, “Controlled electrochemical synthesis of conductive polymer nanotube structures,” *Journal of American Chemical Soccity*, vol. 129, pp. 4483–4489, 2007.

- [37] Y. Wei, C. Chan, J. Tian *et al.*, “Electrochemical polymerization of thiophenes in the presence of bithiophene or terthiophene: Kinetics and mechanism of polymerization,” *Chemistry of Materials*, vol. 3, pp. 888–897, 1991.
- [38] H. Adam, A. Bolz, H. Boy *et al.*, *Fundamentals of Vacuum Technology*, W. Umrath, Ed. Oerlikon, 2007.
- [39] N. Lee and C. Frank, “Surface-initiated vapor polymerization of various alpha-amino acids,” *Langmuir*, vol. 19, no. 4, pp. 1295–1303, 2003.
- [40] X. Chen, M. Anthamatten, and D. Harding, “Vapor deposition and curing of polybenzoxazole precursors,” *Macromolecules*, no. 39, pp. 7561–7565, 2006.
- [41] M. Jacob, C. Easton *et al.*, “Fabrication of a novel organic polymer thin film,” *Thin Solid Films*, vol. 516, pp. 3884–3887, 2008.
- [42] T. Blythe and D. Bloor, *Electrical Properties of Polymers*, 2nd ed. Cambridge University Press, 2005.
- [43] W. E. Tenhaeff and K. K. Gleason, “Initiated and oxidative chemical vapor deposition of polymeric thin films: icvd and ocvd,” *Advanced Functional Materials*, no. 18, pp. 979–992, 2008.
- [44] T. Martin, K. Lau, K. Chan *et al.*, “Initiated chemical vapor deposition (icvd) of polymeric nanocoatings,” *Surface and Coatings Technology*, vol. 201, no. 22-23, pp. 9400–9405, 2007.
- [45] W. Arora, W. Tenhaeff, K. K. Gleason, and J. Barbastasthis, “Integration of reactive polymeric nanofilms into a low-power electromechanical switch for selective chemical sensing,” *Microelectromechanical Systems*, vol. 18, no. 1, p. 97, 2009.

- [46] S. Atanasov *et al.*, “Highly conductive and conformal poly(3,4-ethylenedioxythiophene) (pedot) thin films via oxidative molecular layer deposition,” *Chemistry of Materials*, no. 26, pp. 3471–3478, May 2014.
- [47] S. Armes, “Optimum reaction conditions for the polymerization of pyrrole by iron(iii) chloride in aqueous solution,” *Synthetic Metals*, vol. 20, pp. 365–371, 1987.
- [48] S. G. Im and K. K. Gleason, “Systematic control of the electrical conductivity of poly(3,4-ethylenedioxythiophene) via oxidative chemical vapor deposition,” *Macromolecules*, vol. 40, pp. 6552–6556, 2007.
- [49] B. Winther-Jensen, D. Breiby, and K. West, “Base inhibited oxidative polymerization of 3,4-ethyldioxythiophene with iron(iii)tosylate,” *Synthetic Metals*, vol. 152, pp. 1–4, 2005.
- [50] Y. Ha, N. Nikolov, S. Pollack *et al.*, “Towards a transparent highly conductive poly(3,4-ethylenedioxythiophene),” *Advanced Functional Materials*, vol. 14, no. 6, pp. 615–622, 2004.
- [51] J. Lock, “Chemical vapor deposition of conjugated polymeric thin films for photonic and electronic applications,” Ph.D. dissertation, MIT, June 2005.
- [52] S. G. Im *et al.*, “Conformal coverage of poly(3,4-ethylenedioxythiophene) films with tunable nanoporosity via oxidative chemical vapor deposition,” *ACS NANO*, vol. 2, no. 9, pp. 1959–1967, 2008.
- [53] H. Chelawat, S. Vaddiraju, and K. K. Gleason, “Conformal conducting poly(3,4-ethylenedioxythiophene) thin films deposited using bromine as the oxidant in a completely dry oxidative chemical vapor deposition process,” *Chemistry of Materials*, vol. 22, pp. 2864–2868, 2010.

- [54] Q. Peng, B. Gong, R. VanGundry *et al.*, “‘zincone’ zinc oxide-organic hydrid polymer thin films formed by molecular layer deposition,” *Chemistry of Materials*, vol. 21, pp. 820–830, 2009.
- [55] M. Fabretto, K. Zuber, C. Jariago-Moncunill *et al.*, “Measurement protocols for reporting pedot thin film conductivity and optical transmission: A critica survey,” *Macromolecular Chemistry and Physics*, vol. 212, pp. 2173–2180, 2011.
- [56] R. Brooke, M. Fabretto, P. Hojati-Talemin *et al.*, “Evidence for ‘bottom up’ growth during vapor phase polymerization of conducting polymers,” *Polymer*, vol. 55, pp. 3458–3460, June 2014.
- [57] K. Zuber, M. Fabretto, C. Hall *et al.*, “Improved pedot conductivity via suppression of crystallite formation in fe(iii) tosylate during vapor phase polymerization,” *Macromolecular Rapid Communication*, vol. 29, pp. 1503–1508, 2008.
- [58] D. Evans, M. Fabretto, M. Mueller *et al.*, “Structure-directed growth of high conductivity pedot from liquid-like oxidant layers during vacuum vapcor phase polymerization,” *Journal of Materials Chemistry*, vol. 22, pp. 14 889–14 895, 2012.
- [59] M. Fabretto, K. Zuber, C. Hall *et al.*, “High conductivity pedot using humidity facilitated vacuum vapour phase polymerisation,” *Macromolecular Rapid Communication*, vol. 29, pp. 1403–1409, 2008.
- [60] M. Mueller, M. Fabretto, D. Evans *et al.*, “Vacuum vapour phase polymerization of high conductivity pedot: Role of peg-ppg-peg, the origin of water and choice of oxidant,” *Polymer*, vol. 53, pp. 2146–2151, 2012.
- [61] H. Hosono, H. Ohta, M. Orita *et al.*, “Frontier of transparent conductive oxide thin films,” *Vacuum*, vol. 66, no. 3-4, pp. 419–425, 2002.

- [62] R. Howden, E. McVay, and K. K. Gleason, “ocvd poly(3,4-ethylenedioxythiophene conductivity and lifetime enhancement via acid rinse dopant exchange,” *Journal of Materials Chemistry*, vol. 1, pp. 1334–1340, 2013.
- [63] F. Falkenberg and I. Olefjord, “Influence of mo and n on initiation and repassivation of pots on stainless steels,” in *Passivity and Localized Corrosion - An International Symposium in Honor of Professor Norio Sato*, M. Seo *et al.*, Eds., vol. 99, no. 27. Electrochemical Society, 1999, pp. 404–413.
- [64] Viton vs. buna: Which seal for your applications? Humphrey Products Corporation. Accessed March 2016. [Online]. Available: <http://www.humphrey-products.com/content/viton-vs-buna-which-seal-for-your-applications>
- [65] “Inboard helium leak test of 316 stainless steel swagelok tube fittings with stainless steel tubing,” Swagelok, Product Test Report, 2012.
- [66] 316 stainless steel swagelok tube fittings with advanced geometry back features. Swagelok. Accessed March 2016. [Online]. Available: <https://www.swagelok.com/downloads/webcatalogs/EN/MS-06-16.PDF>
- [67] Speed flanges (iso-kf). Huntington Mechanical Labs. Accessed March 2016. [Online]. Available: http://home.huntvac.com/?page_id=274
- [68] Kf to kf fittings. Ideal Vacuum Products. Accessed March 2016. [Online]. Available: <http://www.idealvac.com/subcatagory.asp?pid=KF-to-KF-Fittings>
- [69] Model 906 convection gauge controller. Duniway Stockroom Corp. Accessed March 2016. [Online]. Available: <http://mavin.com/pictures/db/terrano906-datasheet.pdf>
- [70] 5 gallon vacuum and degassing chamber. Best Value Vacs. Accessed July 2015. [Online]. Available: <http://www.bestvaluevacs.com/5gvac.html>

