Spatial Control of the Conductivity of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Thin Films

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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Abstract

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2016

Poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin films have undergone treatment from rapid thermal processing and direct ultraviolet irradiation at a wavelength of 254 nm. Through various characterization methods, the underlying physical changes as a result of rapid thermal annealing indicate a shift of morphology that correlates to an increase in material conductivity. Through fitting the electrical transport theory of space charge limited current carrier transportation through polymeric materials to experimental results, this shift of morphology can be linked to an increase in the effective mobility of carriers in PEDOT:PSS. Characterization subsequent to various doses of ultraviolet irradiation exhibits up to a 4 order of magnitude loss in conductivity as a result of exposure. This reduction in conductivity has been determined to arise from
a scission process induced by the high energy photons. By applying this previously unexplored direct write patterning technique using ultraviolet exposure, novel device demonstrations of patterned organic light emitting diodes as well as an all PEDOT:PSS capacitive sensing array were implemented. The key feature of such device demonstration being that no physical patterning or structuring of the device was required to obtain proper functionality. Both the rapid thermal annealing and the ultraviolet irradiation are suitable for implementation into a roll-to-roll fabrication process which is critical for taking full advantage of the benefits of polymeric electronic materials such as flexibility and low cost fabrication.
Acknowledgments

I almost feel that if I were to list and name every single individual who has helped me through the past 6 (or 7 if we’re being technical) in both an academic and personal sense, the acknowledgments could quickly become longer than my actual thesis!

However, my sincerest gratitude goes to my supervisor Professor Amr Helmy for his continual guidance, insight, and his encouragement to always push for the best scientific work possible, and to not settle for less. His willingness to offer advice, discuss results, and identify inconsistencies at seemingly any time of the day and week has been crucial in the culmination of this dissertation.

Many thanks to the members of my defense committee, Prof. Tim Bender, Prof. Zheng-Hong Lu, Prof. Wai Tung Ng and Prof. Hany Aziz as well as Professor Nazir Kherani who also served throughout my degree. All have been a pleasure to interact with and for taking the time to go through this thesis and provide critical and welcome feedback. As well, my fruitful interactions with other faculty members such as Professor Joyce Poon, Professor Ofer Levi and Professor Micah Stickel in primarily teaching capacities but also have been welcoming to discuss research activities and provide some helpful opinions.

I would like to thank TNFC, and specifically Henry Lee, Edward Xu, Yimin Zhou, and Harlan Kuntz for training, troubleshooting, problems solving, and just generally putting up with me! The assistance from the cleanroom staff has been invaluable in developing solutions and techniques for the research I’ve carried out. I would also like to acknowledge the feedback and guidance in regards to the spectroscopic ellipsometer modelling, calibration, and operation that I have received from Dr. Michelle Sestak of Horiba Jobin Yvon.

I would, of course, be remiss to forget to mention other amazing members of Professor Helmy’s group (both past and present) that I’ve spent the majority of my time both in the office and in the lab and have had the pleasure to interact with, bounce questions off
of, discuss everything from science to politics to sports along my journey including Dr. Bhavin Bijlani, Dr. Payam Abolghasem, Justin Freedman, Dr. Dongpeng Kang, Dr. Nima Zarein, Charles Lin, Herman Wong, Po-Han Chang, Yiwen Su, Sherri Cui, Rajiv Prinja, Kaustav Nag, Manuchehr Ebrahimi and Janahan Ramanan. Many thanks to other photonics colleagues who have aided me along the way, whether it be a quick conversation in the hallway, an explanation of operation in the cleanroom, borrowing of the odd tool or piece of equipment, or just distracting me with a coffee break along the way and in particular, Dr. Moez Haque, Dr. Fei Ye, Iliya Sigal, Dr. Jianzhao Li, and Dr. Luis Fernandes.

To the massive support network of friends and family in Toronto, Edmonton and elsewhere: there is absolutely no question in my mind that I would be where I am today without the assistance, love, and friendship of those around me. I owe the deepest gratitude to my parents who have continually encouraged me along the way and always been unwaveringly supportive through this chapter of my life as they have with ever other part. Finally, thanks to my fiancée, Jen, for standing with me over the years despite the continually delayed completion date. Her continued tolerance, support and love over the past many years has been overwhelming and I hope to repay her in kind someday.

I guarantee that I’ve neglected to mention someone, as I’ve been involved with a ton of amazing people over the past 7 years, so if you’re reading this and didn’t get named, I apologize profusely.

Looking back at these last 7 years at the University of Toronto, the years and experiences are all blurring into one, I’m not sure if time has flown or crawled by, but I am proud of everything I have accomplished both with an academic outlook and also a personal one – I wouldn’t change the past years for anything.
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>Alq3</td>
<td>tris(8-hydroxyquinolate)aluminum</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DUT</td>
<td>Device under test</td>
</tr>
<tr>
<td>EDOT</td>
<td>Ethylenedioxythiophene</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HFE</td>
<td>Hydrofluoroether</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>IV</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>JV</td>
<td>Current density-voltage</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LV</td>
<td>Light-voltage</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly[2-methoxy-5-(2-ethylhexyloxy)-1,4- (phenylenevinylene)</td>
</tr>
<tr>
<td>NLO</td>
<td>Non-linear optics</td>
</tr>
<tr>
<td>NPB</td>
<td>N,N’-Di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)- 4,4’-diamine</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field effect transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>OLET</td>
<td>Organic light emitting transistor</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
</tr>
<tr>
<td>SCL</td>
<td>Space charge limited</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space charge limited conduction</td>
</tr>
<tr>
<td>TIR</td>
<td>Total internal reflection</td>
</tr>
<tr>
<td>TLM</td>
<td>Transmission line measurement</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet to visible</td>
</tr>
<tr>
<td>VRH</td>
<td>Variable range hopping</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Consumer electronics and computing has been dominated by inorganic materials and in particular silicon based technologies since its inception and widespread development dating back to the discovery of the transistor in 1947. In the latter half of the 20th century, the trend of electronics has been to generate faster, and in general, smaller devices. To realize consumer demands, research into silicon based fabrication and facility control has received hundreds of billions of dollars of funding. Inorganic semiconductors have been found remarkably suitable for computing applications and devices (the most ubiquitous of which is the field effect transistor (FET)) requiring high carrier mobility and stability at common operating temperatures, along with a well-developed theoretical understanding of material characteristics and performance. However, over the past several decades, organic electronic materials have grown into a field of greater significance. The impact of organic electronics in the past two decades has been such that the 2000 Nobel Prize in Chemistry has been awarded to Heeger, MacDiarmuid, and Shirakawa for the study of conducting organic polymers.[1] Polymers being a specific type of organic material – one consisting of many repeated subunits (also known as monomers) to create a longer “chain” of material.

Organic materials have been traditionally investigated and utilized extensively in various optical system design particularly in total internal reflection (TIR) waveguides and are readily available in manufactured optical devices. Organic optical components are of interest due to their inexpensive fabrication, tunable refractive index as a result of processing techniques, transparency at key wavelengths, and the extremely varied number and variety of polymer materials available with a similarly vast range of characteristics.[2] Aside from the wide range of optically transparent polymers, exciting
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polymers exhibiting electro-optic material characteristics have also been discovered. The most influential being the investigation into the use of certain polymers as a second order non-linear optical (NLO) material. In comparison to a benchmark inorganic electrooptic material, lithium niobate (LiNbO_3), NLO polymers can exhibit much higher non-linear coefficients. This allows for lower switching voltages bordering on the sub-volt level, and in turn allows for compatible integration with current electronics.[3] With the aforementioned discovery of electrically conductive and semiconductive organic materials, the exploration into the vast potential of organics for use in a new set of devices with novel functionalities and characteristics was begun.

In contrast to inorganic electronic materials, organics generally exhibit dielectric insulating characteristics with poor electrical conductivity. However, those organic materials that do exhibit relatively high levels of conductivity can be further separated into two particular subsets: small organic molecules and \( \pi \)-conjugated polymers. Traditionally, small organic molecule films are processed under vacuum conditions and often lead to higher degrees of crystallinity in the deposited films themselves. In contrast, polymer films are usually obtained through solution based processing and deposition.[4] \( \pi \)-conjugated conductive polymers allow for disordered hopping of electrical carriers (most often p-type materials) along the polymer chain backbone, whereas in a perfectly saturated polymer no empty states are available.[5], [6] Further discussion on the charge transport mechanism in polymers will take place in Chapter 3, however it is key to note that in general the transport characteristics and conductivity are often orders of magnitude lower than in metallic or doped inorganic semiconductor materials.

Although polymeric (or “soft”) materials exhibit inferior electrical conduction properties when compared to inorganics, they have other highly desirable characteristics that has been driving the motivation into organic electronic research. The overarching ideology behind implementation of organic materials into electronic or optoelectronic devices is often not to improve on silicon device performance, but rather achieve acceptable efficiencies and performance levels while adding certain unique characteristics. Probably
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the ultimate example of such a feature is the capability of organic polymers to maintain structure and conductivity while being physically deformed: in other words flexible electronics. The capability of organic materials to offer flexibility under physical stresses while maintaining a robust structure (i.e. not shattering as a silicon wafer would), combined with preservation of electrical conductivity has contributed to an increasing number of exciting devices including flexible display screens (as shown in Figure 1.1), e-textiles, and energy storage or generation devices.[7], [8]

![Figure 1.1: Photograph of a flexible organic light emitting diode display exhibiting proper functionality under physical deformation. Figure is reproduced with permission from Fig. 6 of Zhou et al. [9] © 2006 AIP Publishing.](image)

While truly flexible consumer electronics are yet to come to fruition, the first commercial organic electronic devices have entered into the market in areas such as smart phones and televisions in the form of organic light emitting diodes (OLEDs). The use of these OLED displays has allowed for fabrication of curved, yet rigid, displays on certain televisions and cellular telephones.

The use of polymer materials also allows for thinner and lighter weight devices. This is primarily due to the allowance for a light-weight plastic or even paper based substrate replacing the traditional relatively heavy silicon or glass substrates.[10]

As polymeric materials are amenable to suspension in a variety of solutions including water, the deposition process is often drastically different compared to the low pressure
vacuum procedures used in silicon processing. This enables deposition approaches such as spin coating, or inkjet printing to create thin films of polymer materials and even control, to some degree, the spatial patterning of materials during deposition. Combined with the use of flexible substrates such as cellulose, plastic, or paper substrates, the implementation of polymers as active electrical materials can pave the way to large area solution processing of devices using roll-to-roll processing techniques. [10]-[13]

It again needs to be emphasized that the adoption of organic electronic materials as a complete replacement for silicon technologies is not a feasible approach. Organic materials suffer from reduced device performance, decreased reliability, environmental degradation and are limited by certain processing or patterning constraints. In particular, the lower carrier mobility in organic electronic materials substantially limits the speed and performance of devices.[14] Due to absorption of higher energy light, ultraviolet (UV) degradation can occur in many organic materials and devices upon exposure to environmental light.[15] Additionally, processing temperatures are limited both due to low glass transition temperatures of many organics along with the potential for carbonization and burning of such materials. There are generally two separate approaches taken for the implementation of organic electronic materials into devices: the first being a hybrid solution, where some of the components in traditional optoelectronics are replaced with organics to offer novel functionality (as is the case with curved OLED displays), the second is to design and develop fabrication architectures with the goal of realizing all-organic devices, thus removing any reliance on inorganic materials. Regardless of the approach taken, continuing research into discovering entirely new materials, or discovering techniques to alleviate the inefficiencies in organic electronic materials is required to further developments in the field.

Of particular interest among the plethora and continually growing database of conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged as a promising organic conducting material due to its favorable electrical characteristics and stability when compared with similar materials. When prepared in a polyelectrolyte complex with
poly(styrenesulfonate) (PSS) as a counterion, a combined poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) polymer is created that is not only electrically conductive, but also forms a stable dispersion in water.[16] This aqueous dispersion offers an avenue to facile and inexpensive deposition, as well as the potential for backend integration with traditional complementary metal oxide semiconductor (CMOS) fabrication technology. PEDOT:PSS has been implemented into a number of applications including solid electrolyte capacitors, antistatic coatings and electrochromic devices. Of particular interest to photonics, PEDOT:PSS has been studied as a highly transparent conductor both as a replacement for indium tin oxide (ITO), and as an additional hole transport layer in photovoltaic or light emitting diode applications.

Given the importance of transparent conducting oxides such as ITO in various optoelectronic devices, the search for a suitable replacement to integrate into flexible device design is critical. As such, significant effort has been made into enhancing the electrical conductivity of PEDOT:PSS to enable it for device implementation (specific techniques will be discussed further in Chapter 4). In order to capitalize on the cost benefits of organic materials in electronics, focus must be applied to techniques that are amenable to large scale organic fabrication processes. In other words, material modification and processing needs to occur in a manner that allows for both effective material performance as well as be appropriate for roll-to-roll processing methods. If both of these constraints are not satisfied, the advantages that solution based polymer processing inherently offers will be ineffective in comparison to vacuum techniques due to either insurmountably inferior device performance or decreased throughput leading to an unrealistically high manufacturing cost.

A second challenge with the use of PEDOT:PSS has been the lack of effective and appropriate patterning techniques. While there are several procedures being actively explored (specific examples will be discussed further in Chapter 3), none have proven themselves to be without tradeoffs. In comparison to inorganic material patterning, polymer films are susceptible to influence from a greater number of solvents or common chemicals and cleaning methods. The use of common photolithographic developers or
stripers, solvent cleaning techniques or plasma processing of PEDOT:PSS films is not always possible due to dissolution, removal, or undesirable modification of the PEDOT:PSS layer. This solvent incompatibility is a major hurdle that will need to be addressed in order to facilitate widespread application of both PEDOT:PSS or other organics in commercial fabrication flows. Compounded by the requirement that any patterning methods need to be suitable for large scale solution processing, many potential organic device applications remain primarily as laboratory demonstrations. Similar to the modification of thin film polymer properties, in order to capitalize on the lightweight, flexible, and inexpensive processing costs associated with polymer electronics, a necessary requirement for patterning is compatibility with roll-to-roll or other large scale processing to make it competitive in the market. This effectively eliminates any patterning techniques that employ standard photolithography process flows involving multiple depositions, exposures, developments and etches. In the roll-to-roll process stream that is highlighted as the most promising for large scale organic electronics, patterning is often performed through screen printing, gravure printing, flexographic printing or inkjet printing, the graphical overview of several of the most common patterning methods is shown in Figure 1.2.[12], [13], [17]-[21]
Figure 1.2: Overview of common patterning techniques such as gravure, flexographic, screen, and rotary printing in use for roll-to-roll fabrication processes. Figure is reproduced with permission from Fig. 3 of Søndergaard et al. [12]. © 2012 Wiley Periodicals, Inc.

As with most engineering issues, there are tradeoffs between the advantages and disadvantages of each of the patterning technologies. With gravure printing, the patterning speed and efficiency can be extremely high, however there is a lack of pattern variability, as a simple pattern can only be repeated many times on the substrate. On the other extreme, while inkjet printing has freedom in terms of structural pattern design, its speed and minimum critical dimension are limitations.

An alternative approach to the physical patterning of a material for proper device operation is to spatially tune the material characteristics of a layer in order to achieve the desired functionality. As a simple case study, this has been the traditional technique to form metal-oxide-semiconductor FET structures on silicon. On a classic p-type silicon substrate, n-type wells can be formed by selectively doping a specific spatial region of the substrate, leading to the desired n-type source and drain within a p-type substrate,
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despite the fact that the silicon wafer itself has not been physically patterned. While this technique is not suitable for every application or design flow, it does offer an alternative to physically removing material to pattern a material layer for a particular function. With respect to polymer materials, this approach of functionalizing as opposed to physical patterning has been implemented for a variety of functionalities. For example, through spatial UV exposure, the surface groups of polymer films can be functionalized to enable protein adhesion in microfluidic polymers allowing for determination of selective protein capture events. [22], [23] Elsewhere, a technique of using direct photopatterning for functionalization has been applied to write optical waveguides by inducing a spatial change in the refractive index of the material. [24], [25] In general, the functionalization of materials is primarily surface based for adherence of selective chemicals onto the surface of a material, however, if the effect is able to penetrate to induce changes below the surface of the film, entire regions of thin film can be tailored as deemed fit.[26]-[28]

Given the current issues with PEDOT:PSS implementation, the approach of this thesis was to explore the transfer of processing techniques from the inorganic domain that may be appropriate for large area organic material processing in order to enhance or create desirable material characteristics. Since the physical patterning of PEDOT:PSS has previously proven to be difficult in practice, the notion of spatially functionalizing its electrical conductivity for specific device applications is explored. By developing such a direct patterning process that can spatially pattern the electrical material characteristics of PEDOT:PSS, new device architectures for electronic and optoelectronic devices could be realized using minimal processing steps. In particular, a suitable application for using PEDOT:PSS is in capacitive touch screen sensing. In current touch input devices, the primary transparent conductor for implementation into a capacitive touch array is ITO. In other device architectures, PEDOT:PSS has proven itself relevant for a material capable of replacing ITO as a contact with high optical transmission across the visible spectrum on flexible substrates. In capacitive sensing design, there are a number of approaches taken to create a suitable structure for 2 dimensional (2D) spatial mapping of a touch event. The challenge with utilizing PEDOT:PSS for such a device is that the
contact material needs to be sufficiently conductive enough to allow for carrier transport to the capacitive elements with limited resistive loss and at acceptable speeds. Additionally, while PEDOT:PSS exhibits high optical transmission across the visible spectrum, thin films do exhibit a slight bluish tinge in comparison to glass slides and ITO. As such, any physical structuring of the PEDOT:PSS film will result in unwanted optical features for proper viewing. Again, a preferable structure would be one in which the PEDOT:PSS film is not patterned physically, but only resistively, resulting in limited visual aberrations for proper viewing through the film.

During the progression of this thesis, the implementation of PEDOT:PSS into a thin film capacitive touch sensor has been commercially realized in a collaboration between Heraeus and Industrial Technology Research Institute, Taiwan (ITRI). The first demonstration of a 3.5” capacitive sensor using PEDOT:PSS was reported in late September 2014, and this has been upgraded to a 7” flexible touch panel integrated with an OLED display in August 2015. [29]-[31] Interestingly, this commercial demonstration also used the approach to resistively pattern the PEDOT:PSS film as opposed to structurally patterning it. The finalized reported device structure of the integrated capacitive sensing device is shown in Figure 1.3.

![Figure 1.3: Schematic of the capacitive sensor element used in the commercial integration of a flexible PEDOT touch screen with a 6” AMOLED display from Heraeus. Figure is reproduced from Fig. 1 of [29].](image)

Heraeus technology involves a chemical patterning using a screen printing technique whereby one of their products, Clevios™ Etch, is printed onto a PEDOT:PSS film which renders the underlying PEDOT:PSS non-conductive before subsequent removal. While
this technology is appropriate for roll-to-roll printing technologies, it does have other limitations such as critical feature dimension being limited to the order of 10’s of microns. This feature size is generally acceptable for human interface devices, however, could be a limitation for other potential uses of PEDOT:PSS in optoelectronic devices that require further miniaturization.
1.1 Thesis Organization

This goal of this thesis is to provide novel and efficient processing alternatives for PEDOT:PSS that are ultimately amenable to roll-to-roll, large area fabrication. Focus will be placed on enhancing the electrical conductivity of PEDOT:PSS which is relatively low when compared to other transparent conductors. A novel method for applying a new patterning concept to the thin PEDOT:PSS film will be characterized and developed for use in electronic and optoelectronic devices that otherwise may not be realizable. Specifically, the application of rapid thermal annealing (RTA) for conductivity enhancement will be explored. The effects of changes within PEDOT:PSS as a result of annealing on the equations governing carrier transport through polymer films will be analyzed. Then, a technique of direct UV irradiation for rendering specific regions of the PEDOT:PSS film insulating as an alternative to film removal will be developed, characterized, and ultimately applied to the design and fabrication of a patterned OLED screen and a capacitive touch sensor array for spatial touch event recognition.

Chapter 1 is the introduction to the topic at hand, along with the motivation behind implementing conductive polymers into optoelectronic devices. The applicability of PEDOT:PSS as either a replacement for ITO in certain applications and the material and processing issues that need to be overcome for widespread implementation is addressed.

Chapter 2 outlines the material characterization methods and fabrication equipment used in evaluating and studying the materials and devices in question.

Chapter 3 provides an in depth background to the polymer PEDOT:PSS and its inherent material, optical, and morphological characteristics.

Chapter 4 introduces the enhancement in conductivity of PEDOT:PSS having undergone RTA and the effect that processing temperature plays on the tuning of material characteristics.
Chapter 5 explores how the particular material changes induced by RTA affect the electrical transport characteristics that govern electrical conduction through a PEDOT:PSS polymer film.

Chapter 6 introduces and studies a direct UV patterning technique to complement the enhancement in conductivity that significantly enhances the resistivity of the polymer film, but enables spatially defined device functionalization. Use in device applications is demonstrated through patterning light emission from both solution processed and small molecule OLEDs.

Chapter 7 involves the use of direct UV patterning in a novel design architecture for development and characterization of a transparent, polymer capacitive touch array.

Chapter 8 concludes the thesis and addresses future potential directions for the use of the knowledge developed within this dissertation.
Chapter 2

Experimental Methods, Techniques, and Equipment

2.1 Rapid Thermal Annealing

RTA is a specialized annealing process which differs from conventional annealing due to the temperature ramp rate of the process.[32] For comparison sake, conventional annealing has ramp rates which are on the range of 10-15°C/min., whereas RTA ovens can achieve ramp rates of up to 200°C/s. RTA results in a substantially different annealing process for several reasons: a non-equilibrium process occurs, high temperatures can be achieved with a limited thermal budget, and for effective material results the anneal time can be reduced from the order of hours down to seconds. While the application of RTA has been used for inorganic process flows to repair semiconductor defects while at the same time preventing dopant ion movement within a material, its use in organic or hybrid materials has not been widely explored. However, in a hybrid inorganic/organic CdTe nanoparticle system, RTA has proven capable of altering the CdTe core crystallinity at temperatures that would normally carbonize the surrounding organic ligands.[33]

The instrument used for RTA was an AS-One system from Annealsys.

2.2 4-Point Probe

A 4-point probe is an electronic testing device used for directly measuring the sheet resistivity of a film. It is a technique that passes current between two of the four probes, while concurrently measuring the voltage difference between the other two probes. In comparison to a simpler two terminal measurement, where the voltage is measured directly from the current supplying contacts, a four probe configuration allows for the elimination of the contact and probe resistance giving a more accurate measurement of the film resistivity. The most common probe configuration is a collinear one, in which
four identical probes are separated by equal distances in a line and is schematically displayed in Figure 2.1

![Diagram](image)

Figure 2.1: Schematic of the common collinear orientation of contacts for use in a 4-point probe measurement. Current is passed along a film of thickness $t$ between the outside probes (1 and 4), and the corresponding voltage is measured between the inside probes (2 and 3).

In this configuration, the current is supplied between the outside probes (1 and 4), and the voltage difference is measured between the inside probes (2 and 3). With known distances between the probes, a resulting effective sheet resistance can be calculated. For an infinitesimally thin film, the sheet resistance relationship between the measured voltage and current relationship is given in Equation 2-1 in which $\rho_s$ is the sheet resistance, $V$ is the measured voltage and $I$ is the applied current. The units of $\rho_s$ are in $\Omega/\square$.[34]

$$\rho_s = \frac{V \pi}{I \ln 2}$$  \hspace{1cm} \text{Equation 2-1}

When taking into consideration a real sample of finite thickness, this equation can subsequently be adapted to extract the real material resistivity of the sample through Equation 2-2, where $t$, is the thickness of the film.

$$\rho_{bulk} = \rho_s \cdot t$$  \hspace{1cm} \text{Equation 2-2}

The instrument used for 4-point probe characterization was a model 101C from Four Dimensions.
2.3 **Raman Spectroscopy**

Raman spectroscopy is an extremely sensitive optical method of analysis that allows for the characterization of low frequency vibrational and rotational modes of a material. Raman active modes are probed through the interaction of single frequency light with a material. When light is incident on a material, various scattering events occur, with the most common type of scattering being elastic Rayleigh scattering, during which photons are scattered back with the same frequency and momentum as was incident. However, in a select few interactions (at a frequency of approximately one in $10^7$ scattering events), the incident light is inelastically scattered due to the loss or gain of energy, to or from a vibrational phonon mode characteristic to a specific atomic bonds in a material.[35] There are two specific types of Raman scattering processes, the first occurs when an incident photon excites the molecule into a virtual energy state from an initial ground state. Upon relaxation, the molecule does not return to its initial ground state, but instead is lowered to an alternate allowed excited state dependent on molecular structure. In this case, the scattered photon have lost some of their initial energy to the molecular system and is referred to as Stokes Raman scattering. Conversely, there is also the probability (aside from at absolute zero) for the initial interaction of the incident photon to be with an initially excited molecular state. Upon relaxation, the molecule relaxes, not to its original excited statue, but now down to the ground state. In this situation, the scattered photon will have gained energy from the molecular system and this process is referred to as anti-Stokes Raman scattering. Figure 2.2 illustrates the aforementioned types of optical interactions that can occur upon interaction of a pump photon with a molecular system. The Stokes scattered signal is generally stronger than the anti-Stokes signal simply due to the fact at appreciable temperatures, the majority of the molecules of the material being investigated will be at ground state.
Figure 2.2: Various optical scattering events upon interaction of single frequency light with a material: a) Rayleigh scattering, b) Stokes Raman scattering, and c) anti-Stokes Raman scattering.

