Charge Injection and Transport in Pentacene Field-Effect Transistors

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2017
ABSTRACT

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Since the seminal discovery of conductive polymers four decades ago, organic electronics has grown from an exploratory field to an industry offering novel consumer products. Research has led to the synthesis of new organic molecules and polymers and their applications: organic field-effect transistors (OFETs), organic light-emitting diodes, and organic photovoltaics. The goal for research as well as for industry is producing low-cost, flexible, and, ultimately, sustainable, electronics.

Although on the rise, organic electronics faces several challenges: air instability, reliability, and scaling, to name a few. And despite that organic devices and larger systems have been demonstrated, there remains a gap in understanding underlying mechanisms behind light absorption, photoconduction, charge transport and conduction in them.

The primary purpose of this thesis is to use a relatively under utilized technique, photocurrent microscopy (PCM), to directly probe charge carriers in pentacene and 6,13-Bis(triisopropylsilylethynyl) (TIPS) pentacene FETs to learn about charge injection and transport. The latter part of the thesis focuses on the use of thiols to modify electrode properties to both increase charge injection efficiency and to provide passivation to low-work function metal electrodes.

It is demonstrated for the first time experimentally by directly probing the OFET channel that top-contact geometry OFETs suffer minimally from a charge injection barrier, and that trap filling and altering of trap density-of-states in the channel is
directly observable with PCM.

PCM was used to investigate grains and grain boundaries in TIPS-pentacene devices. By varying gate bias, it was shown that the PCM maps of grains are not simply a result of varying absorption on the surface of the film; rather, it is an artefact of charge transport between grains and grain boundaries. Through this study, PCM was shown to be a useful, large-area scanning technique, for observing transport in devices with large (on the order of 50 µm) grains. This is particularly relevant as solution-processing films are likely to dominate the flexible electronics industry.

The thiol portion of this thesis compares the impact of two distinct thiols on bottom-contact pentacene FETs: perfluorodecanethiol (PFDT) and pentafluorobenzethiol (PFBT). Using X-ray photoelectron spectroscopy to measure metal oxidation, it was determined that short aromatic thiols are poor choices for low work-function metal passivation. In addition, both passivation and charge injection enhancement can be achieved with long fluorinated alkanethiols. However, there is a trade-off between passivation and on-current. The enhancement of on-current in thiol-treated Cu-electrode pentacene devices is most likely not morphology related, due to the fact that PFDT was found to be in a standing-up orientation on the metal surface.

Additionally, it was demonstrated that although highly electronegative atoms such as fluorine can beneficially modify metal work function, too many fluorine atoms in thiols can lead to too high a work function and a large mismatch between the pentacene highest-occupied-molecular-level and metal work function.
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Acknowledgments

Many people have supported me during my PhD, but I would first like to thank my advisor, Professor Ioannis Kymissis. From the start, John has fostered my creativity and has supported my thought and experimental processes. For that, I am very grateful. I would also like to thank my other committee members for their critiques and scientific discussions, which have made me a better researcher.

I would like to thank all the members of CLUE that I have worked with: Vincent Lee, Jonathan Beck, John Sarik, Marshall Cox, Hassan Edrees, Fabio Carta, Shyuan Yang, Kostas Alexandrou, Willis Kim, Chris Choi, Aida Colon Barrios, Brian Tull, Nadia Pervez and Marco Cavallari. I have had the pleasure of working with them over the past five and a half years and have thoroughly enjoyed our scientific discussions and friendly banter.

I would like to thank the professors with whom I have collaborated on projects: Professor Alon Gorodetsky of University of California Irvine, Professor Xavier Roy of the Columbia University Chemistry Department, and Professor Yvan Bonnassieux from Ecole Polytechnique in Paris, France.

I would like to thank the Masters students and undergraduates, who I have had the pleasure of both mentoring and learning from: Annika Chen, Henry Shulevitz, and Sarah Thompson.

Finally, the love and support of my family.
To my family
Chapter 1

Introduction

1.1 Background and Motivation

The field of organic electronics spun out of the work of Alan Macdiarmid, Alan Heeger and Hideki Shirakawa, for their work on the conducting properties of polyacetylene in the 1970’s. Although it does not conduct well on its own, it was found that when polyacetylene is doped with a halogen vapour, its conductivity can be increased by eleven orders of magnitude. [1]. This contribution earned the trio the 2000 Nobel Prize in Chemistry.

Since this seminal discovery, the organic electronics field has exploded. It has generated immense research on low-cost, flexible electronics, requiring the synthesis of new organic materials by chemists and their characterization and applications by engineers. Figure 1.1 shows several conductive organic molecules whose properties have been well studied and are used in devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).

Although on the rise, organic electronics still faces several challenges: air instability, reliability, and scaling, to name a few. And although organic devices and larger organic systems have been demonstrated, there still remains a gap in understanding the underlying mechanisms behind charge transport and conduction through many
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Figure 1.1: Various conductive organic molecules. a.) Small molecules: i.) pentacene, ii.) TIPS pentacene, iii.) CuPC, and iv.) rubrene. b.) Polymers: i.) Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), ii.) polythiophene, iii.) Poly(3,4-ethylenedioxythiophene) (PEDOT), and iv.) polyaniline
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of these devices.

This thesis focuses on charge injection and transport through pentacene field-effect transistors (FETs). Two topics are discussed: photocurrent microscopy (PCM) and thiol-treated electrodes for OFETs.

In this chapter, electrical and optical properties of organic molecular solids are discussed, and a comparison with inorganic solids are made. OFET operation, fabrication and applications are covered, as well as the organic electronics technological roadmap and the markets that drive it.

1.2 Organic Molecular Solids

Conductive organic molecules are divided into two categories, small molecule (oligomer) and polymer. Small molecules such as pentacene have a low mass and are often thermally evaporated to make thin films. Conductive polymers lend an advantage in being solution processable (i.e., spin-coating and pneumatic printing).

Table 1.1 lists the properties of organic molecular solids and covalently bonded solids such as crystalline silicon (c-Si). In the latter, the unit cell is comprised of atoms held together by via covalent (or ionic or metallic) forces. Contrarily, the constituents in the unit cell of a molecular solid are molecules held together by van der Waals forces, which are far weaker. As a consequence, molecular solids are soft, have low melting temperatures, and can be processed with low-energy methods like low-temperature (< 300 °C) thermal evaporation and solution processing.

Due to weak electronic overlap between molecules, the properties of the resultant solid is similar to that of the individual molecules that comprise it. Therefore, much can be gathered about the molecular solid by studying the properties (i.e., bandgap), of the individual molecule itself. This differs greatly from solids held together by covalent, ionic or metallic bonds [2].

Electron delocalization in a conductive organic molecule arises from its π-conjugated
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<table>
<thead>
<tr>
<th></th>
<th>Organic molecular</th>
<th>Covalently bonded</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit cell forces</strong></td>
<td>Van der Waals</td>
<td>Covalent</td>
</tr>
<tr>
<td><strong>Relevant energy levels</strong> for carrier transport</td>
<td>HOMO and LUMO</td>
<td>Valence and Conduction</td>
</tr>
<tr>
<td><strong>Exciton binding energy</strong> $E_b$</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Bandgap</strong></td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Exciton types</strong></td>
<td>Frenkel and CT</td>
<td>Frenkel, CT, Wannier-Mott</td>
</tr>
<tr>
<td><strong>Effective mass</strong></td>
<td>High</td>
<td>Small</td>
</tr>
</tbody>
</table>

Table 1.1: Comparison of organic molecular and inorganic covalently bonded solids.

backbone: a series of alternating single and double bonds in which carbon atoms are $sp^2$ hybridized. In this configuration, $s$, $p_x$ and $p_y$ orbitals mix in the molecular plane, overlapping into $\sigma$ bonds. These covalent bonds are strong and localize electrons. The leftover $p_z$ orbitals lie perpendicularly to the molecular plane; the overlap between neighboring $p_z$ orbitals form $\pi$ bonds, in which electrons are weakly bound to the atom. Each component of the $p$ orbital lies $120^\circ$ apart from the others, as shown in Figure 1.2 for a benzene molecule. [3]. Some of the energy levels for benzene are also shown.

The energy levels are split between bonding and anti-bonding levels (the division is denoted by the red dotted line). $\pi$ electrons can easily move between the highest-occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). States below the HOMO level are filled, and those above the LUMO are empty but can be filled by exciting electrons (i.e., optically). Note that Figure 1.2 does not show the $\sigma$ and $\sigma^*$ energy levels, which lie below and above $\psi_1$ and $\psi_4$, respectively.

The HOMO-LUMO levels are the analogue to the conduction and valence bands of
covalently, ionically or metallically bonded solids. The transport properties of molecular solids is largely underpinned by the extent to which $p_z$ orbitals from neighboring molecules overlap [2].

The majority of the work done in this thesis is on pentacene-based devices. Like benzene, pentacene ($C_{22}H_{14}$) is a member of the acene family, linear molecules comprised of fused benzene rings. This includes napthalene, anthracene, tetracene, and hexacene. A table of the linear acenes and their properties is shown in Table 1.2 [4]. As the number of aromatic rings increases, the molecular HOMO-LUMO gap and exciton binding energy decrease as a result of increased dielectric screening and increased overlapping of the electron-hole wavefunction [5] [4].

Generally speaking, the binding energy $E_b$ of excitons is Coulombic in origin and in solids is approximated by
Table 1.2: Experimental and theoretical properties of gas-phase oligoacenes [4]: ionization potential (IP), electron affinity (EA), and singlet and triplet excitation energies.

<table>
<thead>
<tr>
<th>Number of Rings</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP (Th.)</td>
<td>9.2</td>
<td>8.0</td>
<td>7.1</td>
<td>6.6</td>
<td>6.4</td>
<td>6.1</td>
</tr>
<tr>
<td>IP (Ex.)</td>
<td>9.0 - 9.3</td>
<td>8.0 - 8.2</td>
<td>7.4</td>
<td>7.0 - 7.2</td>
<td>6.6</td>
<td>6.4</td>
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<tr>
<td>EA (Th.)</td>
<td>-1.2</td>
<td>0.1</td>
<td>0.7</td>
<td>1.2</td>
<td>1.8</td>
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<tr>
<td>EA (Ex.)</td>
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<td>0.5</td>
<td>1.0</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>S₁ (Th.)</td>
<td>4.9</td>
<td>4.0</td>
<td>3.4</td>
<td>2.7</td>
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<tr>
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<td>3.5</td>
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<tr>
<td>T₁ (Th.)</td>
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<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>T₁ (Ex.)</td>
<td>3.7</td>
<td>2.6</td>
<td>1.9</td>
<td>1.3</td>
<td>0.9</td>
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</tbody>
</table>

Table 1.2: Experimental and theoretical properties of gas-phase oligoacenes [4]: ionization potential (IP), electron affinity (EA), and singlet and triplet excitation energies.

\[ E_b = \frac{e^2}{4\pi\varepsilon\varepsilon_0 R} \]  

(1.1)

where \( e \) is the charge of an electron, \( R \) is the physical distance between the hole and electron, \( \varepsilon \) is the dielectric constant of the semiconductor, and \( \varepsilon_0 \) is the permittivity of free space. (Note that this equation applies to spherical molecules and should be corrected for if the molecule deviates from a sphere.)

There are three types of excitons: Frenkel, Wannier-Mott, and charge-transfer (CT). Frenkel excitons have binding energies on the order of 0.1 to 1 eV, Wannier-Mott around 0.01 eV, and CT excitons fall somewhere in between. Frenkel excitons are located either within the same unit cell or on the same molecule. In most organic semiconductors, visible light can create Frenkel excitons, but additional energy \( E > E_b \) is required to separate the hole and electron. Otherwise, the electron-hole pair is localized to the molecule.

\( E_b \) in organic molecular solids is large, due to a small \( \varepsilon \) and \( R \). For instance, in
pentacene, $\epsilon \approx 3.3$ to 3.9 [6] [7], and the electron-hole distance is about the size of a unit cell. For comparison, $\epsilon$ for Si is 11.7. For pentacene, multiple $E_b$ are reported since it has singlet and triplet states (Chapter 2). The singlet binding energy is $\approx 0.1$ eV and that of the triplet binding energies $\approx 0.3$ to 0.5 eV [5]. For comparison, $E_b$ in Si is 14.7 meV, two orders of magnitude smaller [8]. The bandgap of organic molecular solids is also much larger than that of inorganic solids. For instance, the Si bandgap is 1.1 eV, while that of pentacene is $\approx 2.2$ eV.

The large $E_b$ in organic semiconductors is also the reason that the difference between the transport gap ($E_t$) and optical gap ($E_{opt}$) is larger than in inorganic solids. This makes measuring the bangap in organic molecular solids difficult. For instance, the pentacene bandgap has been reported to be anywhere between 2.2 and 2.8 eV. Meanwhile, in inorganic materials, the distinction between $E_t$ and $E_{opt}$ is almost never made.

### 1.3 Organic Field-Effect Transistors

At first glance, an OFET appears very similarly to a Si MOSFET. It consists of source, drain and gate electrodes, a gate dielectric and a semiconductor channel. And like MOSFETs, thermionic emission is the primary injection mechanism. Unlike MOSFETs, OFETs operate in accumulation mode (Figure 1.3 and Figure 1.4). When a large positive (negative) source-gate voltage ($V_{gs}$) is applied, electrons (holes) accumulate to the semiconductor-dielectric interface. When a source-drain voltage ($V_{ds}$) is then applied, current flows from source to drain. In comparison, a MOSFET operating in accumulation is essentially an n-p-n diode, with no current flowing.

The equations governing the operation of a MOSFET in the linear and saturation regions can be used to model an OFET:

$$I_{ds} = \frac{1}{2} \mu C_{ox} \frac{W}{L} [(V_{gs} - V_t)V_{ds} - \frac{1}{2} V_{ds}^2](linear)$$  \hspace{1cm} (1.2)
CHAPTER 1. INTRODUCTION

Figure 1.3: Energy band diagram of a p-type OFET showing the off-state, accumulation mode and depletion mode [9].