- [71] Om-daq-usb-2401. Omega Engineering Inc. Accessed March 2016. [Online]. Available: http://www.omega.ca/pptst_eng/OM-DAQ-USB-2400.html
- [72] High temperature heater tapes. Omega Engineering Inc. Accessed July 2015. [Online]. Available: http://www.omega.ca/pptst_eng/FGS_FGH_FWH.html
- [73] Digital pid temperature controller 220v +max.40a ssr +k thermocouple probe cable. EKS. Accessed July 2015. [Online]. Available: <http://www.ebay.com/itm/Digital-PID-Temperature-Controller-220V-Max-40A-SSR-K-Thermocouple-Probe-Cable-/311402134944>
- [74] Water blocks (liquid cold plates, liquid heat exchangers). Custom Thermoelectric. Accessed July 2015. [Online]. Available: http://www.customthermoelectric.com/Water_blocks.html
- [75] Water discharging through a hose. Accessed December July 2015. [Online]. Available: http://www.engineeringtoolbox.com/water-discharge-hose-d_1524.html
- [76] M. Itano, F. Kern, M. Miyashita *et al.*, “Particle removal from silicon wafer surface in wet cleaning process,” *IEEE Transactions on Semiconductor Manufacturing*, vol. 6, no. 3, pp. 258–267, 1993.
- [77] In-situ polymerisation. [Online]. Available: <http://www.heraeus-clevios.com/en/technology/in-situ-polymerisation.aspx>
- [78] B. Winther-Jensen and K. West, “Vapor-phase polymerization of 3,4-ethyldioxythiophene: A route to highly conducting polymer surface layers,” *Macromolecules*, vol. 37, pp. 4538–4543, 2004.
- [79] C. O’Connell, M. Higgins, H. Nakashima *et al.*, “Vapor phase polymerization of edot from submicrometer scale oxidant patterned by dip-pen lithography,” *Langmuir*, vol. 28, pp. 9953–9960, May 2012.

- [80] “Safety data sheet: 3,4-ethyldioxythiophene,” Sigma Aldrich, 3050 Spruce St., St. Louis, Missouri 63103 USA, SDS, 10 2014.
- [81] T. Prakash and J. Yeom, *Nanofluidics and Microfluidics: Systems and Applications*. Elsevier, 2014.
- [82] NIST. Resistive and hall measurements. [Online]. Available: http://www.nist.gov/pml/div683/hall_resistivity.cfm
- [83] P. Klapetek, D. Necas, and C. Anderson. Gwyddion user guide. Gwyddion. [Online]. Available: <http://gwyddion.net/>
- [84] R. Silverstein, F. Webster, and D. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed. John Wiley and Sons, 2005.
- [85] L. Yue, S. Wang, X. Zhao *et al.*, “Nano-silicon composites using poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) as elastic polymer matrix and carbon source for lithium-ion battery anode,” *Journal of Materials Chemistry*, vol. 22, pp. 1094–1099, 2012.
- [86] B. Winther-Jensen, J. Chen, K. West *et al.*, “Vapor phase polymerization of pyrrole and thiophene using iron(iii) sulfonates as oxidizing agents,” *Macromolecules*, vol. 37, pp. 5930–5935, 2004.
- [87] J. Hwang, I. Schwedeman, B. Ihas *et al.*, “In situ measurements of the optical absorption of dioxythiophene-based conjugated polymers,” *Physical Review B.*, vol. 83, pp. 195 121–195 132, 2011.
- [88] P. Camurlu and L. Toppare, *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Mullen, Eds. Springer-Verlag, 2013.

- [89] E. Kim and J. Bredas, "Electronic evolution of poly(3,4-ethyldioxythiophene) (pedot): From the isolated chain to the prisitine and heavily doped crystals," *Journal of American Chemical Soceity*, vol. 130, pp. 16 880–16 889, 2008.
- [90] F. Tran-Van, S. Garreau, G. Louarn *et al.*, "Fully undoped and soluble oligo(3,4-ethyldioxythiophene)s: spectroscopic study and electrochemical characterization," *Journal of Materials Chemistry*, vol. 11, pp. 1378–1382, March 2001.
- [91] J. Kawahara, P. Ersman, I. Engquist *et al.*, "Improving the color switch contrast in pedot:pss-based electrochromic displays," *Organic Electronics*, vol. 13, pp. 469–474, 2012.
- [92] S. Bratsch, "Standard electrode potentials and temperature coefficients in water at 298.15k," *Journal of Physical and Chemical Reference Data*, vol. 18, no. 1, 1989.
- [93] G. Juska, K. Arlauskas, and M. Viliunas, "Extraction current transients: New method of study of charge transport in microcrystalline silicon," *Physical Review Letters*, vol. 84, no. 21, pp. 4946–4949, May 2000.
- [94] A. Kumar, H. Liao, and Y. Yang, "Hole mobility in optimized organic photovoltaic blend films obtained using extraction current transients," *Organic Electronics*, vol. 10, pp. 1615–1620, August 2009.
- [95] K. Leo. Organic semiconductor world. [Online]. Available: <http://www.iapp.de/orgworld/index.php>
- [96] L. Dai, *Intelligent Macromolecules for Smart Devices - From Materials Synthesis to Device Applications*. Springer, 2004.
- [97] C. Huang, "Organic semiconductor for flexible electronics," *Cornell University*.
- [98] C. Hu, *Modern Semiconductor Devices for Integrated Circuits*. Prentice Hall, 2010.

- [99] K. Molapo, P. Ndangili, R. Ajayi *et al.*, “Electronics of conjugated polymers (i): Polyaniline,” *International Journal of Electrochemical Science*, vol. 7, pp. 11 859–11 875, December 2012.
- [100] C. Hu, *Modern Semiconductor Devices for Integrated Circuits*. Pearson Education, 2009.
- [101] A. Heeger, N. Sariciftci, and E. Namdas, *Semiconducting and Metallic Polymers*. Oxford University Press, 2010.
- [102] H. Klauk, “Organic thin-film transistors,” *Chemical Society Reviews*, vol. 39, pp. 2643–2666, 2010.
- [103] G. Horowitz, “Organic field-effect transistors,” *Advanced Materials*, vol. 10 (5), pp. 365–377, 1998.
- [104] A. Heeger, S. Kivelson, J. Schrieffer, and W. Su, “Solitons in conducting polymers,” *Reviews of Modern Physics*, vol. 60 (3), 1988.
- [105] A. Heeger, “Charge storage in conducting polymers: Solitons, polarons, and bipolarons,” *Polymer Journal*, vol. 17, no. 1, pp. 201–208, 1985.
- [106] J. Bredas, J. Themans, J. Fripiat, and J. Andre, “Highly conducting polyparaphenylene, polypyrrole, and polythiophene chains: An ab initio study of the geometry and electronic-structure modifications upon doping,” *Physical Review B.*, vol. 29, no. 12, pp. 6761–6773, June 1984.
- [107] P. Camurlu, “Polypyrrole derivatives for electrochromic applications,” *Royal Society of Chemistry*, vol. 4, pp. 55 832–55 845, October 2014.
- [108] T. Chung, J. Kaufman, A. Heeger, and F. Wudl, “Charge storage in doped poly(thiophene): Optical and electrochemical properties,” *Physical Review B.*, vol. 30, no. 2, pp. 702–710, July 1984.