By optically filtering out the laser line and Rayleigh scattered light, the remaining scattered light is accumulated by a spectrometer and is reported in terms of a wavenumber (cm⁻¹) shift with respect to the pump wavelength. The collected spectrum can viewed as a molecular fingerprint of the material in question and with appropriate analysis, specific insights to the material being analyzed can be extracted. While Raman spectroscopy has significant potential in material analysis, the most challenging aspect of the technique is the fact that the Raman scattered light is extremely weak. Combined with the relative strength of the laser line and Rayleigh scattering, systems require highly efficient optical hardware in order to filter out the otherwise overwhelming contribution to the spectrum.

The instrument used for Raman characterization was an HR800 spectrometer from Horiba Jobin Yvon, and the primary probe wavelength was 633 nm.

2.4 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is often used as a complement to Raman spectroscopy. Similar to Raman spectroscopy, FTIR also probes and measures the vibrational signature of a molecule or sample. In contrast to a scattering event from a single wavelength pump laser, FTIR uses a broadband infrared (IR) source and subsequently measures the level of transmission or absorption of the sample under
test.[35] A typical absorption spectrum from an FTIR measurement will appear as a set of identifiable spectral peaks corresponding to vibrational modes that absorb specific wavelengths of light upon propagation through the film. An additional difference lies in the selection rules between the two measurement processes. For a Raman active transition, a change in polarization of the molecule is required to occur. In contrast, for an FTIR detectable vibrational mode, the molecule must undergo a change in the dipole moment of the molecule, and as such, completely symmetric molecules will not exhibit any IR absorption lines.[36] In general, due to these differing selection rules, strong Raman active vibrational transitions often exhibit weak IR absorption and vice versa, therefore, in order to build a complete vibrational spectrum of an unknown molecule or material, both techniques are often used in complement.

The instrument used for FTIR characterization was a Tensor II spectrometer from Bruker.

2.5 Atomic Force Microscopy

Atomic force microscopy (AFM) is a method of producing a three dimensional (3D) surface image of a micro or nanoscopic structure. This is in comparison to optical or electron microscopies that readily produce 2D images of images of a sample surface. An AFM measurement allows for the measurement of the z-dimension of a sample as well, or the height of the features on the sample surface. To do this an AFM uses an extremely sharp probe tip to raster scan across the sample surface and generate a topographical image of the surface itself. The probe physically interacts with the sample but in comparison with scanning electron microscopy or scanning tunneling microscopy, a conductive sample is not a requirement. For all characterization in this thesis, the AFM was operated in tapping mode. A schematic of a tapping mode orientation is shown in Figure 2.3.
In this orientation, a piezoelectric controller oscillates a cantilever with an attached AFM tip at its resonant frequency. For monitoring, a laser is focused on and reflected from the back surface of the cantilever onto an X-Y photodetector that detects the change in position of the reflected beam as a result of physical interaction with the sample surface. By deconvoluting the output response of the photodiode, a 3D surface profile of the sample surface can be created.

The instrument used for AFM characterization was a Dimension 3100 AFM from Digital Instruments.

### 2.6 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is a technique in which polarized light of different wavelengths is cast on a film, or layer of thin films at angle and the resulting reflection is carefully measured. Most often, due to thin film reflection and subsequent interference, the gathered light is elliptically polarized and the amplitude ($\Psi$), and phase difference ($\Delta$) between $p$- (ordinary) and $s$- (extraordinary) waves are calculated.[37] The relation between $\Psi$ and $\Delta$ is given below in Equation 2-3, where $\rho$ is the complex reflection ratio, and can be obtained from the ratio of the $p$- and $s$- Fresnel equations.

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta} \quad \text{Equation 2-3}$$
However, as this measurement is an indirect method of analysis, and the refractive index is not explicitly measured, an optical model of the structure using previously measured data or complex dispersion models for thin films needs to subsequently be created. By leaving at least one material or structural parameter as an adjustable variable, an iterative fitting process is then performed by rigorously calculating the reflection coefficients from the idealized model and comparing it to the measured data to minimize the error between the two. With appropriate modelling and resolving a proper fit, the material dispersion curves of the different layers can be approximated from the data. In theory, ellipsometry can be utilized for study of a wide variety of film parameters if properly modelled including thickness, roughness, refractive index, optical anisotropy, and composition.

The instrument used for ellipsometric characterization was a UVISEL ellipsometer from Horiba Jobin Yvon. The UVISEL in particular allows for characterization across the UV, visible, and IR wavelengths.

### 2.7 Ultraviolet-Visible Absorption Spectroscopy

Ultraviolet-visible absorption spectroscopy (UV-Vis) is another absorption based spectroscopy that measures the absorption or transmission of a range of wavelengths of light through the sample under test. It is distinct from FTIR since higher energies of light are used, and as such, the primary absorption mechanism characterized is not the vibrational spectrum of the film but rather the electronic transitions that may take place in a sample. Upon transmission of light through a film, a certain portion is absorbed according to the Lambert law shown in Equation 2-4.[35]

\[
-\log_{10}\frac{I}{I_0} = \alpha l = A
\]

Equation 2-4

In Equation 2-4, \(I_0\) is the initial intensity of light impinging on the sample surface, \(I\) is the measured intensity upon transmission through the sample of path length \(l\), \(\alpha\) is the attenuation coefficient and \(A\) is the absorbance or optical density of the sample. Using this simple characterization, information as to the allowed energy bandgaps and
electronic transitions can be obtained, and in particular, the transparency of the sample for applications requiring visible light transmission can be measured.

The instrument used for UV-Vis spectroscopy was primarily a Lambda 11 Spectrophotometer from Perkin Elmer, however, transmission results were also obtained using the UVISEL ellipsometer.
Chapter 3

PEDOT:PSS Background

An overview of the chemical and physical characteristics of PEDOT:PSS is presented in Chapter 3, with focus on the physical structure and material characteristics of PEDOT:PSS films.

PEDOT is a π-conjugated system of ethylenedioxythiophene (EDOT) monomers creating a polymer chain backbone.[16] Of particular interest early in the discovery of PEDOT, was the oxidative reactions that EDOT would undergo in creating conductive polymeric chains in the presence of appropriate counterions. In general, however, the PEDOT polymer is insoluble in most solvents including water, making it difficult to be fabricated into a readily dispersible solution for industrial or commercial applications. Of particular importance, was the discovery that during polymerization, if polystyrene sulfonic acid was implemented as a counterion to PEDOT, the resulting formulation was readily dispersible in water. It for this reason that the readily processable form of aqueous PEDOT is purchased as a PEDOT:PSS formulation.

3.1 Energy Level Structure of PEDOT:PSS

PEDOT has a forbidden bandgap estimated from of ~1.6-2.2 eV between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO) depending on deposition process, doping, and measurement technique.[33]-[42] Inorganic materials with this large of a bandgap are often categorized as semiconducting or insulating and it is not until material doping takes place that relatively high conductivity is observed. PEDOT:PSS is classified as a p-type polymer, due to its readily electron accepting behavior, however, the process of polymer doping is inherently different from that of inorganic semiconductors. In contrast to silicon, which can be p- or n-type through appropriate choice of substitutional implantation, the p-type doping of
PEDOT:PSS is actually a chemical reaction. During synthesis, the reaction between PEDOT and the PSS counterions results in the oxidizing of the PEDOT and introduces new electronic states in comparison to neutral PEDOT. Also in contrast to inorganic semiconductors, the subsequently introduced charge states are not stored as an excess hole concentration in the valence (or LUMO) band. In conductive polymer p-type doping, the oxidation reaction and introduction of charge carriers leads to a deformation of the entire polymer chain surrounding the oxidation site. This combined charge and lattice distortion in the surrounding material vicinity is referred to as a polaron.[43]-[45] During the doping of PEDOT, excess charge storage is maintained in the form of both polarons and bipolarons (a coupled pair of polarons). These quasiparticles in turn introduce interband energy levels between the HOMO and LUMO level leading to the phenomenon of conductivity in a normally insulating materials.[33] A depiction of this energy level transition is shown in Figure 3.1.

![Energy level depiction of a) Neural PEDOT, b) PEDOT with a polaron state introduced, and c) PEDOT with a bipolaron state introduced.](image)

Due to the fact that polarons obey Fermi-Dirac statistics, with high enough levels of doping, new energy bands within the energy gap of PEDOT are formed, allowing for a variety of new energetic transitions and leads to the relatively high material conductivity observed.
3.2 **Morphological Structure of PEDOT:PSS**

The PEDOT chain within PEDOT:PSS can organize into two different morphological forms: benzoid or quinoid.[47]-[49]. The chemical schematics of benzoid and quinoid PEDOT along with the PSS counterion are shown in Figure 3.2 a) and b) respectively.

![Diagram of PEDOT and PSS](image)

*Figure 3.2: a) Benzoid and b) quinoid morphological forms of the PEDOT polymer.*

The difference between the two being that in the quinoid form, the \( \pi \)-bond is oriented along the polymer backbone between individual EDOT monomers as opposed to between carbon atoms within the thiophene ring in the benzoid form. In the quinoid form, due to the fact that the \( \pi \)-bond is distributed along the polymer backbone chain, it leads to enhanced charge transfer along the length of the polymer.[47], [48] The quinoid form subsequently leads to higher charge delocalization along the polymer chain backbone. Additionally, it has been postulated that the difference in morphological form energetically results in a difference in polymer chain conformation, such that the benzoid form tends to form a polymer structure with coil conformation, while the quinoid form leads to a more linear or extended-coil conformation.[47] The quinoid form of PEDOT:PSS ultimately leads to a material with higher conductivity due to the difference
in polymer chain conformation along with the higher charge delocalization of the charge from the polymer backbone.

3.3 Physical Anisotropy Due to Spincoating Deposition

One of the processing advantages of PEDOT:PSS is its deposition from a water stable dispersion. This allows for nearly universal compatibility with most material systems, as well as enabling facile and inexpensive deposition procedures compared to inorganics that often require vacuum based deposition. The as-purchased PEDOT:PSS formulation in water is a suspension of colloidal gel particles of conductive PEDOT particles surrounded by insulating PSS. It has been confirmed that this phase segregation between the conductive PEDOT areas and the insulating PSS material is maintained upon deposition.[51] Specifically, upon spincast deposition and evaporation of the aqueous solvent, the polymer gel particles flatten to create a layered, lamellar structure of PEDOT grains with sizes on the order of 20-25 nm diameter and 5 nm height.[52], [53] These regions are surrounded and isolated by a thin PSS layer of ~3-4 nm. A schematic of the lamellar film structure is illustrated for clarity in Figure 3.3.

![Figure 3.3: Cross-sectional view of the morphology of a spin-cast PEDOT:PSS film. The PEDOT region is identified by the dark grey color with diameter (d) and height (h). The PSS is shown as a lighter colored film separating the PEDOT grains. Figure is reproduced, with permission, from Fig. 3 of Nardes et al. [53] © 2007 Wiley-VCH Verlag GmbH & Co. KGaA](image-url)
Finally, this leads to a morphologically anisotropic thin film due to the difference of size and ratio of PEDOT to PSS in the directions parallel and perpendicular to the substrate. This anisotropy introduces a number of important material characteristics that must be accounted for in experimental characterization and device design.

3.4 Electrical Conduction Characteristics of PEDOT:PSS

The commonly accepted model for electrical conduction in disordered \( \pi \)-conjugated polymer systems has been developed and is referred to as “hopping” between localized charge carriers (usually polaron or bipolarons). The description of the current conduction mechanism is described through Mott variable ranged hopping (VRH) in a disordered material, whereby a charge carrier carry has an inherent probability to hop from its present state to another localized nearby state at energy levels close to the Fermi energy \((E_F)\).\(^{[53]-[55]}\) Energetic transitions are made possible through interaction with phonons in the disordered material. This leads to a temperature dependent conductivity in the material described by Equation 3-1. Where \( \sigma_0 \) is the limit of conductivity at high temperature, \( T_0 \) is the characteristic temperature of the material, and \( D \) is the dimensionality of the hopping transport process.\(^{[54], [56]}\)

\[
\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{D}} \tag{3-1}
\]

This temperature dependent conductivity change is in contrast to metals, where conductivity decreases with increased temperature. Due to the physical anisotropy of the PEDOT:PSS film when spin cast, electrical conduction in PEDOT:PSS film also displays distinctly anisotropic characteristics, with the in-plane conductivity relationship following a temperature dependency of either \( T^{-1/2} \) or \( T^{-1/4} \), or exhibiting characteristics of 1 dimensional (1D) or 3D VRH respectively.\(^{[56], [57]}\) However, in the out of plane direction, PEDOT:PSS conductivity exhibits a temperature dependency of \( T^1 \), which, in contrast, cannot be explained using the VRH model, as a dimensionality of 0, would be necessary which is impossible. Rather, this temperature dependent conductivity is
governed by the conduction process of nearest neighbor (or Miller-Abrahams) hopping.[52], [54] Across literature, the widespread conflicting reports and conductive behavior of PEDOT:PSS is mostly due to varying PEDOT:PSS grades, deposition methods, and substrate materials.

3.4.1 Secondary Doping Conductivity Enhancement

A variety of approaches have been employed to enhance the conductivity of PEDOT:PSS films either by changing deposition parameters or through post deposition processing. These techniques are generally described as secondary doping processes, with the primary doping being that during the initial synthesis of the PEDOT:PSS solution, to introduce an initial conductivity into the material.[58]

The most widespread technique is through the use of various solvents to either treat the film post deposition, or alternatively be introduced as an additive to the original PEDOT:PSS solution pre-deposition. Both techniques exhibit similar results in that the conductivity when compared to as-grown PEDOT:PSS films is greatly enhanced, in some cases up to 2-3 orders of magnitude depending on the initial grade of the PEDOT:PSS material.

In particular, polar organic solvents with high boiling points such as ethylene glycol (EG) and dimethyl sulfoxide (DMSO), appear to provide the greatest enhancement. Through the use of these solvents to enhance the PEDOT:PSS, conductivities approaching 2000 S cm$^{-1}$ have been reported.[59] Further discussion of secondary doping materials and additives will be covered in Chapter 4.

3.5 Patterning Techniques

Due to the tendency of PEDOT:PSS to be sensitive to certain organic solvents, oxygen, and UV radiation, classical optical lithography materials cannot be directly used for PEDOT:PSS films. To resolve this obvious limitation, a variety of techniques have been
investigated in order to physically structure PEDOT:PSS films.[60] The most common techniques being specialized optical lithography (3.5.1), shadow masking (3.5.2), laser ablation (3.5.3), and stamping (3.5.4), are briefly outlined in the following sections. While each of these techniques has unique capabilities, they also have certain limitations that ultimately detract from the exciting and advantageous material benefits of organic materials – primarily inexpensive, large scale fabrication using roll-to-roll processing.

3.5.1 Specialized Optical Lithography
While there is an extremely wide choice of resist, developer, and etchant chemistries available for patterning inorganic material systems, only a single specialized system has been shown capable for lithographic patterning of PEDOT:PSS films. This system is based on hydrofluoroethers (HFEs) and corresponding solvents.[61], [62] This chemical system is of particular interest since it is nonreactive with organic materials that do not contain fluorinated constituents. A secondary material requirement is that the photoresist be insensitive to the acidic nature of PSS in the PEDOT:PSS films to prevent feature loss resulting from unwanted etching or reaction between the photoresist and the PEDOT:PSS film. Taking both of these material constraints into account, physical patterning using optical lithography has been demonstrated using HFE-7600 as a photoresist, exposure using 365 nm or 248 nm sources, resist development using HFE-7200, etching using oxygen, and subsequent resist removal with propan-2-ol (10%)/HFE-7100. Using a compatible combination of different HFEs and UV exposures, sub-micron patterning was proven that still preserved the conductivity of PEDOT:PSS films. Alternatives to direct optical lithography have also implemented modified lift off techniques using parylene as a mechanical lift off layer.[63]

3.5.2 Protective Layer
Another widely used method of patterning PEDOT:PSS is through the patterned deposition of a protective layer on top of the film through a shadow mask, followed by subsequent plasma etching step. The critical drawback using this technique is that the overlying protective material often cannot be removed, so it must remain and be
implemented into the final device design structure. Such patterning has been demonstrated using a wide variety of protective materials including metals, inorganic insulators along with other organic materials.[60], [65] [66]. The etching plasma gas chemistry can be varied to include both non-reactive argon sputtering and oxygen plasma which is commonly utilized for the removal of many organic materials. A study comparing the etching of PEDOT:PSS with three different gases: CHF₃, O₂, and Ar, observed that although oxygen plasma initially had a higher etch rate (400 nm/min.) when compared to CHF₃ (140 nm/min.), and Ar (40 nm/min.), it did not maintain that constant rate, and would decrease significantly (to 70 nm/min.) after 10 minutes of material etching.[60] If complete removal of a submicron PEDOT:PSS layer is desired oxygen plasma is an adequate gas, however, if a controlled and precise etch depth is required, argon or CHF₃ may be preferred.

3.5.3 Laser Ablation

Material ablation of the PEDOT:PSS films through the use of lasers has been demonstrated for micropatterning. At sufficient fluence levels depending on laser wavelength, the bonds in PEDOT:PSS can be either optically or thermally activated to result in material expulsion from the substrate.[67] Both UV and IR lasers have been shown to achieve ablation of the PEDOT:PSS films due to the higher absorption coefficients of the film outside of the visible range.[68], [69] While this offers a direct and efficient patterning method, several limitations of the process include the transfer of thermal energy to underlying material layers, critical dimensions that are on the order of microns, and uneven material removal.

3.5.4 Stamping

Stamping or micro contact printing is a technique whereby PEDOT:PSS is deposited on a patterned stamp (often made from polydimethylsiloxane (PDMS)) and subsequently brought into contact with a pre-treated substrate resulting in the spatially selective adherence of the PEDOT:PSS to the substrate.[70] Alternatively, the complementary technique referred to as casting can be applied where a thick PEDOT:PSS layer is
initially spun onto the substrate, and then, upon the pressurized application of the stamp, a desired pattern can be achieved.[60] Both of these process flows are shown schematically in Figure 3.4. While stamping has the capabilities of producing extremely narrow linewidths and is generally compatible with roll to roll fabrication systems, challenges can arise with changing pattern design, stamp deterioration, and proper interfacial molecular adhesion to the substrate.

![Fabrication Flow Diagrams](image)

Figure 3.4: Two fabrication flows using PDMS stamps for the patterning of PEDOT:PSS films. Figure is reproduced, with permission, from Fig. 5 of Charlot et al. [60] © 2013 Springer-Verlag Berlin Heidelberg.

### 3.6 Optical Characteristics

Of particular interest to this thesis are the optical characteristics of PEDOT:PSS. The key characteristic of PEDOT:PSS, leading to its widespread commercialization, has predominantly been its transparency across the visible region. To illustrate this, the transmission, absorption and reflection characteristics of pristine PEDOT:PSS are shown in Figure 3.5 a) and the effects of varying film thickness on transmission are shown in Figure 3.5 b).
Figure 3.5: a) Transmission, absorption and reflection spectrum of PEDOT:PSS Clevios PH. b) Relative transmission with respect to film thickness. Figure is reproduced with permission from Fig. 3 of Heraeus-Clevios trade article. [46]

Figure 3.5 not only demonstrates the transparency of the film in the visible region, but also the significant absorption in the UV below 300 nm, as well as the onset of absorption in the IR due to excess free carrier absorption.

An additional unique characteristic of the films stems from its morphological anisotropy. As discussed previously, it has been shown that the physical anisotropy translates in to an electrical conduction anisotropy, however, it has similarly been found to exhibit optical anisotropy.[71] The measured anisotropic differences are shown from a previous study are shown in Figure 3.6 as the differences between the parallel and perpendicular (with respect to the substrate) real and imaginary components of refractive index and absorption coefficient are compared.
Figure 3.6: Optical anisotropy of the real refractive index (top), imaginary refractive index (middle), and absorption coefficient (bottom). Figure is reproduced with permission from Fig. 4 of [71] © 2002 Elsevier Science B.V..

These results, clearly show the optically anisotropic behavior of PEDOT:PSS with a lesser real refractive index and a greater extinction coefficient in the parallel as opposed to the perpendicular direction. This optical anisotropy is attributed to the difference in the relative amount of PEDOT to PSS in the individual indices. By treating the film as being comprised of varying amounts of the individual polymers PEDOT and PSS separately, the ratio of PEDOT to PSS in axis parallel to the substrate is substantially higher than in the normal axis. In other words, the optical characteristics in the parallel direction are much closer to that of only PEDOT and in the perpendicular direction is a more even combination of PEDOT and PSS. Looking critically at the refractive index curves, this makes intuitive sense as the parallel characteristics represent closely a material with high carrier concentration: high absorption and low refractive index, similar to some metals. In the normal axis, the material exhibits characteristics more typical of a
traditional dielectric polymer. While there have been no particular studies that utilize this feature of PEDOT:PSS in device application or design, it may be employed in future engineered structures.
Chapter 4

Conductivity Enhancement from Rapid Thermal Annealing

As discussed in Chapter 3, PEDOT:PSS has several advantageous material characteristics stemming from its organic nature, yet it also has a number of challenges to overcome. A primary concern is its relative conductivity when compared to traditional inorganic conductors, particularly transparent ones such as ITO.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>$6.30 \times 10^7$</td>
<td>[72]</td>
</tr>
<tr>
<td>Gold</td>
<td>$4.10 \times 10^7$</td>
<td>[72]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>$3.50 \times 10^7$</td>
<td>[72]</td>
</tr>
<tr>
<td>ITO</td>
<td>$\sim 1-2 \times 10^5$</td>
<td>[73]</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>$1 \times 10^1 - 1 \times 10^4$</td>
<td>[46]</td>
</tr>
<tr>
<td>Heavily Doped Silicon</td>
<td>$2 \times 10^6$</td>
<td>[74]</td>
</tr>
<tr>
<td>Intrinsic Silicon</td>
<td>$3.1 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>Silicon Dioxide</td>
<td>$10^9 - 10^{16}$</td>
<td>[75]</td>
</tr>
</tbody>
</table>

Table 4.1 outlines the conductivities of a variety of common inorganic materials used in semiconductor device design as well as the inclusion of PEDOT:PSS. The conductivity of PEDOT:PSS is highly variable depending on secondary doping and processing, but is still, in most cases at least an order of magnitude lower than ITO.
4.1 Techniques to Enhance Conductivity of PEDOT:PSS

As touched upon, a variety of approaches have been taken in an attempt to increase the conductivity of thin PEDOT:PSS films. By far the most common, and that currently suggested by the largest manufacturer of PEDOT:PSS (Heraeus-Clevios), is to introduce a polar high-boiling point miscible solvent such as DMSO to the dispersion prior to spincasting the film.[76],[77] While the enhancement effect is largest when using these high boiling point solvents, other additives such as various ionic liquids and alcohols have also been found to increase material conductivity.[47], [76]-[78]

Implementation of small amounts of secondary materials such as carbon nanotubes, graphene, and ZnO or silver nanoparticles into the PEDOT:PSS film have also been shown to enhance thin film conductivity, though not through direct modification of the polymer film itself.[79]-[82]

Another approach involves the use of post deposition processing, which is desirable to allow for selective tuning of material characteristics for a specific application or device. Such processing techniques provide the design engineer with additional tools to adapt, or selectively tailor material properties as desired.

A post-deposition processing method similar adding a secondary solvent to the aqueous dispersion is to chemically treat the as-deposited PEDOT:PSS films. Again, a wide variety of chemical treatments have been explored with varying levels of success including organic and inorganic acids and polar solvents.[83]-[86] Post-deposition treatment removes the requirement of changing the initial dispersion chemistry and as such the film conductivity can be adjusted (only if desired) after the initial deposition.

An alternative post-deposition treatment to solvent treatment is the use of thermal annealing. Different experiments report varying effects of post-deposition annealing, from both a modest enhancement of electrical conductivity to a significant decrease in some cases.[77], [87], [88] This variability in results is a common occurrence when dealing with
PEDOT:PSS experiments due to the wide variety of starting material formulations, processing or deposition conditions, and laboratory environments. What is observed in most cases however, is an increase of material conductivity when treated with temperatures up to ~200-250°C, followed by an onset of conductivity decrease at higher processing temperatures due to material degradation. This conductivity increase has been seen to translate directly into improved device performance of OLEDs and photovoltaic (PV) cells.[87], [89]

4.2 Rapid Thermal Annealing Effects on PEDOT:PSS Films

Previous experiments have initially investigated the morphological changes induced in PEDOT:PSS films and have shown that RTA allows for heating up to 300°C before observed material degradation begins to occur.[90] While the film conductivity and electrical devices were not explicitly investigated, Raman spectroscopic characterization of the annealed PEDOT:PSS films suggested an increase in doping with annealing temperature, along with the transformation into a more PEDOT rich surface through AFM and x-ray photoelectron spectroscopy (XPS).