Figure 1.4: Energy band diagram of p-type and n-type OFETs in the on-state. [10].
\[ I_{ds} = \frac{1}{2} \mu C_{ox} \frac{W}{L} (V_{gs} - V_t)^2 \text{(saturation)} \]  

\[ C_{ox} = \frac{\epsilon_0 \epsilon_{ox}}{t_{ox}} \]  

where \( \mu \) is mobility, \( C_{ox} \) is the capacitance of the gate dielectric, \( W \) is channel width, \( L \) is channel length, \( \epsilon_{ox} \) is the insulator dielectric constant, and \( t_{ox} \) its thickness.

Three standard OFET architectures are shown in Figure 1.5: bottom-contact (BC), top-contact (TC), and top-contact bottom-gate (TC/TG). BC (coplanar) geometry is the most industry relevant, as it allows for photolithographic patterning of electrodes and prevents damage to the semiconducting material, as it is the last layer deposited. However, TC outperforms BC, which will be discussed in greater detail in Chapter 3. Although a top-contact geometry, TC/TG devices lend an advantage in the gate dielectric serving as a barrier to water and oxygen.

Table 1.3 lists the differences between OFETs, a-Si FETs, and c-Si MOSFETs. The organic semiconductor need not be doped to create delocalized carriers (in fact, it is usually not); its p-type, n-type or ambipolar behavior is determined by the Fermi level alignment of the source-drain contacts with that of the channel material.

The vast majority of reported high-performing OFETs are p-channel devices. There is some dispute as to why this is the case, although most agree that the reasons are historic in nature [11]: 1. the use of oxides as the gate dielectric, which are prone to efficiently trap electrons, 2. the use of high work-function electrodes which create a high-energy barrier to electrons, 3. the use of low-work function electrodes which are easily oxidized, and 4. performing measurements in ambient atmosphere, which is known to degrade the material. Indeed, it has been shown that polymers can conduct electrons well on a gate oxide treated with benzocyclobutene (BCB), which removes hydroxyl groups known to trap electrons [12].

As with inorganic devices, the metrics of interest include field-effect mobility \( (\mu_{FET}) \), threshold voltage \( (V_T) \), subthreshold swing \( (SS) \), \( \frac{I_{on}}{I_{off}} \), and leakage current.
CHAPTER 1. INTRODUCTION

Figure 1.5: Schematic of four OFET geometries: a.) bottom-contact bottom-gate (BCBG), b.) top-contact bottom-gate (TCBG), c.) bottom-contact top-gate (BCTG), and d.) top-contact top-gate (TCTG).

$I_{off}$. OFET performance is highly dependent on film morphology, semiconductor thickness, electrode work function, OFET geometry (BC, TC, TC/TG), the quality or nature of interfaces, and of course the conducting properties of the channel material itself.

One key difference between organic and c-Si electronics is processing area. For c-Si, the processing area is set by the wafer size (less than 450 mm). On the other hand, organics and a-Si can be processed in areas on the order of square meters. This is, of course, largely in part due to the fact that organic semiconductors can be fabricated onto both organic and inorganic gate dielectrics; metal and inorganic oxides, for instance, provide reliability for device testing, however, they are rigid. Flexible dielectrics provide the advantage of low-temperature processing and flexibility, but they also create problems such as hysteresis and gate leakage.

OFET performance is complicated by the presence of trap states, which lie in
<table>
<thead>
<tr>
<th></th>
<th>Organic Molecular</th>
<th>a-Si</th>
<th>c-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating mode</strong></td>
<td>accumulation</td>
<td>inversion</td>
<td>inversion</td>
</tr>
<tr>
<td><strong>Transport type</strong></td>
<td>hopping, multiple-trap-and-release</td>
<td>hopping, multiple-trap-and-release, some extended state</td>
<td>extended state</td>
</tr>
<tr>
<td><strong>Gate dependence of mobility</strong></td>
<td>yes</td>
<td>yes</td>
<td>none</td>
</tr>
<tr>
<td><strong>Mobility</strong></td>
<td>low</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td><strong>Carrier type</strong></td>
<td>relies on source/drain and semiconductor $E_F$ matching</td>
<td>relies on doping (mostly n-type)</td>
<td>relies on doping</td>
</tr>
<tr>
<td><strong>Processing area</strong></td>
<td>large</td>
<td>large</td>
<td>small</td>
</tr>
<tr>
<td><strong>Processing temperatures</strong></td>
<td>low</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td><strong>Substrates</strong></td>
<td>flexible/inflexible</td>
<td>flexible/inflexible</td>
<td>inflexible</td>
</tr>
</tbody>
</table>

Table 1.3: Comparison of organic molecular, amorphous silicon (a-Si), and crystalline silicon (c-Si) FETs. Note that the degree to which hopping contributes to transport in a-Si decreases with increased levels of hydrogenation (a-Si:H)
between the HOMO and LUMO levels. Trap states result from grain boundaries, non-ideal dielectric/organic or metal/organic interfaces, oxidation states, water molecules, and other impurities (both desired and undesired). In devices, traps are filled and unfilled with changes in voltage bias. They manifest themselves as bias-dependent mobility, non-zero onset voltage and current hysteresis, making reproducibility and stability a major concern.

Traps can be measured experimentally through electrical or optical characterization. For example, hysteresis in OFET transfer curves demonstrate changes in threshold voltage [13]. Interestingly, hysteresis in OFETs can be a desired effect and an exploited mechanism for non-volatile memory [14] [15] [16].

Transport in OFETs can be through inter-trap hopping, multiple trap-and-release (MTR), and trapping defects in grain boundaries. Hopping and MTR are thermal processes, given by $\mu_{FE} = \mu_0 A e^{-\frac{E_A}{kT}}$, where $E_A$ is the thermal activation energy. Mobility has been shown to be carrier density dependent, and therefore gate-bias dependent. A common equation used for this is $\mu(V_G) = \mu_0(V_G V_T/V_{AA})^\gamma$, where $\gamma$ and $V_{AA}$ are extracted experimentally.

Despite the benefits of organic materials, there are roadblocks leading to their success in the market, including air-instability, reliability and reproducability. Air-instability is caused mainly by oxidation, which leads to trap states in the organic molecule and hence degrades carrier mobility. The deeper the HOMO and LUMO levels are, the less oxidation poses a problem [17].

The biggest competition for organic electronics is a-Si:H, though most likely not where glass is the substrate. Organic materials will be leveraged for their process compatibility with flexible substrates, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polycarbonate and polyamide, which have glass transition temperatures of 70 °C, 120 °C, 150 °C, and 270 °C, respectively [18].
1.4 The Organic Electronics Roadmap

Organic electronics are contenders in low-power applications. These include niche areas, such as radio frequency identification (RFID) tags, sensors, PVs, OLED lighting, thin-film transistor backplanes for displays, non-volatile random access memory devices, and integrated smart systems like smart cards. The individual organic-based components integrated into such systems include OFETs, OPVs, and OLEDs, with OLEDs having already entered the market. OPVs, have shown an upward trend in efficiency [19] [20], but have not yet reached a point of marketability and are considered more viable in the consumer electronics market rather than in large-area power supply. OFETs have been integrated into logic circuits [21] [22] [23] but are also a strong candidate as transducers in gas sensing, as they are a streamlined alternative to the existing bulky chemical sensors in use today [24].

The exact reported value of the organic electronics industry differs from report to report, but the projected number lies somewhere around 70 billion dollars by the year 2026. All reports agree on three major attributes of the industry: 1. that the market for organics has been growing and will continue to grow, 2. that the market is driven primarily by display and lighting technology, and that 3. the Asia Pacific region dominates the field. Philips, Sony, Samsung and LG are amongst the top investors and producers of organic electronics, with products such as the LG Curved Smart TVs and the Samsung Galaxy line of smart phones.

The Organic and Printed Electronics Association (OEA) is a leading international association for setting standards in the organics industry and defines the roadmap looking ahead. Like the inorganic electronics roadmap, the organics roadmap is bent on improving the resolution of fabrication processes while maintaining high throughput.

The roadmap is continuously updated as new applications, materials and processing techniques emerge. The roadmap is driven by the following metrics: complexity, operating frequency, operating voltage, lifetime, efficiency, cost, and sustainability,
Figure 1.6: Existing and projected mobilities of organic small molecule and polymer FETs in comparison to mobilities of a-Si and poly-Si [25].

with the end goals being true flexibility (conformality, rollability and stretchability) [25].

Silicon has been the gold standard for transistor technology, while organic electronics currently has no gold standard semiconductor. There is little consensus on material choice, applications, and fabrication processes. This is largely attributed to how nascent the field is and the continuous synthesis of new materials. Put another way, it is far easier optimize a technology once an agreement on materials is made. Unlike the inorganic world, however, it is likely, given the myriad disparate applications of organic electronics, that there may not necessarily be a need for one gold standard material. Instead, materials will most likely be synthesized and tailored for each individual application.
CHAPTER 1. INTRODUCTION

Figure 1.7: The existing and projected applications of organic devices based on the Organic Electronics Roadmap [25].

1.5 Scope of Research

The primary purpose of this thesis is to use a relatively under utilized technique, photocurrent microscopy (PCM), to directly probe charge carriers in pentacene field-effect transistors (FETs) to learn about charge injection and transport in devices. Specifically, the first half of the thesis is devoted to a discussion of the theory and use of PCM, followed by a demonstration of experimental PCM measurements of pentacene FETs, with an emphasis on device architecture and morphology.

Chapter 2 is a review of the current body of work concerning photocurrent studies of pentacene OFETs, as the technique applied to organic materials is rather new,
and its applications are varied. Chapter 3 demonstrates experimental PCM on pentacene FETs, showing how the signal changes with device geometry, voltage bias, morphology, electrode and gate dielectric treatments, and laser wavelength. Chapter 4 compares two thiols used to alter the charge injection barrier in pentacene FETs and to simultaneously passivate low-workfunction metal electrodes. A summary is presented along with a plan for future work to build on top of the work done in this thesis. Lastly, the Appendix demonstrates work done on other novel materials: graphene, graphene oxide and superatomic co-crystals.
Photocurrent spectroscopy (PCS) and photocurrent microscopy (PCM) are powerful tools that can probe the mechanisms of charge generation and transport in organic semiconductor devices. There has been significant progress in the use of these techniques, which has yielded a number of insights into the underlying materials and operation of devices. Despite the potential for PCS and PCM to become standard tools, a consensus has not been reached on its uses and mechanisms that produce the photoresponse. This is particularly true for measurements of pentacene devices, as the energy dynamics of pentacene are complex. Accordingly, this chapter summarizes the current body of PCS and PCM of pentacene devices, offers interpretations of the data, and discusses which questions remain unanswered. The reviewed work has been divided into four categories based on the goals of the study and the technique used: PCS, PCM, mobility, and trap density-of-states.
CHAPTER 2. REVIEW OF PHOTOCURRENT MICROSCOPY OF PENTACENE DEVICES

2.1 Introduction

As mentioned in Chapter 1, among the most researched organic semiconductors is pentacene, $C_{22}H_{14}$. Owing to its high hole mobilities [26] and low processing temperatures, pentacene is a popular material for organic field-effect transistors (OFETs) [27] [28], light-emitting diodes (OLEDs) [29] [30] and photovoltaics (OPVs) [31] [32] [33]. Its solution-processable counterparts are also widely studied, due to their potential for roll-to-roll fabrication [34] [35] and printing.

A significant research effort is driven by inquiry into the optical and transport properties of organic semiconductors. Salleo et al. [36], review the most widely used optical spectroscopy, x-ray and scanning probe techniques for investigating structure and charge transport. Atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM) and electrostatic force microscopy (EFM) construct spatial maps of electric field, workfunction, charge concentration and morphology. Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) produces orientation details, while optical, Raman and IR spectroscopies generate complimentary details of energy states.

Photocurrent spectroscopy (PCS) and microscopy (PCM) are powerful techniques that exploit mechanisms such as internal photoemission and photoconductance to analyze energy states and transport. Photocurrent measurements have been used to study nanostructures such as quantum dots [37] [38] [39], nanowires [40] [41] [42], carbon nanotubes [43] [44] [45], and graphene [46] [47] [48] [49]. Despite its growth and potential as a standard tool, there remains much debate on its uses and the mechanisms that produce the photoresponse, particularly in the case of pentacene, due to its complex energy dynamics.

Interpreting PCM and PCS results requires knowledge of optical and electrical properties of the materials under investigation. The pentacene absorption spectrum in Figure 2.2 shows peaks at 1.83, 1.97, 2.1, and 2.2 eV. The two lower energy transitions are singlet excitons localized to a single molecule. The singlet
states are characterized by a Davydov splitting of 0.1 eV, which is a result of two translationally variant pentacene molecules within one unit cell, and which is also responsible for its herringbone structure. The two higher transitions are charge transfer (CT) excitons, which travel between neighboring molecules. Out of all the oligoacenes, pentacene and its derivatives are popular for photovoltaics due to the relatively small binding energy, low bandgap and efficient singlet exciton fission. 6,13-Bis(triisopropylsilylethynyl)pentacene This is due to increased overlapping of e-h wave function as the more aromatic elements are added to the molecule.

Transient absorption spectroscopy on single-crystal pentacene has demonstrated that singlet states undergo rapid exergonic fission into triplets [50], which relax via interaction with gap states or free carriers. Efficient singlet fission can also occur in polycrystalline pentacene [51] and TIPS pentacene [52]. Because triplet states possess energies less than half of singlets, the process does not require thermal input [51]. Owing to this and its efficiency, the singlet fission process has been recognized as a potential mechanism to achieve high efficiency OPVs and to surpass the Shockley-Quiessar limit [31] [33] [51].

2.1.1 Photocurrent Measurement Basics

A typical photocurrent setup is shown in Figure 2.1. The light source can be an LED, a laser, or a broadband lamp paired with a monochrometer, depending on the spatial and spectral resolution desired. In a scanning apparatus either the stage or optics can move. In some cases, large parts of the device are illuminated, and scanning is not utilized. For high spatial resolution, scanning galvo mirrors scan the light source, and an objective lens focuses the light to a diffraction-limited (∼λ/2) spot size.

Data collection generally proceeds as follows. The device is simultaneously DC biased and illuminated, and the output current is measured. The measured current consists of the DC current and a perturbation current induced by the illumination (photoresponse). If the illumination is modulated, the photoresponse can be isolated.
There are two types of photocurrent studies: PCM and PCS. PCM generates spatial maps of photocurrent activity. PCS measures the photocurrent response as a function of incoming light wavelength. A number of experiments can be performed, depending on the parameter swept (voltage bias, frequency of light modulation, wavelength or position of the light source). The technique can be used for potentiometry if the light source is scanned in space, simultaneously collecting information about mobility and contact resistance. If the wavelength and voltage bias are swept, photocurrent probes energy states and recombination methods.