- [109] J. Bredas and G. Street, "Polarons, bipolarons, and solitons in conducting polymers," *Acc. Chem. Res. UCLA*, vol. 18, pp. 309–315, 1985.
- [110] O. Bubnova, Z. Khan, H. Wang *et al.*, "Semi-metallic polymers," *Nature Materials*, vol. 13, pp. 190–194, February 2013.
- [111] R. Kline and M. McGehee, "Morphology and charge transport in conjugated polymers," *Journal of Macromolecular Science, Part C: Polymer Reviews*, vol. 46, pp. 27–45, 2006.
- [112] T. Hasegawa and J. Takeya, "Organic field-effect transistors using single crystals," *Science and Technology of Advanced Materials*, vol. 10(2), 2009.
- [113] R. Pierret, *Semiconductor Device Fundamentals*. Addison-Wesley, 1996.
- [114] E. Meyer, "Atomic force microscopy," *Progress in Surface Science*, vol. 41, pp. 3–49, 1992.
- [115] What is atomic force microscopy? JPK Instruments. Accessed December 2014. [Online]. Available: <http://usa.jpk.com/what-is-atomic-force-microscopy.432.us.html>
- [116] G. Binnig, C. Quate, and C. Gerber, "Atomic force microscope," *Physical Review Letters*, vol. 56, no. 9, March 1986.
- [117] R. F. Egerton, *Physical Principles of Electron Microscopy - An Introduction to TEM, SEM, and AEM*. Springer, 2005.
- [118] P. Griffiths and J. De Haseth, *Fourier Transform Infrared Spectrometry*, 2nd ed. John Wiley and Sons, 2007.
- [119] T. Owen, *Fundamentals of UV-visible spectroscopy*. Agilent Technologies, 2000.

- [120] B. Faust, *Modern Chemical Techniques: An Essential Reference for Students and Teachers*. The Royal Society of Chemistry, 1997.
- [121] V. Carey, *Liquid-Vapor Phase-Change Phenomena - An Introduction to the Thermodynamics of Vaporisation and Condensation Processes in Heat Transfer Equipment*. Hemisphere, 1992.
- [122] Boiling points of water at various elevations. Engineering Toolbox. Accessed December 2014. [Online]. Available: http://www.engineeringtoolbox.com/boiling-points-water-altitude-d_1344.html
- [123] R. Mortimer, *Physical Chemistry*, 3rd ed. Elsevier Academic Press, 2008.
- [124] J. Mikielwicz and D. Mikielwicz, *Chemical Engineering and Process Technology*. Encyclopedia of Life Support Systems (EOLSS), 2010, vol. 2.
- [125] Selenophene. National Institute of Standards and Technology. Accessed December 2014. [Online]. Available: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C288051&Mask=4&Type=ANTOINE&Plot=on>
- [126] H. Hertz, "On the evaporation of liquids especially mercury in vacuo," *Ann. Phys.*, vol. 17, p. 177, 1882.
- [127] M. Knudsen, "Maximum rate of vaporization of mercury," *Ann. Phys.*, vol. 47, p. 697, 1915.
- [128] M. Herman, W. Richter, and H. Sitter, *Epitaxy: Physical Principles and Technical Implementation*, ser. Materials Science. Springer-Verlag, 2004, vol. 62.
- [129] D. Moss, *Pressure Vessel Design Manual*, 3rd ed. Elsevier, 2004.

Appendix A

Electronic Theory of Polymers

A.1 Organic Semiconductor Band Formation

Figure A.1.1: Orbital Overlap in Covalent Bonds [95]

In organic chemistry the majority of bonds are covalent - a 'sharing' of electrons between atoms to complete pairs and fill orbitals. Figure A.1.1 shows a covalent double bond between two carbon atoms. For each atom in the diagram, two of p orbitals from the atom - the ones in the same grey plane as the atoms themselves - hybridize with one s -orbital to create three new sp_2 orbitals [42]. One new sp_2 orbital from each atom directly overlaps longitudinally with the other, forming a σ -bond. The unhybridized 'vertical' p_z orbitals can indirectly overlap and form a π -bond. This π -bond results in delocalized electron clouds above and below the atom as shown in the diagram.

For organic molecules to have a conduction path, a conjugated backbone formed of alternating single and double bonds is necessary. As shown in Figure A.1.2, this conjugation leads to a continuous p-orbital overlap between atoms; thus allowing delocalized electrons to move freely between atoms in the chain. If the conjugation stops, then the overlap does as well. This has important implications because the electrons can no longer move easily between orbitals - effectively localizing them. One exception to the rule is that some atoms such as nitrogen and sulfur can provide filled p-orbitals for continuous overlap between conjugated segments [96].

Figure A.1.2: Orbital Overlap in Conjugated versus Non-Conjugated Oligomers [97]

The addition of more atoms to the chain causes the bonding and anti-bonding energy levels of the p_z and sp^2 orbitals to split into more levels - adhering to the Pauli Exclusion Principle for fermions [1]. As the number of levels in the chain increases, they begin to form continuous one-dimensional bands. In organic physics, the edges of these bands are called the “Lowest Unoccupied Molecular Orbital” (LUMO) and “Highest Unoccupied Molecular Orbital” (HOMO) respectively. These LUMO and HOMO levels are analogous to the conduction and valence bands (CB and VB) respectively.

Figure A.1.3: Energy Levels of Ethylene [1]

Figure A.1.3 shows the energy levels for ethylene; the second simplest form of carbon-carbon bonding [1]. As aforementioned, with the addition of a second atom the energy levels split from two to four. Most important is the fact that the p_z or π bonding and π^* anti-bonding levels have a smaller band gap, or energy difference between their band edges, than that of the sp^2 or σ levels. For this reason the LUMO and HOMO bands from the π bonds are responsible for semiconducting/insulating properties of polymers. Another interesting fact is that in a single polymer chain, the p_z conduction or LUMO band is not continuous or in other words the electrons in the pseudo-band are localized. This is due to the lack of overlap in the p_z orbitals for the anti-bonding states. Therefore, the electrons have to hop or tunnel to neighbouring atoms; they cannot move freely as in the valence band.

Note that this model is more for an isolated polymer chain; when many polymers are in a close proximity there is intermolecular overlap which leads to a very complex system. In comparison, inorganic semiconductors like silicon have four sp^3 -hybridized orbitals and bond to form crystal lattice structures [98]. This allows for fully delocalized electrons in continuous three-dimensional bands.

Figure A.2.1: Thermal Promotion in Semiconductor Bands [99]

A.2 Free Carriers and Doping in Polymers

Recalling the continuous band structure of inorganic semiconductors, at a temperature of absolute zero the conduction band is empty and the valence band is full. In this scenario, the semiconductor is an electrical insulator since the electrons are immobilized [98]. When the temperature is increased, energetic electrons are thermally promoted to the conduction band leaving behind holes in the valence band. As shown in Figure A.2.1, the electrons in the conduction band can move almost freely since there are empty spaces available. Similarly, electrons in the valence band can begin to move since there are empty spaces available, though not quite as many. The latter concept is simplified by thinking of each hole as a quasi-particle; then with the valence band being virtually empty of holes, they can move about freely.