To study the electrical effects of RTA on the PEDOT:PSS films, three characterization techniques were used: ITO/PEDOT:PSS/Al structures were fabricated to investigate the conductivity perpendicular to the substrate, along with 4-point probe and transmission line measurement (TLM) structures to investigate the material conductivity parallel to the substrate. Annealing temperatures were constrained to 200°C, not specifically due to PEDOT:PSS constraints, but rather, due to a limitation of the commercially purchased ITO substrates. Initial electrical characterizations appeared to exhibit extremely variable breakdown characteristics of the diodes, before it was discovered RTA at temperatures above 200°C results in deterioration of the ITO substrate. To confirm this hypothesis, a control batch of ITO was processed separately without PEDOT:PSS deposition and electrically characterized. While the first several voltage sweeps (from -5 to 5 V) through the ITO resulted in the expected ohmic conduction, with repeated bias, significant
electrical degradation could be observed. Figure 4.1 shows the effects of 25 consecutive voltage sweeps of ITO films annealed at temperatures between 200 and 300°C. At temperatures above 200°C, significant, non-linear electrical effects are apparent after even 5 repeated bias sweeps due to ITO contact degradation.

![Graphs showing current-voltage characteristics](image)

Figure 4.1: Effect of repeated bias on the current-voltage (IV) characteristics of commercial ITO substrates having undergone a) no secondary annealing, and RTA processing at b) 200°C, c) 250°C, and d) 300°C.

4.2.1 Electrical Conductivity Characterization

With the substrate limitation of ITO, annealing of the PEDOT:PSS films for electrical characterization was performed at 150, 175, and 200°C. The annealing took place in an inert Argon atmosphere, with a temperature ramp rate of 25°C/s before a 30s hold at maximum temperature. The annealing chamber is not actively cooled, so the cooling rate is determined solely through interaction with the gas flow through the chamber and blackbody radiation. A graph of the ideal and actual temperatures during a typical 30s anneal at 200°C is shown in Figure 4.2.
Figure 4.2: Graph depicting a typical RTA process at 200°C of pyrometer temperature (black line) and set point temperature (red) plotted against the overall time of the complete process flow. The minimum readable temperature from the pyrometer is 100°C resulting in the discrepancy below 100°C.

The TLM structures consisted of aluminum contacts with side lengths of 500 μm, thermally evaporated onto the polymer films through a shadow mask. For this experiment, the PEDOT:PSS film was spun at 1000 RPM for 45s followed by a 5 minute soft bake at 105°C resulting in approximately a 300 nm thick film. The distance between contact pads was designed to vary from 300 to 3550 μm. The IV relationship and subsequent resistance measurements were obtained using a HP4155 Semiconductor Parameter Analyzer.

Figure 4.3: Plotted measured values comparing the absolute resistance between pads compared to lineal distance in a TLM study. Linear curve fits have been applied to the data and are shown as dashed lines overtop the
data. The unannealed curve is shown in black, 150°C in red, 175°C in blue, and 200°C in green.

In Figure 4.3, the raw resistance measurements from the TLM structure are shown. By performing a linear fit of the resistance with respect to distance, an estimation of sheet resistance can be extracted by multiplying the slope of the fit by the width of the contacts. In this case, the sheet resistance values could be seen to decrease monotonically with increased annealing temperature as shown in Table 4.2. This decrease in sheet resistance was confirmed using a traditional 4-point measurement obtained by a Four Dimensions Model 101C 4-point probe. The results of the 4-point measurements are shown in Table 4.3. While not displaying identical measurements, the values are on the same order of magnitude, and more importantly, highlight the same trend of a decrease in sheet resistance with an increase in annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope $(\Omega/\mu$m$)$</th>
<th>Intercept $(\Omega)$</th>
<th>Sheet Resistance $(\Omega/\square)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>0.12265</td>
<td>1121</td>
<td>61</td>
</tr>
<tr>
<td>150°C Annealed</td>
<td>0.10792</td>
<td>389</td>
<td>54</td>
</tr>
<tr>
<td>175°C Annealed</td>
<td>0.08461</td>
<td>442</td>
<td>42</td>
</tr>
<tr>
<td>200°C Annealed</td>
<td>0.07328</td>
<td>373</td>
<td>36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sheet Resistance $(\Omega/\square)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>76</td>
</tr>
<tr>
<td>150°C Annealed</td>
<td>33</td>
</tr>
<tr>
<td>200°C Annealed</td>
<td>25</td>
</tr>
</tbody>
</table>

From the TLM results, an additional change in regards to contact resistance with the aluminum can be extracted. From the $y$-intercept values obtained from the linear fit to
data as shown in Table 4.2, it is observed that with increased annealing temperature, the intercept decreases. While there is a deviation in the results after annealing at 175°C, this is simply associated with measurement error. By annealing at 150°C, the intercept (and associated contact resistance), decreases by a factor of 2.88. Creating an ohmic contact to PEDOT:PSS is critical to device performance, and simply by applying a 30s rapid anneal at 150°C, the conductive interface from Al to PEDOT:PSS can be improved. The actual contact resistance at each contact is the half of the intercept so in the best case scenario with annealing at 200°C, the resistance at each contact is approximately 137 Ω in comparison to that of 560 Ω of the unannealed film.

4.2.2 Raman Spectroscopy of PEDOT:PSS Having Undergone RTA

In order to further analyze the physical effects of RTA on the PEDOT:PSS thin films, two non-destructive characterization methods were performed on the PEDOT:PSS samples. The first being an optical characterization using Raman spectroscopy, and the second being a physical characterization of the PEDOT:PSS surface using AFM.

4.2.2.1 Raman Spectroscopy Applied to PEDOT:PSS Films

Raman spectroscopy has been used previously to analyze PEDOT:PSS systems as well as a theoretical evaluation of the Raman modes inherent to an EDOT monomer.[91] This enables a sound theoretical and experimental foundation to base the analysis of the effects of RTA on the thin PEDOT:PSS films. A typical spectrum acquired from a thin 100 nm PEDOT:PSS film on silicon is shown in Figure 4.4 overlaid with the normalized spectrum of the silicon substrate the film was spun on. The identifiable Raman modes associated with the PEDOT:PSS after the silicon background is removed are found in Table 4.4.
Figure 4.4: Sample Raman spectra from 110 to 2000 cm$^{-1}$ of PEDOT:PSS on a silicon substrate shown in red. The overlaid black trace is that of the silicon substrate.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Mode Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>438</td>
<td>Oxyethylene ring deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>578</td>
<td>Oxyethylene ring deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>704</td>
<td>Symmetric C-S-C deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>855</td>
<td>O-C-C deformation</td>
<td>[92]</td>
</tr>
<tr>
<td>988</td>
<td>Oxyethylene ring deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>1098</td>
<td>C-O-C deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>1133</td>
<td>C-O-C deformation</td>
<td>[91]</td>
</tr>
<tr>
<td>1240</td>
<td>C$<em>{\alpha}$-C$</em>{\alpha}$ (inter-ring) stretch + C-H bend</td>
<td>[91]</td>
</tr>
<tr>
<td>1260</td>
<td>C-C (inter-ring) stretch</td>
<td>[91]</td>
</tr>
<tr>
<td>1367</td>
<td>Symmetric C-C stretch</td>
<td>[91]</td>
</tr>
<tr>
<td>1430</td>
<td>Quinoid type C$<em>{\alpha}$-C$</em>{\beta}$ (-O) symmetric stretch</td>
<td>[93]</td>
</tr>
<tr>
<td>1450</td>
<td>Benzoid type C$<em>{\alpha}$=C$</em>{\beta}$ (-O) symmetric stretch</td>
<td>[93]</td>
</tr>
<tr>
<td>1535</td>
<td>Asymmetric C-C stretch</td>
<td>[91]</td>
</tr>
<tr>
<td>1561</td>
<td>Doping induced asymmetric C-C stretch</td>
<td>[98]</td>
</tr>
</tbody>
</table>
For analysis specifically of the conductive PEDOT polymer, the wavenumber region of interest is located from 1000-1600 cm\(^{-1}\), since the lower wavenumber modes are primarily associated only with the insulating PSS.

4.2.3 Raman Characterization of PEDOT:PSS Having Undergone RTA

Raman spectra of the films annealed at different temperatures were obtained and the overlay of the results are shown in Figure 4.5. The spectra have been normalized to the magnitude of the silicon mode at 940 cm\(^{-1}\) and offset for clarity with the unannealed at the bottom (black) up to the sample annealed at 200°C at the top (green). While the magnitude of the Raman signal from the PEDOT:PSS film appears to be increasing with annealing temperature in comparison to the unannealed sample, there are a number of uncontrolled variables during measurement that can alter the signal intensity such as the film thickness at the specific measurement location, inconsistent focus between samples, and variability in signal from the underlying silicon substrate.

![Figure 4.5: Overlay of complete Raman spectra of the annealed samples. The spectra correspond to no annealing (black), at 150°C (red), and 175°C (blue) and at 200°C (green). The spectra have been normalized to the silicon background.](image)

For investigation of the changes within the PEDOT:PSS film itself, a comparative study between amplitude and positions of certain modes to others of the same film is required. To explore the morphological changes in the PEDOT:PSS structure, the key region of interest is further narrowed to focus specifically on the modes contributing to the feature
peak at ~1450 cm\(^{-1}\). While not intuitively obvious, from the mode assignment in Section 4.2.2.1, this mode is actually a convolution of two separate symmetric C-C (-O) modes correlating to slightly different morphological structures of the PEDOT polymer. Figure 4.6 shows an enhanced view of the region of the spectra that change with increased annealing. For each spectra, the fitted Gaussian-Lorentzian modes for the benzoid type C-C bond (at ~1430 cm\(^{-1}\)) and the quinoid type C-C bond (at ~1455 cm\(^{-1}\)).

![Figure 4.6: Change in the contribution of Raman spectra of the C-C mode at ~1450 cm\(^{-1}\) from the peak fits of quinoid and benzoid modes at 1430 and 1455 cm\(^{-1}\) respectively. The spectra correspond to no annealing (black), at 150\(^\circ\)C (red), and 175\(^\circ\)C (blue) and at 200\(^\circ\)C (green).](image)

<table>
<thead>
<tr>
<th>Annealing Temp. ((^{\circ})C)</th>
<th>Quinoid</th>
<th>Benzoid</th>
<th>Peak of Combined Mode (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak (cm(^{-1}))</td>
<td>Amplitude (a.u.)</td>
<td>Peak (cm(^{-1}))</td>
</tr>
<tr>
<td>Unannealed</td>
<td>1429</td>
<td>959</td>
<td>1453</td>
</tr>
<tr>
<td>150(^\circ)C</td>
<td>1428</td>
<td>1190</td>
<td>1453</td>
</tr>
<tr>
<td>175(^\circ)C</td>
<td>1426</td>
<td>1391</td>
<td>1455</td>
</tr>
<tr>
<td>200(^\circ)C</td>
<td>1427</td>
<td>1417</td>
<td>1455</td>
</tr>
</tbody>
</table>

A distinct change in mode amplitudes can be observed in the Raman spectra. With increased annealing temperature, the ratio of quinoid to benzoid contribution is seen to
increase. For clarity, Table 4.5 outlines the fitted values for the two morphological peaks in question. Confirming the subjective observation of the spectra in Figure 4.6, the amplitude ratio of the quinoid:benzoid peak ratio increases with increased annealing temperature. As a result of this change in contribution from each of the morphologies, there is an overall blue shift of the convoluted mode from C-C/C=*=C mode from 1436 cm$^{-1}$ to 1425 cm$^{-1}$. This shift has been previously correlated to a conversion of film morphology from the benzoid to quinoid type PEDOT grain.[93] The conclusion of this analysis is that the annealing is causing a change in the film morphology to form one with a higher ratio of quinoid PEDOT to that of benzoid. As the quinoid morphology has an extra π-bond along the polymer chain backbone, a higher delocalization of charge between monomers can be achieved, which, in turn increases carrier mobility along the chain and through the film.

An additional observation is a blue shift in the spectral feature at ~1257 cm$^{-1}$. This peak is again a combination of two related, but separate modes assigned to a C=*=C (inter-ring) stretch + C-H bend at 1240 cm$^{-1}$, and an isolated C-C (inter-ring) stretch at 1260 cm$^{-1}$. With increased annealing temperature the peak of this combined mode is observed to shift from approximately 1260 cm$^{-1}$ to 1257 cm$^{-1}$ as displayed in Figure 4.7.

![Figure 4.7: Observation of the progressive blue shift of the peak correlating to the inter-ring convolution mode from 1260 cm$^{-1}$ in the unannealed (black) spectrum to 1257 cm$^{-1}$ with annealing at 200°C (green).](image)
This particular interring bond in the benzoid form of PEDOT is a single bond between carbon atoms in neighboring thiophene rings, however in the quinoid form, this would take the form of a more energetic double bond as previously depicted in Figure 3.2. As Raman spectroscopy of is an inelastic interaction of light with the allowed phonon vibrations in the polymer, a blue shift is indicative of an increase in bond strength. Taking both of these conjectures into account, the blue shift of the interring mode observed is interpreted as a shift from a lower energetic interring single C-C bond, to an energetic C= C. This interpretation aligns well with the previous analysis that highlighted a morphological shift from benzoid to quinoid morphologies.

It should be emphasized that the previous Raman analysis portraying a morphological shift is not an absolute change from benzoid to quinoid, but rather a relative one as the Raman signal is gathered from the ensemble of molecules within the measured area. The films characterized are not wholly comprised of either benzoid or quinoid PEDOT, but are a combination of both forms simultaneously. With increasing RTA temperature up to 200°C, the relative amount of PEDOT taking the quinoid with respect to benzoid morphology increases leading to the observed decrease in sheet resistivity. In other polymer systems, traditional annealing has been investigated to find similar conductivity enhancements as a consequence of an enhancement in polymer order.[94],[95] While such a crystallinity effect was not directly characterized through techniques such as x-ray diffraction (XRD), that is not necessarily to say that there is no enhancement in crystallinity occurring. There has, in fact, been at least one indication from literature than annealing may affect the crystalline order of a PEDOT:PSS film, although the observation is very subjective in analysis.[96] Raman spectroscopy is also able to give an indication of changes in polymer crystalline order. This is performed through the relative comparison of peak widths of the vibrational modes and has been applied for use both in nanoparticle and polymer systems.[33],[97] However, analysis of the fitted Raman modes of PEDOT:PSS as shown in Appendix B, did not explicitly indicate any change or enhancement in conductivity with annealing. It is acknowledged that the PEDOT crystallinity may be changing with annealing, which could contribute to the observation
of the identified morphological shift from benzoid to quinoid PEDOT. However, such a change was not directly explored using other characterization techniques and may be of interest to investigate in the future.

The specific implications of RTA on carrier transport relationship and the impact on device operation is explored in Chapter 5.
Chapter 5

Effects of RTA on Space Charge Limited Conduction

In Chapter 4, the effects of RTA on the sheet resistance of PEDOT:PSS was studied through both direct 4-point probe measurements as well by a TLM structure. While it was demonstrated that the lateral, sheet resistance of PEDOT:PSS decreased with appropriate processing, the effects on normal conduction through the film were not explored. Despite PEDOT:PSS being commonly used as a highly transparent conductor or a hole transport layer in PV and OLED applications, the detailed IV relationship of transport normally through the polymer film has not been directly investigated. The spectroscopic and morphological analysis of the changes induced in PEDOT:PSS films with RTA have been analyzed by Raman and AFM, however, these changes on an isolated thin film often deviate from ideality when implemented into more complex device architecture. To elucidate the processing potential of RTA on PEDOT:PSS thin films for application in functional device designs that require current conduction normal to the substrate, single carrier hole transport diodes comprised of ITO/PEDOT:PSS/Al were fabricated for study. Although PEDOT:PSS has previously been shown to undergo ionic transport under bias, the time scale for such changes is on the minute range and also at much higher bias levels.[99] Since these scans were taken with a sweep rates of greater than 1V/s, any contribution from ionic movement to the analysis is expected to be negligible.

5.1 Space Charge Limited Carrier Conduction with Exponential Trap Distribution

The mechanisms of current conduction through disordered media including polymers has been investigated for many decades. The present theoretical understanding of electrical
transport through organic diodes is based primarily on the space-charge limited conduction (SCLC) with an exponential distribution of carrier traps.[100], [101] This theory has been found most appropriate for describing the electrical conduction through inherently insulating media, including disordered polymers. Fitting experimental IV curves through organic media to SCLC theory has been utilized in other studies to extract values such as carrier mobility.[102]-[104] While this method may not be as potentially accurate as other methods such as time of flight analysis it does allow for a relative estimate of parameter extraction with an extremely simplified device structure and analysis.

In its simplest form, SCLC can be observed during experimental observations of a squared power law dependence \( J \propto V^2 \) of current on voltage through semiconducting or insulating materials. Basic SCLC is governed by a relationship known as Child’s Law as shown in Equation 5-1.

\[
J = \frac{9q\varepsilon_r\varepsilon_0\mu V^2}{8d^3}
\]

Equation 5-1

In Equation 5-1, \( J \) is current density, \( q \) is elementary charge, \( \varepsilon_r \) is the relative permittivity of the dielectric under test, \( \varepsilon_0 \) is dielectric permittivity of free space, \( \mu \) is carrier mobility, \( V \) is the applied voltage, and \( d \) is the thickness of material. When taking into account material non-idealities, this relationship can been adapted to take into consideration the presence of traps in disordered materials such and the presence of a Schottky barrier. If there is assumed an exponential distribution (with respect to energy) of carrier traps in the real organic material, the previous equation is modified as shown in Equation 5-2.

\[
J = q^{l-1}\mu N_V \left( \frac{2l + 1}{l + 1} \right)^{l+1} \left( \frac{l \varepsilon}{l + 1 H_b} \right)^{l+1} \frac{V^{l+1}}{d^{2l+1}}
\]

Equation 5-2
In Equation 5-2, \( l \) is an exponential parameter defined by Equation 5-3, \( N_V \) is the density of states in the valence band, and \( H_b \) is the total trap density in the material.

\[
l = \frac{T_C}{T}
\]

Equation 5-3

In Equation 5-3, \( T_C \) is the characteristic temperature of an exponential trap distribution in the material, and \( T \) is the temperature during the test. Ultimately, taking into account non-idealities in a real system has been expanded to identify four separate regions of current conduction mechanism, each following a different theoretical formula.[105], [106]

![Figure 5.1: Identification of four separate regions of current conduction through a single carrier organic diode with the presence of a Schottky barrier. The IV behavior in Region 1 corresponds to low field ohmic relationship, in Region 2 a trap filling SCL relationship is encountered, in Region 3, the majority of the traps have been filled and the traditional \( J \propto V^2 \) SCLC relationship is observed, and in Region 4, due to the presence of a Schottky barrier, the relationship tends back towards an ohmic one. Figure is reproduced with permission from Fig. 5 of [106] © 2009, EDP Sciences, SIF, Springer-Verlag Berlin Heidelberg and modified to label numbers according to conduction regions in this thesis.]

A graphical depiction of the four regions is shown in Figure 5.1 and can be identified as follows:

- **Region 1**: At low bias levels, bulk transport through the material due to thermal carriers or doping is capable of transporting the low level of injected carriers, and as such, is defined through a traditional ohmic relationship as defined in Equation
5-4, where \( p_0 \) is the carrier concentration of holes (or could also be electrons in other materials) in the material.

\[
J = q\mu p_0 \frac{V}{d}
\]

Equation 5-4

- Region 2: At moderate bias levels, bulk transport through the material is unable to transport the entirety of the injected carriers into the material, and as such, a space charge begins to develop at one of the contact interfaces. In a real disordered system and assuming an exponential distribution of traps with respect to energy in the organic material, a current density-voltage (JV) relationship according to Equation 5-2. The subsequent current density will have a power law dependence on applied bias which is greater than 2 (\( J \propto V^x \), where \( x > 2 \)).

- Region 3: At a sufficiently high applied bias, the carrier injection from the contact is such that the distribution of traps in the material are effectively completely filled, and the power law dependency of current density on voltage decays to the more common SCLC as previously outlined in Equation 5-1 with a squared relationship between current density and voltage (\( J \propto V^2 \)).

- Region 4: In certain devices with appropriately designed contacts, a 4th region can be encountered at even higher biases, whereby a Schottky barrier is not infinitely large at the injecting junction will further limit the JV dependency from the ideal SCLC and the relationship will adjust towards a second region of linear or ohmic dependency.

These 4 theoretical current transport regions have been developed specifically for application to a single carrier device in which the active material exhibits an exponential distribution of carrier traps.
5.2 ITO/PEDOT:PSS/Al Electrical Diode Characterization

Depending on the study, material preparation, and processing of the PEDOT:PSS film, the precise work function is reported to vary between 4.8-5.4 eV, with the most commonly accepted level to be that of around 5.0 eV.[107] In a similar manner, the work function of ITO can vary depending on stoichiometry and processing between 4.2-4.7 eV, with the commonly accepted level being around 4.5 eV.[108] As such, an estimation of energy level alignment of the ITO/PEDOT:PSS/Al electrical diode is shown in Figure 5.2.

![Energy level alignment diagram](image)

Figure 5.2: Energy level alignment of the ITO/PEDOT:PSS/Al electrical diodes fabricated for characterization of normal current transport through PEDOT:PSS thin films.

While the exact energy levels of the ITO and PEDOT:PSS are not fixed, what is known is that the work function energy level of both contacts is certainly less than that of PEDOT:PSS. Since PEDOT:PSS is a hole transporting material, the ITO/PEDOT:PSS/Al diode can be assumed to be a hole-only carrier device. Assuming an ITO work function of 4.5 eV and a PEDOT:PSS work function of 5.0 eV, the barrier to electron injection barrier from either of the contacts into the PEDOT:PSS material, will be greater than that of hole injection, again lending credence to the assumption of a single carrier, hole-only device.
Figure 5.3: Measured current with respect to bias on a log-log scale of the unannealed device assuming hole injection into the PEDOT:PSS from the ITO contact (positive bias applied to the ITO contact). Identifiable regions are labelled according to the various regions that define current transport through an organic diode. A blue dotted line depicting a purely ohmic relationship as well as dashed red line depicting a traditional SCLC $J \propto V^2$ current relationship for reference.

Figure 5.4: Measured current with respect to bias on a log-log scale of the unannealed device assuming hole injection into the PEDOT:PSS from the Al contact (positive bias applied to the Al contact). Identifiable regions are labelled according to the various regions that define current transport through an organic diode. A blue dotted line depicting a purely ohmic relationship as well as dashed red line depicting a traditional SCLC $J \propto V^2$ current relationship for reference.

Two scenarios of current transport were studied using the fabricated devices: carrier injection from the ITO contact is shown in Figure 5.3 and carrier injection from the Al contact is shown Figure 5.4. Both Figure 5.3 and Figure 5.4 are measured results from the as-grown (unannealed) devices. Of note is the fact that when holes are injected from
the ITO contact, only the first two regions of current transform are obtained at realizable bias levels. If the device is biased above the levels measured, either Joule heating or electrical breakdown causes film spalling of the PEDOT:PSS layer. The specific mechanism of failure was not investigated, but similar results have been reported elsewhere.[109] The applied electric field was subsequently governed to prevent the onset of film spalling, which would detrimentally affect the electrical transport characteristics through the film.

Similar measurements were made for annealed diodes at 150°C, 175°C and 200°C. An overlay of the current characteristics of the fabricated samples are shown in Figure 5.5 for ITO injection and Figure 5.6 for Al injection. While Figure 5.5 and Figure 5.6 are the measured IV relationships for a single device, to obtain an appropriate level of confidence in the process, the fitting procedure was performed across a number of tested diodes (from 4-8 depending on the specific yield from that particular sample) and the combined data set was used to determine specific device parameters as a statistical average along with determination of variability in samples.

![Figure 5.5: Comparison of current vs. voltage curves of samples annealed at different temperatures with hole injection from the ITO contact.](image)
Figure 5.6: Comparison of current vs. voltage curves of samples annealed at different temperatures with hole injection from the Al contact.

One clear difference to note with annealing, is that the conductivity normal to the substrate increases with annealing temperature in a similar trend to the material conductivity parallel to the substrate as previously noted in Chapter 4. While this might have been expected, due to the electrical and morphological anisotropy of the PEDOT:PSS films. The magnitude of current enhancement is somewhat difficult to pinpoint to an absolute, since the degree of enhancement varies depending on what regime of current conduction the device is being operated in. With carrier injection from the ITO contact, the specific level of conductivity enhancement with RTA at 200\(^\circ\)C can be estimated at electric field levels below 1 \(\times\) 10\(^4\) V/cm to be on the order of a single order of magnitude in the ohmic transport region. Conversely at higher electric field levels, the level of conductivity enhancement decreases to just over a factor of 1.5 at higher biases levels. This indicates that the electrical conductivity enhancement is highly dependent on the current conduction mechanism: at low biases in the linear relationship region, the effect of RTA on current conduction is more prominent than at higher biases where conduction follows either trap filling or classic SCLC. This can be understood through the differences in transport phenomenon, for in the low bias ohmic regime, the carriers are being transported by the film through hopping mechanisms. At higher biases, the PEDOT:PSS conductivity is unable to transport the higher levels of injected current, a space charge accumulates, and subsequently SCLC dominates the transport characteristics. So, while the physical material conductivity is determined to increase
with annealing, this conductivity enhancement does not translate equally across the entire operating bias level due to a fundamentally different mechanism of carrier transport.