Photoexcitation alone does not guarantee charge separation in a device. Energy is required to overcome the large Coulombic force between holes and electrons in organic semiconductors [53]. Electric fields can play a vital role in exciton dissociation. The excitons in photodiodes and solar cells dissociate once the hole-electron pair diffuses toward a heterojunction. Strong internal electric fields can also dissociate excitons in the case of some Schottky barriers. However, several effects may work simultaneously to produce the photoresponse in any material: the thermoelectric Seebeck effect, the photovoltaic effect, drift/diffusion of free carriers, diffusion of excitons, and the
bolometric effect [46]. Much of the literature pertaining to photocurrent studies of pentacene use the photovoltaic response to explain results, while few have investigated (for example) bolometric effects [54]. The Seebeck effect is not usually used to explain the photoresponse in pentacene devices.

2.1.2 Pentacene Photophysics

Pentacene is a linear acene with a 2.2 eV highest occupied molecular orbital (HOMO) - lowest unoccupied molecular orbital (LUMO) gap [55]. The pentacene absorption spectrum in Figure 2.2 shows peaks at 1.83, 1.97, 2.1, and 2.2 eV. The two lower energy transitions are singlet excitons localized to a single molecule. The singlet states are characterized by a Davydov splitting of 0.1 eV, which is a result of two translationally variant pentacene molecules within one unit cell, and which is also responsible for its herringbone structure. The two higher transitions are charge transfer (CT) excitons, which travel between neighboring molecules.

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Given the potential for singlet fission to take place in pentacene, a PCS or PCM study of pentacene must carefully consider the paths that excitons take and hence the illumination wavelength utilized. For instance, when wavelengths between 635 and 660 nm are used, excitons in pentacene are unlikely to split into hole-electron pairs and contribute to the current as charge carriers. A more likely scenario is that singlets will undergo fission and that the resulting triplets will fill empty traps, thus facilitating
Figure 2.2: (Top) Absorption spectrum of thin-film pentacene on glass measured with UV-VIS spectroscopy. Transitions occur at 1.83, 1.97, 2.1 and 2.2 eV. (Bottom) Energy level diagram of pentacene illustrating singlet fission and charge transfer transitions.
transport of injected charge carriers. It is important to note the improbability that illumination will produce charge carriers in pentacene, unless the generated exciton is sufficiently close to a heterojunction that supplies a strong enough electric field to facilitate dissociation.

2.2 Photocurrent Spectroscopy

Spectrally resolved photocurrent has been used to measure fundamental optoelectronic properties and to verify material parameters such as the HOMO-LUMO gap. More importantly, comparison of a photocurrent spectrum with the semiconductor absorption spectrum can also shed light on transport mechanisms in devices and the energy states that contribute to transport.

2.2.1 PCS of OFETs versus Schottky Diodes

As a vast majority of pentacene photocurrent studies are on OFETs, here we present a study on pentacene Schottky diodes. This study is highlighted in particularly to show that PCS measurements can be heavily affected by the presence of a strong heterojunction.

Lee et al. measured current-voltage curves of Al/pentacene Schottky diodes under illumination [56]. Under reverse bias, the photoresponse was greatest at 630 nm (1.97 eV) and 490 nm (2.5 eV). The photocurrent and pentacene absorption spectra under zero bias are shown in Figure 2.3. Due to the diode structure, there exists a large enough electric field within the pentacene layer to facilitate dissociation of excitons created by illumination. The authors offer that the peaks in the spectral response is due to the primary gap of pentacene being at 1.97 eV and unoccupied molecular orbitals lying higher at 2.5. However, since the publication of this study, there has been much progress in pentacene photophysics, and we argue here that the large response at 1.97 eV may be a result of singlet fission, as this potentially doubles the
number of charge carriers dissociated by the heterojunction. The peak at 2.5 eV, on the other hand, is mostly likely attributed to the creation of CT excitons, which can move more easily to neighboring molecules.

In sharp contrast to these results are those from a PCS study on pentacene FETs by Jia et al. [57]. Recent progress in organic electronics has led to surface modification of electrodes and gate dielectrics prior to deposition of the organic semiconductor. One
method that has shown promise in improving bottom-contact OFET performance is UV-ozone treatment of the gate dielectric. [57] investigated how UV-ozone treatment of parylene (used here as the gate dielectric) affects the performance of pentacene FETs. Standard device characterization showed improved performance in UV-ozone treated samples, namely an increase in source-drain current and hole mobility and a decrease in threshold voltage. The authors propose that carboxyl groups in the gate dielectric introduced by the treatment act as electron traps, therefore preventing recombination and facilitating hole transport (possible trap-assisted dissociation). In addition, deep trap get filled as a result of the increased hole concentration, leading to a higher mobility.

Spectral photocurrent was used to measure pentacene energy states in UV-ozone treated and untreated samples (the latter referred to in the study as air-free samples). Figure 2.4 shows a comparison of the photoresponse spectra. Peaks occur at 668 nm (1.85 eV), 630 nm (1.96 eV), 588 nm (2.11 eV), and 544 nm (2.28 eV). The greatest
photoresponse is measured at photon energies associated with singlet excitons that are known to undergo fission into triplet states. There is also a small peak between 300 nm (4.1 eV) and 400 nm (3.1 eV), which grows with increasing magnitude of gate voltage. This wavelength range is associated with energies sufficiently high enough to break apart the exciton in pentacene (greater than 2.95 eV).

In Fig. 2.4, the photoresponse for those wavelengths above approximately 475 nm appear to be unchanged as a result of the UV-ozone treatment, while those associated with CT and higher-energy excitons exhibit an increase. Part of the explanation lies in the fact that in this energy range, pentacene absorption is a minimum, and transmission is a maximum. Therefore, more high energy photons than low energy photons penetrate the pentacene layer and reach the parylene. However, it remains unclear as to why the introduction of -COOH groups produces an enhancement in photoresponse for high energy photons.

Note the contrast between the spectra in [56] and [57], mainly the presence of a peak at 2.5 eV in the former and the lack of the peak in the latter. This is entirely due to the fact that one device contains a strong interal electric field and that in the other, PCS data was taken by illuminating the middle of the OFET channel, which lacks a strong enough electric field to facilitate dissociation. It is possible that the photoresponse in the latter case is due not to creation of charge carriers, but instead photoconductance.

2.2.2 The Effects of Semiconductor Thickness on PCS

We note here that in [56], a relatively thick pentacene layer was used (200 nm) and that this can have a serious impact on PCS results. This was shown in a study by Gorgolis et al. [58], which investigates the effect of film thickness on photocurrent spectra. The plots in Figure 2.5 reveal an inverse relationship between absorbance and photocurrent (referred to as responsivity) up to around 2.2 eV; that is, local minima in absorbance correspond to local maxima in photocurrent. Such a relationship
is referred to as antibatic. Figure 2.5 shows that as the pentacene thickness increases, the behavior of the photoresponse plot switches from symbatic to antibatic. The authors propose the following mechanism. A higher recombination rate is expected at the surface of the semiconductor due to a high surface density of states. The recombination rate is also higher for strongly absorbed light, but as the film gets thicker, weakly absorbed light is more uniformly absorbed through the film. Therefore, charges generated beneath the surface can better survive surface recombination, giving rise to a higher photocurrent than in the case of strongly absorbed light. It is possible that \[56\] observed an antibatic response, given their film thickness (200 nm). It is therefore imperative that special attention be paid to device dimensions in analysis of photocurrent results.

### 2.3 Photocurrent Microscopy (PCM)

Spatially mapping the photoresponse of OFETs can shed light on the effects of morphology and geometry on carrier-injection efficiency and device performance. Spatially resolved photocurrent, or photocurrent microscopy (PCM), can also assess local mobility, electric field, and potential in the channel. Although similar plots have been generated using KPFM, it measures surface states, and channel dynamics in OFETs can only be inferred. On the other hand, in PCM, photons penetrate the semiconductor, generating excitons that interact with energy states along the conduction path. Therefore, PCM offers a significant advantage over KPFM.

Several studies have used PCM to investigate bottom-contact OFETs in particular. Bottom-contact geometries are considered to be a highly relevant geometry for industrial applications of thin film transistors [59] [60] [61]. However, bottom-contact devices suffer from lower charge injection efficiencies than top contacted devices [62]. PCM is a useful tool for studying these charge injection barriers, as it exploits internal photoemission, and the magnitude of internal electrical fields can be inferred.
Figure 2.5: Superimposed absorption (blue) and photocurrent (red) for various pentacene film thicknesses: 18, 50, 80, 247 and 357 nm [58].
Figure 2.6: 1D photocurrent map from pentacene bottom-contact FETs, plotted for various gate voltages [63].

from the measured photoresponse.

2.3.1 Photocurrent vs. Photoconductivity

Fiebig et al. generated 2D photocurrent maps of pentacene bottom-contact OFETs using 633 nm illumination [63], the peak absorption wavelength for pentacene.

The measured photoresponse as a function of position in the OFET channel is shown in Fig. 2.6. The most prominent feature is the peak near the source, the positively biased contact. Although the contacts were photolithographically patterned, considerable inhomogeneity in photocurrent was observed. This is most likely a result of morphological defects, as pentacene forms smaller grains near the edge of the contact region and is likely to suffer from structural disorder at the interface.

The authors suggest that the photoresponse is a consequence of two distinct phe-
nomena, photocurrent and photoconductivity. The former is the result of electron-hole pair generation, separation, and subsequent transport to the contacts. A small carrier lifetime would limit the ability for charges to directly travel to the contacts, limiting the photocurrent effect to parts of the channel close to the contacts. Photoconductivity, on the other hand, is an increase in conductance at the illumination spot due to photogeneration and filling of trap states.

The posited theory offers that each mechanism contributes to the photoresponse at different parts of the channel: both photocurrent and photoconductance near the source, and photoconductance away from the source. Near the source, photogenerated electrons travel successfully to the source contact, while away from the source, they are far less likely to make it to the drain contact due to recombination with both injected holes from the source and photogenerated holes.

Kim et al. provide an explanation for the photoresponse peak on the source side [64]. The authors demonstrate via simulations of bottom-contact pentacene OFETs that a sharp drop in potential at the source contact occurs simultaneously with a large discontinuity in charge concentration at the source-pentacene interface, forcing charge to be injected from an area of low hole concentration at the contact to an area with high concentration in the channel. The drop in potential indicates the presence of a large electric field at this interface, which is needed to push charges against the concentration gradient. This explains the peak in photocurrent, as the photoresponse is proportional to the product of mobility and electric field.

2.3.2 PCM, ”Hot Spots” and Contact Resistance

Tsen, et al. [65] offer a slightly different interpretation of the source-side photoresponse peak, making it an interesting comparison to the previous study. PCM was used to examine low charge injecting efficiencies in bottom-contact pentacene FETs arising from an injection barrier. 2D photocurrent maps were generated (Figure 2.7) using 658 nm illumination, one for which source-drain voltage $V_{DS} = 0$, and one for
CHAPTER 2. REVIEW OF PHOTOCURRENT MICROSCOPY OF PENTACENE DEVICES

Figure 2.7: 2D photocurrent maps from pentacene FETs showing "hot spots" [65].

which $V_{DS} < 0$. For the former case, no response was measured except for at the contacts, indicating the presence of a strong electric field at the metal-semiconductor interface.

For $V_{DS} < 0$, photocurrent maps feature a peak on the source contact, consistent with [63]. In Figure 2.7, the same spots that arise in the "zero-biased" data contribute to large signals in the "non-zero biased" devices. It was concluded that these "hot spots" act as point-like contacts between the gold and semiconductor. It was observed that the more spots present in the $V_{DS} = 0$ map, the better the device performance when $V_{DS} < 0$.

The authors used the photoresponse to calculate the resistance of each hole-injecting point contact ("hot spot"), further demonstrating the utility of PCM. The point contact resistance was on the order of GΩ, while the channel resistance was on the order of a few hundred MΩ, indicating the significant role that the point-contacts
CHAPTER 2. REVIEW OF PHOTOCURRENT MICROSCOPY OF PENTACENE DEVICES

play in charge injection. Their study shows that ironically, although the source-side peak in photoresponse is a marker of high resistance, it is simultaneously a marker of good contact between the semiconductor and metal.

2.4 Mobility

Significant debate surrounds the nature of transport in single crystal and disordered pentacene, as high mobility values alone do not provide definitive proof of extended state band-like transport. In addition, it is not clear where the transition between single crystal and disordered transport may occur.

Transport via multiple trapping-and-release (MTR) has been found in thin film pentacene devices [66] [67]. In TIPS pentacene, a negative value of the thermal coefficient of mobility, $\frac{d\mu}{dT}$, has been found, indicating band-like transport [68]. However, the authors indicate that this result may be misleading and may not be the result of extended state transport, but instead of lattice fluctuation limiting transport. On the other hand, Minder et al. conclude that TIPS pentacene is one of the only organic molecules to exhibit band-like transport in an FET configuration, while single-crystal pentacene is not [69].

These conflicting results show that a single measurement is not enough to confirm that one transport type prevails over another. Multiple techniques are needed; photocurrent measurements are yet another useful tool for this. Channel mobility in OFETs is typically measured assuming a transport model, such as the classic long channel MOSFET equations, variable range hopping, or multiple trap-and-release. However, the mobility value attained is highly model-dependent, and the model used is often inappropriate for the semiconductor under investigation. Here, we review studies that demonstrate the potential for photocurrent measurements to allow for a model-free mobility measurement, from which a transport model can be inferred.
Figure 2.8: (Left) Photocurrent efficiency plotted against illumination wavelength for various gate voltages. (Right) Mobility and charge concentration derived from photocurrent data.