As shown in Figure A.2.2, the band gap - the energy difference between the conduction and valence band edges - dictates the properties of the material [100]. When the band gap is too large there are intrinsically very little free carriers in the material and it acts like an insulator. When the band gap is non-existent (or in other words there is band-to-band overlap) the material is a semimetal conductor - actual metals have partially empty conduction bands. With a band gap somewhere in between, materials will exhibit semicon-

Figure A.2.2: Band Gaps and Material Properties [98]

ductor properties. For semiconducting materials, as the temperature increases the average electron has greater energy and the odds of its thermal promotion also rise. Therefore with increasing temperature the number of free carriers will also rise coinciding with a measurable increase in conductivity. For organic materials, specifically polymers, the band gap is on average much larger compared to traditional inorganic semiconducting materials such as silicon with a band gap of around 1.1 eV. As such, there are much less free carriers at room temperature in polymers compared with silicon [29]. As a result, many polymers are intrinsically insulating and are notably used as protective sheathing for electrically conducting wire. For use in electronics, other than as insulators, they are somewhat less desirable because of this behaviour.

As previously mentioned, the overlapping π bonds in the conjugated carbon backbone allow for delocalized electrons and create a continuous 1D HOMO band [96]. However, with no holes in the valence band, charges cannot move freely and current cannot flow. In this state the polymer is not of much use, so the number of free carriers in the polymer must be artificially increased.

In inorganic semiconductors creating holes in the valence band – outside of thermal promotion – is referred to as p-type doping [100]. This is achieved by introducing electron acceptor type materials like Boron that are charge neutral but have valence electrons numbering less than four – equal to that of the intrinsic material. When forming

the covalent bonds in the lattice the p-type dopant atoms generate a deficit of electrons; though the conduction band concentration remains unchanged. Conversely, n-type doping introduces electron donor type materials such as Phosphorus or Arsenic with a valence of five or greater thus producing excess electrons in the lattice and creating electrons in the conduction band.

For polymers, n and p type doping can occur through several processes [96, 101]. Chemical doping is most similar to inorganic doping involving the introduction of foreign materials. For p-type doping, electrons are removed from the conjugated backbone via oxidization of the polymer by atoms like Chlorine or Bromine. Note that the atom is securely bonded to the polymer molecule altering its chemical structure. Conversely, atoms of alkali metals such as Sodium are used to donate electrons to the polymer via reduction.

The electrochemical doping process is similar insofar as an electrolyte intercalates into the polymer chain using an applied electric field between electrodes [96]. As the electrolyte goes into and between atoms in the insoluble polymer chain, it temporarily adds or removes electrons to the chain. When the applied field is removed or reversed and the electrolyte exits the polymer and the polymer returns to its intrinsic state.

Last is field-effect doping. As its name suggests, it is also the method of formation of the conductive channel in the organic field effect transistor. In an OFET, its semiconducting substrate is composed of polymer chains. Differing from a MOSFET, the channel is formed in an OFET by charge accumulation [102]. By applying a gate bias the polymer chains are field effect doped and become conductive. Physically, electrons or holes are drawn onto the polymer chains near the semiconductor dielectric interface hopping from neighbouring chains.

It is important to note that while polymers can be n-type doped, the new conduction electrons still have a difficult time moving through the chain since the conduction band is not as continuous and the electrons are more localized to specific atoms. This leads most polymers to be more suited to p-type doping when a conductive polymer is desired [103].

As such there has been much more research on p-doped conducting and semiconducting polymers.

Unfortunately, in order to make complimentary transistor structures both n-type and p-type are required. The use of both together in MOSFET technology to create Complimentary Metal Oxide Semiconductor (CMOS) significantly reduced the energy consumption, switching speed, and output high and low levels [29]. Luckily, the π^* anti-bonding levels can be forced into forming a continuous conduction band in the presence of large molecules such as fullerenes (e.g. C_{60} a.k.a. Buckyball). However, these polymer molecules must be artificially produced.

A.3 Charge Carriers and Transport in Polymers

The actual processes after the chemical doping of polymers are much more involved. The carriers in this case are not simply electrons or holes. When the polymer becomes doped and a charge imbalance is produced, part of the polymer is deformed thus breaking the alternating single-double bond pattern in the backbone [104]. Figure A.3.1 shows a neutral soliton in trans-polyacetylene (TPA), the simplest deformation. Not to be confused with soliton waves which can pass through each other, this soliton is non-linear excitation in the lattice displaying a wave function resembling its namesake. Electronically, solitons introduce new states at mid-band inside the band gap leading to new optical transitions. The more a chain is doped, the more deformations that are produced up to a maximum theoretical level.

This kink in the chain is a bond-alternation domain wall separating the two possible phases of conjugation. The effect of this lattice or chain relaxation can stretch over several monomer units with a soliton in PA being measured up to $14a$ - the equilibrium bond length. The surprisingly large width of the soliton facilitates movement of the deformation along the chain. More technically, the “variation of the system energy as the center of the [soliton]

Figure A.3.1: Neutral Soliton in Polyacetylene [104]

moves relative to the lattice is very small” [104]. If the deformation was localized to only one or two units, then large barriers would be present between units requiring tunnelling or hopping to circumnavigate. However, this is not the case as mobility and resulting conductivity of carriers is measured to be high, suggesting metallic transport mechanisms. Furthermore, the large width results in an effective mass on the scale of electrons validating the treatment of the soliton as a quantum particle.

There are various types of these charge carrying chain deformations that include solitons, polarons, and bipolarons [96]. Figure A.3.2 shows a few varieties of each in TPA, with differing associated spin and charge values. The polaron is a combination of charged and neutral solitons whilst the bipolaron is a combination of like charged solitons.

TPA has a twofold degenerate ground or neutral state with both phases being equal in energy - assuming an infinitely long chain. For other polymers with more complex structures such as polythiophene (PT), boasting an aromatic ring, the two possible phases of conjugation are not equivalent. Thus for the non-degenerate PT, the symmetry induced soliton cannot exist. Charge carriers are limited to polarons and bipolarons. Focus on these non-degenerate polymers will be emphasized as PEDOT is one such example.

Figure A.3.3: Non-Degeneracy in Polythiophene [105]

It has been demonstrated through several comprehensive experiments that the population and make-up of these carriers changes with the level or extent of doping in poly-

Figure A.3.2: Charge Carriers in Trans-Polyacetylene (Modified from [96])

mers [106, 107, 108]. Figure A.3.4 shows an approximation for the electronic structure at undoped, lightly doped, medium doped and heavily doped progressing from left to right. Using polypyrrole (PPy) as a case study, in the lightly doped state the first carriers to appear are polarons which introduce two new levels in the $\pi - \pi^*$ band gap. If it is p-type doped, then the polarons would appear as positively charged with only one electron in the lower state. Upon further doping the concentration of polarons increases; however, they begin to pair up and change into bipolarons that are more energetically or thermodynamically favourable [109]. In PPy bipolarons have a binding energy of 0.69 eV compared with 0.12 eV for a single polaron. Accordingly, bipolarons have a stronger geometric relaxation over the four PPy rings shown in Figure A.3.4 leading to the two gap states being further away from the band edges.