While difficult to explicitly identify without the reference lines associated with the different regimes, the previous observations from the as-grown samples shown in Figure 5.3 and Figure 5.4 hold for all of the annealed samples as well. To reiterate, for hole injection from the ITO contact, only two regimes of current conduction can be achieved within the limits of our applied bias: the initial ohmic and subsequent trap filling SCLC regimes. However, when holes are injected from the Al contact, all four regimes of current conduction can be identified: ohmic, trap filling SCLC, ideal SCLC, and finally an injection limiting Schottky regime. From these observations, while specific numeric values of work functions energy levels cannot be extracted from the current analysis, the relative work functions of the two contacts with respect to each other can be. As holes as carriers energetically flow “upwards” there is expected to be an energy barrier from both the ITO and Al contact into the PEDOT:PSS. What was initially uncertain, due to the variety in reported ranges of both ITO and PEDOT:PSS, is the magnitude of injection energy barriers from the respective contacts into the PEDOT:PSS, both relative to each other or absolute. Through the observation of the transitions between different current transport regimes, it can be concluded that the Schottky barrier at the Al/PEDOT:PSS interface is greater than that at the ITO/PEDOT:PSS interface, as the Schottky restricted SCLC regime is achievable at a lower bias level.

5.2.1 Parameter Fitting Procedure for ITO/PEDOT:PSS/Al Diodes

To extract the most material information from the RTA devices, a theoretical fitting of current conduction to the experimentally measured data, analysis is focused on the carrier injection from the Al contact so as to cover more regimes of current conduction. Numerical parameters were extracted using the mathematical fitting procedures in Origin Lab 8.0.
The fitting procedure followed starts by initially applying Equation 5-1 to the trap filled SCLC regime, which is labelled as region 3 in Figure 5.4. Since the thickness of the PEDOT:PSS layer was independently measured to be approximately 100 nm by AFM, and using the assumption that the relative permittivity of PEDOT:PSS is equal to 2.2 (presuming the refractive index is around 1.5 as in [16]), the only variable parameter is hole carrier mobility (μ). By fitting initially in this regime across the various annealed samples, comparative average values for hole mobility from each tested stack can be extracted and are displayed in Figure 5.7. The error bars shown in Figure 5.7, are obtained by plotting the maximum and minimum values from each of the samples tested.

![Figure 5.7: Average values of hole mobility extracted from fitting of Equation 5-1 to the ideal SCLC region with respect to temperature. Error bars correspond to the maximum and minimum values of the individually measured and fit](image)

The unannealed value of PEDOT:PSS carrier mobility was found to be approximately equal to 0.01 cm² V⁻¹ s⁻¹ which is slightly lower in comparison to other reports measuring the mobility through a variety of means including Hall effect measurements, FET, and optical spectroscopy to be between 0.045 cm² up to 1.5 cm² V⁻¹ s⁻¹ in an unprocessed pristine state.[110] This difference in carrier mobility is again attributed to differences in film formulation, processing and measurement technique. Afterwards, by applying Equation 5-1 to the trap filling SCLC (Region 2 in Figure 5.4), and using the hole mobility numbers from the previous fit, experimental values for available density of states (N_t) and total trap density (H_t) can be determined. As the range of biases where trap
filling SCLC (Region 2) can be applied isn’t definitively defined, the central point of the mathematical fit, was chosen to corresponded to the point with the greatest power relationship between I and V. The specific central point for each device was located by numerically calculating the second derivative of current with respect to voltage, and evaluating at what bias the second derivatie is equal to zero. Visually on the graph, this can be estimated by the point on the IV curve where the curve changes concavities (from up to down). The fitted values for $N_V$ and $H_b$ with respect to RTA temperature are shown in Figure 5.8 and Figure 5.9 respectively. In contrast to the hole mobility values, there is no discernible change within variation of either of these values with respect to the annealing temperature and their average values are $N_V = 1.54 \times 10^{18}$ cm$^{-3}$ and $H_b = 3.67 \times 10^{17}$ cm$^{-3}$.

![Figure 5.8: Values of effective density of states extracted from fitting of Equation 5-2 to the trap filling SCLC region with respect to RTA temperature.](image)
Figure 5.9: Values of total trap density extracted from fitting of Equation 5-2 to the trap filling SCLC region with respect to RTA temperature.

Lastly, shifting to the low bias region of the IV curve (Region 1) and again using the previously extracted mobility values, values for the carrier concentration can now be determined through fitting to Equation 5-4. The values fitted for hole concentration from the low bias ohmic regime with respect to annealing temperature are shown in Figure 5.10.

Figure 5.10: Values of effective hole concentration in PEDOT:PSS at the Al contact extracted from fitting of Equation 5-4 to the linear or ohmic current conduction region with respect to RTA temperature.

With respect to annealing temperature, although the material conductivity enhances, from this analysis it is not due to an increase of hole concentration as the value stays nominally constant on the order of 7-8 x 10^{14} cm^{-3}. 
By fitting the data from the specific regions of current conduction, a variety of parameters defining the current conduction mechanism through thin polymer films have been extracted. By comparing the parameter values between the different temperature annealed samples, it is found that with annealing, only the carrier mobility within the PEDOT:PSS film is being affected. Revisiting the results from Chapter 4 as well as the IV curves in Figure 5.3 and Figure 5.4, the increase in measured conductivity as a result of RTA is associated with the increase in carrier mobility. This enhancement of carrier physically arises from a morphological transition towards quinoid form PEDOT which is known to be more efficient in carrier transport. Considering potential localized surface effects on the PEDOT:PSS, as indicated from the TLM measurements in Chapter 4, there is a decrease in contact resistance from the Al contact to the PEDOT:PSS. While this is instructive to take into account for future device design using appropriate electrical contacts, the decrease in contact resistance is not solely responsible for the increase in conduction through the film itself as observed in Figure 5.5 and Figure 5.6. However, the increase in the carrier mobility parameter as extracted from the fitting regime of only 35% also is unable to completely account for the overall order of magnitude change depending on the applied bias. There is a greater degree of conduction enhancement through the device at the lowest of biases. In this regime there is a combined effect of both the contact resistance as well as the material charge conduction that is contributing to the increase in current transport. However, at higher biases, PEDOT:PSS mobility is not as influential on the J-V relationship as the system is now injection limited by the contact and not bulk limited by material transport. Hole mobility is still a relevant parameter in the SCLC relationships as shown by its presence in the current governing equations. Ultimately, the measurements from Chapter 4 indicating a decrease also take into account potential differences in contact resistance and are designed to specifically measure the resistance of the material being tested. Further exploration of the particular effects of the RTA on PEDOT:PSS thin films with respect to changing the injecting contact was not undertaken, but may prove valuable in the
future for discerning additional surface effects with respect to the adjacent electrode materials.

Being able to anticipate the precise changes in a material due to processing is key in device implementation where a variety of films and interfaces are required to exhibit specific properties in order to maintain device function. In particular, as PEDOT:PSS is often used as either a highly transparent contact or a hole transport layer in a PV or OLED cell, it is of key importance that not only the resistive losses be minimized for highest efficiency, but also, the energy level alignment in the device be maintained for appropriate function. Through the use of RTA, the conductivity is seen to increase through a morphological change in the material allowing for increased carrier transport through the film. On the other hand, if additionally, the carrier concentration was being adjusted through the process, the inherent Fermi level within the layer would be also changing and potentially adversely affecting the energy level alignment between layers in the device.

While the manipulation of density of states, total trap density and carrier concentration has not been indicated through rapid thermal processing, utilizing this characterization offers an alternative method of approximation of such values and has been demonstrated using purely electrical characterization. Admittedly, the relatively large errors may be obscuring some additional underlying effects of RTA on the SCLC parameters. The size of error was primarily due to the range of IV data from the different tested films, however this was further compounded when taking into account additional error introduced during the fitting procedure. In particular, the effects fitting for trap density and effective density of states from the trap filling SCLC (Region 2), was highly dependent on the range of electric field values used. In efforts to prevent a fitting bias, a standardized range of voltages around a central bias point corresponding to the peak exponential relationship between was utilized. It was additionally noted through this standardization, that this voltage point may actually be increasing as shown in Figure
5.11, but with the large variation in peak exponential bias point within similarly annealed devices, no correlation could be confirmed.

![Graph showing peak exponential bias voltage vs. annealing temperature.](image)

Figure 5.11: Average voltage at which the peak exponential relationship between $J$ and $V$ was located, and subsequent centering point for the mathematical fit to JV data for the trap filling SCLC equation.

Despite the potential inaccuracy of this parameter fitting to SCLC for parameter extraction when compared to more intricate experimental techniques such as time of flight measurements or specialized structures to evaluate field effect mobility in organic semiconductors, this facile test device consisting of just two contacts and the PEDOT:PSS film being evaluated offers a reasonable estimate that is in line with other previous measurements of the mobility. Additionally, while there is a relatively high level of error associated with the extracted values, the fitting procedures was identical for all the tested devices, thus offering an appropriate relative estimate of hole mobility to identify the changes in current conduction with RTA temperature. The enhancement in conduction through the PEDOT:PSS layer with RTA at 200°C shows a modest enhancement of, on average, just under 1 order of magnitude at low bias levels. However, this rapid thermal technique allows for a material change occurring on the order of seconds and as such could offer a promising processing technique for high throughput manufacturing, especially when used in concert with other suitable techniques of material enhancement such as chemical additives for increasing doping.
Chapter 6

Conductivity Quenching Using Flood UV Irradiation

The application of RTA to enhance the conductivity and performance or reduce energy consumption of electrical organic devices is of little consequence without spatial nano- or micropatterning techniques. Discussed in Chapter 3.5 were several common approaches to patterning of PEDOT:PSS thin films. Each of those has their specific advantages or drawbacks, with a common concern being the lack of high throughput patterning for an organic device fabrication process stream. One of the key process innovations that enabled the revolution of the semiconductor industry was the development of photolithography in device patterning. Photolithography works by irradiating a UV light onto a polymeric thin film, a change in film solubility can be induced to selectively pattern the photoresist and subsequently the underlying material. This procedure often proves extremely challenging when being applied to patterning organic films due to the fact that photoresist developers and solvents often interact detrimentally with similarly composed materials. In particular, for PEDOT:PSS, UV photolithography has only been demonstrated using a highly specialized photoresist/developer combination as discussed in Chapter 3.5.1, but is not a commonly applied technique.

Based on the knowledge that relatively high energy photons in the UV spectrum are capable of inducing significant changes in other polymers, through either scission or crosslinking, it was expected that similar effects may be encountered when applying UV irradiation directly to a PEDOT:PSS thin film. In fact, direct UV exposure has been applied to other organic semiconductors allowing for facile material removal upon exposure.\[111\], \[112\] In contrast to the developed photolithography polymers, the focus of
these experiments focused on the concept of inducing appropriate spatial material changes to the PEDOT:PSS film to allow for functionalizing of the film for device application without the subsequent requirement of material removal. Simplifying the fabrication process stream in such a manner would allow for direct device creation by functionalizing the film as opposed to physically patterning the device through multiple sequential fabrication steps.

6.1 Reported Effects of UV Irradiation on PEDOT:PSS Thin Films

There are a wide variety of reports of the effects of UV irradiation on properties of PEDOT:PSS films. Most common is the application of UV irradiation to tune the work function of PEDOT:PSS for appropriate energy level engineering at the material interface with other films in a device.[113], [114] In particular, by tuning the PEDOT:PSS work function in OLED or PV devices an enhancement of performance efficiency can be realized.[115], [116] Although PEDOT:PSS is generally assumed to degrade with UV exposure in the presence of oxygen, the specific effects of UV irradiation on the structure of is not as well studied. There are several conflicting reports in some cases indicating a modest increase in conductivity, and others a drastic decrease. [113], [114], [117], [118] Lastly, while PEDOT:PSS exhibits relatively high transmission to wavelengths in the visible regime, and generally absorbing across the UV spectrum, recent reports have also demonstrated that exposure to high energy gamma and X-ray radiation results in scission events in the conductive PEDOT polymer creating free radicals and subsequently disrupting the conductive pathways through the polymer.[119], [120] Although the exposure and conductivity degradation upon exposure to high energy irradiation is generally viewed as a detriment to device lifetime, this study is investigating the potential use for UV exposure to directly and spatially influence the film characteristics for device creation.
6.2 Experimental Investigation into the effects of UV Irradiation on PEDOT:PSS

For initial material investigation of the effects of UV irradiation on thin film properties of PEDOT:PSS, a thin polymer film was spincast onto ITO, Corning glass 2947, and also a silicon wafer. The spin parameters were chosen such that the resulting film thickness on glass and ITO were ~100 nm, whereas on silicon a thicker ~200 nm film was deposited for better characterization signal from optical characterizations. Prior to deposition, the PEDOT:PSS under brand name Clevios F HC was filtered through a 0.22 µm filter to remove any larger particulates from the initial aqueous polymer dispersion. Following deposition, a 10 minute bake at 125°C to remove any residually remaining solvent from the film. The films were then exposed to UV from a Spectroline XL-1500 UV Cross-linker at three separate doses of 24.9, 48.3, and 71.6 J/cm² in an air atmosphere. The spectral output of the Spectroline XL-1500 is located at 254 nm which is below the estimated absorption edge of PEDOT:PSS at λ ~ 320 nm.[16] The output spectrum of the cross-linker is shown in Figure 6.1 and confirmed through communication with the manufacturer is that there is no spectral output below 252 nm.

![Spectral Energy Distribution of Germicidal Lamp](image)

Figure 6.1: Spectral energy distribution of the Spectroline XL-1500 UV Cross-linker as supplied by the manufacturer.

In Figure 6.1, while there is some measureable energy output at wavelengths longer than 254 nm, they are significantly weaker (less than 5% in all cases) and all material changes
are attributed to the 254 nm output. Subsequent to exposure, Al contacts were thermally evaporated onto the PEDOT:PSS film through a shadow mask.

6.2.1 Effect of UV Irradiation on PEDOT:PSS Conductivity

Similar to the RTA experiments studied in Chapter 4, investigations into the effects of UV annealing on both directions (normal and parallel) to substrate were explored. To characterize the in-plane conductivity (sheet resistance), 4-point probe measurements were taken on each of the exposed films on insulating glass to prevent any substrate contributions to conductivity. The difference in sheet resistance between the RTA experiments in Chapter 4 and here are twofold. For one, the thicknesses are different, with the RTA films being more than double the initial thickness of the UV experiments. Secondly, despite best efforts of maintaining the PEDOT:PSS dispersion under vacuum conditions and in a fridge, aging effects were observed as a portion of the polymer was no longer dispersible in water and had to be removed from the formulation prior to deposition. Given that PEDOT is indispersible in water whereas PSS is, it is assumed that the majority of this precipitated material is PSS. The subsequent films would then have a higher relative proportion of PSS to PEDOT causing the lowered conductivity observed. Of key importance however, is that the results shown in Table 6.1, clearly indicate a significant increase in sheet resistance with UV exposure.

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>Sheet Resistance (Ω/□)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.19 x 10²</td>
</tr>
<tr>
<td>24.9</td>
<td>3.39 x 10⁴</td>
</tr>
<tr>
<td>48.3</td>
<td>1.07 x 10⁶</td>
</tr>
<tr>
<td>71.6</td>
<td>2.39 x 10⁷</td>
</tr>
</tbody>
</table>

The precise effects of UV exposure on lateral material conductivity can be directly extracted from the application of Equation 2-2, whereby the material resistance ($\rho$) is dependent not only on the measured sheet resistance ($\rho_s$), but also the film thickness ($t$).
In previous investigations of effects of UV exposure on PEDOT:PSS films however, decrease of film thickness has been documented, so it is important to directly measure the film thickness changes as a result of UV exposure. Thickness measurements were taken across a step interface using a Dimension 3100 AFM, and the results are shown below in Table 6.2.

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>108</td>
</tr>
<tr>
<td>24.9</td>
<td>80</td>
</tr>
<tr>
<td>48.3</td>
<td>74</td>
</tr>
<tr>
<td>71.6</td>
<td>66</td>
</tr>
</tbody>
</table>

Utilizing these measured values of both sheet resistance and film thickness, lateral material resistivity can be calculated and are graphically shown in Figure 6.2.

![Figure 6.2](image)

Figure 6.2: Changes in sheet resistance (red circles) and lateral material resistivity (black squares) with respect to UV exposure energy displayed on a lin-log scale.

As can be seen with increased exposure to UV irradiation, the sheet resistance of the previously conductive PEDOT:PSS film increases significantly, by over 4 orders of magnitude. The effects are attributed to an actual material change as well, not simply to a change in material thickness as measurements were taken to eliminate the effects of
film thickness, and the calculated resistivity increases in a similar manner. Akin to previous experiments, the anisotropic behavior and difference in material processing effects was taken into consideration. Figure 6.3 displays the conduction with respect to bias of a pristine PEDOT:PSS film and that which has undergone 71.6 J/cm² of UV irradiation. While the resistivity is not directly measured, the current conduction through the film is observed to decrease with exposure. Of note is that in contrast to the conductivity change parallel to the substrate of nearly 4 orders of magnitude, in the normal dimension, there is only a factor of ~10 change.

![Graph showing current density-voltage curves](image)

Figure 6.3: Current density-voltage curves of the electrical transport normal to the substrate of the pristine PEDOT:PSS film (black), and the UV exposed with 24.9 (red), 48.3 (blue) or 71.6 J/cm² (green) are displayed on a lin-log scale.

Additional material characterization methods were undertaken to further investigate this difference in effect, and determine the precise mechanism through which the film conductivity is being disrupted.

### 6.2.2 Raman Spectroscopic Characterization

The effects of UV irradiation dose on the morphology of PEDOT:PSS films spun on silicon substrate was performed. Figure 6.4 displays the changes across the region of interest of the Raman spectra of PEDOT:PSS. While not explicitly shown, all previously identified modes of the PEDOT:PSS film could be identified in all samples thus ensuring
that the films are not significantly disrupted and still intact, similar to previous Raman investigations in Chapter 4. Of interest, there were two Raman vibrational modes in particular that were observed to change with increased UV exposure. Those modes are highlighted with asterisks in the figure, are located at ~1250 cm\(^{-1}\) and ~1440 cm\(^{-1}\) and are assigned to a Cα-Cα intrerring stretch, and a symmetric Cα-Cβ (-O) respectively.

![Raman spectra](image)

Figure 6.4: Raman spectra of PEDOT:PSS films having undergone UV exposure. The black curve is from as-grown PEDOT:PSS, red is from 24.9 J/cm\(^2\), blue is from 48.3 J/cm\(^2\), and green is from 71.3 J/cm\(^2\) irradiation of UV light. Two particular modes of interest have been highlighted and labelled.

Turning attention initially to the intrerring stretch at ~1250 cm\(^{-1}\), it can clearly be observed that with increased UV exposure the strength of the mode decreases noticeably. To quantify this loss in mode strength, the values of normalized amplitude (compared to the strong peak at 1440 cm\(^{-1}\)) and peak location for the mode at 1250 cm\(^{-1}\) are shown in Table 6.3.
Table 6.3: Effects of UV exposure on the amplitude, and peak wavenumber of the Cα-Cα
interring stretch at ~1250 cm⁻¹

<table>
<thead>
<tr>
<th>UV Exposure Energy (J/cm²)</th>
<th>Normalized Amplitude</th>
<th>Central wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.207</td>
<td>1255</td>
</tr>
<tr>
<td>24.9</td>
<td>0.126</td>
<td>1252</td>
</tr>
<tr>
<td>48.3</td>
<td>0.099</td>
<td>1251</td>
</tr>
<tr>
<td>71.6</td>
<td>0.081</td>
<td>1250</td>
</tr>
</tbody>
</table>

From the values shown in Table 6.3, the peak amplitude of the interring stretch can be calculated to decrease to 40% of its initial value. Although in previous studies UV exposure has been associated simply with breakdown due to enhanced oxidation of the PEDOT:PSS film, these observations indicate that there is another mechanism in play.[121] In particular, the decrease in strength of the interring bond between EDOT monomers is indicative of a scission event within the conductive PEDOT grain. Additionally, this observation fits well with the measured decrease in film conductivity that has previously been observed when PEDOT:PSS was exposed to high energy radiation. As the interring bonds are broken through this polymer scission event, the average polymer chain length is systematically decreased. The decrease in chain length interrupts the relatively efficient conductive pathways along the PEDOT chain backbone, and results in the observed decrease in conductivity. At each of these scission locations, rather than the efficient nearest neighbor transport between conductive EDOT monomers, additional hopping events are required to maintain conduction though the polymer. UV exposure induced polymer scission can also explain the difference in conductivity decrease between the in-plane and out-of-plane conduction. As it was previously discussed that with spin coating the PEDOT:PSS forms into a lamellar structure with a relatively large number of insulating PSS barriers in the normal direction as compared to the parallel one. As such, assuming that the scission even occurs evenly throughout the thin film, the process will have more effect in-plane due to the already larger percentage of PEDOT to PSS in that dimension. Lastly, also of interest, is
the fact that with UV exposure, the interring stretch mode also undergoes a slight blue shift from 1255 cm\(^{-1}\) down to 1250 cm\(^{-1}\). While this blue shift has not been previously identified as a result of either, it could act as an indicator of UV exposure and degree of scission of PEDOT:PSS in future experiments.

The second identified mode of interest is the \(\text{C}_\alpha\text{-C}_\beta\) \((-\text{O})\) stretching mode of the thiophene ring at \(\sim\)1440 cm\(^{-1}\). This assignment of a single mode is actually a misnomer, as spectral shape is actually the result of two individual \(\text{C}_\alpha\text{-C}_\beta\) \((-\text{O})\) vibrations, one belonging to the benzoid form of PEDOT:PSS which is centered at \(\sim\)1450 cm\(^{-1}\), and one belonging to the quinoid form which is centered at \(\sim\)1430 cm\(^{-1}\). Following a baseline removal and peak fitting routine, Figure 6.5 depicts the deconvolution of the spectral feature into its two components along with the combined fit and its comparison to the raw data (colored dashed line and solid grey line respectively). Further analysis highlighting the change is shown in which is the numerical fitted values for the benzoid and quinoid peak centers and amplitude ratio. As can be seen, with UV exposure, the amplitude ratio of quinoid to benzoid decreases continuously from its original value of 4.67 down to 1.62. While the amplitude ratio cannot be used to specifically determine the precise percentage of quinoid to benzoid morphology in the film, in a relative sense it can be concluded that with increased exposure, the film undergoes a shift from quinoid to benzoid.
Figure 6.5: Deconvolution of Cα-Cα (~O) stretch mode at ~1440 cm⁻¹ into the underlying quinoid (~1420 cm⁻¹) and benzoid (~1450 cm⁻¹) components. The raw data is shown in light grey, with the combined fit overlaid as a colored, dotted line. The various spectra with changing UV irradiation are offset on top of each other.

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>Quinoid/Benzoid Amplitude Ratio</th>
<th>Benzoid Peak Center (cm⁻¹)</th>
<th>Quinoid Peak Center (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.67</td>
<td>1451</td>
<td>1421</td>
</tr>
<tr>
<td>24.9</td>
<td>1.94</td>
<td>1451</td>
<td>1426</td>
</tr>
<tr>
<td>48.3</td>
<td>1.66</td>
<td>1450</td>
<td>1428</td>
</tr>
<tr>
<td>71.6</td>
<td>1.62</td>
<td>1450</td>
<td>1433</td>
</tr>
</tbody>
</table>

While the previously examined decrease of the interring stretch mode clearly indicates that a scission process is occurring which adequately explains the decrease in film conductivity, this morphological shift may also play a part. It was previously discussed that the quinoid morphology is associated higher conductivity along the polymer due to the fact that this morphology preferentially forms into a linear chain type that allows for higher delocalization of charge. As such, this decrease in quinoid form is also indicative of a decrease in polymer conductivity, however, it cannot be definitively determined
whether this morphology shift is a direct cause of the decrease or rather a secondary consequence of the chain scission. Due to an excess of scission events, a large number of dangling bonds will be created that will be prone to subsequent reaction, and potential reorganization into the less conductive benzoid morphology.

Taking the entirety of the Raman investigation into account, the decrease in conductivity due to UV irradiation can be correlated with a polymer scission event in which the interring bonds between EDOT monomers are being broken. The conductivity decrease may in fact also be contributed to by a shift in film morphology, however, the morphological change in the film could also be a secondary effect of the scission process and subsequent reaction at the newly created dangling bond sites.

6.2.3 FT-IR Spectroscopic Characterization

In complement with the Raman spectroscopy, FTIR characterization on the various films was performed. The FTIR characterization was studied in absorption mode by measuring the IR absorption of the thin films on a silicon substrate. Figure 6.6 displays the raw FTIR spectra of the thin PEDOT:PSS films. Given that the spectra have not been adjusted or artificially offset from each other, in the short to mid-IR wavelengths (from 2000-4000 cm\(^{-1}\)), a decrease in absorption with increased UV exposure is observed. This decrease in overall IR absorption is attributed to the decrease in delocalized charge carriers. In highly conductive PEDOT:PSS with a large number of available charge carriers, there is high absorption above 2000 cm\(^{-1}\).[121] With UV irradiation, the decrease in absorption and correlated level of free charge carriers in the film is in good agreement with all other observations indicating a decrease in film conductivity.
Figure 6.6: Raw FTIR spectra of the PEDOT:PSS films having under gone no UV exposure, along with 24.9, 48.3, and 71.3 J/cm².

This is again, a relative comparison, as there is no defined amount of absorption with respect to free carrier concentration. There are a variety of other considerations affecting the level of absorption in a PEDOT:PSS film including the initial starting material formulation, but also the thickness and deposition technique. As it is not simply due to the free charge carriers, a definitive relationship between absorption and free carrier concentration in the film cannot be established.