2.4.1 Model-Free Mobility Measurements

Breban et al. made model-free mobility and average hole density measurements in pentacene OFET channels using photocurrent measurements [70]. A critical observation served as the launching point for their analysis: DC source-drain current and photocurrent possess third-order and second-order gate voltage dependencies, respectively. The following rudimentary forms of source-drain current ($I_{ds}^{dc}$) and photocurrent ($\delta I_{ds}^{\lambda}$) as functions of the gate ($V_g$) and drain ($V$) voltages are:

$$I_{ds}^{dc} = -e \frac{W}{L} \int \mu(V_g,V)n(V_g,V)dV$$

(2.1)

$$\delta I_{ds}^{\lambda} = -e \frac{W}{L} \delta n \int \mu(V_g,V)dV$$

(2.2)

where $W$ and $L$ are the width and length of the channel, respectively, $\mu$ is mobility, $n$ is the concentration of free carriers, and $e$ the elementary charge. It is assumed that
the concentration of photogenerated carriers is source-drain voltage \( V \) independent. Given the simplicity of equation 2, \( \mu \) can be solved for independently by measuring \( I_{ds}^\lambda \) as a function of \( V \). The known form of mobility is then substituted back into equation (1), and the form of \( n(V_g, V) \) is derived. Using this method, it was determined that \( \mu \sim V_g^{1/3} \), which verifies that charge transport is most likely a multiple-trap-and-release process.

Figure 2.8 shows the author’s final results of mobility and hole density as a function of gate voltage. Mobility is both gate voltage and carrier concentration dependent, corroborating that transport should be modeled by trap-and-release mechanisms.

### 2.4.2 Spatially Resolved Mobility Measurements

Jia et al. produced two different field-effect mobility values, one each for the linear and saturation regimes [57]. Their assumptions were similar to those of the previous authors, and both studies found one higher degree of \( V_{GS} \) dependency of source-drain current than for photocurrent. Equations for photocurrent and DC source-drain current were used to solve for mobility:

\[
I_{DS} = -\frac{W}{L} \mu(n_{ind}) C_i n \left( V_{GS} - V_{th} - \frac{V_{DS}}{2} \right) V_{DS} \quad (2.3)
\]

\[
I_{PC} = \frac{W}{L} \mu_{FET}(n_{ind}) n_{PC} V_{DS} \quad (2.4)
\]

where \( I_{DS} \) and \( I_{PC} \) are the DC drain current and photocurrent, respectively. The current dependencies on gate voltage were calculated by fitting \( I_{DS} \) vs. \( V_{GS} \) and \( I_{PC} \) vs. \( V_{GS} \) curves. Comparison of the results to the forms for \( I_{DS} \) and \( I_{PC} \) in equations 3 and 4 reveal that \( \mu_{FET} \) in the linear region \( \sim V_{GS}^{1.20} \), and as expected, due to the additional factor of \( V_{GS} \) in the first equation, \( I_{DS} \sim V_{GS}^{2.21} \).

The saturation region is more complex, as \( \mu_{FET} \) is dependent on position in the channel. Therefore, an approximate average relationship of \( \mu_{FET} \sim V_{GS}^{0.9} \) was estimated. Note that the exponent in the linear regime is greater than that in the
Figure 2.9: Local mobility: Linear region (top two curves) showing constant mobility, and saturation region (bottom three curves) showing a decrease in mobility toward the drain.

saturation regime, which could be justified as follows. As $V_{GS}$ increases, an increasing number of traps get filled, which accounts for the rapid increase of mobility in the linear region. However, once $V_{DS}$ approaches the saturation region, most traps are already filled and mobility does not rise as steeply with increasing $V_{GS}$.

In a related study, Jia et al. calculated position-dependent mobility in both the linear and saturation regions [71]. Results shown in Fig. 2.9 are consistent with their previous work, indicating that mobility in the linear region is relatively constant throughout the channel, due to the spatial uniformity of both traps and charge carriers. In contrast, mobility in the saturation region is dependent on position in the channel, dropping from source to drain. Due to the reduced concentration of charges on the drain side, traps remain unfilled, effectively reducing the mobility in that part of the channel.
2.5 Trap Density-of-States

The presence of deep traps in organic semiconductors leads to some limitations in device performance. Traps produce variability and unpredictability in device operating parameters, as evidenced by hysteretic OFET transfer curves. Traps can be introduced by impurities [26] [72], bias stress [72] [73], and interfacial effects between organics and inorganics [74]. Given the influence of localized states on device performance, it is imperative to study the trap density-of-states (DOS). Photocurrent techniques are an effective means to estimate the trap DOS by sweeping the frequency of light modulation or illumination wavelength.

2.5.1 Probing Trap States with Modulated Illumination

Kounavis showed that the timescale associated with a trap is dependent on the depth of the trap [75]. In pentacene, shallower traps are quickly filled and emptied, as they are within a few kT of the valence band, while deeper traps are filled and emptied on longer time scales. Accordingly, the interaction between majority carriers and gap states was found to be related to both the phase and amplitude of photocurrent. A key relationship involving the energy probed below (above) the conduction (valence) band was extracted [75]:

\[
E_C - E_{\omega n}^i = kT \ln \left( \frac{c_n^i N_C}{(\omega^2 + (\omega_i^t)^2)^{1/2}} \right) \quad (2.5)
\]

\[
E_V - E_{\omega p}^i = kT \ln \left( \frac{c_p^i N_V}{(\omega^2 + (\omega_i^t)^2)^{1/2}} \right) \quad (2.6)
\]

\[
\omega_i^t = n_{dc} c_n^i + p_{dc} c_p^i \quad (2.7)
\]

where \( E_C, E_V, E_{\omega n}^i \), and \( E_{\omega p}^i \) are the conduction band, valence band, probed electron gap state and probed hole gap state energies, respectively. \( N_V \) and \( N_C \) are the DOS at the band edges, \( c_n^i \) and \( c_p^i \) are the carrier capture coefficients at the probed
energy levels, and $\omega_t$ is a threshold frequency. In the argument of the natural log, the numerator is the attempt to escape frequency ($\sim 10^{10}$ Hz) and the denominator the thermal emission frequency. Trap depth can be swept by changing either the bias illumination strength, modulation frequency, or temperature. A change in illumination bias alters the density of free carriers, $N_v$ or $N_c$.

Gorgolis et al. used the above results to measure the trap DOS in polycrystalline pentacene 2-terminal devices [76]. Two 660 nm LEDs were used, one for modulation and one for bias. Note that 660 nm photons generate singlet excitons in pentacene, which split into triplets that relax via localized traps. It is worthwhile to question, then, whether the following results would be different if a wavelength generating CT
excitons were used.

It is proposed that high frequency (HF) and low frequency (LF) regimes exist, where $\omega \gg \omega_i$ and $\omega \ll \omega_i$, respectively. HFs probe shallow trap states, since they are associated with shorter timescales, while LFs probe deeper trap states. Large phase differences between incoming modulated light and photoresponse are expected in the HF regime, since free carriers are delayed due to their interaction with empty traps. For LFs, phase shifts are negligible, as deeper states are mostly occupied. Data in Fig. 2.10 validates this theory. Phase differences are indeed large for HFs. With increasing bias, the phase drops for LFs; as the density of free carriers increases, more traps get filled, and free carriers interact with fewer empty states.

The demarcation between unfilled (shallower) and filled (deeper) traps is $\omega_s$ and is readily observed where data from two bias values overlap (shown in Fig. 2.10 at 1 kHz and 40 kHz). The presence of multiple $\omega_s$ values means that the trap Fermi energy shifts toward the valence band as bias increases, because more traps get filled with increasing illumination bias. As modulation frequency increases, the trap depth approaches the HOMO level, and the data overlap indicates that at these energy states, regardless of how many traps are filled due to the bias strength, trap filling and emptying is dominated by temperature fluctuations.

The calculated trap DOS in the right panel of Fig. 2.10 reveals a metastable and stable DOS. The metastable DOS was observed in photocurrent amplitude and phase plots as a shoulder feature for devices that were measured in air (not shown). Those devices measured after being in vacuum for several days did not exhibit the shoulder or the metastable states. The deep exponential trap distribution is a hallmark of structural disorder, and the metastable Gaussian trap distribution is a sign of adsorbed water molecules.
2.5.2 Photocurrent as a Complementary Technique

Lang et al. studied bias stress-induced traps in single-crystal pentacene OFETs [77]. A previous study [78] using space-charge limited current (SCLC) measurements had found that bias stress produces trap states centered at 0.38 eV above the valence band.

Two complementary techniques, photocurrent and photoquenching, were used to observe these trap states. Photoquenching is useful for studying traps, as the extent of photoquenching indicates the magnitude of trap states that prevent radiative decay. Photoquenching data was obtained by first biasing the devices at a high voltage for the purpose of introducing traps and subsequently illuminating them at a lower voltage.
while measuring current. The photoquenching data is related to the inverse of the
time that the SCLS decays to its pre-stress value.

Figure 2.11 shows spectral photocurrent and photoquenching data from single-
crystal pentacene. Photocurrent data from polycrystalline pentacene [55] is superim-
posed. The devices that produced photocurrent data were not bias stressed.

Differences between the two batches of photocurrent data between 1.5 and 2.2 eV
is argued to be attributed to the different decay paths that triplets follow in polycrys-
talline and single-crystal pentacene. In single crystals, there exist stronger interac-
tions between triplet-excitons and trapped carriers, and in polycrystalline pentacene
there are stronger triplet exciton quenching interactions. Although the photocurrent
data in this study played a more qualitative role (it was not used to extract trap
DOS), we include it in this report, as Fig. 2.11 illustrates that spectral photocurrent
is a useful tool for visualizing the existence of trap states and comparing the effects
of disorder on the distribution of energy states in organic semiconductors.

2.6 Conclusion

Although there is potential for PCS and PCM to become standard tools, further
progress is required for researchers to 1. come to a consensus on the mechanisms that
produce the photoresponse and 2. understand the full utility of the technique.

There are many questions that remain at large. For instance, what is the nature
of the photoresponse when no heterojunction exists in the illumination spot? Is it
trap-assisted dissociation, or is trap filling simply facilitating the transport of injected
carriers? Which conditions create free carriers, and which merely facilitate transport
of existing free carriers through the device? In addition, how do measurements differ
with higher probe wavelengths? Most of the studies discussed exploit pentacene’s
peak absorption wavelength, but is there something to be learned about CT excitons
with the use of shorter wavelengths?
CHAPTER 2. REVIEW OF PHOTOCURRENT MICROSCOPY OF PENTACENE DEVICES

This chapter has shown that PCM and PCS are powerful tools that rival conventional scanning techniques that probe only surface states and are highly sensitive to the surface-environment interface. Here, the most recent progress in photocurrent measurements of pentacene devices has been presented, but more importantly, it has been demonstrated that the photoreponse can be exploited for spectroscopy, microscopy, potentiometry, measuring trap states, and spatially resolving contact resistance and mobility.
Chapter 3

Photocurrent Microscopy of Organic Field-Effect Transistors

In this chapter, the ‘true’ channel potential in top- and bottom-contact (TC and BC) architectures is measured with PCM. The impetus for this study is shown in Figure 3.1, which are plots of simulated channel potential in TC and BC pentacene OFETs [64]. There are two key points to be drawn from the results. The first is the drop in potential (rise in electric field) at the source-channel boundary in bottom-contact OFETs not observed in top-contact devices. This has been measured using KPFM in a number of studies.

The second attribute is the disparity between surface states (orange) and channel states (black). Among its various disadvantages (small scan areas, long scanning times, frequent probe tip replacement), KPFM is sensitive only to surface states, a drawback for devices with thick films or for probing states lying well beneath the film surface. Contrarily, PCM can directly probe the OFET channel via light penetration through the device stack.

The chapter starts with a brief description of advantages and disadvantages of BC and TC geometries, followed by a discussion of the photocurrent generation model and underlying assumptions that frame it. Experimental results from TC and BC
pentacene and TIPS pentacene FETs are then presented, demonstrating the impact of device geometry, film morphology, voltage bias and laser wavelength on the measurement.

3.1 Top and Bottom-Contact Devices

BC OFETs are more industry-relevant than TC OFETs. In BC fabrication, the semiconductor layer is patterned last, which minimizes damage to the film. The electrodes can be photolithographically patterned if desired, allowing for high resolution features. Additionally, when electrodes are deposited prior to the semiconductor,
it affords the opportunity to treat the contacts (i.e., with self-assembled monolayers) to modify surface energy and improve charge injection from the electrode to the semiconductor.

Despite these advantages, BC FETs suffer from low carrier injection efficiency and low source-drain current in comparison to TC FETs. The underlying mechanisms behind this remain debated. The following reasons have been suggested: 1. mismatch in pentacene growth on metals versus gate dielectrics, 2. inherent artefact of the geometry, 3. during deposition of TC electrodes, the overlying metal penetrates the semiconductor and increases contact surface area, and 4. TC provides a larger surface area for injection [79]. There is very little evidence supporting the latter two mechanisms. A simple back-of-the-envelope estimate suggests that carriers encounter much larger series resistance through the depth of the semiconductor than through the metal electrode. Carriers in TC geometry are therefore most likely injected into the channel through the corners of the electrode, like in BC devices.

The mismatch between pentacene growth on metal and that on oxides occurs on two levels: in the first few monolayers and in over all grain size. SEM and AFM have shown that pentacene forms smaller grains on metal than on oxides (Figure 3.2). X-ray diffraction has demonstrated that the first few monolayers grow in a lying-down orientation on metals, while they take on a standing-up orientation on oxides. This mismatch is a result of the difference in surface energies between metals and oxides.

The most compelling argument that the disparity between TC and BC FETs is the geometry itself comes from the aforementioned simulations from Figure 3.1. [64]. The simulations demonstrate that in TC OFETs, the semiconductor is always in contact with the insulator, hence there is continuity in hole concentration throughout the entire channel. In the BC case, the carrier concentration abruptly increases from the contact to the channel, giving rise to a resistive region at the source contact. The discontinuity in carrier concentration gives rise to contact-limited transport in BC not found in TC geometry.
Figure 3.2: Scanning electron microscope image of pentacene on a.) SiO$_2$ and b.) thermally evaporated Au.
In addition, the charge carriers in TC geometry must transport through the thickness of the semiconductor before accessing the channel. The gate voltage drop across the semiconductor layer results in the channel potential not being coincident with the surface potential, which drives the need for a technique that can probe the true OFET channel.

### 3.2 Mechanism of Current Generation in PCM

The majority of the visible spectrum supplies insufficient energy to split electron-hole pairs in many organic materials (unless the excitation occurs near a heterojunction, as in photovolatics). Therefore, for organic semiconductors with a large $E_b$, free carrier generation does not give rise to the photoresponse.