Figure A.3.4: Electronic States Introduced Through Doping in Polypyrrole (Modified from [107])

With the knowledge of carrier spin (polarons have half spin and bipolarons are spinless), Electron Spin Resonance (ESR) measurements have been performed by many researchers. Consensus is that in the light doping regime, as the doping level increases so does the ESR signal indicating a larger population of polarons. Upon further increase in doping, the ESR signal shrinks to nearly zero suggesting that bipolarons begin to dominate. At even higher doping levels, bipolaron states begin to split into bands as observed by optical studies. It is also important to note that while these new states are being introduced in the band gap they are removing states in the conduction and valence bands - widening the previously defined band gap. However, it is still theoretically possible to have the bipolaron band merge with the valence band. This would result in a partially filled valence band leading to semi-metallic properties in one dimension. Bubnova et al. [110] have reported a reduction in conductivity with increasing temperature for highly doped PEDOT consistent with semi-metal activity. Furthermore, their Ultraviolet Photoelectron Spectroscopy (UPS) measurements indicate a significant population of states above the Fermi-level coinciding with semi-metal band overlap.

Figure A.3.5: Propagation of Chain Deformations [109]

There are several different forms of charge transport, which will be briefly addressed. The first is intra-chain transport in which free carriers move along the conjugated backbone of the chain [102]. As the charge moves along the chain, the deformation also moves. This limits the speed of charge transport with phonon movement; hence the maximum theoretical speed that could be achieved would be that of sound in the polymer. As these quantum particles propagate along the chain they eventually reach the ends of polymers at which point interchain transport occurs. Note that the gaps between polymer chains often referred to as ‘grain boundaries’ are energetic barriers for carrier movement. However, contrary to common belief, they are not traps for carriers; the traps occur in the chains as localized orbitals often caused by conjugation defects. These traps contain free carriers and prevent them from contributing to current flow. Often the traps are first saturated at which point they become less problematic.

Moving on to interchain transport, it occurs when carriers switch from one chain to the next [102]. Several different vying mechanisms are theorized to be responsible for interchain transport; tunnelling, hopping, and phonon-assisted hopping are three mainstream methods mostly agreed upon by the scientific community. Hopping refers to the particle gaining energy to jump over an energy barrier and subsequently lose the energy falling back in-band. Tunnelling refers to the particle ‘warping’ through the barrier and appearing on the other side. This quantum phenomenon is only possible if the tail of the particle’s associated wave function stretches beyond the energy barrier - indicating a non-zero probability

for the particle existing in that spot. All three have in common the fact that their probability of occurrence increases with reduced energy barrier sizes between chains. This variable physically depends on the extent of “intermolecular overlap of neighbouring molecules” [102].

‘Stacking’ the π bonds on top of each other is one way in which to decrease the interchain energy barriers [102]. The delocalized p_z orbitals begin to vertically overlap to an extent, facilitating movement between chains. This aspect adds another dimension in which the carriers can travel unimpeded. This mode of interchain transport can even be more favourable than intra-chain transport in situations where there are lots of traps and defects along the chain-lengths. Since significant π bond stacking only occurs in one axis, the orientation of the polymer in the semiconductor films of OFETs is important as charge transport is mostly desired on the horizontal plane, not depth-wise.

In general, interchain transport is very important for overall carrier mobility in OFETs as the polymers chains in the substrate are not long enough to span between the drain and source so the carriers must switch between chains at some point. Furthermore, the “conjugated molecules are typically longer than the persistence length, so a charge is not expected to be able to travel the full length of a molecule before having to hop to a neighbor” [111]. It is important to note that the resulting mobilities of these polymer films in OFET structures are nowhere near that of the current industry titan, silicon. In terms of hole mobilities, the highest seen with an organic semiconductor has been around $40 \text{ cm}^2/(\text{Vs})$ though the average is closer to $1 \text{ cm}^2/(\text{Vs})$; whereas for moderately doped silicon it is at least an order of magnitude higher, sitting around $450 \text{ cm}^2/(\text{Vs})$ - with even higher electron mobilities around $1450 \text{ cm}^2/(\text{Vs})$ [112, 102].

Appendix B

Characterization of Conducting Polymer Films

There are a plethora of tests used in research and industry to characterize conducting organic films. Mirroring the same desired characteristics, many stem from a long history in the silicon industry. The tests themselves are run to determine their quality and hence applicability to devices. In this appendix, a select few tests that were available at the time will be enumerated and described.

B.1 Four Point Probe Measurement

For organic conducting films, one of the most important parameters is their conductivity or resistivity. One of the simplest and quickest methods of extraction is the four point probe test. Figure B.1.1 shows the setup for the test. Four small probes aligned co-linearly and spaced equidistantly are lowered onto the film or device under test (DUT). “Typical probe radii are 30–500 nm and probe spacing [‘s’] ranges from 0.5 to 1.5 mm” [11]. A current source is connected to the outer two probes while the inner two measure the voltage drop across the middle.

Figure B.1.1: Four Point Probe Measurement Setup [113]

Figure B.1.2 helps to illustrate why the simpler setup of using only two probes to both source the current and measure the voltage drop is not common practice. The two probe setup obviously uses two probes which are connected to Source-Measurement Units (SMUs). A current is sourced from one probe to the other and the voltage difference is measured on those probes.

Figure B.1.2: Comparison of Resistances in 2 and 4 Point Probe Measurements [11]

The total resistance measured in the 2 probe setup is given by Equation B.1.1 where R_W is the resistance of the probe and the wire connecting it to the SMU, R_C is the contact resistance between the probe and DUT, and lastly R_{DUT} is the resistance of the actual device under test. The resistances of the wire and contacts are referred to as parasitic resistances

since they reduce the voltage drop across the DUT if a fixed voltage or current is applied. Note that the current being sourced is independent of the parasitic resistances.

$$R_{Total-2Probe} = \frac{V_{meas}}{I_{source}} = 2R_W + 2R_C + R_{DUT} \quad (B.1.1)$$

With the voltage being measured across the current source, the voltage drop across the parasitic resistances R_C and R_W is included in the measurement skewing the result. With the four point probe setup, there is minimal current flow across the inner wires and contact resistances. This is due to the fact that the voltmeter has very high input impedance. As such there will be an almost negligible voltage drop across R_W and R_C which gets added onto the voltage drop measured across the DUT. With the voltmeter measuring almost exactly the voltage drop across the DUT, the resistance measurement has eliminated contact resistance.

Since there is 3D current spreading between the outer probe tips, the measured resistance is not equivalent to the sheet resistance (R_S). To obtain the sheet resistance and hence the resistivity of the DUT, the current spreading must be accounted for using modelling. For the case where the probe spacing is more than half the thickness of the sample ($s > t/2$), it can be assumed that the current spreading in the vertical direction is negligible. With that assumption in hand and for a large area sample relative to probe spacing, the sample can be treated as an infinite sheet. Given that the voltage drops logarithmically away from a point current source on an infinite sheet according to Equation B.1.2; where I is the current, ρ_s is the sheet resistivity in $\Omega/\square$, and r is the distance away from the current source in m.

$$\phi - \phi_0 = -\frac{I\rho_s}{2\pi} \ln(r) \quad (B.1.2)$$

Knowing the inner probes are spaced $1s$ and $2s$ away from the current source, the potential difference or voltage is calculated as:

$$V = \phi_1 - \phi_2 = (\phi_2 - \phi_0) - (\phi_1 - \phi_0) = -\frac{IR_S}{2\pi} \ln(r_2) - \left(-\frac{IR_S}{2\pi} \ln(r_1)\right) = \frac{IR_S}{2\pi} \ln\left(\frac{r_1}{r_2}\right)$$

$$\Rightarrow R_S = \pi \frac{V}{I} \frac{1}{\ln(2s/1s)} = \frac{V}{I} \frac{\pi}{\ln(2)} = 4.5324 \frac{V}{I}$$

To obtain the resistivity in $\Omega \bullet \text{cm}$ the sheet resistance is simply multiplied by the thickness, t , in cm. From there the conductivity is simply the inverse.