Figure 6.7: FTIR data with underlying absorption removed. Peak positions in the unexposed PEDOT:PSS film are labelled, and two significant modes of interest are highlighted with asterisks at 1520 and 1720 cm⁻¹.

To expand the analysis beyond the simple comparison of overall absorption, a baseline fit was performed to remove the effects of the underlying free carrier absorption and focus on the changes in molecular absorption. The results of this baseline removal are shown in
Figure 6.7. Also in Figure 6.7, peaks for the unexposed film have been labelled and two key absorption modes of interest are highlighted at 1520 and 1720 cm$^{-1}$.

The peak at 1520 cm$^{-1}$ is associated with the absorption of a C=CC bond, and in PEDOT:PSS films, it has been reported as an indicator of conjugation length.[122] With increased exposure, the amplitude of the mode decreases to the point that it is difficult to discern above the background with maximum exposure. Since it can be seen to decrease with exposure in a similar manner as the interring stretching mode from the Raman investigation, and has been identified as an indicator of conjugation length, this mode can be associated with the interring double bond of the quinoid morphology of PEDOT:PSS. As only the quinoid morphology contains an interring carbon double bond, and the Raman results show that the thiophene ring is still intact despite a shift in morphology, this C=C mode also corroborates the hypothesis of a scission event. In particular, a scission event that is primarily occurring along the polymer chain backbone in the quinoid morphology of PEDOT:PSS.

A second mode at 1720 cm$^{-1}$, also can be observed to significantly in amplitude with increased UV irradiation. While this mode has not been explicitly linked to a particular molecular absorption in PEDOT:PSS films through theoretical studies, it has been associated in other reports to correspond to the level of doping in a PEDOT film.[123] In the context of the UV irradiation on PEDOT:PSS, the increased irradiation causes a decrease in doping of the thin film, which can subsequently be detected in the deterioration of the absorption peak at 1722 cm$^{-1}$. Taking all of the FTIR data into account, the changes in the IR absorption can be explained through the previously predicted scission process of the PEDOT chain from Raman spectroscopy, leading to a decrease in conjugation length, and correlated decrease in conductivity and doping.

Finally, a number of other modes aside from the two previously discusses can be identified with comparison to literature and are labelled with assigned mode in Table 6.5. [121], [124]-[126]
Table 6.5: Assignment of FTIR absorption peaks to vibrational modes of PEDOT:PSS

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Mode Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>927</td>
<td>C-S (str)</td>
</tr>
<tr>
<td>970</td>
<td>C-S (str)</td>
</tr>
<tr>
<td>1078</td>
<td>C-O (str)</td>
</tr>
<tr>
<td>1133</td>
<td>Oxyethylene ring (str)</td>
</tr>
<tr>
<td>1188</td>
<td>C=C (str)</td>
</tr>
<tr>
<td>1355</td>
<td>C=C (str)</td>
</tr>
<tr>
<td>1523</td>
<td>C=C or C-C (str)</td>
</tr>
</tbody>
</table>

The above modes have been cited for the unexposed film, however, upon the fitting procedure, although the magnitudes of the modes in Table 6.5 were relatively invariant with UV exposure, several of them experienced blue shifts in terms of their peak location. Figure 6.8 depicts the shift of the central wavenumber of a number of PEDOT:PSS modes as a result of UV exposure.

![Figure 6.8: Shift in select FTIR modes as a result of UV exposure. Values of the shift in mode is shown with respect to the unexposed central position listed in Table 6.6.](image)

While some modes shifted more significantly than other, all, including the C-C (str) mode at ~1520 cm$^{-1}$ progressively shifted with increased UV exposure. The absolute fitted values for the center of each of the peaks is shown in Table 6.6. Although this shift has
not previously been associated with a decrease in polymer conjugation length, the increase in absorption peak locations is indicative of a progressive change in molecular bond energy with UV irradiation. In future experiments, this relative shift can now be associated both with a decrease in material conductivity and PEDOT conjugation length.

Table 6.6: Fitted values of the central wavenumbers of the assigned PEDOT:PSS FTIR absorption modes.

<table>
<thead>
<tr>
<th>FTIR Vibrational Assignment</th>
<th>0 J/cm² UV exposure</th>
<th>24.9 J/cm² UV exposure</th>
<th>48.3 J/cm² UV exposure</th>
<th>71.6 J/cm² UV exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C or C-C (str)</td>
<td>1523 cm⁻¹</td>
<td>1527 cm⁻¹</td>
<td>1532 cm⁻¹</td>
<td>1535 cm⁻¹</td>
</tr>
<tr>
<td>C-C (str)</td>
<td>1355 cm⁻¹</td>
<td>1374 cm⁻¹</td>
<td>1375 cm⁻¹</td>
<td>1376 cm⁻¹</td>
</tr>
<tr>
<td>C=C (str)</td>
<td>1188 cm⁻¹</td>
<td>1199 cm⁻¹</td>
<td>1208 cm⁻¹</td>
<td>1210 cm⁻¹</td>
</tr>
<tr>
<td>Oxyethylene ring (str)</td>
<td>1133 cm⁻¹</td>
<td>1138 cm⁻¹</td>
<td>1141 cm⁻¹</td>
<td>1142 cm⁻¹</td>
</tr>
<tr>
<td>C-O (str)</td>
<td>1078 cm⁻¹</td>
<td>1083 cm⁻¹</td>
<td>1087 cm⁻¹</td>
<td>1088 cm⁻¹</td>
</tr>
<tr>
<td>C-S (str)</td>
<td>970 cm⁻¹</td>
<td>977 cm⁻¹</td>
<td>981 cm⁻¹</td>
<td>982 cm⁻¹</td>
</tr>
<tr>
<td>C-S (str)</td>
<td>927 cm⁻¹</td>
<td>934 cm⁻¹</td>
<td>934 cm⁻¹</td>
<td>935 cm⁻¹</td>
</tr>
</tbody>
</table>

6.2.4 AFM Characterization

AFM characterization was used to investigate both the surface profile of the PEDOT:PSS films as well as the thickness of films in relation to exposure. The decrease in film thickness has already been documented in Table 6.2 so Section 6.2.4 will focus specifically on the analysis of the surface profile of the PEDOT:PSS films.

Figure 6.9 shows the 2D height profiles of the 4 investigated samples of PEDOT:PSS films. Subjectively it appears that with increased exposure, the initially rough film with well-defined peaks and valleys are gradually eroded with increased exposure to the point that there are very few well defined regions. For clarity, a 3D image of the PEDOT:PSS surface of the unexposed sample is shown in Figure 6.10, distinctly showing the rough surface profile consisting of the nanometer size hills. These nanometer sized elevated
regions have been associated with the conductive PEDOT grains surrounded by a background of insulating PSS.\[53\]

![Figure 6.9](image1.png)

Figure 6.9: Height images of the PEDOT:PSS films having undergone UV exposure of 0, 24.9, 48.3, and 71.6 J/cm\(^2\), a) – d) respectively.

![Figure 6.10](image2.png)

Figure 6.10: 3D surface profile of the unexposed PEDOT:PSS sample displaying distinct peaks and valleys corresponding to separate polymer phases of PEDOT and PSS respectively.

A larger size and surface coverage of these elevated areas has been associated with higher conductivity in vertical transport through the film. This initial analysis is mirrored in a more objective manner when comparing the calculated average roughness and particle statistics of the images across a 100 \(\mu \text{m}^2\) area. The measured values for RMS roughness,
average peak height and average peak diameter of the elevated grains are tabulated in Table 6.7. Evaluating the film roughness indicates that with UV exposure comparing the as-grown to fully exposed, the surface roughness decreases. Although there is a slight discrepancy between the 24.9 and 48.3 J/cm² samples, the decrease in roughness with UV exposure is ultimately evident and is in general agreement with other reports in literature. Associated with surface roughness is the level of doping of the PEDOT:PSS film. The surface roughness can also be correlated to both a higher degree of phase separation between the conductive PEDOT and insulating PSS regions and in turn an increase in conductivity of the thin film itself.[90], [127] Secondly, looking at the particle analysis statistics of the elevated PEDOT grains, a clear decrease in grain height and diameter can be observed between noted. Comparing the two extremes of the unexposed film and the film exposed with 71.6 J/cm², the PEDOT grains have decreased their average height by 60%, and their average diameter by 45%.

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>RMS Roughness (nm)</th>
<th>Average Height of Peaks (nm)</th>
<th>Average Diameter Peaks (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.622</td>
<td>27.6</td>
<td>811</td>
</tr>
<tr>
<td>24.9</td>
<td>5.708</td>
<td>21.4</td>
<td>747</td>
</tr>
<tr>
<td>48.3</td>
<td>5.838</td>
<td>24.3</td>
<td>725</td>
</tr>
<tr>
<td>71.6</td>
<td>2.398</td>
<td>11.1</td>
<td>440</td>
</tr>
</tbody>
</table>

Along with the height images, phase scans were performed to further illustrate the changes in surface morphology due to the effects of UV irradiation. Figure 6.11 shows the phase image comparison of the unexposed and variably exposed film PEDOT:PSS films.
Figure 6.11: Phase profile images of the PEDOT:PSS films having undergone UV exposure of 0, 24.9, 48.3, and 71.6 J/cm², a) – d) respectively.

In Figure 6.11 a) across the 100 µm² area, a very clear distinction can be identified. These separated phases can be correspondingly mapped to the nanoscale hills from the height AFM images in Figure 6.9. However, upon UV exposure, Figure 6.11 b)-d), this phase distinction decreases until with the highest UV exposure, no definitive phase difference across the surface of the film can be observed. The loss of phase distinction between the PEDOT and PSS regions is understood again through the scission of the PEDOT chains upon exposure. The size and coverage of the conductive areas decreases with exposure and after 71.9 J/cm², the PEDOT regimes cannot be discerned from the AFM scans. The reduced phase distinction arises from the fact that upon chain scission, dangling bonds are created within the conductive PEDOT grain, allowing for permeation of radical species from the surrounding PSS into the PEDOT regions. This decrease of PEDOT conjugation length combined with the introduction of PSS or other species into the conductive regions of the film, acts in concert to decrease the conductivity of the film upon UV irradiation.
6.2.5 Spectroscopic Ellipsometric Characterization

Spectroscopic ellipsometry was utilized to investigate optical changes in complex refractive index of PEDOT:PSS for the potential for utilization of UV irradiation for optoelectronic mode engineering. For this study on the UV effects on PEDOT:PSS, variables were limited to thickness, refractive index, and anisotropy.

The measurements were performed on thicker (1.5K RPM spin speed) PEDOT:PSS on a silicon substrate to optimize the measureable signal for appropriate fitting. For all samples, the measurements were taken in a standardized configuration involving a modulator angle of 0° and an analyzer angle of 45° at an angle of incidence of 55°. Spectra were gathered between 0.6 to 5 eV with a step size of 0.05 eV.

To achieve an appropriate optical model and best fit experimental results to spectroscopic theory, an initial reference scan of the silicon substrate used was taken prior to PEDOT:PSS deposition, to account for any non-idealities, dopants, and factor in the oxide layer on the substrate surface. The PEDOT:PSS was modelled as a uniaxially anisotropic material based on previous studies outlining the morphological and optical anisotropy evident in spin-cast PEDOT:PSS. A classical dispersion model consisting of a linear combination of an ideal Drude oscillator and a Lorentz oscillator was adopted to describe the dispersion in PEDOT:PSS thin films. The specific mathematical dispersion equation used is shown below in Equation 6-1 where $\varepsilon$ is the complex refractive index, $\omega$ is the frequency of light, $\varepsilon_s$ is the value of the static dielectric function at zero frequency, $\varepsilon_\infty$ is the high frequency dielectric constant, $\omega_r$ is resonant frequency of the Lorentz oscillator, $\Gamma_0$ is the damping factor of the Lorentz oscillator, $\omega_p$ is the plasma frequency of the Drude oscillator, and $\Gamma_D$ is the collision frequency of the Drude oscillators.

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\omega^2 - \omega_r^2 + i\Gamma_0 \omega} + \frac{\omega_p}{-\omega^2 + i\Gamma_D \omega}$$  \hspace{1cm} \text{Equation 6-1}

This classical model is appropriate for PEDOT:PSS as it combines parts of both the Lorentz (commonly used for insulating or semiconducting materials) as well as Drude
(commonly used for metallic materials) dispersion equations and is often adequate for describing materials that somewhat exhibit conductive behaviour (for example ITO). In contrast to amorphous ITO however, that of PEDOT:PSS has both an ordinary (parallel to the substrate) as well as an extraordinary (perpendicular to the substrate) component that are distinct from each other. For the iterative fitting procedure, the thickness of the PEDOT:PSS film as well as all the variables in the dispersion model for PEDOT:PSS were allowed to vary. A representative example of the graphical of results of a typical fitting procedure of the unexposed PEDOT:PSS are shown in Figure 6.12. As can be seen the optically simulated reflection from the modelled PEDOT:PSS film (solid line) mirrors very closely to the experimentally gathered data (dotted line) across the entire wavelength range (0.6 to 5 eV). It should be noted, that the y axis values of $I_s$ and $I_c$ (the first and second Fourier transform harmonics from the measured signal itself) in Figure 6.12 are related to $\Psi$ and $\Delta$ through Equation 6-2 and Equation 6-3.

\[
I_s = \sin(2\Psi) \sin(\Delta) \quad \text{Equation 6-2}
\]

\[
I_c = \sin(2\Psi) \cos(\Delta) \quad \text{Equation 6-3}
\]

Figure 6.12: Graphical example of appropriateness of fit of modelled optical reflection from PEDOT:PSS dispersion relations (continuous line) to experimental data from the unexposed PEDOT:PSS film (dotted line) with a $\chi^2$ error value of 2.19.
The goodness of fit is determined through minimization of a calculated $\chi^2$ error value, visually determining the fitted curve to the data, as well as evaluating the error bars on the resultant fitted values.

Table 6.8: Fitted Values for Thickness and Dielectric Model Variables for PEDOT:PSS Samples

<table>
<thead>
<tr>
<th></th>
<th>0 J/cm²</th>
<th>24.9 J/cm²</th>
<th>48.3 J/cm²</th>
<th>71.3 J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Error</td>
<td>Value</td>
<td>Error</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.19</td>
<td>-</td>
<td>1.57</td>
<td>-</td>
</tr>
<tr>
<td>Height (nm)</td>
<td>211</td>
<td>18</td>
<td>170</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>152</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_\infty$</td>
<td>1.75</td>
<td>0.05</td>
<td>1.99</td>
<td>0.07</td>
</tr>
<tr>
<td>$\epsilon_S$</td>
<td>2.20</td>
<td>0.03</td>
<td>2.42</td>
<td>0.03</td>
</tr>
<tr>
<td>$\omega_t$</td>
<td>6.41</td>
<td>0.10</td>
<td>6.33</td>
<td>0.17</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>1.08</td>
<td>0.01</td>
<td>1.27</td>
<td>0.01</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>0.33</td>
<td>0.01</td>
<td>1.01</td>
<td>0.06</td>
</tr>
<tr>
<td>$\Gamma_D$</td>
<td>0.88</td>
<td>0.04</td>
<td>0.99</td>
<td>0.05</td>
</tr>
<tr>
<td>Extraordinary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_\infty$</td>
<td>1.52</td>
<td>0.15</td>
<td>2.20</td>
<td>0.07</td>
</tr>
<tr>
<td>$\epsilon_S$</td>
<td>2.15</td>
<td>0.03</td>
<td>2.45</td>
<td>0.04</td>
</tr>
<tr>
<td>$\omega_t$</td>
<td>6.97</td>
<td>0.36</td>
<td>5.82</td>
<td>0.20</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>0.43</td>
<td>0.06</td>
<td>0.59</td>
<td>0.05</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>0.10</td>
<td>0.08</td>
<td>1.22</td>
<td>0.14</td>
</tr>
<tr>
<td>$\Gamma_D$</td>
<td>1.01</td>
<td>0.23</td>
<td>1.04</td>
<td>0.17</td>
</tr>
<tr>
<td>Ordinary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fitted values for the PEDOT:PSS layer for all samples are shown in Table 6.8. Using these values, the subsequent real and imaginary ($n$ and $k$ respectively) refractive index relationship can be developed for both the ordinary and extraordinary
directions in PEDOT:PSS and are related to the previous dispersion models through Equation 6-4.

$$\tilde{\varepsilon}(\omega) = (n + ik)^2$$  \hspace{1cm} \text{Equation 6-4}$$

To further corroborate the good fit of the ellipsometric modelling, the loss in thickness was measured again by AFM. A comparison of the film thickness measurements from SE and AFM is shown in Table 6.8Table 6.9. As can be seen, the modelled value is in close agreement with the directly measured thickness and is within the fitted error values for all cases.

Table 6.9: Comparison of film thicknesses between the ellipsometric fit and the directly measured thickness from AFM

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>SE Film Thickness (nm)</th>
<th>AFM Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>211</td>
<td>204</td>
</tr>
<tr>
<td>24.9</td>
<td>170</td>
<td>172</td>
</tr>
<tr>
<td>48.3</td>
<td>156</td>
<td>156</td>
</tr>
<tr>
<td>71.6</td>
<td>152</td>
<td>147</td>
</tr>
</tbody>
</table>
Figure 6.13: Real ($n$) and imaginary ($k$) refractive index curves of the unexposed (black), and UV irradiated films at 24.9 (red), 48.3 (blue), and 71.6 J/cm$^2$ (green), for both the ordinary ($\parallel$) and extraordinary ($\perp$) components of PEDOT:PSS.

Figure 6.13 is a comparison of the fitted refractive index values with respect to wavelength of the anisotropic PEDOT:PSS. Before looking the effects of UV exposure, it is important to comprehend the differences between the parallel and perpendicular refractive index curves. It can be seen that in the pristine unexposed case, across the visible and IR spectrum, the real refractive index of the parallel component of PEDOT:PSS has a lower value than that of the perpendicular direction. In contrast, the imaginary component, while both are relatively low across the visible regime (being one of the trademark uses of PEDOT:PSS as a highly transparent conductor), the perpendicular component is significantly lower than the parallel component, especially when moving into the IR regime. The general trends of the curves as well as the absolute values are also in close agreement with the previously report anisotropy previously reported and shown in Figure 3.6. This anisotropy as explained previously is a result of the PEDOT:PSS being the dominant species in the parallel component of the dispersion equation with the conductive PEDOT grains forming island like pancake structures, whereas in the perpendicular direction, the PSS becomes more significant due to lamellar
structure of PEDOT and PSS components. If thought of in terms of a ratio between PEDOT and PSS, in the parallel direction, the vast majority of this lamellar structure is PEDOT based, whereas in the perpendicular direction, the ratio of PSS is much larger. The PEDOT, due to its relatively high conductivity and free carrier concentration absorbs much more than the insulating PSS, causing an increase in the absorption (related to k) in IR regime in the PEDOT rich ordinary direction.

As a subjective observation of the refractive index curves, the effects of UV irradiation generally cause an increase in the refractive index in both components of the thin film. This effect is fairly consistent across the entire wavelengths investigated, however discrepancies can be noted in the farthest regions of IR (1200-2000 nm). The increase in refractive index is attributed to in part to a densification of film due to the polymer scission. As the PEDOT chains are broken and the phase definition between PEDOT and PSS regions is lost. The electrostatic forces maintaining physical separation between the conductive PEDOT grains and the surrounding PSS are diminished as the broken bonds offer available sites for interaction with inherent radical species or even the surrounding PSS itself. The increase in refractive index, particularly in the infrared region, cannot be entirely explained by a densification however as will be discussed shortly. The discrepancy between the changes in refractive index and densification are attributed to the effects of changing morphology and polymer scission within the PEDOT polymer.

In order to explore and estimate the potential effects of pure densification on the refractive index of the PEDOT:PSS films, analysis using a simple effective index model at 600 nm was performed where the PEDOT:PSS films are relatively transparent and free carrier effects on the refractive index curves should not be as prevalent. The extracted refractive index values used for this model are taken from the ellipsometric measurements at a $\lambda=600$ nm are given in Table 6.10 along with film thickness changes for the two variations of initial starting thicknesses initially deposited.
Table 6.10: Thickness and refractive index at λ=600 nm of PEDOT:PSS films having undergone UV exposure

<table>
<thead>
<tr>
<th>UV Exposure (J/cm²)</th>
<th>Measured Thickness (nm)</th>
<th>n∥</th>
<th>n⊥</th>
<th>Measured Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>204</td>
<td>1.425</td>
<td>1.475</td>
<td>108</td>
</tr>
<tr>
<td>24.9</td>
<td>172</td>
<td>1.472</td>
<td>1.554</td>
<td>80</td>
</tr>
<tr>
<td>48.3</td>
<td>156</td>
<td>1.505</td>
<td>1.607</td>
<td>74</td>
</tr>
<tr>
<td>71.6</td>
<td>147</td>
<td>1.501</td>
<td>1.607</td>
<td>66</td>
</tr>
</tbody>
</table>

Two models were compared to the extracted results: the first assuming that the entire thickness change is due to densification of the material, the second assuming that there is a densification of the material that is also aided by a constant etch rate of the top surface of the film. For the modelling of the etch and densification process, the assumption was made that the effective index at 600 nm was essentially unchanging in both orientations between 48.3 J/cm² and 71.6 J/cm². Therefore, the change between these irradiation steps in thickness was due purely to a slight material etch of ~0.35-0.4 nm/(J/cm²). This was based on the fact that the fitted refractive index values were very similar as well as the thickness decrease was approximately consistent regardless of the starting thicknesses. Additionally, by assuming that no additional densification is occurring with increased irradiation, the effective values of refractive index given in Table 6.10 of the films having undergone the highest exposure are assumed to be of the PEDOT:PSS film itself and not an effective mix with air. The comparison of the most accurate of the two aforementioned models at λ=600 nm for both optical axes are shown in a) and b) of Figure 6.14. The as deposited film parameters used to model the pure densification process are: initial filling fraction (polymer:void) = 0.7, n∥ = 1.51, n⊥ = 1.61. The as deposited film parameters used to model the densification and etch process are: initial filling fraction (polymer:void) = 0.85, n∥ = 1.51, n⊥ = 1.61.
Figure 6.14: Comparison of modeled effective index values for pure densification (red) and for densification with etch (blue) to that of the ellipsometric values (black). Comparison at $\lambda=600$ nm in a) and b) and $\lambda=1600$ nm in c) and d) for both optical axes is compared.

It is found through comparison of the models, that the model allowing a slight etch is more accurate to the fitted ellipsometric data than that of pure densification. At $\lambda=600$ nm, the modeled values for both the parallel and perpendicular modes are within 3% error in all cases. Applying both models to the IR wavelength of $\lambda=1600$ nm as seen in Figure 6.14 c) and d), the etch and densification model correlates to the change in the perpendicular refractive index within 2% error. However, this deviates significantly to greater than 10% error when comparing to the parallel component of refractive index at $\lambda=1600$ nm. Since the conjugated polymer tends to create a lamellar structure upon spincasting, the high carrier mobility in the film will provide an optical screening effect in the IR wavelengths most prevalent in the orientation parallel to the substrate. The effect
of increased UV exposure on the refractive index properties in the IR, cannot be sufficiently attributed to an etch and densification process, and the additional changes in refractive index are observed as a result of the scission process taking place in the PEDOT polymer. The PEDOT scission event correspondingly reduces the level of free carriers in the material that are preferentially oriented parallel to the substrate, thereby more significantly affecting the refractive index parallel to the substrate. With this analysis, the filling fraction of polymer to air in the as deposited PEDOT:PSS polymer can be estimated to be approximately 0.85. The subsequent change in refractive index across the visible and IR spectrum and decrease in film thickness with irradiation can be correlated to a combination of densification and etching of the surface of ~0.35 nm/(J/cm²) along with a PEDOT scission process proposed by the previous characterizations. This conclusion is supported by the previously exhibited data in AFM that highlight the loss in phase separation on the surface of the film itself. The IR refractive index parallel to the substrate in which the PEDOT polymer chains are preferentially oriented for high conductivity, initially displayed relatively low real refractive index, but high absorption akin to the refractive index relationship of materials with high carrier concentration. However, with exposure, the abnormally low refractive index for a polymer material increases significantly to display a more traditional and higher value and can be correlated to the 4 order of magnitude decrease in material conductivity. When comparing the real refractive index of the film itself, it can be seen the initial difference between the two components becomes less significant with exposure. This is again a result of the loss of phase definition within the film itself due to the polymer scission, and can be viewed as a homogenization of the two components of the refractive index. In other words, with increased exposure, the film becomes less anisotropic, since the lamellar structure initially created that resulted in a differing amount of polymer constituents depending on the direction of propagation through the film is continually degraded, leading towards a film that exhibits increased isotropic behaviour.
These observed trends in the refractive index curves in Figure 6.13 are also evident in the numerical fitting parameters of the classical dispersion model as well. As mentioned, the values of refractive index (both real and imaginary), generally increase with exposure, and this change is reflected in the actual values of the high frequency and static dielectric constants ($\epsilon_\infty$ and $\epsilon_s$ respectively) both generally increase as well. In the ordinary component, $\epsilon_\infty$ increases from its original value of 1.75 up to 2.17 after full exposure, and in a similar manner $\epsilon_s$ also increases from 2.20 up to 2.57. This trend is consistent in the extraordinary component as, $\epsilon_\infty$ increases from its original value of 1.52 up to 2.43 (there is a slight discrepancy in this trend as the film having undergone 48.3 J/cm$^2$ actually had a larger value of 2.50) and $\epsilon_s$ also increases from 2.15 up to 2.65. This may have been expected from the increase in values in the Figure 6.13 with exposure.