To start, the current in an OFET is proportional to the product of charge, mobility and electric field. For a device with mobility $\mu$ and channel width $W$, the DC-bias current $I_{DS}(y)$ and photocurrent $I_{PC}(y)$ as a function of position $y$ are:

\[
I_{DS}(y) = \frac{dV_{ch}(y)}{dy} \mu(y) Q W
\]

\[
I_{PC}(y) = \frac{dV_{ch}(y)}{dy} \mu(y) Q_{PC} W
\]

where $\frac{dV_{ch}(y)}{dy}$ is the electric field in the channel, $Q = C_{ox}(V_{gs} - V_t - V_{ch}(y))$ is the capacitive charge density, and $Q_{PC}$ is the excess charge on top of the DC-bias charge.

In the linear region, it can be assumed that $Q$ is constant along the channel, and therefore $\mu$ is independent of $y$ as well. Using these two assumptions, Eq. 3.2 can be integrated [71] to yield:

\[
V_{ch}(y) = \frac{1}{\mu Q_{PC} W} \int_0^y I_{PC}(y) dy
\]

Equation 3.3 implies that in the linear regime of an OFET, the photocurrent at position $y$ in the channel is proportional to the electric field at $y$. It also suggests
that PCM can be exploited for potentiometry.

It is important to note the limitations of the linear model. For instance, it is invalid in cases in which electron-hole separation is possible. Additionally, the linear model breaks down in cases where the carrier concentration is not constant along the channel (i.e., in saturation mode or in linear mode of a device with large grain boundaries).

It is largely agreed upon that the source of the photoresponse is the following. Photons penetrate the channel, where they are absorbed by pentacene. Holes are excited just enough to interact with and fill trap states, allowing the holes that are responsible for conduction to move from source to drain less impeded by traps. The laser source therefore creates a localized increase in mobility (photoconduction). The perturbation current measured on top of the DC current is a result of this mechanism.

3.3 Fabrication

Pentacene FETs were fabricated on 500 um-thick degenerately doped Si wafers, serving as the substrate and gate. The gate dielectric was thermally grown 300 nm SiO$_2$. Si wafers are a convenient substrate/dielectric system for studying the physics of organic semiconductors, due to the growth of a high-quality, stable dielectric [17].

Substrates were cleaned in a sonicator in acetone and isopropylalcohol, rinsed with de-ionized water, and baked to remove residual water. All electrodes were evaporated through a shadow-mask in an $\approx 2 \times 10^{-6}$ Torr vacuum chamber within a nitrogen-filled glovebox. A 5 nm Cr film was deposited as an adhesion layer. Cr helps noble metals to adhere better to the substrate, as the first few monolayers of the Cr form an oxide with the gate dielectric, while the last few monolayers form an alloy with the metal.

For BC devices, once electrodes were deposited, substrates were transferred within the glovebox to a pentacene chamber, in which $\approx 30$ nm of pentacene were deposited
at a rate of 0.11 Å/s in $\approx 10^{-7}$ Torr vacuum. The semiconductor was also patterned using a shadow-mask. The order of the electrode-semiconductor deposition was of course reversed for TC devices.

As will be discussed later in this chapter, some of the BC devices were exposed to UV-ozone treatment. For these, indium-tin-oxide (ITO)-patterned glass substrates were used. ITO served as the gate and 200 nm parylene-C as the gate dielectric. Patterning of the electrodes and semiconductor were identical to the fabrication mentioned above.

The accumulation layer in pentacene FETs has experimentally shown to be $\approx 0.9$ nm thick (less than 1 monolayer), and the depletion layer $\approx 5$ nm thick (3 to 4 monolayers) [80]. Therefore, the bulk of the deposited pentacene serves only to protect the channel from oxygen and water. All pentacene devices had $W/L = 30$, with $L = 100 \, \mu m$.

TIPS pentacene devices were fabricated using thermally evaporated electrodes and pneumatic printing (Figure 3.3) of the semiconductor [81]. TIPS pentacene was dissolved in toluene, with a concentration of 16 mg/mL; the printing direction was parallel to the channel length in order to minimize the number of grain boundaries along the charge carrier’s path.

### 3.4 Experimental PCM Setup

The PCM setup consists of a Super K supercontinuum laser with a 350 nm to 850 nm wavelength range. The laser beam’s optical path includes several mirrors, tunable filters for varying light source power, a photodiode, and scanning galvo mirrors. The confocal setup allows for only light reflecting off of the focal plane to enter the photodiode. A rotating shutter allows the source light to be switched easily from the broadband microscope light to the laser beam.

The sample is placed on a stage and brought into focus with the broadband
The laser beam is diffraction limited. The width of the beam is approximately:

$$R = \frac{1.22\lambda}{NA}$$

where $\lambda$ is the laser wavelength, and $NA$ is the numerical aperture of the lens. The microscope objectives range from 4x, 10x, and 40x, depending on the field-of-view and magnification desired. For the 40x, 10x and 4x lenses, $NA = 0.60, 0.30,$ and $0.10$, and $R = 1.3 \text{ um}, 2.7 \text{ um},$ and $8.1 \text{ um},$ respectively.

A Labview program runs the entire experiment, rastering the beam at the desired rate, number of points and number of lines.

Devices were measured in air. Prior to each measurement, the OFETs were biased.
Figure 3.4: PCM setup used for the measurements. The cryo pump was not used for these results. All measurements in this thesis were done in air. Image credit: Nathan Grabor.

and left on for several minutes; it was observed that PCM measurements could not be collected until the current stabilized.
3.5 Experimental PCM Results

3.5.1 Results from TC and BC Pentacene OFETs

Figures 3.5 a.) and b.) demonstrate the differences in the photocurrent signal between TC and BC devices. In the latter, a strong signal appears at the source-semiconductor interface; in the former, the PCM image has a rectangular profile. According to equations 3.2 and 3.3, the PCM profiles suggest that in BC geometry, a large electric field exists at the source-semiconductor interface and that TC geometry lacks this feature.

Potential profiles were generated by integrating the photoresponse in the channel (Figure 3.5 c) and d.)). These results corroborate the aforementioned simulations from [64]. KPFM has generated similar profiles for BC devices, demonstrating an abrupt drop at the source electrode. Here, another drop (high electric field) appears at the drain side, suggesting that charge carriers are met with high resistance there as well. It is most likely attributed to morphology. Note that had the photocurrent signal been measured well into the electrodes, the potential profile would have flattened out.

It is noteworthy to mention that in many BC FETs, there is no photocurrent signal except at the source-semiconductor interface, while the photocurrent signal is present along the entire channel length in TC FETs. Although the aforementioned linear model predicts the shape of photocurrent profile, it does not describe or explain how the photoresponse is generated. If in fact the photoresonse is a result of photoconduction, the reason that $I_{PC} = 0$ within the channel in many devices remains unexplained.

3.5.2 Varying Voltage Bias and Wavelength

The gate bias $V_{gs}$ plays a pivotal role in trap filling. When the device is on, the carrier concentration in the channel is set by $C_{ox}(V_{gs} - V_f)$. However, not all of these carriers contribute to conduction at the same time. At any point in time, a fraction of them
Figure 3.5: Photocurrent maps of bottom-contact and top-contact devices with a wavelength of 635 nm. $V_{gs} = 20V$. 
fill and empty trap states (this is why $V_t$ is nonzero for OFETs despite operation in accumulation mode). Consequently, measurements were done to see the effects of gate bias on the photoresponse.

2D reflection and PCM maps for a BC device with Cu electrodes is shown in Figure 3.7 and a 1D cross-section in Figure 3.8. Prior to adjusting the voltage bias, the device was shut off entirely to allow enough time for traps to empty, which is approximately a few microseconds.

There is very little change in the photoresponse as a function of $V_{gs}$ on the source-side, which is dominated by the charge-injection barrier. In the middle of the channel, the PCM signal increases slightly. In organic FETs, the role of the gate is to move the Fermi level in the channel, not to change the charge injection barrier. Therefore, changes in the source-side charge injection barrier is minimal. The signal within the channel does change with gate voltage, although only slightly, from $\approx 1 \times 10^{-10}$ A to $\approx 3 \times 10^{-10}$ A. A very different trend is observed when source-drain voltage $V_{ds}$ is varied, as shown in Figure 3.10. The photoresponse at the source contact is directly proportional to $V_{ds}$.

Increasing $V_{gs}$ accumulates more holes in the channel, but does not change the velocity of the carriers. For pentacene devices, the aforementioned linear model states that photocurrent is sensitive to the electric field in device, not the number of charge carriers. The minimal response of the photocurrent to changes in $V_{gs}$ corroborates this. $V_{ds}$, on the other hand, simply controls the speed at which carriers are transported from source to drain; it does not control the concentration of those carriers. The potential drop across the high-resistance source-channel junction increases with increasing $V_{ds}$, because $I_{PC}$ measures the extra 'effort' (electric-field) required to match the increase in current. And as $V_{ds}$ increases, more potential is dropped over the contact resistance.

In Figure 3.9, the PCM map for $V_{DS} = -4V$, a distinct but faint peak shows up on the drain side. This is most likely due to the morphology at the drain-semiconductor
Figure 3.6: Measurements of TC OFET, clockwise from top left: photodiode (reflection) signal, photocurrent signal, photocurrent signal in a 3D plot, and the output curves for the device.
Figure 3.7: Reflection and PCM results for bottom-contact devices with Cu electrodes. Source-gate voltage is varied to show the effect on the charge injection barrier and overall PCM signal.
Figure 3.8: 1D photocurrent scan for the device in Figure 3.7 for different gate voltages.
Figure 3.9: Reflection and PCM results for bottom-contact devices with Cu electrodes. Source-drain voltage is varied to show the effect on the charge injection barrier and overall PCM signal.
interface. If the junction is not a clean interface, the mobility at that point is small. But since the current must be the same everywhere, the electric field is large to compensate.

### 3.5.3 Treated Bottom-Contact Devices

As will be discussed in further detail in the following chapter, substrate surface energy heavily impacts device performance. Metals can be treated to modify their surface energy. For instance, hexadecanethiol treatment has been shown to create large grains on Au, with devices seeing an increase in carrier mobility [59]. In addition, polymethylmethacrylate (PMMA) has been used as a thin buffer layer in both BC and TC devices. These devices showed improvements in both pentacene crystal growth and in field-effect mobility.

In addition, many gate dielectric oxides such as SiO$_2$ suffer from dangling bonds that manifest themselves as trap states in the semiconductor channel. These traps
states can cause serious problems in charge transport, reducing mobility and increasing threshold voltage. For this, octadecyltrichlorosilane (OTS) is a popular gate dielectric treatment.

In some cases, deliberate formation of trap states on the dielectric surface can be leveraged to trap the minority charge carrier. An example of this is UV-ozone treatment. During UV light exposure, high-energy oxygen species are formed, which bond to organic dielectrics such as parylene-C. These -OOH groups are known to be electron traps and can be exploited in p-type devices. C-V measurements show that flatband and threshold voltages monotonically shift to lower values with increased UV-zone exposure [82]. In Chapter 2, it was mentioned that PCS revealed increased photoresponse at low wavelengths in UV-ozone treated devices. These measurements demonstrate the formation of trap states.

PCM was measured on UV-ozone treated bottom-contact devices. The parylene-C gate dielectric (see fabrication section) was UV-ozone treated for 20 minutes prior to pentacene deposition. The output curves are shown in Figure 3.14 and demonstrate a high on-current comparable to TC device performance. The PCM profile is rectangular and mimics that of a top-contact device.

3.6 TIPS Pentacene and Grain Boundaries

3.6.1 The Role of Grain Boundaries in Charge Transport

Although organic single-crystal devices have boasted high mobilities, they are not conducive to large-area processing. Soluble materials like TIPS-pentacene lend an advantage in this respect. However, one downside is the formation of grain boundaries (GBs), 2D interfaces between neighboring grains that are thought to limit transport. Both mobility and extent of hysteresis have been shown to depend on grain size [83].

Existing theory models the GB as a back-to-back Schottky barrier, as the density of free carriers within GBs is lower than within the grain [84]. The energy barrier
Figure 3.11: Output curves of BC devices fabricated on ITO-patterned glass substrates with 200 nm parylene as the gate dielectric. $V_{gs}$ ranges from 0 to -15 V.

associated with a GB is estimated to be around 100 meV [83], with the mobility within the grain being around $10^{-8}$ cm$^2$/Vs [83]. It has also been shown that transport in single GB FETs is dominated by the GB, not by the contacts, and that the GB is a gate-voltage dependent bottleneck to hole transport [85].

TIPS-pentacene FETs can have mobilities on the order of 1 cm$^2$/Vs, but the values generally rely on the direction of grain growth and the extent of crystallinity. Mobilities of those devices in which grains are formed parallel to the channel can be an entire order of magnitude higher than those with grains perpendicular to the channel [86]. The deposition method (i.e., spinning, drop-casting, pneumatic printing), drying time, solvent type and solution concentration all impact device performance. Variations in deposition have been explored, including using inert gas injection to
3.6.2 2D Photoresponse Maps from TIPS-pentacene FETs

Given the role of GBs in charge transport, the 2D photoresponse of TIPS pentacene BC and TC OFETs was measured with PCM. Equations 3.1 to 3.3 implicitly state that the electric field at a GB should be large due to lower mobility and charge carrier density than in the grains. As the photoresponse is proportional to the electric field, it was hypothesized that the photoresponse is also larger in the GB than in the grain.
Figure 3.13: Output curves for a BC UV-ozone-treated FET. Treatment was 20 minutes long. $V_{gs}$ ranges from 0 to -20 V.

itself. A schematic of this concept is shown in Figure 3.15.

Figures 3.16, 3.17, 3.18, 3.19, 3.20 are observed photoresponse and reflectance maps from BC FETs. The white line indicates the location of the drain. The horizontal black lines demarcate the lateral extent of the signals.

There are two key features from this result. The first is that like BC pentacene devices BC TIPS pentacene demonstrate peaks in photoresponse at the source. Second, the position and extent of the signals in the y-direction are correlated with the source-semiconductor heterojunction, and in the x-direction is clearly correlated with the spatial extent of the grains.
Figure 3.14: PCM map of uv-ozone treated bottom-contact FET with parylene-C gate dielectric.