$$\sigma = \rho^{-1} = [R_S \bullet t]^{-1} = \frac{I}{4.5324 V t} \quad (\text{B.1.3})$$

B.2 Atomic Force Microscopy

The quality of polymer films is not only judged by their conductivity but several other important aspects; these include film thickness, crystallinity, conformity and chain orientation. Atomic force microscopy (AFM) is a widely used technique in modern surface science and nanoscale technology. Under good conditions AFM can yield resolution on the Angstrom scale allowing individual atoms and their spacing to be resolved [114]. This rivals Transmission Electron (TEM) and Scanning Tunnelling Microscopy (STM) and exceeds that of scanning electron microscopy (SEM). Furthermore, AFM has less restrictions on sample composition and thickness compared to TEM and STM. Figure B.2.1a shows a diagram of a typical AFM setup. AFM employs a very small and sensitive cantilevered probe tip. Extremely sensitive xy positioners in the form of piezoelectric crystals move the sample underneath the probe allowing it to laterally scan with high resolution. The cantilever is deflected by forces from the sample usually in the range of 10^{-11} N to 10^{-6} N ; deflection can be caused by electrostatic, magnetic, capillary, van der Waals, covalent and ionic forces.

Figure B.2.1: Atomic Force Microscopy

Over the years several deflection sensors have been employed. At the time of conception of the AFM - accredited to Binnig et al. [116] - an electron tunnelling sensor, also used in STM, was used in the prototype to measure deflection. However, due to several disadvantages, including sensitivity to contaminants and the magnitude of an unwanted measurable force being exerted by the tunnelling beam, other sensors were explored [114]. Optical interferometry, laser beam deflection, and capacitance sensors all exert less pressure on the probe tip under proper operating circumstances.

For the test measurements in this thesis, the AFM employed a laser deflection sensor as shown in Figure B.2.1b. The principle of operation is based on a collimated laser beam reflecting off the backside of the cantilever; the reflected beam is incident on a two or four segmented photodiode also known as a Position Sensitive Detector (PSD). As the cantilever deflects, the reflected beam changes angle and so does position on the photodiode. As the spot shifts from the middle of the diode, one segment of the photodiode becomes more illuminated than another generating more current. A differential signal is obtained which is amplified and processed by low noise electronics. Due to the use of these circuits, the resolution of the sensor is limited by the thermal noise floor.

There are several modes of operation which make it a versatile device [114, 116]. The first category of modes involves minimal movement of the cantilever and requires making 'contact'. This contact or static mode requires raising the sample with the z piezo to deflect the cantilever to an equilibrium amount. In the most common equiforce mode, as the force and deflection on the cantilever change due to several factors, the z piezo raises or lowers the sample to restore the previous equilibrium force. Slowly scanning and moving the sample up and down, the movement of the piezos are recorded giving a high resolution profile. Alternatively, the sample height can remain fixed while the change in deflection is measured; this often yields lower resolution but with higher scanning speeds. The major disadvantage of these contact methods is that due to the close proximity of the probe tip, the frictional force can damage the surface, removing weakly bound molecules. In certain instances this is acceptable but if further characterization is required, the subsequent measurements will be different.

As opposed to the static method, the dynamic method involves moving or oscillating the cantilever near its resonant frequency using a piezoelectric crystal at the end of the cantilever. The dynamic method is further sub-divided into tapping mode and non-contact mode. With non-contact modes the probe tip is spaced slightly further away around 50 Å to 150 Å. At this distance the van der Waals and other forces are still experienced by the tip but to a lesser extent. As the probe oscillates up and down in one location, the strength of the forces experienced by the cantilever fluctuate with distance to the surface. As a result, the oscillation frequency of the cantilever changes slightly. This frequency modulation (FM) is monitored closely and compared between spots in the scan to determine relative topological information. For the intermittent contact or tapping mode the oscillating probe comes much closer to the sample surface. As such, the forces cause a measurable change in the amplitude of oscillation. Compared to FM, the amplitude modulation (AM) can have a higher resolution as the forces close to the surface are much stronger. This thesis mainly

employs the tapping mode for obtaining topological information and average thickness of polymer films.

B.3 Scanning Electron Microscopy

While AFM provides the highest possible resolution, it is a relatively new and therefore less ubiquitous tool. As scanning electron microscopes (SEM) are more readily available in the lab environment, they were used almost exclusively when imaging initial films. There are many variants of SEMs with different sets of supplemental equipment or accessories. The base imaging in a SEM operates by focusing a collimated electron beam onto the sample with a small spot size, typically ~ 10 nm [117]. The primary electrons that compose the beam penetrate into the sample and interact mainly with atomically bound electrons through multiple elastic and inelastic collisions. Some of the primary electrons elastically collide and are backscattered towards the surface of the sample. A number of these electrons are reflected within range to exit the sample and be captured by the SEMs detectors forming a measurable current known as the backscattered-electron signal.

Additional base functionality of SEMs include secondary-electron imaging. As the primary electrons collide with the atomic electrons in the sample, many are excited and ejected from their atoms as “secondary electrons”. These electrons have energies on the order of tens of electronvolts (eV) making “the average distance that a secondary [electron] travels in the solid [...] very small, typically one or two nm” [117]. If the secondary electrons are generated close to the surface of the sample, and have enough kinetic energy - mostly valence electrons - they may emerge from the sample and be collected.

Figure B.3.1 shows the schematic diagram for a SEM. The electron beam is generated by a field-emission electron source or heated-filament source then collimated and shrunk through a series of condenser lenses and apertures. Since the energy range of secondary and backscattered electrons is so large, a smaller incident beam or probe must be

Figure B.3.1: Schematic Diagram of a SEM [117]

used to receive a focused image. A smaller probe leads to better resolution but captures less area. This is circumvented by the implementation of a raster scan. The x and y-axis scanning coils in the SEM are fed asymmetric sawtooth waves which generate magnetic fields to deflect the electron probe, effectively sweeping it across the substrate. Historically, CRT monitors were employed to view SEM images with the scanning coil signals also being directed to the CRT electron gun “in exact synchronism” - similarly deflecting the electrons onto the phosphor screen and mapping out the points [117]. The output signal of the detector was used to modulate the voltage across the electron gun in the monitor thus adding contrast to the perceived image.

B.4 Fourier Transform Infrared Spectroscopy

In the past, Fourier Transform Infrared Spectrometry (FTIR) was a cornerstone in chemical analysis of organic material [118]. Its position diminished with the widespread use of mass spectrometry, Nuclear Magnetic Resonance (NMR), and X-ray Photoelectron Spectroscopy (XPS). Although these aforementioned methods yield much information on the chemical

Figure B.4.1: Electronic, Vibrational, and Rotational Energy Levels [119]

structure of samples, FTIR provides further complementary knowledge which cannot be otherwise obtained. The operating principle of FTIR lies in supplying IR photons to induce transitions between the “quantized [rotational and] vibrational energy states” [118]. In doing so, a molecule’s structure is probed.

The energy difference between electronic levels is on the order of 100 kJ/mol [120]. For vibrational and rotational level differences, the differences are reduced to the orders of 1 and 0.01 kJ/mol respectively. As such, lower energy photons in the IR range are required to induce adjacent level changes. One would expect vibrational state transitions to generate discrete absorption lines in the spectrum [84]. However, vibrational state transitions must be accompanied by rotational changes as well. Since there are a multitude of rotational states to and from which transitions can occur a pseudo-continuum forms leading to broader absorption peaks or bands instead of lines. The location of absorption peaks is dictated by several variables including the relative masses of constituent atoms in a molecule, bond lengths or strengths, and geometrical arrangement. Though every molecule has vastly different and unique IR spectra, often signature peaks of specific bonds or attached functional groups and moieties can be identified. Due to the influence of other atoms in the molecule affecting geometry by rotating and stretching bonds, they do not always occur

Figure B.4.2: Michelson Interferometer

at the exact same wavenumber. Instead regions of occurrence are defined where they are oft detected. Using this knowledge, additional information on organic molecules can be gained.