6.2.6 UV-Vis Absorption Characterization

Lastly, UV-Vis absorption was used to characterize the effects of UV exposure to PEDOT:PSS films and the measured absorbance results are shown in Figure 6.15.

![Figure 6.15: UV-vis absorption measurements of the PEDOT:PSS films under test. The results have been scaled to each other to account for thickness differences.](image)

The results of the UV-vis absorption spectra were taken normal in transmission mode, so they act to corroborate the relative characteristics of the changes in $k$ with respect to wavelength and as in both, the trend is for the overall absorption to increase with exposure. However, what is also important to note is that the general functionality of the
PEDOT:PSS as a highly transparent material across the visible spectrum is not significantly perturbed. While, after irradiation, there is a slight increase in absorbance, greater than 90% transmission is maintained across the visible spectrum. This characteristic of maintaining visible wavelength transmission would obviously be important for applying this patterning process to thin film transparent devices. The increase of the absorption edge in the UV regime also aligns with the decrease in $\omega$, (or absorption edge of the Lorentzian oscillator) in the dispersion model of the PEDOT:PSS film.

The absorbance also plays a key role in the determination of the maximum thickness of the PEDOT:PSS film allowable for relatively homogeneous scission through the complete thickness of the film. From the UV-vis data, at 254 nm, the normalized absorbance values with increased exposure (from no exposure to maximum tested exposure of 71.6 J/cm²) are 0.087, 0.260, 0.291, and 0.372, respectively. These absorbance values correspond to optical depths (where the intensity at 254 nm drops to a value of $1/e$) of 2335, 775, 702, and 567 nm again from no exposure to maximum tested exposure. While a gradient with film thickness is unavoidable, in order to ensure as homogeneous effect of the exposure throughout the film as possible, a limitation of a 25% difference exposure between the top surface and bottom surface of the PEDOT:PSS film was chosen. Using a simple Beers-Law calculation, to maintain 75% energy exposure at the bottom of the film when compared to the top of the film (assuming a worst-case, no change in film thickness), a maximum thickness of ~160nm is acceptable.

6.2.7 Root Cause of PEDOT:PSS Conductivity Quenching

The overarching results remain that with UV exposure, the optical, morphological, and conducting characteristics of the PEDOT:PSS film can be directly altered through UV exposure. This allows, not only for tuning of film parameters morphologically, or conductively, but also for optically for additional functionality and applications if applied in a spatially selective manner. Direct measurements indicate the loss of conductivity through UV exposure and while other previous studies have suggested the same, there
has been contradicting evidence as to that conclusion, along with limited explanation as to the physical mechanism. Taking into account the variety of characterizations carried out on the PEDOT:PSS thin film samples, the evidence clearly suggests the loss of conductivity due to a scission process specifically within the PEDOT grains of the polymer film. This decrease in polymer chain length is evidenced explicitly through the decrease in amplitude of the interring vibrational modes in Raman and FTIR spectroscopy. Additionally, circumstantial characterization using AFM indicates a loss in phase definition between the PEDOT and PSS grains that are formed into a lamellar structure during spin coating. This loss in phase distinction aligns with the conjecture of polymer scission due to the excess bonding sites being created at the scission edges, and subsequent reactions occurring between the surrounding PSS or radicals within. The loss in PEDOT grain morphology is again corroborated with the SE characterization indicating both a film etch and densification causing an increase of refractive index combined with the additional changes in the IR regime as a result of the loss of delocalized free carriers in the film.

Through application of this UV induced scission process, the bulk film properties can now be tailored to suit a specific application. In addition, as the technology to spatially define UV exposure onto a substrate has been well developed by the semiconductor industry, the possibility for spatially defined functionalization of a thin PEDOT:PSS film is possible using this quenching technique.

6.3 Application of UV Irradiation for Device Patterning

As a demonstration of the suitability of such a direct spatial modification of the conductivity of PEDOT:PSS, two device applications were investigated. Both take advantage of the key feature of visible transparency.
6.3.1 Patterned Solution Processed OLED Emission

PEDOT:PSS is often utilized as a highly transparent hole injection or transport layer in OLEDs. As has been demonstrated in the previous section, with UV irradiation, the conductivity of the film can be diminished by orders of magnitude depending on irradiation dose. However, also apparent from the electrical characterization is that the conductivity change in the normal direction does not change as significantly as in the parallel direction to the substrate. In OLEDs the critical conduction path is predominantly normal to the substrate in order to achieve recombination in an emissive layer between contacts.

For demonstration of the application of the UV irradiation, two distinct OLED devices using poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-(phenylenevinylene)] (MEH-PPV) were fabricated. The physical structure of the two are identical with PEDOT:PSS spun onto a conductive ITO substrate to achieve an initial thickness of ~100 nm, followed by spincoating of MEH-PPV to a thickness of ~90 nm. An Al cathode was evaporated on top of the MEH-PPV through a shadowmask followed by an oxygen plasma ash to remove all polymer material not protected by the Al contacts. The ultimate structure is one of ITO/PEDOT:PSS/MEH-PPV/Al, and is one that has been applied elsewhere to study the effects of PEDOT:PSS on OLED efficiency.[128], [129] The only difference between the two devices was that in one sample, prior to MEH-PPV deposition, the PEDOT:PSS film was exposed to 71.6 J/cm² of UV irradiation. The cross sectional area of the diode was 0.25 mm². The IV characteristics of the diodes were measured through the HP4155A semiconductor parametric analyzer. For optical power characterization output was collected through a 10X objective lens and the amplitude and spectral output was measured using the Raman spectrograph. Since the Raman spectrograph is not calibrated for power with respect to an arbitrary input, only a comparative difference between the two diodes could be obtained. The electroluminescent spectral output of the non-irradiated MEH-PPV OLEDs as collected through the Raman output is also typical of other reported values with the largest peak occurring at ~580 nm along with a
secondary shoulder at ~625 nm,[131] A sample output spectrum from an unexposed MEH-PPV diode is shown in Figure 6.16.

![Figure 6.16: Spectral electroluminescent output of a non-irradiated OLED (black) and a one with the PEDOT:PSS layer irradiated with 71.6 J/cm² (green). The output power has been enhanced 6.5x for clarity. Overlaid in dashed lines on the right axis is the change in transmission of the PEDOT:PSS layer.](image)

It can be seen that there are spectral output differences between the pristine and irradiated diode. As the emissive layer is not exposed at all due to the irradiation taking place prior to deposition, the change in spectral output is associated with two changes in the PEDOT:PSS layer. The first is confirmed by the difference in transmission through the PEDOT:PSS film which has been overlaid on the right y-axis for clarity. The difference in output spectrum shape above 650 nm can be correlated to the difference in slope from the transmission spectrum. The slight shift in the output peak cannot be sufficiently explained by the change transmission through the exposed PEDOT:PSS film. Rather, the previously explored change in refractive index results in an alteration in the waveguide modes between the layers and as a result changes the outcoupling efficiency. The output efficiency of the entire stack was not explicitly model due to the fact that MEH:PPV is also known to display anisotropic material behavior with refractive index values again dependent on initial dispersion formulation and deposition parameters. However, around the approximate emission wavelength (600 nm), MEH:PPV has been found to have n~2.[130] Without explicitly taking into account the anisotropies of both
the refractive indices of organic films across the entire spectral range of light output, a change in the refractive index of PEDOT:PSS will cause a perceived change in the spectral output of the emitted light due to an alteration of the emission angles and TIR based losses within the OLED structure. In general terms, the increased index of refraction with UV exposure will bring the refractive index of PEDOT:PSS closer to that of MEH:PPV, thus increasing the critical angle and decreasing the overall amount of TIR losses.

![Graph](image)

Figure 6.17: JV characteristics of the unexposed (black) and UV irradiated (green) OLEDs.

Figure 6.17 compares the JV characteristics of the unexposed and exposed diodes. As designed, under the same bias conditions, the current conduction through the irradiated diode was drastically reduced. For clarity, the information of both Figure 6.17 and Figure 6.19 are displayed on a lin-log scale for better comparison in Figure 6.18.
Figure 6.18: LIV OLED data from Figure 6.17 and Figure 6.19 displayed on a log-lin scale for clarity.

Subsequently, the difference in current conduction is identified as between 1 and 2 orders of magnitude depending on the bias applied.

Figure 6.19: LV characteristics of the unexposed (black) and UV irradiated (green) OLEDs.

Figure 6.19 shows the light-voltage (LV) characteristics of the same fabrication run of OLED diodes characterized in Figure 6.17. The measure of optical power for the LV curve was obtained by integrating the area under the spectral curve with respect to wavelength. The exact same diodes were not compared, due to diode lifetime issues as a result of not being encapsulated. As expected, the irradiated devices exhibited much less output power after device “turn-on” was achieved. The rationale behind the decrease in both current conduction and also light output is due to the excess voltage drop across the relatively resistive irradiated PEDOT:PSS film. As a result, the irradiated diode is unable
to achieve sufficient turn-on voltage for a finite optical output at tested voltages. Voltages were limited to 15 V due to the fact that above which (beginning from 16-20 V depending on the specific device), film spalling due to significant heating and subsequently near immediate device destruction occurred. Optical power and current characterization were taken on a timescale allowable for appropriate comparison, however, it was noted that with continued operation, the optical output would degrade. The change of output power with respect to 5 minutes of operation is shown in Figure 6.20.

![Graph showing output power versus wavelength.](image)

**Figure 6.20**: Loss of output power with respect to time across a time span of 5 minutes. Each scan is taken 1 minute apart.

With this significant difference in optical output verified, the next extension was to investigate the capabilities of UV irradiation to spatially pattern output from a single OLED device. UV irradiation of a square grid pattern was performed through a foil shadowmask with 150 μm linewidths with a pitch of 500 μm.
Figure 6.21: Spatially patterned light emission from an OLED diode by subjecting the PEDOT:PSS layer to spatially selective UV irradiation.

Figure 6.21 is an optical image of the optical output from a single patterned OLED biased at 13 V. Three other test diodes on the same substrate can also be seen that are not biased. The expected non-emissive grid pattern due to UV irradiation is clearly visible, even with room lights on. The critical feature in this demonstration is that none of the OLED layers are physically removed; the entire stack is maintained intact and the only additional processing required is UV exposure. In particular, in the emissive region of interest, neither the Al cathode or ITO anode have been physically patterned which has previously been the method of choice for pixelating or patterning output from an OLED display. The capability of developing such a patterning process whereby no material removal is required allows for a facile method of patterning light emission in a manner suitable for polymeric material systems.

6.3.2 Patterned Small Molecule OLED Emission

While the previous demonstration using MEH:PPV was an instructive example of the potential capabilities of PEDOT:PSS, the entirely solution based fabrication process is relatively inefficient in OLED performance when compared to the state-of-the-art small molecule or phosphorescent based organic emissive architectures. These small molecules are primarily thermally evaporated in vacuum deposition chambers and generally offer significantly higher performance metrics in comparison with solution processed materials. The drawback with such systems results from the requirement of high vacuum deposition
Chapter 6: Conductivity Quenching Using Flood UV Irradiation

constraints, thereby increasing the fabrication cost and limit compatibility with high capacity and low cost manufacturing.\cite{132} Although with future material and device fabrication advances, the efficiencies may improve to allow for an efficient all solution based device, the focus of this dissertation is solely on the tailoring of PEDOT:PSS.

To highlight the cross platform suitability of the effects of patterning PEDOT:PSS for control of OLED output, a second demonstration using small molecule evaporation was fabricated. In a similar manner to the previous OLED, PEDOT:PSS was spun onto cleaned and O$_2$ plasma treated ITO substrates at a speed of 1000 RPM resulting in initial film thicknesses of 106 nm. The PEDOT:PSS layers is again utilized to act as a hole injection layer into the overlying emissive organic films. The effects of using polymeric hole injection layers on the transparent anode have generally resulted in improved device efficiencies, however, significant variability in performance can be identified even as a result of differences in cleaning procedure of the substrate.\cite{133}-\cite{137} Following PEDOT:PSS deposition, the PEDOT:PSS films were exposed with 75 J/cm$^2$ of UV irradiation through an aluminum foil shadowmask. The irradiated pattern was a set of 8 parallel, 2 mm wide lines with a pitch of 2.5 mm. Following patterning, two additional organic layers were thermally evaporated onto the substrate: directly onto the PEDOT:PSS layer was a 500 nm layer of N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), and secondly on top of that, a 600 nm layer of tris(8-hydroxyquinolinate)aluminum (Alq$_3$). Finally, to serve as the cathode, an ultrathin 1 nm layer of LiF then a 100 nm layer of Al was deposited through a shadowmask to form a 2 mm wide cathode.

The top view of the overall device structure is shown in Figure 6.22 a), and the cross section is shown in Figure 6.22 b). For a comparison to a baseline structure without the use of PEDOT:PSS, the NPB, Alq3, and cathode layers were also deposited onto a patterned ITO substrate consisting of 8, 1 mm wide lines with a pitch of 2.5 mm. For characterization, a bias was applied between the ITO and Al contacts using a Hewlett Packard 4140B pA meter/DC voltage source, and the output current limited to 10 mA to
prevent burning of the devices. Light output measurements were measured using a Minolta LS-110 luminance meter and a custom designed Labsphere integrating sphere.

![Diagram](image)

Figure 6.22: a) Top view of the fabricated small molecule OLED device. b) Cross section of the emissive OLED stack.

Upon turn on, the patterned emission due to UV irradiation could be distinctly identified optically. An optical image of this patterned emission is shown in Figure 6.23, in which the clear delineation between illuminated portions of the LED bar can be observed.

![Image](image)

Figure 6.23: Optical image of the patterned light emission from the fabricated device under test. (Inset)Magnification on the space between illuminated regions highlighting the difference in light emission between the unexposed and exposed PEDOT:PSS regions.

An investigation of the IV curve of the entire array of LEDs was complicated due to the fact of current governing from the testing equipment itself. As was observed with the MEH:PPV OLEDs, the exposed regions are not actually completely dark as can be seen
in the magnified micrograph in the inset of Figure 6.23, but have a much lower light output as a result of the higher material resistance and subsequent lowered current density with exposure. A quantified comparison of the amount of luminance from the bright and dim regions of patterned OLED array is shown in Figure 6.24. In a similar manner, albeit, slightly decreased efficiency with respect the MEH:PPV OLEDs previously studied, a factor of 6 difference in output power is obtained.

![Comparison of the luminance with bias of the unexposed (high luminance) and UV irradiated (low luminance) regions of the OLED.](image)

As an aside, also observed in Figure 6.24, is the effects of the current governing from the power supply. The maximum allowable current (10 mA) through the OLED was reached at a bias of 3.6 V, which is only 1.2V higher than the turn on voltage, that was identified to occur above 2.4 V. For a more appropriate comparison on the effects of implementing PEDOT:PSS with that of a baseline OLED fabricated without PEDOT:PSS (hereafter referred to as “Baseline OLED”), a single illuminating pixel of LED was isolated by physically removing the connecting Al electrode from the remaining array (hereafter referred to as “PEDOT:PSS OLED”). Figure 6.25 is a comparison of the J-V curve and Figure 6.26 is that of the L-V curve between the Baseline OLED and that the PEDOT:PSS OLED. Comparing the two OLED devices, it can be seen that the additional PEDOT:PSS layer is limiting the current density within the device and subsequently the luminance as well at any given bias. This is to be expected, as the PEDOT:PSS is both adding an additional resistive pathway for carriers, and additionally preventing leakage electron transport from the ITO contact.
Figure 6.25: Comparison of current density with respect to applied bias (JV) characteristics of the baselined and PEDOT:PSS OLEDs characterized.

Figure 6.26: Comparison of luminance with respect to applied bias (LV) characteristics of the baselined and PEDOT:PSS OLEDs characterized.

While the conductivity of the device and luminance with respect to bias is found to decrease with the addition of PEDOT:PSS, the current efficiency (Figure 6.27) and photoluminescent efficiency (Figure 6.28) of the device with respect to current density are found to be improved upon due to the electron blocking effects of the layer along with a preferential alignment of energy levels to lower the energetic barrier for hole injection from the anode into the adjacent organic material. This effect has been widely studied in previous experimental demonstrations of PEDOT:PSS use in OLEDs.[133], [135], [138]
Figure 6.27: Comparison of the current efficiency with respect to current density of the baseline and PEDOT:PSS OLEDs characterized.

Figure 6.28: Comparison of the photoluminescent efficiency with respect to current density of the baseline and PEDOT:PSS OLEDs characterized.

This characteristic of the PEDOT:PSS layer limiting current density with voltage, but enhancing efficiency within the OLED has both advantages and disadvantages and necessitates a decision being made as to the tradeoff required with implementation. In other studies, it has been highlighted, that the performance and optimization of OLEDs implementing PEDOT:PSS is highly dependent on the interface between not only the ITO but also that of the overlying organic as well as thicknesses of all the materials involved in transport.[139], [140] Generally, the PEDOT:PSS hole injection layer ranges between 20-100 nm, however, if the initial film is too thin, with UV patterning, the inherent etching as a result of the process may lead to direct contact between the ITO and the overlying NPB, thereby negating or decreasing the effects of the PEDOT:PSS layer. Lastly, the spectral output from the OLEDs is compared in Figure 6.29. The slight
redshift of the peak intensity from 528 nm in the Baseline OLED to 544 nm in the device with a PEDOT:PSS hole injection layer is attributed to both additional absorption through the PEDOT:PSS layer, but is also be a result of exciton energy loss as a result of having carriers transported through an additional layer of material.

![Comparison of spectral output](image)

Figure 6.29: Comparison of the spectral output of the baseline and PEDOT:PSS OLEDs characterized.

The designed experiment and demonstration using PEDOT:PSS as a hole injection layer was to highlight the patterning process of the OLED, that is compatible with small organic molecule thermal evaporation. As has been shown, the process allows for the preferred illumination of untreated areas of the OLED while maintaining the desired advantages accompanying the use of a PEDOT:PSS interfacial layer. This quantitative device comparison between OLEDs with a PEDOT:PSS hole injection layer, and without, has shown to be maintain the beneficial optoelectronic properties as expected with the implantation of a hole injection layer. Coupled with the capabilities of defining brightly and dimly emitting regions across the OLED using an extremely facile and single step irradiation process, allows for arbitrary pattern definition, particularly in applications where inexpensive devices are critical, yet fully dynamic functionality may not be necessary. It should be noted that the hole injection layer has not been optimized for this device, rather, this is an extension of the UV patterning technique which could prove beneficial towards certain applications. Ultimately, the eventual goal would be towards fully addressable and pixelated display technologies. While the fully addressable demonstration has not been demonstrated, the progress towards such technology using an
inexpensive and facile patterning mechanism has been shown through the linear definition of a pixelated array.
Chapter 7

Highly Transparent Organic Capacitive Touch Sensors

The successful demonstration of the OLED patterning through modification of the PEDOT:PSS layer only took advantage of the conductivity reduction in the normal direction. The effects of UV irradiation of 3 orders of magnitude more effective in conductivity change in the direction normal to the substrate. To demonstrate the potential for spatial patterning in a device that takes better advantage of the full decrease in conductivity parallel to the substrate, PEDOT:PSS was implemented as a conductive contact in a capacitive touch sensor array exhibiting high transparency across the visible spectrum.

With the ubiquitous nature of smartphones, tablets, and hybrid laptops being implemented into society over the past 10 years, essentially every single consumer electronics user has interacted with some form of touch interface. A wide variety of techniques have been implemented for imparting touch input functionality into electronic devices including resistive, capacitive, and IR sensing.[141] The use of capacitive touch screens has become the most influential, as this technology is the most prevalent in virtually all current electronics that involve a touch interface. Key requirements of a generic capacitive touch screen include being relatively transparent, being able to identify a touch event (ideally multi-touch capable), and be compatible with the underlying technology. Capacitive touch screens that locate a touch input or interpret gesture from the user, and are based on the concept of electric field perturbation by the users finger (or suitable stylus). In most commercial technologies, ITO is utilized as the contacts to
the capacitive element and is required to be physically patterned in the designed electrode pattern of choice. ITO, however, suffers from several incompatibilities for implementation with future organic and structurally flexible devices. Of primary concern is the characteristic of ITO to be brittle and subsequently break or significantly lose conductivity when bending occurs after deposition on a flexible substrate.[142], [143] Additionally, techniques for depositing ITO onto substrates are often vacuum based and occur at significantly high temperatures, resulting in incompatibility with common flexible substrate materials or any underlying organic layers that are not properly protected. These drawbacks are all detrimental to proposed large scale, high throughput organic electronic device techniques, specifically roll-to-roll processes.

To counteract the issues with ITO implementation in a flexible capacitive touch panel architecture, a variety of design approaches and materials have been explored. For example, to achieve an appropriate balance between transparency and conductivity, fabrication of experimental electrodes has also been approached by creating thin grids or meshes of opaque conductive material such as metal foil.[144], [145] While this solution can be effective for application in PV cells, to allow the majority of light to interact with the active absorbing material, it is not an acceptable solution for display technologies in that the then metal grids will create optical aberrations that interfere with proper viewing of an underlying LED screen. Alternative solutions using different transparent conductive materials such as silver nanowires, graphene, nanoparticles, carbon nanotubes and conductive polymers have also been explored.[146]-[153] The primary challenge in switching the electrode material is ensuring a high material conductivity as charge carriers need to be transported efficiently in order to detect the changes in capacitance with an appropriate response time. A second issue with many of these novel materials include incompatible deposition environments for high throughput organic fabrication (such as the vacuum deposition techniques for graphene). While significant research has been focused on the deposition and material characteristics of potential transparent electrodes, the mechanics of patterning are generally still reliant on traditional optical lithography to create the required overlapping row and column electrodes for an
addressable capacitive touch sensor. Such methodology does not lend itself to the predicted advantages of fabricating organic materials into a high through large scale fabrication process. Obviously material characteristics are a key parameter in device performance, but since organic materials will never be able to compete directly with inorganic electronic materials, the areas where they do excel such as inexpensive, room temperature and pressure deposition and compatible patterning methods need to be exploited.

In particular, the use of PEDOT:PSS in capacitive touch sensors has been identified in only a few cases.[149]-[151] Of critical importance is the recently reported integrated demonstration from Clevios, however, aside from that, the use and patterning PEDOT:PSS as a transparent electrode in capacitive touch screens is limited.[31] The most appropriate demonstration involved the deposition of patterned PEDOT:PSS using inkjet printing, followed by a subsequent deposition of a transparent dielectric polymer to prevent a short being created at the intersection points between row and column traces, followed again by a second deposition of PEDOT:PSS on top of the dielectric to create an electrical connection row electrodes.[149] The resulting device was able to appropriately sense touch events by measuring capacitance changes between row and column traces, however, the method of fabrication is limiting in terms of sequential depositions, and spatial resolution that is inherent to inkjet printing. Additionally, using laser ablation and micromolding patterning techniques, appropriate electrode designs have been created, however, no device characteristics reported.[150] In order to ultimately be competitive in the market, capacitive sensing technology must be available in a scalable, high throughput fabrication process along with being compatible to the underlying electronics and materials it is being integrated with. This is where the developed UV irradiation architecture from Chapter 6 for spatially resistive patterning can excel in comparison to other serial process flows such as inkjet printing and laser ablation. Desired device functionality can be provided through the UV induced resistive patterning without requiring physical material removal or secondary resist deposition and development.
7.1 Capacitive Sensor Electrode Design

There are a variety of touch input sensor technologies that have been utilized for commercial applications. Such technologies include resistive sensing, projected capacitance sensing, IR detection and acoustic wave sensing. The most common are the electrical techniques that sense a resistive or capacitive change due to a touch event. Currently, the consumer electronics market is dominated by projected capacitance touch panels that are inherent to nearly all smartphones, tablets and touch enabled personal computers.

7.1.1 Projected Capacitive Sensing Technology

As the concept suggests, projected capacitive sensing is a technology that relies on the measurement and subsequent change of capacitance due to electromagnetic interference at, or between one or more electrodes. The benefits of projective capacitive sensing include multi-touch input (if designed properly), high optical transmissivity assuming a highly transparent conducting electrode material is used, proper operation in extreme environments given the active layers and electronics are encapsulated appropriately, along with the potential for being transferred onto plastic or flexible substrates for future organic applications.[155] In contrast, the technology does suffer from low signal to noise ratio and a relatively high cost (as compared to a resistive sensing option). In order to be able to determine a spatial touch even, a 2D array of individually addressable conductive traces is required to be fabricated. There are two types of projected capacitance architectures used for 2D touch sensing applications: self capacitance, and mutual capacitance. Regardless of the sensing architecture, the supporting sensing integrated circuits need to be able to individually either drive or sense a signal for each of the rows and columns.

7.1.1.1 Self Capacitance

Self capacitance is a based on taking a measurement of capacitance between a selected trace/electrode and the ground plate. In the circumstance that a finger or conductive stylus is brought near to the electrode, a parallel capacitive path to ground is created,
subsequently increasing the capacitance measured from that electrode to ground. A modelled circuit diagram of this method of sensing is shown in Figure 7.1.