The photoresponse and reflection signals for another TIPS pentacene BC FET are superimposed in Figure 3.20. Generally, where the reflectance is higher, the photoresponse is lower. These are areas of lower photon absorption.

Photoresponse maps from TC TIPS pentacene devices are shown in Figures ??, 3.21, 3.22. The reflectance images are shown as well in black-and-white. The raw photoresponse maps were normalized in order to highlight the contrast between photocurrent in the grains, otherwise the changes in the response were difficult to discern. This was done by finding the largest value of the photocurrent in the map and dividing the values in all pixels by that number. Note that the images are inverted from
Figure 3.15: Schematic of a possible photoresponse from grains and grain boundaries within a TIPS pentacene device. As the DC current density must remain the same everywhere, the electric field is expected to be large in areas where mobility and charge density are reduced. Region 1 denotes the grain and region 2 the grain boundary.

Like many of the previous results, the photocurrent in these maps increases with gate voltage bias. Although the hypothesis concerning peaks in photocurrent at GBs was not corroborated, the decreased contrast between grains with increasing $V_{gs}$ shows that trap filling and altering of trap DOS in the channel is directly observable with PCM. In addition, due to the drastic changes in the photocurrent maps with increasing $V_{gs}$, these maps are a direct observation that the behavior of the photoresponse breaks from the linear model when the device is in saturation.
Figure 3.16: Reflectance (top) and photocurrent (bottom) maps for a TIPS pentacene BC device. $\lambda = 660$ nm. Units of current in the PC map are amperes. $V_{ds} = V_{gs} = -40$ V.
Figure 3.17: Reflectance (top) and photocurrent (bottom) maps for a TIPS pentacene BC device. $\lambda = 630$ nm. Units of current in the PC map are amperes. $V_{ds} = V_{gs} = -40$ V.
Figure 3.18: Reflectance (top) and photocurrent (bottom) maps for a TIPS pentacene BC device. $\lambda = 545$ nm. Units of current in the PC map are amperes. $V_{ds} = V_{gs} = -40$ V.
Figure 3.19: Photocurrent (top) and reflectance (bottom) images for a BC OFET. The probe wavelength was 545 nm, which is likely energetic enough to split holes and electrons. The white line demarcates the drain side of the OFET, while the black lines indicate the extent of the photocurrent signal along the width of the device.
Figure 3.20: Photocurrent and reflectance superimposed to demonstrate correlation between the two signals for a BC OFET.
Figure 3.21: Photocurrent maps of TC TIPS pentacene FETs for increasing $V_{gs}$ (left column) and increasing $V_{ds}$ (right column). $\lambda = 630$ nm.
CHAPTER 3. PHOTOCURRENT MICROSCOPY OF ORGANIC FIELD-EFFECT TRANSISTORS

Figure 3.22: Reflection (top) and photocurrent (middle and bottom) maps of TIPS pentacene FETs for two different gate voltage biases $\lambda = 630$ nm.
Figure 3.23: Reflection (top) and photocurrent (middle and bottom) maps of TIPS pentacene FETs for two different voltage biases, $\lambda = 630$ nm.
CHAPTER 3. PHOTOCURRENT MICROSCOPY OF ORGANIC FIELD-EFFECT TRANSISTORS

3.7 Undesired Effects in PCM

It is important to note the impact that optical confinement may have on the measurement. Figure 3.24 shows the stacks of materials at the electrodes and in the channel, with each layer labelled with its respective thickness and refractive index.

The condition for waveguiding within a dielectric is $n_1$ less than $n_2$ and $n_3$, where $n_1$ is the inner refractive index and $n_2$ and $n_3$ the indices of the outer materials. A lower refractive index on the outside of the stack ensures high reflectivity and optical confinement. In both regions of the device, the pentacene/SiO$_2$/Si stack is flanked by lower refractive indices (air and/or metallic electrode). In fact, light is likely to be even more confined within the electrodes than in the middle of the channel for two reasons. The first is due to the high reflectivity of the metal and the second is that the laser beam angle of incidence at the edges of the field-of-view are much larger.

Figure 3.24: Stack of materials in the two regions of interest, the electrodes and in the middle of the channel. Both regions show that there is likely optical confinement within the pentacene/SiO$_2$/Si stack, given that it is flanked by materials with lower refractive indices.

<table>
<thead>
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<th>Thickness</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Metal</td>
<td></td>
<td>n = 0.18</td>
</tr>
<tr>
<td>Pentacene</td>
<td>30 nm</td>
<td>n = 1.56</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>300 nm</td>
<td>n = 1.46</td>
</tr>
<tr>
<td>Si</td>
<td>500 um</td>
<td>n = 3.83</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td>n = 1</td>
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<tr>
<th>Layer</th>
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<td>300 nm</td>
<td>n = 1.56</td>
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<tr>
<td>SiO$_2$</td>
<td>500 um</td>
<td>n = 1.46</td>
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<tr>
<td>Si</td>
<td></td>
<td>n = 3.83</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td>n = 1</td>
</tr>
</tbody>
</table>
Figure 3.25: PCM map of a BC device where parylene-C was used as encapsulation. Periodic features in the map are a result of waveguiding caused by the encapsulation.

than in the channel due to the fact that the zero point for the scanning mirrors are set to be in the middle of the channel.

Although an undesired effect, the fact that wave guiding occurs to a greater extent within the metal-pentacene-SiO$_2$-Si stack bolsters the argument that TC devices do not benefit from a larger charge injection area, as we do not see a large photocurrent signal at the source or drain.

Figures 3.25 and 3.26 demonstrate waveguiding due to a thin layer of parylene-C encapsulating the OFET. There is a clear periodic photocurrent signal indicating optical confinement. Although none of the major conclusions from the study come from this device, these two figures do show that the experimentalist must take into account any undesired artefacts in the photocurrent signal due to the device stack-up.

There exist additional mechanisms that contribute to low spatial resolution in PCM. The first is the laser beam width, which ranges here from 1 to 8 µm. The second mechanism is that shadowmasking does not result in a sharp edge at the electrode-
semiconductor interface, which could create undesired scattering at the corners.

## 3.8 Conclusions

For the first time, it was experimentally demonstrated by directly probing the channel that TC geometry suffers minimally from a charge injection barrier and that trap filling and altering of trap DOS in the channel is directly observable with PCM. PCM was used to investigate grains and grain boundaries in TIPS-pentacene devices. By varying gate bias, it was shown that the PCM maps of grains were not simply a result of varying absorption in the film, rather, it is an artefact of charge transport between grains and grain boundaries. Also, the TIPS pentacene results are a direct observation that the behavior of photocurrent breaks from the linear model when device is in saturation mode, as expected.

Additionally, as a large-area scanning technique, PCM was shown to be useful for observing transport in devices with large grains. This is particularly relevant
as solution-processable films are likely to dominate the flexible electronics industry. The observed maps can provide a more accurate estimate of the true W/L, as not all printed areas of the grains form working transistor channels.
Chapter 4

Thiolated Electrodes for OFETs

Substrate surface energy is a crucial factor underpinning the growth of organic molecules. For example, the first few monolayers of pentacene grow horizontally on metals and vertically on high-energy surfaces such as SiO$_2$ (Figure 4.3). The lying-down arrangement prevents ordered packing and optimized overlapping of $p_z$ orbitals.

OFET performance is largely impacted by the quality of interfaces. This includes the electrode/organic, dielectric/organic, and, if applicable, organic/organic interfaces (the latter pertains to heterojunction devices). The electrode/organic interface determines charge-injection efficiency, while the dielectric/organic interface can introduce trap states and impacts carrier transport within the channel.

Thiols, which form self-assembled monolayers (SAMs), are used to modify both the surface energy of metals and their work function. Due to their high affinity to metal, the wide variety of thiols available, and ease of deposition, thiols are a prime candidate for contact engineering.

In this chapter, two thiols, pentfluorobenzenethiol (PFBT), and perfluorodecanethiol (PFDT), are used to treat electrodes in bottom-contact pentacene FETs. The modified electrodes and devices are characterized using a number of methods to determine thiol impact on low work function metal passivation and device performance.
4.1 Thiols

Thiols consist of a sulf-hydryl group covalently bonded to an organic group. The three parts of a thiol are the ligand (head group), the space group, and the terminal functional group (Figure 4.1). Thiols come in many varieties: alkane or aromatic, fluorinated or nonfluorinated. Alkanethiols are saturated, containing only single carbon bonds, while aromatic thiols are unsaturated.

Thiols can be deposited via solution or vapor deposition. When dissolved in solvent, the hydrogen from the sulfhydryl group dissociates, leaving behind a sulfur ion, which readily bonds to a metallic surface. Properties of thiols can be measured with techniques such as X-ray photoelectron spectroscopy (XPS), contact angle measurements (Figure 4.2), optical ellipsometry [88], and infrared spectroscopy [88].

Generally speaking, the HOMO-LUMO gaps of conjugated thiols are smaller than that of alkanethiols. In addition, the resistance of conjugated thiols is less dependent on molecular length than that of alkanethiols [89]. For short conjugated thiols, the conduction mechanism is off-resonance tunnelling, but as the length of the thiol increases, transport switches from tunneling to hopping, which is highly temperature
dependent, but weakly length dependent. [90] [91].

A number of studies have used thiols to modify OFET performance. A comprehensive study on alkanethiols has shown that beyond a certain length, mobility declines with alkanethiol length [92]. As the molecule gets longer, the tunnel barrier widens, and the probability of injection decreases. This leads to fewer carriers in the channel with which to fill traps, thereby decreasing mobility.

Many studies have demonstrated the ‘odd-even effect’. In alkanethiols, conductance is typically higher with an even number of methylene groups in the alkyl spacers. Break-junction measurements have corroborated this effect by showing that alkane thiols with an odd number of methylene groups exhibit higher resistance due to an apparent tilt [93].
Figure 4.3: Schematic showing how the orientation of pentacene molecules is affected by substrate surface energy. The first few monolayers grow in a lying-down fashion on SiO$_2$ (left), while they grow in an upright manner on top of thiols (right).

At small voltage biases ($\leq 1$ V), conduction through alkane thiols and short aromatic thiols is predominantly tunneling. The resistance of a single molecule can be estimated with the Landauer formula:

$$ R = \frac{\hbar}{2e^2T} = \frac{12.9k}{T} $$

and

$$ T \propto e^{-2\sqrt{\frac{mE_gk}{\hbar}}} $$

where $T$ is the transmission function from one contact to another, $E_g$ is the molecule bandgap (2 to 3 eV), and $L$ is the length of the molecule. The longer the molecule, the greater the resistance. For $L = 5\text{Å}$ and $E_g = 2$ eV, $R \approx 2.1M\Omega$ [94].
Break-junction measurements are one of the best methods for determining the conductivity of single molecules [95]. For alkanethiols and short π-conjugated thiols, they have demonstrated temperature-independent carrier transport, implying tunneling rather than sequential hopping. The conductance of alkanethiols is known to decay with increased molecular length. Measured resistances of alkanethiols range from 87Ω to 35 MΩ, depending on the number of carbons [96].

The magnitude of the electric field experienced by a thiol in a breakjunction measurement is most likely much larger than that experienced by a thiol in an OFET. For instance, in a breakjunction measurement, if the average thiol is approximately 0.1 nm in length, then the electric field for an applied voltage of 1 V is $10^{10}$ V/m. In a pentacene FET such as that in Figure 4.3 with an applied voltage of 10 V, the electric field is $10^5$ V/m and $10^8$ V/m for gate lengths of and 100 µm and 100 nm, respectively. As the electric fields in the latter case are far smaller, it can be inferred that carrier transport through a thiol in a FET is most likely a tunneling mechanism as well.

The thiolated Au surface is a well studied system, as Au is inert and S has a strong affinity to Au. But there is a growing interest in using thiols on lower work-function metals such as Cu and Ag. They are cheaper, and Cu is already widely used for electrodes and interconnects. Their one drawback is oxidation. For the pentacene system in particular, a lower work function produces a larger charge-injection barrier, as the HOMO level of pentacene is 5.2 eV.

When using low work function metals, thiols can solve both the obstacles of oxidation and a high charge-injection barrier. Because thiols are self-limiting and only grow monolayers, they serve as a convenient mechanism for changing the properties of electrodes without contributing too much to series resistance. It has already been shown that pentafluorobenzenethiol (PFBT) improves the performance of pentacene FETs with low-work function electrodes [97] [98].

In addition, thiols have demonstrated the potential for passivating low-work func-
Laibinis, et al [99] looked at preventing oxidation of Cu with alkanethiols. It was found that the longer the thiol, the more effective it is as a barrier to oxygen.

In this chapter, two thiols were investigated: PFBT and perfluorodecanethiol (PFDT). They are shown in Figure 4.4. PFBT is an aromatic thiol and PFDT an alkanethiol, and both are fluorinated.

PFBT was chosen due to prior work done on Au, Ag and Cu. Electrical measurements have shown that PFBT increases on-current by several orders of magnitude in Ag and Cu electrode pentacene FETs [97]. UPS measurements have shown that PFBT moves the work function of Au, Ag, and Cu closer to the HOMO level of pentacene [97]. And a comparison of PFBT with a non-fluorinated alkanethiol showed that PFBT reduces the difference between electrode work function and pentacene HOMO level more than the alkanethiol [100]. This is attributed to the fluorina-
tion, which provides a strong dipole moment on the metal surface, reducing its work function.

PFDT was chosen, because it offers the linearity and length of an alkanethiol (ideal traits for passivation), as well as fluorination, which should alter the metal work function more than a non-fluorinated alkanethiol. Note that PFDT contains many more F atoms than PFBT.

Four mechanisms are investigated in this chapter: potential for passivation, modifications to metal work-function, and measurement of pentacene tilt angle on the substrate surface.

4.2 Electrical Characteristics of PFBT- and PFDT-treated FETs

Pentacene FET output curves for bare Cu, PFBT/Cu and PFDT/Cu devices are shown in Figures 4.5 to 4.7, and subthreshold swing curves in Figure 4.8. Threshold voltage was extracted by finding the $V_{gs}$ value when $\sqrt{I_{ds}} = 0$ V. The results demonstrate that both PFBT and PFDT improve on-current: $V_T$ for bare Cu, PFDT-treated and PFBT-treated devices are -9.1 V, -3.7 V, and 0.8V, respectively.