Standard FTIR setups employ a Michelson interferometer as shown in Figure B.4.2. A broadband mid-IR spectra is generated by heating a filament to a specific temperature to emit blackbody-like radiation. The most prevalent source for such wavelengths is the 'Globar', a silicon carbide rod heated to roughly 1300 K [118]. The spectra is collimated into a fine beam and shone incident on a beam-splitter. For mid-IR wavelengths, the splitter is composed of KBr - which is nearly transparent in that range - and a germanium coating of exact thickness to yield 50% reflectance. After the beam splitter, these two rays reflect off fully-silvered mirrors and return to the beam splitter. Each ray splits again with half of each passing through to the detector - a pyroelectric sensor. This sensor measures very slight changes in its temperature due to the incident IR waves. It is normally sealed away in a temperature and humidity (0%) controlled environment with KBr glass as its aperture.

With the current setup described, spectral information cannot be resolved from the resulting sensor readings. This is accomplished by producing a time-dependent interfero-

gram which is subsequently Fourier transformed into the frequency domain. By moving one of the mirrors in the interferometer, the path length changes and the two incident beams develop a phase shift between each other. The mirror is accurately stepped by a piezoelectric positioner at regular time intervals to emulate a continuous constant rate movement. To obtain satisfactory resolution of less than 4/cm, scans lasting several seconds are taken.

The linear absorption coefficient (absorbance) or transmissivity of a sample of uniform thickness, b in cm, at various wavelengths - $\alpha(\tilde{\nu})$ and $T(\tilde{\nu})$ respectively - is extracted through the application of Beer's Law. It states that the "transmittance of a pure sample of thickness b (cm) at wavenumber $\tilde{\nu}$ " is given as by Equation B.4.1 where $I_0(\tilde{\nu})$ is the incident intensity.

$$T(\tilde{\nu}) = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = e^{[-\alpha(\tilde{\nu})b]} \quad (\text{B.4.1})$$

B.5 UV-Visible Spectroscopy

Similar to FTIR spectroscopy, UV-Vis spectroscopy examines transitions between electronic states in molecules. As the energy difference between electronic levels is much greater, higher energy photons corresponding to the UV (200-400 nm) and visible (400-700 nm) are employed.

In conjugated polymers, the possible electronic states which transitions can be made to and from are shown in Figure B.5.1. Note that the n -levels correspond to lone pair states which do not participate in conventional bonding. The larger the transition, the higher the photon energy needed. In the UV-visible spectrum, the most commonly observed absorption peaks are associated with $\pi - \pi^*$, $n - \pi^*$, and $n - \sigma^*$ transitions. The rest of the transitions from bonding levels are "too high a frequency to measure easily" [120]. Analogous to the intermediate rotational states between vibrational states, the intermedi-

Figure B.5.1: Optical Transitions Between Electronic States [120]

ate vibrational states between electronic states give rise to continuous bands of absorption instead of discrete lines. This phenomenon is visualized in Figure B.4.1.

The standard spectrophotometer for UV-vis measurements has few similarities. To acquire such a broad range over both the UV and visible spectra, two separate sources are often used [119]. A hydrogen or deuterium bulb for UV and an incandescent bulb for visible. These two sources are superposed by reflecting both off a mirror into one single beam. This beam is then passed through a prism or diffraction grating to spatially spread the wavelengths. A monochromatic beam of particular wavelength is selected using a slit and passed through a beam splitter or rotating segmented mirror allowing for incidence on both a reference and sample. The sample and reference are typically held inside cuvettes in solution form. The cuvettes along with other components are made from silica glass which has a lower absorption in the UV range compared to more commercially available glass. The beams exiting the reference and sample are recorded by a wavelength independent detector which records intensity as number of counts per second. To generate a spectra, the slit is shifted scanning over all the wavelengths.

Another common design exists where a full spectrum beam is passed through the sample then dispersed by a grating or prism. The output is incident on an array of non-wavelength sensitive diodes which is resolved into a spectra using the intensity registered by each diode and their corresponding spatial location.

Figure B.5.2: Typical UV-Vis Spectrophotometer Setups [119]

To obtain transmissivity or absorbance Equation B.4.1 is used again. While the transmissivity yields information on the electronic structure of materials, in this instance it can also provide important information on the performance of PEDOT as a transparent conductor for use in such devices as solar cells or touch screens. The more transmissive, the more efficient the end product will be for either collecting or emitting visible light.

Appendix C

Vaporization Theory

As many vacuum deposition systems use reactants in vapour form, the mechanics of vaporization can be extremely relevant. Vaporization is defined as the phase transition from a liquid to a gas. It is sub-divided into two categories, evaporation and boiling [121]. Boiling is a vigorous physical reaction that occurs when the average kinetic energy of all the molecules in the liquid exceeds a threshold value; this temperature is well-known as the boiling point. In this process the average molecule found in the bulk of the liquid has enough kinetic energy to break free of the attraction exerted by its nearest neighbours. Macroscopically, vapour bubbles can be seen forming in the bulk of the liquid and rapidly rising to the surface, releasing the gaseous molecules into the atmosphere. Evaporation, can occur below the boiling point of a liquid. While the average kinetic energy of a molecule is not enough to escape from the bulk liquid, some molecules do have kinetic energy which exceeds the threshold. Notably, molecules at the surface with fewer nearest neighbours experience less attraction and a lower barrier to vaporization. Thus evaporation is mostly undergone by surface molecules which have greater than average kinetic energy.

It is well known that the boiling point of water is roughly 100 °C; less known is the fact that the boiling temperature varies with elevation. Water can boil at a lower temperature at the peak of Mount Everest (72.0 °C) than at sea level (100.0 °C) [122]. This can be

Temperature Range for Fit (K)	A	B	C
234.0-387.5	3.75976	1331.417	-33.354

Table C.0.1: Antoine Coefficients for Selenophene [125]

attributed to the change in the ambient pressure. To explain this phenomenon, the concept of vapour pressure must be understood.

Consider a closed system partially filled with a pure liquid substance at thermodynamic equilibrium. Evaporation will occur with energetic molecules escaping the surface, reducing the mass of the liquid (though total mass remains constant) [123, 124]. At some point when enough vapour has been formed, the rate of evaporation and condensation will balance. The pressure exerted by the vapour on the container or system is called the ‘equilibrium vapour pressure’ or more simply, ‘vapour pressure’. For a given temperature, a higher vapour pressure indicates a higher rate of evaporation in an open environment. If the temperature of a substance is raised, then the average kinetic energy is also increased. Accordingly, more surface molecules have the energy necessary to evaporate and exert force on the container. By inference, vapour pressure must have a positive correlation with temperature. There are several different models for this relationship including the Clausius-Clapeyron Equation shown below; where P is the vapour pressure, L is the specific latent heat of vaporization, R is the gas law constant, T is the temperature, and c is a constant.

$$\ln P = -\frac{L}{R} \left(\frac{1}{T} \right) + c \quad (\text{C.0.1})$$

Another common mathematical regression for the relationship is the Antoine Equation given below.

$$\log_{10} P = A - \frac{B}{C + T} \quad (\text{C.0.2})$$

The three constants A , B , and C are often measured and reported for a variety of substances such as selenophene.