![Figure 7.1: Schematic of self capacitance sensing mechanism. The inherent capacitance shown in a) is effectively increased due to a secondary parallel capacitance to ground when a conductive stylus or finger being brought close to the electrode as shown in b).](image)

For spatial detection, the capacitance is measured sequentially across each of the rows and columns resulting in a total number of measurements to be made equal to the sum of the number of rows and column electrodes in order for the location of a single touch to be determined. The measured capacitance is continually monitored and compared to a base value of capacitance. A drawback of this method, however is the inability to handle multi-touch input. Since a capacitance change only indicates to the microcontroller that there is a touch somewhere along the trace, and the exact location is determined by simultaneously measuring a change across one of the perpendicular traces. In the case of a multi-touch input as shown in Figure 7.2, there is an inherent ambiguity as to the precise location of the touches due to two potential ghost points being created. It is because of this multi-touch ambiguity that the preferred method of sensing in modern devices has shifted to a mutual capacitance method.
Figure 7.2: Illustration of the erroneous detection points (red circles) due to “ghosting” as a result of a multi-touch event (green circles) in a self-capacitance architecture.

### 7.1.1.2 Mutual Capacitance

A mutual capacitance sensing architecture is the current solution to enabling multi-touch input in modern capacitive touch screens. Rather than measuring the capacitance between a conductive trace and ground in self capacitance methods, mutual capacitance detects a capacitance change between two separate electrodes. In general, this is measured between a row and a column electrode, and the detection of a touch at the intersecting node of the electrodes is enabled. Conceptually, at each of individual intersections between row and column traces, a small capacitor is formed. Upon the introduction of a conductive object near a measured node, a secondary field can be created between the object by effectively shunting away some of the fringing field between the electrodes as shown in Figure 7.3. Several advantages of mutual capacitance sensing include the enabling for multi-touch input, higher spatial sensitivity, and is more resilient to external electromagnetic interference. However, these advantages come as a trade-off, due to the fact that an increased number of measurements need to be made to map the entire panel (the number of individual capacitance measurements is now equal to the number of row electrodes multiplied by the column electrodes, as opposed to an addition in the self-capacitance case), requiring additional computing circuitry and signal processing. As well, not only is the base value of capacitance between electrodes much
smaller due to the significantly smaller cross sectional area (only the intersection between capacitors defines the area as opposed to the entire length and width of the electrode to ground in the self-capacitance case), but since only a fraction of the fringing field is stolen from the capacitor, the measured change in capacitance is often extremely small, on the femtofarad level. Due to the lowered level of capacitance values and change, the external sensing circuitry is required to be relatively complex when compared to the self-capacitance variety in order to be able to sense subsequent changes in capacitance.

![Figure 7.3: Schematic of an unperturbed capacitive element shown in a) created at the intersection between a row and column electrode, and in b) the effects of bringing a conductive object close to the node in question. Electrode material has a thickness of \( h \) and dielectric interlayer has a thickness of \( d \).](image)

### 7.1.1.3 Physical Electrode Design

A common method to increase the sensitivity of mutual capacitance devices is to enhance the amount of fringing field and subsequent coupling effect of interference of a conductive object inducing a touch event. This can be achieved by altering the electrode pattern from a simple rectangular cross hatch to a structure of interlocking diamonds as shown in Figure 7.4. Different design considerations need to be made in order to maximize the fringing field,
Using the variable assignments shown in Figure 7.3 and Figure 7.4, a value of the capacitance per unit length of each intersection of electrodes is given in Equation 7-1, where \( t \) is the electrode trace width, \( \epsilon \) is the permittivity of the dielectric material between the traces, \( d \) is the thickness of the dielectric, \( h \) is the thickness of the electrode material, \( w \) is the length of the side of the diamond, and \( k \) is a coefficient of sensing.

\[
C_{\text{sensing}} = k \frac{t^2 \epsilon}{d} + k \frac{8\pi w \epsilon}{\log\left(\frac{4d}{h} \right)} \tag{Equation 7-1}
\]

In Equation 7-1, the coefficient of sensing \( (k) \) is 1 when the sensor is untouched and during a touch event is equal to \( s/(s+d) \), where \( s \) is the distance from the conductive object to the top of the electrode surface. The first term in Equation 7-1 is the capacitance contribution from the overlapping electrode necks, and the second term is the contribution from the fringing field between row and column electrode diamond structures.
Figure 7.5: Generalized fabrication process of a single (a) and dual (b) substrate electrode capacitive touch panel. Coloring does not imply different material, but rather differentiates between eventual row and column structures.

This conductive diamond shaped structure is often patterned in one of two approaches: single or dual substrate. Generalized process flows for both are shown in Figure 7.5. In Figure 7.5 a) there is an initial deposition of electrode material on the substrate, subsequent deposition and patterning of a dielectric interlayer to prevent shorts between electrodes, and the completion of the structure by depositing and patterning the missing conductive column traces. In Figure 7.5 b), the complete row and column electrodes are patterned on different substrates, subsequent deposition of a dielectric interlayer and completion of structure by aligning and bonding the two substrates together.

7.1.2 PEDOT:PSS Capacitive 2D Sensor Fabrication Design

Applying the technique of UV resistive patterning to PEDOT:PSS requires several additional considerations that are not as critical to traditional sensor design using ITO. The primary one is that pristine PEDOT:PSS has inherently at least an order of
magnitude lower conductivity that ITO (see Table 4.1). Combined with the fact that in order to ensure proper spatial patterning of the PEDOT:PSS film, the film needs to be kept thin as well (preferably on the order of sub-150 nm). This is due to the penetration depth limitation of the 254 nm UV light that was discussed in 6.2.6. As such, the ultimate design featured a thicker trace width \((t)\) of 0.5 mm as opposed to the more common 20 \(\mu m\) size traces of ITO and the electrode thickness \((h)\) was chosen as 100 nm. Combined with this wider electrode trace, aluminum contacts were evaporated on both sides of the active region of the sensor in order to provide the best contact and lowest resistance to all locations along the row and column electrodes. As a consequence of enabling a simplistic, single step exposure process flow, a dual substrate design as illustrated in Figure 7.5 b) was necessary. Lastly, due to the dual substrate process, an alignment step to ensure appropriate intersection of the diamond shaped electrodes was required. As this non-standard process flow was not automated for use with an optical stage, it was necessary to perform this alignment by hand, and therefore, the gap \((g)\) between electrodes was increased to 0.5 mm to prevent potential undesirable electrode overlap. Further design decisions included creating an array with a pitch \((p)\) of 2.5 mm in order to be compatible with common electrical connector contact widths to allow for ease of interfacing between external measuring equipment. Finally by designing an array of 8 electrodes for both the rows and columns, millimeter scale resolution across the active area of the device could still be achieved. As a result of previous design decisions, the parameter of diamond width \((w)\) was calculated as 0.9 mm. The choice to use SU-8 as a dielectric interlayer was primarily based on optical transparency, but also taken into account was chemical availability and previous expertise of this photoresist for robustly flip chip bonding substrates together. From the SU-8 data sheet, the approximate permittivity of SU-8 is \(4 \varepsilon_0\).

Combining the above designed and selected values with Equation 7-1, an estimated value of capacitance of each element can be calculated using a dielectric thickness \((d)\) of 5 \(\mu m\) of \(C_0 = 1.92\ pF\). Upon characterization of the eventual measured values, the average of the 64 capacitive elements was found to be 2.33 pF with a standard deviation of 1.17 pF.
The significant variability across the array results from variability in the thickness of both the dielectric and organic layer, slight misalignment during the bonding procedure, as well as measurement error due to resistive losses along the PEDOT:PSS traces.

### 7.2 Capacitive Sensor Characterization

For all touch event characterization, measurements were made using an HP4248A LCR meter capable of femtofarad measurements at a frequency of 100 kHz using an applied voltage of 0.1 V. The touch events introduced were performed through the use of a conductive stylus connected in series to a 100 pF capacitor and a 1.5 kΩ resistor, which is an approximation of the electrical model of a human body.

#### 7.2.1 1 Dimensional Mutual Capacitance Detection

Prior to implementing the designed 2D sensor array, an initial demonstration of capacitance sensing was tested by creating a capacitive element parallel to the substrate between conductive lines as opposed to vertically. The key purpose of this demonstration is that the occurrence of a spatial touch event could be event could be identified using a structure that is fabricated out of a single material and single layer through functionalization. The general fabrication process was similar in manner to the X-Y grid fabrication, with the exception that rather than a 3D structure with the capacitive sensing element created between bonded substrates, with UV exposure, a capacitive element could be created along the plane of the thin PEDOT:PSS film itself.
Figure 7.6: Single layer planar capacitive sensing element.

Figure 7.6 displays the general process flow and device structure. PEDOT:PSS is spincast on a transparent glass substrate. UV irradiation is designed such that the capacitive sensor is created between parallel conductive lines. This also takes advantage of the greater change of conductivity with exposure parallel to the substrate as opposed to in the normal direction. However, as there is no explicit insulator deposited or fabricated in between conductive plates, there is a finite conductance between the contacts as well that may influence results and introduce inconsistencies. In order to both prevent any change in material characteristics during testing and mimic the expected eventual separation of conductive stylus from the PEDOT:PSS film, a glass slide cover was bonded on top of the patterned PEDOT:PSS film for encapsulation. For testing the three sensor structure, a touch event across the three sets of pads was cycled verifying that such an even could both be identified and was repeatable. The average measurements of both capacitance and conductance under the given experimental configuration are shown in Table 7.1.

It can be observed that upon a touch event across the measured element, a large change in capacitance (anywhere from a worst case 180% change up to over 400% difference can be measured. Due to the fact that the touch event is effectively creating a parallel capacitive path between the two contacts, the capacitance subsequently increases in magnitude as schematically shown in Figure 7.7.
Table 7.1: Capacitive and Conductance Change Measured Across Conductive PEDOT:PSS Lines Upon a Touch Event

<table>
<thead>
<tr>
<th>Measured Element</th>
<th>Touch Location</th>
<th>Capacitance (pF)</th>
<th>Conductance (μS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>n/a</td>
<td>1.34</td>
<td>1.06</td>
<td>106</td>
</tr>
<tr>
<td>1</td>
<td>4.0</td>
<td>2.8</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>1.31</td>
<td>0.95</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>1.33</td>
<td>1.01</td>
<td>106</td>
</tr>
<tr>
<td>n/a</td>
<td>1.33</td>
<td>1.3</td>
<td>75</td>
</tr>
<tr>
<td>1</td>
<td>1.28</td>
<td>1.27</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>2.4</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>1.30</td>
<td>1.26</td>
<td>78</td>
</tr>
<tr>
<td>n/a</td>
<td>1.88</td>
<td>1.82</td>
<td>68</td>
</tr>
<tr>
<td>1</td>
<td>1.81</td>
<td>1.77</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>1.80</td>
<td>1.76</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>6.2</td>
<td>78</td>
</tr>
</tbody>
</table>

Figure 7.7: Schematic of the lateral capacitance demonstration of a) the unperturbed structure, b) the structure with a touch event introduced, and c) the equivalent circuit of the structure with a touch event.
The large degree of variability during the touch event is due to the inconsistent nature of
the physical touch. Slight changes in position as well as areal coverage across the
conducting lines will change the coupling between the finger and the sensor. Also
tabulated in Table 7.1, is the measured conductance and change between the two
conductive traces. While there may be slight variation as a result of a touch event, there
is neither a consistent change, nor a significant one in comparison to the unperturbed
case. While a slight decrease may have been expected due to the addition of an alternate
parallel resistance, the magnitude of the introduced resistance through 2 mm of a glass
slide would be much greater than the present inherent in-film resistance and as such is
inconsequential. Any differences in measurements are subsequently attributed to errors in
the sensing mechanism of the sensing circuitry.

7.2.2 3x3 Array Proof of Concept

As an initial proof of concept of a 2D capacitive sensing array, PEDOT:PSS was spincast
onto two 5.1 x 7.6 cm transparent glass substrates. Following deposition, three
conductive lines are patterned into the PEDOT:PSS film through selective UV
irradiation. Lastly, SU 8-2007 is spincast onto both substrates and flip chip bonded to
each other, effectively creating an array of capacitors with electrical contacts accessible
on either side of the device. A schematic of the final structure is shown graphically in
Figure 7.8.
Figure 7.8: Schematic of 3x3 spatial addressable capacitive touch sensor array fabrication.

With this device, direct electrical connections were made sequentially to each of the conductive PEDOT:PSS read lines to a HP4284A LCR measurement unit. For each combination of electrical connections to the read lines, the baseline capacitance was measured, along with the change in capacitance upon a finger touch event at each of the conductive intersections. Table 7.2 shows the measured capacitance of each element without any touch event on the device.

Table 7.2: Measured Capacitances of each Conductive Intersection Without a Touch Event

<table>
<thead>
<tr>
<th>Event</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>2.73 pF</td>
<td>3.00 pF</td>
<td>2.88 pF</td>
</tr>
<tr>
<td>Y2</td>
<td>2.47 pF</td>
<td>2.18 pF</td>
<td>1.77 pF</td>
</tr>
<tr>
<td>Y3</td>
<td>1.66 pF</td>
<td>1.78 pF</td>
<td>1.47 pF</td>
</tr>
</tbody>
</table>

Upon a touch, due to the mutual inductance of the finger perturbing the electric field, and effectively creating a parallel capacitor to draw charge away from the developed capacitor, the measured capacitance would fall. Figure 7.9 depicts the change in
capacitance at each of the 9 capacitive elements tested upon a touch at the specific location where the color map is located.

![Color coded change of measured capacitance at each capacitive element (Fig. 7.9)](image)

Figure 7.9: Color coded change of measured capacitance at each capacitive element following a touch event at the specific location.

The maximum capacitance change due to a touch even was greater than 5% from its unperturbed value, for all cases with the exception of the bottom left element (corresponding to contacts at X₁ and Y₃ in Figure 7.8). Critical as well, is that fact that there was a measurable difference in terms of percentage change between the element that was contacted and those surrounding it. While there is still some crosstalk from the touch on an element and its neighbors, the element located below the physical touch exhibited the greatest capacitance change when compared to the surrounding sensors.

### 7.2.3 8x8 Interlocking Diamond Structure Testing

Both previous capacitive touch sensor demonstrations take advantage of the greater, 4 order of magnitude reduction in material conductivity. In order to improve on the spatial resolution the previously designed array from 7.1.2 was created and characterized. While several iterations of the capacitive test structure were fabricated, the characterization reported here is primarily on the best working and completed prototype.

#### 7.2.3.1 Fabrication Procedure

Boroaluminosilicate glass slides with dimensions of 2.54 x 7.62 cm were used as the dual substrates and were initially ultrasonic cleaned with acetone and subsequently oxygen plasma cleaned for 10 minutes at 100 W with an O₂ pressure of 0.5 mTorr. PEDOT:PSS
was then spun onto cleaned at 2000 RPM for 45 s. The resultant film thickness was approximately 100 nm thick before UV exposure. For resistive patterning, the films were irradiated by a Spectroline XL-1500 Crosslinker through an electroformed Ni shadow mask. For proper functionality and obtaining a large enough contrast between conductive and resistive regions, a total exposure energy of 75 J/cm² was required. Following the UV patterning, aluminum contacts were thermally evaporated through a second shadow mask onto the PEDOT:PSS films at the edges of the substrate. This allowed for appropriate electrical contact to the polymer traces, yet did not interfere with the highly transparent characteristics of the two PEDOT:PSS layers and SU-8 bonding layer within the active sensing region. The Al contacts were thermally evaporated on both ends of the conductive PEDOT:PSS traces to provide a minimum of resistance along the polymer trace and achieve the possible performance. Proper monitoring and timing of the flip chip bonding sequence involving SU 8 are required to ensure a robust bond between substrates. Initially, a transparent film of SU 8-2007 was spun on one of the slides to the desired thickness of 5 μm and soft baked at 95°C for 5 minutes. Following this soft bake, hotplate temperature was lowered to 60°C. At 85°C the second slide is brought into contact, PEDOT:PSS side down, with the SU-8 covered slide and pressure is applied by rolling a cylinder across the surface till the temperature reaches 75°C to create a homogeneous interface between the two slides. As the hotplate temperature continues to decrease to 60°C a 1 kg weight is maintained on top of the device to achieve a robust contact and bond. The entire structure is then baked on the hotplate for an additional hour with the aid of a 1 kg weight to maintain proper adhesion. A representation of the finalized device is shown in Figure 7.10.
Figure 7.10: Schematic of dual substrate fabricated sensor array with 8 rows (Y1-Y8) and 8 columns (X1-X8) resistively patterned into PEDOT:PSS separated by an SU-8 dielectric layer with aluminum contacts on both edges of the active layer.

### 7.2.3.2 Electrical Characterization

To ensure that appropriate irradiation and proper resistive patterning was achieved, electrical IV measurements were taken on the individual PEDOT:PSS films measuring the change in conductivity between aluminum contacts on opposing sides of the eventual active area. A representative IV measurement is shown in Figure 7.11 on a log-lin scale. An initial electrical baseline is obtained across an expected conductive PEDOT:PSS trace between X4-X4. Subsequent measurements offset by a single resistively patterned region are shown between X4-X3/X5. Beyond one offset contact, no measured signal above the noise floor was obtainable.

Figure 7.11: Electrical IV measurements on the log-lin scales between opposing aluminum contacts on the same substrate demonstrating
significant conductivity loss with irradiation. Measurements are shown for contacts on the same conductive electrode (X4-X4) and offset by one resistive regime (X4-X3 and X4-X5).

From these results it can be calculated that the material conductivity (discounting contact losses) along the PEDOT:PSS trace is \( \sim 460 \text{ S/cm} \), which aligns within the expected range given in Table 4.1. Also of key importance is the greatly reduced current once a UV patterned region is introduced between adjacent contacts. At a bias of 1V an order of magnitude difference is observed with a single introduced region, and with two regions introduced a conductive loss of over 3 orders of magnitude can be measured. Due to the non-linear relationship between bias and conduction due to conduction regime, by limiting the measurement voltage to less than 1V, the contrast between contacts can be magnified, and at \( \sim 0.1 \text{ V} \) approaches the expected 3-4 orders of magnitude contrast between adjacent contacts. It is found that this level of contrast is sufficient to provide appropriate spatial location of a touch event as shown through characterization in the next section.

### 7.2.3.3 Touch Event Characterization

For touch event characterization, an initial baseline of each of the capacitive sensors was initially measured to determine the magnitude of initial capacitance at each crossing electrode. The base capacitances are displayed in as a surface map in Figure 7.12.

![Figure 7.12: Color map of the measured capacitances of the unperturbed array.](image-url)
The raw measurement values range from 0.856 pF up to 5.326 pF, with an average of 2.10 pF with a standard deviation of 1.25 pF. This, however, is a slightly misleading variance, since there can be observed a clear increase in capacitance along the top and bottom edges of the array, and in particular along rows $Y = 1$ and $Y = 8$. If two separate means and standard deviations are calculated for the electrodes $Y = 1$ and $Y = 8$, and $Y=2$ to $Y=7$, values of $3.82 +/− 1.07$ pF and $1.52 +/− 0.65$ pF are obtained respectively. This is attributed to inconsistencies in both the thickness of the insulating dielectric SU8 layer between the two glass substrates, but also differences in contact resistance from the aluminum traces to the PEDOT:PSS film itself. More precisely, the method of fabrication involves a pressure rolling step to create an appropriate bond between the slides, and the width of the rolling cylinder used is exactly 2.25 cm. Although efforts were made to homogenize the applied rolling pressure, it appears as if the initial point of pressure, along the center of the slides along both the X and Y direction create a measureable difference in interlayer thickness. If it assumed that the difference is solely due to dielectric thickness, applying Equation 7-1 the difference in interlayer thickness between the two regions can be calculated to be between 2.7 and 5.2 $\mu$m. This very slight difference may arise from an uneven application of pressure during the fabrication process, or even roughness of the underlying glass substrate itself. By documenting the initial baseline, a relative comparison of the capacitance before and after a touch can be analyzed for determination of the spatial location of a touch.

Following the measurement of the initial baseline values, capacitive measurements were made at each of the 64 coordinates dependent on a touch event being initiated on the top substrate surface at each of the 64 coordinates individually. Due to the significant variability of the initial base capacitances, for proper determination of a touch event, the individually measured change in capacitances is normalized to the maximum change across the array. A representative example of the normalized capacitive measurements is shown in Figure 7.13 upon a stylus touch at location $X = 3$, $Y = 3$. 
Figure 7.13: Measured changes in capacitance at each of the 64 intersecting elements of the electrode array upon a touch event located at X=3, Y=3.

In Figure 7.13, with normalization to the maximum change for each capacitive intersection, the location of the touch event can clearly be observed.

For each touch event, the measured values could be interpolated into a representative color map displaying the relative change of capacitance across the entire array. While there was some noise and ambiguity of the touch location in several of the measurements, the touched coordinate measured the largest change in 78% of the touch events, of the remaining error readings, 17% reported a nearest neighbor displaying the highest capacitance change, and only 5% measurements indicated an erroneous touch more than 1 coordinate away. A representative example of a color map properly operating touch event is shown in Figure 7.14 with the stylus centered at coordinate X=3, Y=3.
Figure 7.14: Characteristic example of an accurately measured touch event displaying the measured relative change in capacitance upon a touch event occurring at position X=3, Y=3.

One of the encountered errors in measurements that contributed to location ambiguity, was cross talk between neighboring electrodes. In some iterations, maximum capacitance change was observed, not only at the location of the touch stylus, but also at one or more of the nearest neighboring intersections. An example of a touch event that results in cross talk between neighboring electrode crossings as shown in Figure 7.15, wherein the stylus was placed at position X = 4, Y = 7, however a maximum capacitance change was measured not only at that intersection, but also at the neighboring X = 4, Y = 6 location.

Figure 7.15: Example of a nearest neighbor error in the measured relative change in capacitance upon a touch even occurring at position X=4, Y=7. Not only is the maximum change registered at the touched coordinate, but it is also measured at the adjacent coordinate X=4, Y=6.
While this behavior is obviously undesirable, as previously stated, this was observed in only 17% of the cases tested. A second error encountered, was a significant display of maximum or near maximum capacitance change registered simultaneously from a number of points across a common electrode. For example, a particular device displayed significant capacitance change across the majority of the X=6 electrode intersections when the stylus was located at X = 6, Y = 1. This is the result of a single PEDOT:PSS trace being improperly exposed resulting in a significant errors along the entirety of the trace as shown in Figure 7.16. In such situations, to alleviate these issues the accumulation of signal averaging could be increased to obtain a higher signal to noise ratio at the cost of measurement time. Further analysis of the improperly reporting electrode, X=6, was performed by taking an electrical measurement between aluminum electrodes across the PEDOT:PSS trace. The IV characteristics are displayed in Figure 7.17 and clearly indicate a 2 order of magnitude loss of current conduction at a 1V bias when compared to the expected values measured in Figure 7.11. This implies that the expected conductive PEDOT:PSS electrode was inadvertently exposed during the resistive patterning procedure, and subsequently results in an improperly operating electrode.

Figure 7.16: Example of an improperly defined electrode. Current is not being conducted properly along the length of an electrode and as such similar capacitance change values are being read across the entire X=6 electrode although the touch event is taking place only at X=6, Y=1.
Figure 7.17: IV curve measured between contacts across improperly reporting electrode X = 6 displaying a distinct loss of conductivity in comparison to previously measured unexposed PEDOT:PSS traces.

Due to the abnormally high resistivity of the trace, carriers are not efficiently transferred from the contacts to the intersection between the row and column electrode, and as a result, the change in capacitance is erroneously distributed along the entire trace. Since devices exhibiting such characteristics are not properly conducting current to the measuring electrode, cross talk between the individual elements, a solution of averaging could not alleviate the problem, and appropriate data for touch locations on such a trace was unobtainable.

### 7.2.3.4 Transparency Characterization

Transparency is a key metric in regards to capacitive touch sensors for user interface. For proper viewing of underlying display screens. In that regard, the transmission of visible light, between 400-800 nm, through the fabricated sensor was measured and compared to transmission through a reference device which had not undergone any patterning. The transmission results are shown in Figure 7.18 and are taken with reference to two glass substrates, mimicking the eventual structure of the completed capacitive array.
Figure 7.18: Transmission characteristics through an unpatterned sensor array (blue) and the finalized patterned device (green).

Due to the small critical dimension of the patterning and the sampling beam spot size being 1 mm in diameter, the transmission spectra compiled using the averages of 5 individual measurements. This takes into account potential differences in polymer film thickness and also exposure dose differences between exposed and unexposed regions and gives an average transparency of the entire film. The results corroborate the previous characterization of a single thin film having undergone exposure from Section 6.2.6, where increased exposure reduced transparency in the visible regime. The completely patterned device was capable of transmitting over 80% of light across the visible spectrum. To further illustrate the high level of transparency within the active area of the array, an image of a completed array overlaid on a ruled paper is shown in Figure 7.19.

Figure 7.19: Image of a completed sensor array overlaid on a ruled paper exhibiting the visible transparency within the active region.
With this level of transparency the capacitive touch screen is competitive with the transparency of ITO touch screens which exhibit around 85% transmission.
Chapter 8

Conclusions and Future Direction

PEDOT:PSS, while having been discovered over a decade ago, is still relatively unexplored in regards to the commercial material advantages it offers to organic electronic devices. It has been applied in a vast number of electronic and optoelectronic applications, however, the precise material characteristics of different PEDOT:PSS thin films can vary drastically with processing, deposition and starting formulation. This has led to a wide range of inconsistent, and occasionally contradicting, results in literature. While the original concept for this thesis began with the intentions of implementing PEDOT:PSS into optoelectronic waveguide structural stacks and active devices, it became clear that the material science and fabrication procedures required for appropriate use did not yet exist in literature. Therefore a transition to the application of appropriate processing techniques, optical and electrical characteristics and subsequent material changes in PEDOT:PSS was necessary to develop the foundation for moving forward into device integration.