Due to long pump-down periods during the pentacene deposition process, many batches of devices performed poorly, comparable to those without thiol treatment. The thiol layer most likely desorbed over time inside the vacuum chamber. Various desorption mechanisms have been reported, both in air and in vacuum. In air, desorption is a result of sulfonation; the thiolate reacts with oxygen or water [101]. Desorption can also occur in vacuum via a hydrogen elimination process which results in desorption of the chain groups, while the thiol head groups remain on the copper surfaces, forming Cu$_2$S following the decomposition of the hydrocarbon fragments [102].
Figure 4.5: Output curves for bare Cu bottom-contact pentacene OFETs. For the output curves, $V_{gs}$ ranges from 0 to -40 V with steps of -10 V.

4.3 Passivation of Cu Electrodes

PFBT and PFDT were tested for their potential for metal passivation. It is reasonable to hypothesize that the ability of a SAM to act as a barrier to oxygen relies heavily on its length and packing density. Some fluorinated thiols, due to the high electronegativity of fluorines, are known to pack in a way that minimizes interaction between F atoms. This has been shown for PFBT on Au. Readily seen in Figure 4.9, PFBT molecules arrange themselves so that their F atoms face the relatively neutral cores of neighboring benzene molecules, rather than a F atom [103]. This forms a herringbone pattern.

X-ray photoelectron spectroscopy (XPS) was used to measure the oxidation state
of Cu films. In XPS, X-rays impinge the sample surface, are absorbed by electrons, and the electrons are subsequently expelled from the sample into a detector. These electrons are referred to as photoelectrons. Rather than scanning the energy of incoming X-rays, the detector scans and filters for electron kinetic energies. Since the X-ray and electron kinetic energies are known, the binding energy (BEs) of the electrons can be calculated from

\[
E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)
\]  

(4.3)

where \(E_{\text{kinetic}}\) is the electron kinetic energy and \(\phi\) is the detector work function. Depending on the X-ray energy, XPS can measure core or valence electrons. Core XPS is far more convenient for differentiating between atomic species due to the large dif-

Figure 4.6: Output curves for PFBT-treated Cu bottom-contact pentacene OFETs. For the output curves, \(V_{gs}\) ranges from 0 to -40 V with steps of -10 V.
Figure 4.7: Output curves for PFDT-treated Cu bottom-contact pentacene OFETs. For the output curves, \( V_{gs} \) ranges from 0 to -50 V with steps of -10 V.

...ferences in core binding energies amongst the elements. A Phi XPS system was used. During measurements, the chamber pressure was on average around \( 5 \times 10^{-10} \) Torr.

Si substrates approximately 1 inch x 1 inch were solvent cleaned, rinsed with deionized water and baked prior to metal deposition. An adhesion layer of 5 nm Cr was crucial in this study, as it was found that the thiol layer can grow between the substrate and metal, eventually causing the metal film to lift off. Cu was thermally evaporated inside a chamber at \( 10^{-6} \) Torr. Immediately following deposition, the samples were soaked in a 1 % by weight thiol in ethanol solution.

It was discovered that when thiol deposition was done either in air or within a nitrogen-filled glovebox with regular ethanol, neither thiol prevented passivation. Ultimately, deposition was done using an anhydrous ethanol thiol solution in the glove-
Figure 4.8: Subthreshold swing curves of pentacene FETs with Bare, PFBT-treated and PFDT-treated Cu electrodes for $V_{ds} = -40$ V. The horizontal axis is the absolute value of gate voltage.
CHAPTER 4. THIOLATED ELECTRODES FOR OFETS

Figure 4.9: From [103]: On the left, high resolution STM image of well-ordered packing of PFBT on Au(111). On the right, yellow circles correspond to Au atoms and cyan to PFBT. The length of \(a\) is approximately 5.6 Å, which provides enough spacing for oxygen molecules (300 pm in length) to diffuse to the substrate.

Samples were then either immediately transferred out of the glovebox to the XPS instrument or were left out in air. Contact angle measurements confirmed thiol deposition.

Pure Cu metal shows two large peaks Cu 2p\(_{1/2}\) and Cu 2p\(_{3/2}\), attributed to spin-orbit coupling (Figure 4.11). Oxidized Cu surfaces demonstrate the two usual photoelectron lines as well as several satellite features, depending on the extent of oxidation (Cu\(_2\)O vs. CuO). Cu\(_2\)O is similar, but contains weak satellites between the two main peaks. Meanwhile, the CuO spectrum is the more distinguishable of the the Cu oxides, with much stronger satellites.

The satellite features in the 2p spectra of 3d-transition metal oxides is a result of shake up (SU) processes [105]. Upon X-ray absorption, photoelectrons are created, and the atom is left in an excited state. During the atomic relaxation process, some
of the energy can be imparted to electrons remaining in the atom. If the energy is sufficient enough, photoelectrons are created and show up as secondary peaks in the detector. The exact nature of the SU process has been found to be strongly correlated to the covalency and the paramagnetic (or diamagnetic) nature of the metal oxide [105].

Figures 4.13 to 4.15 show the Cu 2p spectra for unaged and 24-hour aged PFDT and PFBT-treated Cu films. The PFBT/Cu films became heavily oxidized, while the PFDT/Cu films remain passivated.

It is noteworthy that pure Cu should contain no satellite features. Unfortunately, the slight oxidation of Cu during deposition and possibly during transfer to the XPS chamber could not be avoided. Therefore, the ‘bare’ Cu 2p spectrum does contain CuO. However, the important result is that further oxidation did not take place to the ‘bare’ Cu samples treated with PFDT, which the data suggests.
Figure 4.11: Cu2p XPS spectra for freshly-depoisted Cu. The small satellites around 945 eV indicate that the Cu was slightly oxidized during deposition or during transfer to the XPS chamber.

4.4 Work Function Analysis

Ultraviolet photoelectron spectroscopy (UPS), also a photoelectron process, expels valence band electrons from the sample surface. UPS is more surface sensitive than XPS; as UV photons cannot penetrate as deeply into the sample, the majority of the signal comes from the surface. The principle behind the measurement is shown in Figure 4.16.

The Fermi edge is shown at 0 eV binding energy as a sharp drop in the signal. To the left of this are several peaks which correspond to valence band energy levels. The broad peak from 8 eV to 14 eV is a result of photoelectrons which inelastically
Figure 4.12: Cu2p XPS spectra for oxidized Cu. The sample was oxidized by heating on a hotplate at 300 °C.

scatter and show up in the detector as lower kinetic energy electrons. Therefore, these electrons show up in the spectrum as having higher binding energy. The work function calculation is:

\[ WF(\phi) = E_{\text{photon}} - |E_{\text{fermi}}| - E_{\text{onset}} \]  \hspace{1cm} (4.4)

where \( E_{\text{fermi}} \) is the absolute Fermi level calibration from the biased sample, and \( E_{\text{onset}} \) is the edge slope intercept with respect to the background. The advantage of UPS over Kelvin probe measurements is that an absolute value is measured in the former, while a relative number is measured in the latter and requires a calibration sample.

UPS was done at Drexel University with a Phi system. A stage bias of 9 V was used. Measurements were done in vacuum using a He I source with \( E_{\text{photon}} = 21.2 \text{ eV} \).
The measurement is shown in Figure 4.17. The top plot shows superimposed spectra of the two samples, and the bottom plot zooms in on the cut-off region, showing cut-offs of 7.005 eV and 6.931 eV. Because the Fermi edge on both samples were not sharp enough, a clean, sputtered Au sample was used for calibration. Its spectra (not shown) showed a Fermi edge at -8.721 eV. Therefore, the work functions of the PFDT/Au and PFDT/Cu samples came out to 5.548 eV and 5.474 eV, respectively.

Table 4.1 lists measured work functions of PFBT and PFDT on Au and Cu for comparison. An asterisk is placed next to the UPS work function measurements; all other values were acquired through Kelvin probe by our Ecole Polytechnique collaborator, Dr. Sungyeop Jung.

Previous work on PFBT has found work function changes between bare and treated Au and Cu to be 0.1 eV and 0.23 eV, respectively [98]. According to Ta-
Figure 4.14: Cu2p spectrum of PFBT/Cu aged in air for 24 hours.

<table>
<thead>
<tr>
<th></th>
<th>Bare</th>
<th>PFBT</th>
<th>PFDT</th>
</tr>
</thead>
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<tr>
<td>Au</td>
<td>5.10</td>
<td>5.23</td>
<td>5.54*, 5.32</td>
</tr>
<tr>
<td>Cu</td>
<td>4.85</td>
<td>5.24</td>
<td>5.47*, 5.18</td>
</tr>
</tbody>
</table>

Table 4.1: Work function values from UPS (with asterisk) and Kelvin probe measurements.
ble 4.1, the changes for PFDT treated Au and Cu are 0.45 eV and 0.33 eV, respectively. These numbers indicate that PFDT has a greater impact on work function than PFBT, as expected, due to the greater number of F atoms on the molecule.

4.5 Synchrotron XPS Results

Near-Edge X-ray Absorption Fine Structure (NEXAFS) data were collected at the ALOISA beamline at Elettra Synchtron in Trieste Italy. Synchrotron sources offer several advantages over benchtop X-ray sources. The most important one is brilliance, which is a metric that represents both the brightness and the angular spread of the beam (i.e., a laser beam versus a lightbulb). Synchrotron sources also provide a greater level of coherence and polarizability.
In the previous section, XPS was used to fingerprint molecular species, namely Cu oxide. NEXAFS, on the other hand, probes unoccupied energy levels around an absorption edge, up to around 50 eV above that edge. X-rays are absorbed by electrons in occupied levels, which are excited to unoccupied levels. Upon decay, the electron either transfers its energy to another (Auger) electron or releases a photon. Either the kinetic energy of the Auger electron or the energy of the photon are measured. At ALOISA, it is the former.

Unlike XPS, NEXAFS offers polarization dependence, which reveals information about molecular orientation on a substrate. This 'search light effect' is shown in Figure 4.18 for a benzene molecule chemisorbed on Ag(110). It is particularly useful for molecules that contain highly directional bonds, such as π-conjugated systems. When X-rays are polarized parallel to the direction of the bond, absorption is at a
Figure 4.17: UPS measurement of PFDT/Au and PFDT/Cu.
maximum. At the ALOISA beamline, the polarization state is changed by rotating the sample stage with respect to the X-ray beam. NEXAFS was used to determine the orientation of pentacene on top of the thiols.

The substrates were 1.5 x 1.5 cm pieces of SiO₂/Si. To save time due to pump down, each sample consisted of one Au stripe, one Ag stripe, and one Cu stripe, with 1 mm spacing in between each stripe. A Au stripe was patterned across the top to short all three together so that the entire sample could be grounded during the measurement. The metals were thermally evaporated and patterned with a shadowmask. 5 nm Cr
were deposited first as an adhesion layer. PFDT and PFBT were deposited via soaking in a 1\% by weight solution in anhydrous ethanol for 30 minutes inside a nitrogen-filled glovebox. The samples were then sealed inside heat-seal bags to prevent oxidation during transport to the synchrotron.

NEXAFS data from Cu are shown in Figures 4.19, 4.20 and 4.21. The orientation of pentacene molecules on the substrate can found using the following equation for tilt angle:

\[
\phi = \sin^{-1} \left( \frac{2\cos^2(\theta)}{I_\nu/I_\sigma + 3\cos^2(\theta) - 1} \right)
\]  

(4.5)

Given that in all three cases the first few peaks of the s-polarization data are much larger than those in the p-polarization data, it is obvious that pentacene is in a
standing up orientation. The tilt angles for bare Cu, PFBT/Cu, and PFDT/Cu are 82°, 78°, and 70°. The most likely reason for the high tilt angle on bare Cu is that the metal is slightly oxidized (see passivation section). As it was impossible to acquire pure Cu films from the thermal deposition, the substrates provided a surface energy allowing for only slightly tilted (from the surface normal) pentacene monolayers.

4.6 Conclusions

In summary, this study examined the impact of two distinct thiols on bottom-contact pentacene FETs. By using XPS to measure metal oxidation, it was determined that
short aromatic thiols are poor choices for low work-function metal passivation. In addition, both passivation and charge injection enhancement can be achieved with long fluorinated alkanethiols, however, there is a trade-off between passivation and \( I_{on} \). The enhancement of \( I_{on} \) in thiol-treated Cu-electrode pentacene devices is most likely not morphology related, due to the fact that PFDT was found to be in a standing-up orientation on the metal surface. Lastly, it can inferred that although highly electronegative atoms such as F can modify metal work function, too many F atoms in thiols can lead to too high a work function and a mismatch between the pentacene HOMO level and metal work function.
Chapter 5

Conclusions and Future Work

In summary, this thesis demonstrated that photocurrent microscopy (PCM) is a powerful technique for measuring transport in OFETs. To the author’s knowledge, this is the first time top-contact pentacene and TIPS pentacene devices have been analyzed with PCM. It was demonstrated that PCM can be used as a method of potentiometry, and the mechanism of photocurrent generation was shown using TIPS pentacene measurements. Meanwhile, the latter half of this thesis showed that thiols can be used for contact enhancement and passivation simultaneously. There appeared to be a trade-off between passivation and device performance.

The photocurrent work in this thesis is a stepping stone for more advanced measurements. Among the possible routes to further this study are the following: 1. using polarizers to correlate grains orientation and photoresponse, 2. comparing the photoresponse of photolithographically patterned and shadow-masked electrodes, and 3. measuring the energy level of trap states at a TIPS pentacene grain boundary using PCM.

For additional thiol work, there exist a plethora of metals and metal compounds that can be further explored. An example is aluminum, which has a work function of approximately 4.08. Unlike Cu, Al’s oxide is self-limiting. In addition, Al is cheaper and lighter than Cu. Aluminum was the original choice for interconnects in integrated
circuits. The impetus behind the switch from Al to Cu was increased current densities that led to electromigration effects in Al, as well as the higher conductivity in Cu which allowed for scaling. However, since the applications of organic electronics will certainly not be integrated circuits and will be limited to low current density systems, aluminum could be worth exploring. Passivation would be extremely crucial, since aluminum oxide is an insulator.