Figure C.0.1: Graph of Vapour Pressure of Water [122]

A more technical definition for the boiling point is the temperature at which the vapour pressure of the substance equals the ambient pressure. In the case of atmospheric pressure, 101.325 kPa, the boiling point of water is 100 °C, examining the vapour pressure curve for water it can be seen that at 100 °C it is approximately equal. More importantly, if the ambient pressure is lowered, the temperature required for the substance to have an equal vapour pressure is also lowered. This principle is employed to evaporate or sublime substances with relatively high atmospheric boiling points while keeping the temperature to a moderate level. To have operating pressures lower than atmospheric, vacuum vessels are employed.

To reiterate, the hydrostatic or ambient pressure acting on the liquid plays an important role in vaporization. In 1882 Heinrich Hertz investigated the evaporation rate of Mercury [126]. He discovered that the rate of evaporation depends heavily on difference of the vapour pressure, p_{vap} , and the hydrostatic pressure, p_h , acting upon it. With further research by Knudsen in 1915, it was discovered that the state of the liquid's surface also played an important role and a coefficient of evaporation, consequently α_v , was included to generalize the expression [127]. A final equation known as the Hertz-Knudsen equation,

shown below, was composed expressing the net number flux of molecules escaping, j_{HK} [128].

$$\Phi_{HK} = \frac{dN_e}{A_e dt} = \frac{\alpha_v [p_{vap} - p_h]}{\sqrt{2\pi m k_B T}} \quad (C.0.3)$$

As described by the above equation, there will be net evaporation in a closed system until the hydrostatic pressure of that particular species reaches its vapour pressure for that temperature. Conversely, when the hydrostatic pressure exceeds the vapour pressure, net condensation occurs. In standard vacuum deposition systems, a continuous pump is applied removing the gaseous species causing the hydrostatic pressure at the liquid interface to effectively be null. As a result boiling ensues until all reactant is spent or the pump rate is reduced. This pseudo steady-state system has been thoroughly studied and applied. For a pump-isolated system, the situation becomes more complex and dynamic with an ongoing competition between evaporation and condensation. The condensation can be modelled as ‘Langmuirian absorption’ with a similar expression as the above. Given a non-isothermal environment - surfaces with different temperatures - the rates of evaporation, transport, and condensation become more involved. At this point simulation of the competing processes becomes necessary.

Appendix D

Pressure Vessel Mechanical Design

D.1 Stress Calculations

Below is a sample calculation for the maximum tensile stress found at the center of a simply supported cylindrical lid, $\sigma_{max,center}$. For AISI 316 stainless steel the maximum Poisson ratio value is $\nu_{SS316,max}=0.275$. For a $t=3/8''$ thick lid that spans a gap of $d = 2r = 13.5''$, the maximum stress at the center is estimated to be:

$$\sigma_{max,center} = \frac{3[3 + \nu]pr^2}{8t^2} = \frac{3[3 + 0.275](101.325kPa)(0.17145m)^2}{8(0.009525m)^2} \cong 40.32MPa$$

Comparing this with the minimum yield strength for 316 stainless steel, $\sigma_{SS316,min} = 205MPa$, there is a safety factor of about 5x engineered with the $3/8''$ thick lid. Dropping the thickness to $1/4''$ reduces the safety factor to about 2x which was deemed to be insufficient given extra possible loading. Similarly, the corresponding deflection for the $3/8''$ scenario is given below:

$$y_m = \frac{[5 + \nu]pr^4}{64[1 + \nu]}D^{-1} = \frac{[5 + \nu]pr^4}{64[1 + \nu]} \left\{ \frac{Et^3}{12[1 - \nu^2]} \right\}^{-1} = \frac{12[5 + \nu][1 - \nu]pr^4}{64Et^3}$$

$$y_m = \frac{12 [5 + 0.275] [1 - 0.275] (101.325 \text{ kPa}) (0.17145 \text{ m})^4}{64 (190 \text{ GPa}) (0.009525 \text{ m})^3} \approx 3.82 * 10^{-4} \text{ m}$$

Thus at the center of the lid the deflection is less than 1 mm. For the cylindrical shell, a different design methodology was employed. Following code established by the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel (BPV) Handbook, a thickness was first assumed and a number of intermediate parameters were calculated with the help of graphs to estimate a collapsing pressure [129]. First, the length to diameter and diameter to thickness ratios were calculated.

$$L/D_0 = 14.5''/13.5'' \approx 1.07$$

$$D_0/t = 13.5''/(1/8'') = 108$$

Using these ratios in Figure D.1.1, a Factor A of 0.0014 was estimated for the shell. Then Factor A was used in Figure D.1.2 below to extract a Factor B of about 9000 Pa. With Factor B in hand, the maximum allowable pressure was calculated as:

$$P_a = \frac{4Bt}{3D_0} = \frac{4(9000)(1/8'')}{3(13.5'')} = 111 \text{ kPa}$$

This is just slightly above ambient pressure, thus it is suitable for full vacuum application. Note that the safety factor is already built into the ASME design process.

D.2 Finite Element Analysis Stress Simulations

In COMSOL Multiphysics Simulator, the geometry for the outer vacuum vessel was reproduced. Two separate parts were generated in the program; the cylindrical shell including

Figure D.1.1: ASME BPV Code Shell Stress - Graph of Factor A (Modified from [129])

Figure D.1.2: ASME BPV Code Shell Stress - Graph of Factor B (Modified from [129])

bottom wall, and the top lid. The shell was set at a thickness of $1/8''$, and the bottom to $1/2''$. For the lid, the thickness was set to $3/8''$ and 8 counterbored holes were included. These holes represent the bulkhead feedthroughs for the valve stems; their effect on the load distribution will be examined later. A pressure of 15 psi or atmosphere was applied to the outer surfaces with no counteracting internal pressure to emulate absolute vacuum conditions. Figure D.2.1 shows the von Mises stresses throughout the volume of the vessel as well as the resulting deflection. As can be seen, the maximum stress indicated by the colour scale is $\sigma_{lid,max}=3723 \text{ psi}=25.675 \text{ MPa}$ which falls well below the minimum yield strength of 316 stainless steel, $\sigma_{SS316,min}=205 \text{ MPa}=29.732 \text{ kpsi}$. For a thinner lid of $1/4''$ the simulation indicates a stress of over double at 7931 psi. In the cylindrical shell the stress is reduced three-fold due to the bracing by the convex shape against the pressure. Examining the deflection throughout the volume, the maximum lies at $y_{lid,max}=4.28 \times 10^{-3} \text{ in}=1.08 \times 10^{-4} \text{ m}$ or about 4 mils. The hand calculations overestimate the maximum stress and deflection by about a factor of two and four respectively.

Since both methods yield stresses of the same order of magnitude well below the minimum yield stress, the current pressure vessel design is acceptable.

Figure D.2.1: COMSOL Finite Element Simulations of Exterior Pressure Vessel

Briefly returning to the effect feedthrough holes have on the structural integrity of the lid, Figure D.2.2 shows a zoom of Figure D.2.1a around one of the eight counterbored holes. As can be seen, the stress is increased or concentrated at the edge of the holes compared to the flat surfaces nearby. The inner edge in particular, has high concentrations almost rivalling the stress found at the rim. The walls of the counterbored holes hold very well and show less stress compared to the flat surface inside and immediately surrounding the hole. Since the stress is still 10x less than the yield strength, the inclusion of the holes poses no additional faults in the lid design.

Figure D.2.2: COMSOL von Mises Stresses Near Counterbored Holes