8.1 Summary of Contributions

A point form summary of the contributions from this thesis are listed below followed by a subsequent more detailed discussion on the particulars of this thesis.

- Amalgamated a wide breadth of literature on the background, processing techniques, and material potential of PEDOT:PSS in organic electronic device design.

- Demonstrated the decrease in material resistivity of PEDOT:PSS thin films through the application of RTA.
- Associated the specific electrical changes effects of RTA to a shift in morphology of the PEDOT:PSS thin films.

- Explored the effects RTA has on the theoretical equations governing carrier transport through PEDOT:PSS and identified an increase of carrier mobility and decrease in contact resistance with respect to annealing temperature.

- Proposed an alternative method of imparting functionality to PEDOT:PSS films using a UV induced scission process to spatially modulate the film conductivity as opposed to physically patterning the film itself.

- Characterized the specific electrical, optical and morphological effects that UV irradiation has on the PEDOT:PSS film.

- Designed fabricated, and characterized two demonstrations of organic electronic devices (an OLED and a capacitive touch sensor panel) that utilized the aforementioned UV induced scission process for imparting appropriate device functionality.

This dissertation began by emphasizing the trend in commercial devices towards lightweight, physically flexible optoelectronic components such as OLEDs. In particular, the focus on a relatively well known, and commercially available conductive organic polymer, PEDOT:PSS, was identified. The limited body of scientific literature dealing with the physical electronic conduction phenomena and optical material characteristics of PEDOT:PSS, as well as the lack of effective patterning techniques compatible with large area high throughput fabrication technologies motivated this research.

Initial experimentation were centered on resolving one of the issues related to PEDOT:PSS: that being the relative low conductivity when compared to other transparent conductors, and in particular ITO. Specifically, the application of
RTA, a post-deposition processing technique, was investigated, explored and characterized. The effects of RTA were found to reduce the sheet resistivity from 76 Ω/□ in the unannealed sample to 25 Ω/□ after a 30s anneal at 200°C as measured by a 4-pt probe. A set of variably spaced Al contacts were also thermally evaporated onto a PEDOT:PSS film for corroboration and the subsequent calculated sheet resistance was observed to decrease from 61 Ω/□ in the unannealed sample to 36 Ω/□ after the anneal at 200°C. The root cause of the conductivity increase arising from the annealing process was investigated through a variety of material characterization techniques. Important to this dissertation in particular was the optical characterization using Raman spectroscopy. Using Raman spectroscopy it was confirmed that the polymer was not undergoing significant carbonization or deterioration. A shift in polymer morphology from the benzoid form to that of the relatively more conductive quinoid was observed. This observation was identified by a spectral change in a vibrational mode of PEDOT:PSS centered at approximately 1430 cm⁻¹. This spectral feature is the convolution of two separate modes corresponding to the quinoid form (~1425 cm⁻¹) and the benzoid form (~1453 cm⁻¹). By comparing the ratio of the magnitudes of the peak amplitudes within each spectrum the relative ratio of quinoid to benzoid PEDOT morphologies was found to increase. Additionally, a second spectral change also corresponding to a transition to quinoid morphology was identified through a shift in the central wavenumber of an interring C=C/C=C mode at 1260 cm⁻¹. With increased annealing temperature, this mode underwent a discernible blue shift indicating a relative increase in bond energy within the film. Important to this observation is the understanding that the benzoid form of PEDOT exhibits a single C=C interring bond, whereas the quinoid takes the form of a double bond. Both spectral observations are attributed to the shift of PEDOT film morphology to become more quinoid like. As Raman spectroscopy is primarily a qualitative assessment of the material being investigated, AFM and XPS studies were
undertaken to verify this change in polymer morphology, however, they are not discussed as a part of this thesis.

To evaluate the implications on potential device performance and the particulars of the effects of RTA on the current transport relationship normally through a PEDOT:PSS film was evaluated. By fabricating single carrier diode structures using ITO/PEDOT:PSS/Al the IV relationship was found to exhibit trap limited SCLC conduction where the precise relationship between current and applied bias is dependent on the applied bias level. At low bias levels, where carrier transportation is material limited by the PEDOT:PSS, an ohmic relationship could be identified. With continually higher bias levels, the relationship progressively transitioned into a trap filling state exhibiting a relationship of $I \propto V^2$, before decaying to theoretical $I \propto V^2$, and finally beginning the transition towards a final linear regime. The eventual linear relationship under the highest applied bias was never reached due to device heating and subsequent film spalling. Differences in magnitude and transport characteristics were discovered depending on which contact the carriers were being injected into the film. When biased with hole injection from the Al, the current relationship progressed through all of the theoretical SCLC regimes, whereas using the same bias levels and injecting from the ITO contact, the current relationship was limited to the traditional $V^2$ law and never began a decay towards the final linear region. By applying a progressive fitting regimen to measured data across the different regimes of current conduction, various parameters from the SCLC could be extracted. When comparing parameter values with respect to RTA temperature, the single parameter that was observed to change was an increase of carrier mobility from 0.0095 to 0.0128 cm$^2$V$^{-1}$S$^{-1}$, or an increase of 34.7%. Found to be unchanging within the noise level of the data were extracted values for hole concentration, density of states, and trap density in PEDOT:PSS films with approximate values of $7.4 \times 10^{14}$ cm$^{-3}$, $1.5 \times 10^{18}$ cm$^{-3}$, and $3.7 \times 10^{17}$ cm$^{-3}$ respectively.
Conclusions and Future Direction

To alleviate material patterning challenges and to allow for implementation of PEDOT:PSS into processes that are compatible with high throughput large scale fabrication, a novel design approach of etch-free device functionalization was devised. In comparison to the traditional structural patterning of films for device definition, UV irradiation was used to spatially render desired regions of the PEDOT:PSS film highly resistive. Previous reports had primarily indicated a change work function of the film along with a reduction of conductivity of PEDOT:PSS due to UV irradiation, and the specific breakdown mechanism and effects on film characteristics had not been elucidated. By varying the exposure level of UV light on the surface of the film, a significant and monotonic increase in sheet resistance was measured from $720 \ \Omega/\square$ in the as-deposited films to $2.39 \times 10^7 \ \Omega/\square$ after $71.6 \ \text{J/cm}^2$ of UV irradiation. Concurrently, an overall decrease of film thickness was observed on the order of 40-60 nm with full exposure. The thickness decrease was not observed at a constant rate, and was thickness dependent implying that the decrease may not be due solely to material etching, but also densification with exposure. An approximation of the etch rate using an etch and densification model was found to be $\sim 0.35 \ \text{nm/(J/cm}^2\text{)}$. Taking the thickness decrease into account with the sheet resistance measurements, the in-plane material conductivity of the PEDOT:PSS film was calculated to decrease from 130 to $6.34 \times 10^3 \ \text{S/cm}$, or over 4 order of magnitude decrease. The loss in conductivity normal to the substrate plane was not as significant due to the material anisotropy, and only exhibited between 1 and 2 order of magnitude decrease of conductivity. To evaluate the specific changes occurring in the film with UV irradiation, physical and optical material characterizations were employed.

Raman spectroscopic analysis identified a notable change in several vibrational modes of interest. Most critical was the significant decrease in the interring stretch mode at $1250 \ \text{cm}^{-1}$. The mode amplitude after normalization to an accompanying
PEDOT mode decreased to 40% of its unexposed value indicating a relative loss in the amount of interring bonds between EDOT monomers. A second change was again a shift in morphology, however, in comparison to the previously observed transition towards a quinoid morphology upon thermal processing, with UV exposure the opposite effect was identified and a transition towards a more benzoid form of PEDOT:PSS was identified.

With FTIR analysis, corroborating results were obtained whereby two particular modes corresponding to an interring mode indicating conjugation length of the PEDOT chain at 1520 cm\(^{-1}\), and a mode reported to be associated with the level of doping in PEDOT:PSS located at 1720 cm\(^{-1}\) were both found to diminish with UV exposure. A concurrent qualitative change in the overall IR absorption spectra was also observed that with increased exposure, the underlying magnitude of IR absorption background decreased and was identified as a loss in the level of delocalized free charge carriers in the film.

Through height and phase imaging with an AFM, the surface of the PEDOT:PSS film was seen to undergo a loss of surface roughness. The surface of PEDOT:PSS films has been elsewhere described as consisting of nanometer sized elevated grains of PEDOT surrounded by lower lying PSS regions. A decrease in roughness and the amount of elevated regions indicate a decrease in the surface composition of conductive PEDOT grains. This loss of phase segregation was verified using phase imaging, as the separation between conductive PEDOT grains and the PSS background was eroded and homogenized with UV exposure.

The direct electrical measurements, Raman, FT-IR, and AFM characterizations all indicate that there is a loss in the level of conductive PEDOT regions within the film. In particular, the long conductive PEDOT chains are being subjected to a polymer scission process that decreases the conductivity of the film.
Lastly, spectroscopic ellipsometry and UV-vis spectroscopy was used to probe the changes in optical characteristics of the PEDOT:PSS films to eventually enable future implementation into optoelectronic devices and structures. The optical characterization of the anisotropic PEDOT:PSS films demonstrated that UV exposure leads to an increase in real refractive index and extinction coefficient of the films across all dimensions of the film. Extraction of refractive index curves from fits to the spectroscopic data across the visible to IR wavelengths were enabled. Similar to the anisotropic effects of exposure on conductivity, processing had different effects on the film as it enacted a relatively more significant change in the optical characteristics parallel to the substrate as opposed to those normal to the substrate. This is explained by the physical anisotropy of the film upon deposition, where if one were to look at the ratio of PEDOT to PSS parallel to the substrate it will be of significantly higher value as opposed to out of plane. Since the UV exposure is inducing a polymer scission event primarily within the PEDOT portion of the film, a greater change in the dimension with a higher PEDOT ratio is understood.

Following the study of material effects of the UV induced scission process, design of electronic and optoelectronic structures taking advantage of this processing technique were approached. As an initial device example demonstrating the applicability of this spatial patterning process, OLED devices were fabricated. A comparison of ITO/PEDOT:PSS/MEH:PPV/Al, OLED stacks were created with both unexposed and irradiated PEDOT:PSS layers. As was expected with an emissive stack that exhibits orders of magnitude higher resistivity, the current density and related optical output power was significantly higher in the device with the unexposed PEDOT:PSS. To further highlight the potential capabilities for OLED output patterning, a similar stack was fabricated in which a grid pattern was exposed into the PEDOT:PSS layer. With no physical patterning, and complete OLED stack structurally intact, a patterned output could be obtained
due to the polymer scission process produced by UV exposure. A similar demonstration was applied to a different material system using thermally evaporated organic molecules NPB and Alq. The fabricated OLED stack of ITO/PEDOT:PSS/NPB/Alq/LiF/Al was created with a UV patterned PEDOT:PSS layer. The emissive output was subsequently patterned upon operation. When comparing diodes with a PEDOT:PSS hole injection layer to baseline diodes without, although the absolute current and luminance vs. applied bias was decreased with the hole injection layer, the current and photoluminescent efficiency was calculated to perform as well if not better than the devices without PEDOT:PSS.

As the mechanism of OLED carrier transport occurs in the normal direction to the substrate, an alternative device of particular importance to current consumer electronics that requires carrier transport parallel to the substrate was developed. This dissertation culminated in the design, fabrication, verification, and characterization of a set of highly transparent capacitive touch sensor arrays. Through application of spatial adaptation of PEDOT:PSS film conductivity using UV irradiation, several demonstrations of mutual capacitive sensing arrays were realized. The highlight being a flip-chip bonded, 8x8 capacitive sensor array fabricated using an SU-8 dielectric interlayer. The sensor array was designed using a common interlocking diamond pattern structure with the diamond electrodes being functionalized into the PEDOT:PSS film using direct UV exposure. The sensor array was capable of locating a touch event from a conductive stylus mimicking the capacitance of a human body. An average capacitance across each of the 64 elements creating the array was found to be 2.10 as compared to the expected designed value of 1.92 pF. Despite some common errors due to crosstalk between capacitive elements, a single touched location across the array was identified in over 75% of the measurements on a properly fabricated device, neighboring element crosstalk resulted in an ambiguous touch detection on 17% of
the touch events, and only in 5% of the touch events, did the data indicated a completely incorrect location of the stylus. Of importance, in particular for future implementation with an underlying emissive display, the transmission of visible light through the PEDOT:PSS electrodes and dielectric interlayer was greater than 80% between 400-800 nm.

8.2 Future Prospects

Moving forward there are several routes for progression of this research to be discussed. An initial area of interest is to continually expand and investigate the UV patterning process for implementation with flexible substrates and fabrication architecture. The UV exposure process is inherently compatible with a transition to flexible substrates. One of the key focusses of this dissertation was to allow for a simplified transition to a flexible platform. Without the solvent compatibility restraints as are present with the use of organic developers and etchants to physically pattern a film, the choices of material for implementation as a substrate is essentially unlimited. This will enable the use of the best possible substrate for development taking into account factors such as cost, green or recycled materials, reactivity and transparency. Of course, this compatibility extends further than just the substrate to impact other potential materials, whether those be emissive or waveguiding materials, gain media or other novel layers, for whatever device design is used, there should be no compatibility issues during the UV patterning of a PEDOT:PSS layer. Transitioning to a flexible substrate system could, however, pose slightly different material challenges, especially if the characteristic anisotropy of PEDOT:PSS is imperative to device operation. This is due to the fact that the root mechanism behind the realization of material optical and electrical anisotropy is inherent in the deposition technique of spincoating. While spray coating may also provide the similar anisotropic characteristics due to the velocity at which the PEDOT:PSS material is directed towards the substrate, other common non-contact techniques used in roll-to-roll fabrication may not. Conversely, if the
anisotropic material characteristics are not mandatory or if they are detrimental, the UV induced patterning should operate in a similar manner and provide multiple orders of conductivity decrease in, now potentially both the parallel and normal directions to the substrate.

There is also additional room for exploration into alternative effects of RTA and UV processing on PEDOT:PSS films. Specifically, further investigation into the effects that RTA and UV irradiation may take on the crystallinity of the PEDOT:PSS films may be of significance. This was not explicitly characterized for any of the samples, and would provide valuable insight into the potential effects of processing on the stacking and order within the polymer film itself. Additionally, while the traditional contacts used in OLED and organic PV devices are often ITO and Al, an extensive exploration of the variation of contact metals, charge injection barriers, and the consequences of processing on electrical contact PEDOT:PSS creates with these materials would be of great use in device optimization and design. Lastly, while significant changes have been studied on the effects of RTA and UV irradiation on the conductive PEDOT polymer in the PEDOT:PSS formulation, no material investigation of the potential effects of UV exposure on the PSS counterion was explored. UV irradiation is known to affect, in a variety of manners, many organic molecular systems, so it might be expected that the UV patterning process could also affect the PSS. Although the PEDOT has been primarily associated with the loss in conductivity of the thin polymer film, the role of UV effects on PSS has not been explored. An enhanced and rigorous study into the contributions of the material changes in PSS could further enhance the understanding of the photodegradation process that is occurring. This would be particularly insightful and useful to the community due to the vast range of formulations that PEDOT:PSS is created or supplied in. Specifically, the ratio of PEDOT to PSS in many dispersions can range from 1:1 up to 1:30, allowing for a wide range in chemical properties and conductivity.[154] While the UV
patterning process developed has focused on a specific, high conductivity formulation consisting of a ratio of PEDOT:PSS of 1:2.5, due to the fact that PEDOT:PSS with different ratios, solid contents, or pH, the effects of UV irradiation on other material systems could differ in results. It is therefore important to study the effects of UV patterning not only on the PEDOT component, but also that of PSS.

It may also be of interest to expand the tested parameters of the variables used in RTA to explore potential differences on film characteristics. This dissertation focused specifically on the temperature of annealing based on similar previous experiments.[90] There exist a significant number of additional variables that may be optimized with RTA to achieve the maximum material enhancement. These include adjusting the temperature heating rate, the annealing atmosphere, and the temperature hold time. Any of these may adjust the specifics of the non-equilibrium annealing process to provide greater benefit than was observed in this thesis. It is also may be of potential use to explore the effects of varying the substrate material. As RTA takes non-equilibrium processes to an extreme limit, the specific heat capacity and thermal conductivity of the substrate itself may adapt the overall effects of annealing. The electrical measurements with respect to RTA conductivity enhancement were primarily obtained on boroaluminosilicate glass slides, whereas to optimize the optical signal, the Raman characterization was performed on a silicon substrate. It has been assumed within these experiments that the thermal load of the substrate is inconsequential to the heating process due to the drastically different equipment as opposed to traditional oven annealing. The RTA equipment used performs such heating rates through a set of high intensity optical bulbs as opposed to resistive coils in hot plates or ovens. As such, the initial point of exposure is the PEDOT:PSS film being adapted, and the substrate material is assumed to have negligible consequence. However, explicitly exploring this variable along with the other aforementioned
variables in RTA would allow for a more complete optimization of parameter space for applying this process to thin PEDOT:PSS films.

Of particular interest to the community is the ongoing development of organic field effect transistors (OFETs) and with added light emitting functionality, organic light emitting transistors (OLETs). In these devices, as PEDOT:PSS does not exhibit luminescent or field effect switching characteristics, the PEDOT:PSS film is only suitable for acting as an electrode material as has been demonstrated elsewhere.[156]-[158] It would be of extreme value to transfer the developed patterning procedure for use in an OFET structure. In fact, a preliminary shadowmask for thin film patterning has already been designed, however, due to complications with the supplier being able to achieve the required specifications for the mask, it was not available for device development prior to the completion of this thesis. One of the potential concerns with the use of the use of this patterning technique for implementation into an OFET architecture is that the degree of resistivity change is not significant enough. This is more of a concern in organic transistors, since most demonstrated devices require relatively high (on the order of 10s of volts) gate biases and the magnitude of source to drain current is often on the nano to micro amp level depending on dimensions and materials used. As such, even highly resistive films may mask the desired field effect characteristics. Further material processing research will most likely be needed in order amplify the conductivity modulation. One approach would be simply to increase the total irradiated power to the film, and see how much further the effect can be utilized. A second technique could be to vary the radiation wavelength in order to see if a stronger effect could be obtained, although a tradeoff between absorption induced scission events and penetration depth to properly expose films of sufficient thickness would need to be taken into consideration. A third, and potentially most interesting option of enhancing the scission process is to introduce an additional nanomaterial into the PEDOT:PSS matrix to act as a plasmonic coupler to the
incident UV light and provide an enhancement of the electromagnetic field within
the film. This technique has been applied in a variety of other fields, and in
particular surface enhanced Raman spectroscopy (SERS), whereby, metal
nanoparticles are designed to provide optical resonance at a particular range of
wavelengths, which subsequently enhances the electric field from the pump laser in
the vicinity of the nanoparticles, leading to up to 10 orders of magnitude
enhancement of detection capability. In the case of enhancing the electric field in
the UV region of the spectrum, a shift away from the commonly utilized noble
metals towards alternatives such as aluminum, or rhodium are required. [159]-[161]
Furthermore, adding conductive nanostructures to the PEDOT:PSS matrix may
also act to enhance the conductivity of the unexposed film as has been observed
through the addition of silver or carbon based nanostructures.[79], [82] If proven,
the enhanced technique would allow for a larger contrast between conductive and
insulating regions, as required for the implementation into OFETs but also acting
to improve performance of other demonstrated devices.

In combination with the UV surface patterning technique offered, the
complimentary efforts from the initial studies of enhancement of material
conductivity with RTA can be investigated in concert with other traditional means
of enhancement such as secondary doping with organic solvents or acids. While
RTA does not provide as substantial an improvement of conductivity as these
chemical processes, it does have the advantage of being applied post-deposition of
the film, so it could be used as a complement to other methods, combing both
enhancement techniques. This thesis has focused primarily on material studies and
introduced a platform for the use and patterning of PEDOT:PSS into
optoelectronic devices. While functionality has been demonstrated, the efficiency,
yield, and performance of devices has not been addressed or optimized, and there is
significant room for improvement in the design and fabrication of these devices.
The understanding and insight into the particular effects of RTA on the SCLC
relationships governing current transportation normally through a PEDOT:PSS film, will aid in such optimization.

A second broader topic of future research is to shift the focus from the use of PEDOT:PSS as a highly transparent electrode material to explore other potential applications such as active switching in a polymer waveguide structure. Similar approaches using ITO have been modeled to provide switching, modulation or directional coupling in hybrid or plasmonic waveguide structures.[162]-[164] The general concept would be to implement PEDOT:PSS into a waveguide structure that allows for biasing in anticipation that a similar accumulation region based switching mechanism will be formed in the PEDOT:PSS as it is in ITO.[165] Fitting to an optical model of the structure show a nanometer thick change in the PEDOT:PSS film similar to what might be expected for an accumulation layer, however further experiments need to be designed to confirm this. Although, PEDOT:PSS may not be as appropriate as inorganics for implementation into CMOS compatible silicon optical structures, it can offer some unique and exciting advantages to all-polymer optics. Specifically, the material optical anisotropy is a characteristic not often found in non-crystalline materials and could be utilized for polarization control and manipulation of light propagating in a properly designed structure. In conjunction with the material bias investigation, proper design of a low loss, compact waveguide structure will need to be explored compatible refractive index materials, the most probable of which are other organic polymers. The method of waveguiding could be aided or entirely achieved through the UV polymer scission process that has been shown to tune the refractive index of the PEDOT:PSS. Regardless, with the unique properties that PEDOT:PSS exhibits of high optical transparency, conductivity, anisotropy, and potential of tuning of refractive index with bias, the implementation into both passive and active waveguide structures is one of high potential.
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Appendix A: List of Journal Publications and Conference Presentations


7- **S. A Rutledge** and A. S Helmy, “Etch-Free Patterning of PEDOT:PSS for Optoelectronics”, *2015 Conf. on Lasers and Electro-Optics (CLEO)*, San Jose, CA (*May 2015*).


## Appendix B: Detailed Fits of Raman Modes from Chapter 4 and Chapter 6

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<th>Peak Assignment</th>
<th>0°C Wavenumber (cm⁻¹)</th>
<th>150°C Wavenumber (cm⁻¹)</th>
<th>175°C Wavenumber (cm⁻¹)</th>
<th>200°C Wavenumber (cm⁻¹)</th>
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<td>854.74</td>
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<td>988.49</td>
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<td>1096.39</td>
<td>18.74</td>
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<td>C-O-C deformation</td>
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<td>26.51</td>
<td>1131.96</td>
<td>24.78</td>
<td>31.65</td>
<td>31.82</td>
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<td>C-C (-H) interring</td>
<td>1247.16</td>
<td>75.85</td>
<td>1247.28</td>
<td>81.53</td>
<td>50.28</td>
<td>53.43</td>
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<td>64.63</td>
<td>1257.69</td>
<td>64.16</td>
<td>13.92</td>
<td>15.00</td>
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<td>Symmetric C-C</td>
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<td>1365.91</td>
<td>114.78</td>
<td>10.21</td>
<td>22.98</td>
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<td>Quinoid C-O-C</td>
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<td>428.85</td>
<td>1424.70</td>
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<td>39.75</td>
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<td>227.04</td>
<td>1454.20</td>
<td>258.11</td>
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<td>32.37</td>
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<td>123.25</td>
<td>1532.07</td>
<td>122.94</td>
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<td>32.59</td>
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<td>Doping induced C-C</td>
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<td>1563.89</td>
<td>102.14</td>
<td>29.48</td>
<td>30.38</td>
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Table 8.2: Complete list of fitted modes from the UV study in Chapter 6

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<th>Peak Assignment</th>
<th>Wavenumber (cm⁻¹) A W</th>
<th>Wavenumber (cm⁻¹) A W</th>
<th>Wavenumber (cm⁻¹) A W</th>
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<td>24.9 J/cm²</td>
<td>48.3 J/cm²</td>
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<tr>
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<td>1106.04 14.18 21.60</td>
<td>1102.16 16.01 19.29</td>
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<td>1134.22 12.38 26.75</td>
<td>1130.54 16.92 43.18</td>
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<tr>
<td>C-C Interring stretch</td>
<td>1220.97 12.74 30.47</td>
<td>1220.97 12.74 30.47</td>
<td>1220.77 13.10 37.73</td>
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<tr>
<td>C-C Interring stretch</td>
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<td>1251.49 33.73 32.77</td>
<td>1251.08 24.99 30.21</td>
</tr>
<tr>
<td>Symmetric C-C stretch</td>
<td>1365.43 47.29 31.95</td>
<td>1365.43 47.29 31.95</td>
<td>1367.93 19.26 12.32</td>
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<tr>
<td>Quinoid C-C</td>
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<td>1427.69 221.84 44.63</td>
<td>1428.09 189.35 39.74</td>
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<tr>
<td>Benzoid C-C</td>
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<td>1453.38 96.60 33.53</td>
<td>1450.28 113.96 31.30</td>
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<td>1533.16 43.43 19.68</td>
<td>1535.38 29.75 17.18</td>
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<td>1557.52 60.31 36.36</td>
<td>1559.31 52.73 34.35</td>
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</tbody>
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Appendix C: Comprehensive Set of Capacitive Colormaps from Chapter 7
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