The work on PFBT versus PFDT raised many questions regarding conduction in thiols. Future thiol work can entail a systematic study of thiols where only one variable is tuned. For instance, a comparison of thiophenol with pentafluorothiophenol (PFBT). Here, the variable tuned is fluorination versus nonfluorination. Since conduction through both thiols is mostly likely the same, thereby reducing the number of introduced variables, this study would be optimal for testing only the effect of fluorination on metal work function and on pentacene growth.
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Appendix A

XPS of Graphene and Graphene Oxide

A.1 XPS of Radiated Graphene

Graphene boasts incredible mechanical strength [107], superior carrier mobilities [108], and unique optical properties [109]. Although graphene FETs for circuitry are impractical due to ambipolarity, the FET is a useful and convenient platform to study carrier transport phenomena under various conditions.

There is considerable interest in investigating the effects of harsh environments on devices, especially those that are a source of ionizing radiation, such as space environments. Ionizing radiation includes high-energy electrons, alpha and beta particles, gamma rays, x-rays and ultraviolet radiation. In this study, graphene FETs were radiated with gamma and electron-beam radiation at Brookhaven National Laboratory (BNL). Fabrication and electrical characteristics measured before and after exposure was performed by Dr. Kostas Alexandrou. Details concerning fabrication and I-V characteristics can be found in [110].

Gamma radiation dosages were 2.2 kGy and 26.4 kGy. Devices were exposed to gamma radiation both in air and in a nitrogen environment, to determine whether
### Table A.1: Content of C1s XPS for treated and untreated graphene samples.

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>UV-ozone</th>
<th>26.4 kGy</th>
<th>E-beam</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>66.4</td>
<td>40.0</td>
<td>46.8</td>
<td>52.9</td>
</tr>
<tr>
<td>C-OH</td>
<td>16.4</td>
<td>38.4</td>
<td>27.7</td>
<td>20.8</td>
</tr>
<tr>
<td>C-O-C</td>
<td>9.7</td>
<td>7.6</td>
<td>15.3</td>
<td>9.4</td>
</tr>
<tr>
<td>COOH</td>
<td>7.5</td>
<td>14.0</td>
<td>10.2</td>
<td>16.9</td>
</tr>
</tbody>
</table>

The damage is attributed to the radiation alone, the environment or both. E-beam radiated devices were exposed only in air. Note that the devices were top-contact back-gate (the heavily-doped Si substrate acted as the gate), so that the graphene was completely exposed to the environment.

![Figure A.1: Carbon 1s XPS data from three different devices: (i) non-irradiated, (ii) UV-ozone treated samples, and (iii) samples exposed to a gamma ray dosage of 26.4 kGy.](image)

XPS was employed to investigate the effects of the ambient environment on non-encapsulated irradiated devices. XPS spectra were collected using a Phi system with a standard Mg Kα source and spot size of 100 um.

In Figure A.1, C1s XPS spectra from three different device configurations are
presented. Peaks were fit using a Gaussian-Lorentzian blend. The data are comprised of four peaks positioned at 284.5 eV, 285.2 eV, 286.4 eV, and 288.6 eV, corresponding to C-C, C-OH, C-O-C, and -COOH bonds, respectively.

Table A.1 shows the percent area that each peak makes up of the total C1s spectral area. UV-ozone-exposed graphene suffers from high oxygen adsorption and doping, while others have shown that gamma radiation induces ozone formation in air. For these reasons, a UV-ozone treated sample was included in our XPS measurements, to compare its oxygen content to that of the gamma irradiated sample. Both UV-ozone and 26.4 kGy gamma radiation treatment show similar trends. The main carbon peak decreases in area, while the C-OH, C-O-C, and -COOH peaks increase in area. These results clearly indicate that gamma irradiation increases the adsorption of oxygen, resulting in degraded electronic performance. A passivation layer is therefore crucial to isolate the graphene channel from oxygen if devices are to operate reliably in a radiation-heavy environment.

The second form of radiation under consideration was beta radiation, which are high-energy electrons or positrons emitted during atomic nuclei decay processes. A 1.5 MeV Van de Graaff was used to irradiate the samples. The dosage was \(2.35 \times 10^{15} \text{ e/cm}^2\) for 16 minutes. XPS results from electronic beam-radiated blanket graphene samples are shown in Figure A.2. Similar components to the gamma radiated graphene was found at 284.6 eV, 285.5 eV, 286.8 eV, 289.0 eV and a possible fifth component at 290.4 eV.

The above XPS results are consistent with FET I-V measurements, which demonstrate shifts in Dirac point and an increase in mobility degradation with increasing radiation dosage. Oxygen groups present in the semiconductor degrade lattice crystallinity, leading to smaller mobilities. In addition, a reasonable hypothesis is that carboxyl groups form on the surface of the gate dielectric as well. It is possible that these oxygen groups form electron traps; their presence in the gate dielectric surface and in the graphene lattice would contribute to the shift of the Dirac point toward
APPENDIX A. XPS OF GRAPHENE AND GRAPHENE OXIDE

Figure A.2: Carbon 1s XPS data from a beta radiation-treated sample. The dosage was $2.35 \times 10^{15} \text{ e/cm}^2$ for 16 minutes.

positive voltages, a clear sign of increased hole conduction and decreased electron conduction.

This data demonstrates the damage done to the graphene lattice due to ionizing radiation, and to an extent, explains the changes in I-V characteristics of irradiated graphene devices. Although the results are convincing, they are incomplete. A comprehensive study would measure changes not only in the channel, but in the source, drain, gate dielectric and the gate. In addition, while the encapsulated devices show promise in protecting devices from radiation damage, it would be beneficial to measure the effects of radiation over time on the encapsulation material. This is crucial,
as this study pertains to environments in which electronic devices can be sent off for long periods of time, months if not years or decades.

A.2 XPS of Graphene Oxide for Humidity Sensors

Graphene is a promising candidate for sensors, due to its high surface-to-volume ratio and high conductivity. It can make for small, light and effective sensors. Graphene oxide (GO) is a functionalized form of graphene, made by oxidizing graphite, and is easily processable due to its solubility in water, a major advantage over graphene. As it is laced with oxygen groups, GO is more resistive than pure graphene. However, once deposited, its electrical conductivity can be improved through a reduction process.

There has been recent interest in using GO for humidity sensing due to its unique electrical and chemical properties [111] [112] [113]. Reduced GO (rGO) is an eligible candidate for humidity sensing as well, but it poses problems for flexible substrates due to the high temperature processing involved with reduction.

Although rGO humidity sensors have been demonstrated, further work is required to optimize performance, as a compromise exists between film sensitivity and conductivity. In addition, performance relies heavily on the relative humidity (RH) of the environment. For instance, in high relative humidity (HRH), greater than 55%, a ‘swelling effect’ occurs, in which water molecules intercalate into GO layers, thereby increasing interlayer distance and subsequently film resistance. This mechanism has been reported to cause in sensors hysteresis and degradation of humidity sensitivity [114] [115]. Therefore, in this study, angle-resolved XPS (ARXPS) was used to demonstrate permanent water trapping in rGO after HRH exposure, and to correlate water content in the films with device behavior.

rGO films for ARXPS measurements and humidity sensors for electrical characterization were fabricated and electrically characterized by collaborators at the De-
To prepare the ARXPS samples, GO and rGO solutions were spun onto glass substrates at spin speeds of 3000 and 6000 rpm. A different number of reduction steps were used for each rGO sample, ranging from no reduction to 5 iterations. Thermal reduction was done under forming gas (H2/N2:5/95) [116]. Two samples were placed in HRH for observing the swelling effect. HRH (≥85%) samples were exposed for at least 450 seconds using a Capriccio T-253 cool mist ultrasonic air humidifier.

Figures A.3, A.4 and A.5 show ARXPS results from three different types of samples. The measurements were taken four months after the exposure date to test the temporal extent of swelling.

Deconvolving oxygen species in O1s spectra can be problematic. Identification of water is particularly difficult, as the oxygen within water can take on many binding energies depending on what the molecule is physisorbed to [117]. However, it is clear that the sample exposed to low RH exhibits more symmetry in its O1s spectra, while the HRH samples demonstrate clear increased asymmetry. This indicates the possible addition of an oxygen-containing species in the HRH samples.

It is also noteworthy that changes in the spectra are evident at high angles (i.e., 60-65 degrees), indicating that water intercalation into the rGO flakes occurs deep within the film. The height of the spectra between 534 and 535 eV at these angles is particularly high relative to the rest of the peak.

It is highly likely that water from the upper rGO layers was desorbed over the four month period, especially when the samples were placed within the high vacuum XPS chamber. Therefore, data from smaller angles should not be scrutinized as closely as those from larger angles.

Electrical measurements of devices (not shown) demonstrate a permanent current decrease in sensors after HRH exposure. Specifically, the current through the rGO sensors remains stable under RH = 32%. When the RH is increased to 85%, the
current abruptly increases by 190%. Before the RH recovers to 32%, the current decreases by 100% (compared to the initial value) and stabilizes over time. This permanent current decrease after HRH exposure reveals permanent effects that can be attributed to water trapping inside the rGO flakes and/or damage of the rGO flake structure during water absorption and desorption. The aforementioned ARXPS measurements support this theory.

In summary, rGO samples demonstrated a permanent water trapping effect upon exposure to HRH. The existence of trapped water molecules inside the rGO layer was detected with ARXPS.
Figure A.4: Oxygen 1s ARXPS data from a 5rGO 3000 rpm sample exposed to high relative humidity.
Figure A.5: Oxygen 1s ARXPS data from a 5rGO 6000 rpm sample exposed to high relative humidity.
Appendix B

Thermoelectric Properties of a Superatomic Cocrystal

Sustainability is currently steering advancements in energy technology. With approximately two-thirds of all used energy wasted as heat, there is considerable ongoing research in waste heat recovery and reuse, with thermoelectricity (TE) a contender amongst alternative energy sources.

Although it is the common opinion that TE’s are inefficient and subsequently of little use, they prove greatly beneficial in niche applications where conventional cooling methods are cumbersome. An example is TE generators for satellites and space probes [118]. There is also interest in waste recovery for automotive power generation [119] and using human body heat to power electronics [120].

In thermoelectric materials, a temperature gradient across the material sets up a measureable voltage:

\[ \Delta V = -\alpha \Delta T \]  
\[(B.1)\]

where \( \alpha \) is the Seebeck coefficient (both \( \alpha \) and \( S \) are used in the TE literature). The larger the Seebeck coefficient, the greater the voltage across the material for a given temperature gradient. The figure-of-merit of thermoelectric materials is \( ZT \):
where $\lambda$ is total thermal conductivity, and $\sigma$ is electrical conductivity. The ideal TE material has a low $\lambda$ and a high $\sigma$. Figure B.1 shows the general trends in $\sigma$, $\lambda$, $\alpha$, and $Z$. Insulators of course have high $\alpha$ but are poor TE materials due to low electrical conductivities. Metals exhibit the inverse trend. Doped semiconductors, on the other hand, can offer a happy medium between the two.

Figure B.1: Electrical conductivity $\sigma$, thermal conductivity $\lambda_e$ (electron) and $\lambda_l$ (lattice), Seebeck coefficient $\alpha$ and $Z$ as a function of carrier concentration [121].

Electrical and thermal conductivities are often coupled due to the heat that charge carriers transport in conductive materials. Decoupling $\lambda$ from $\sigma$ has been the defining challenge for inorganic TE materials. However, with the advent of novel materials and advancements in nanotechnology, there has been a recent thrust for using nanos-
structuring to reduce $\lambda$ (increase $ZT$) by increasing phononic scattering. Phononic scattering can occur on different scales: atomic, nanoscale and mesoscale, each scattering phonons of different wavelengths.

This study measures the thermoelectric properties of an intercalated two dimensional binary superatomic cocrystal (SAC), synthesized by Evan O’Brien and Rose Kann in the Roy Group, Department of Chemistry at Columbia University. The solid is comprised of a specially designed cluster with bulky ligands, $\text{Co}_6\text{Te}_8(\text{PnPr}_3)_6$, combined with three equivalents of $\text{C}_{60}$, $[\text{Co}_6\text{Te}_8(\text{PnPr}_3)_6][\text{C}_{60}]_3$. The solid consists of alternating fullerene layers (FL) and cluster layers (CL), where one electron has been transferred from the CL to the FL per formula unit. The electron is delocalized among three fullerenes and can move through the FL. Tuning of the solid’s electronic properties was accomplished by intercalating the electron acceptor tetracyanoethylene (TCNE) between the FLs and CLs, which depleted the FL of mobile electrons and reduced the CL. The resultant solid is $[\text{Co}_6\text{Te}_8(\text{PnPr}_3)_6][\text{C}_{60}]_3[\text{TCNE}]_x$, where $0 \leq x \leq 2$.

The measurement apparatus was built inside of a glovebox with an inert atmosphere to keep the material from degrading (Figure B.4). The synthesized material was cold pressed into 5 mm diameter pellets approximately 1-2 mm in height. Initially, the pellet was sandwiched between a ceramic heater and a cooling block whose temperature was controlled with a TE cooler external to the glovebox. The setup was later simplified to consist of two digitally-controlled heaters. In this configuration, for an $\alpha$ measurement at temperature $T$, the heaters were held at temperatures $T+5$ and $T-5$, and the voltage was read off of an SMU held in constant current ($I = 0$ nA) mode (Figure B.3). For a $\sigma$ measurement at $T$, both heaters were held at $T$, while applied voltages were swept from 0 to 100 mV and the current read off of the SMU kept in constant voltage mode. To ensure accuracy of the measurement, after temperatures were changed between data points, approximately 20 minutes were allowed to pass, which was sufficient time for the pellet to thermalize and the voltage
and current readings to reach stable values. Double-sided adhesive Cu foil was used as the electrodes on the pellet. The hot side of the pellet was grounded during all measurements.

The fully intercalated sample was not used, as its $\sigma$ was too low to accurately measure. Measurements were taken up to 100 °C, because the properties of the compound drastically change at these temperatures. Upon heating above 100 °C, $\sigma$ increased and $\alpha$ decreased. This was attributed to polymerization of the FLs, which increased the mobility of the electrons in the FL. This was confirmed with Raman spectroscopy (measurement by Rose Kann).

Thermal conductivity measurements were performed by Dr Wee Liat Ong at Carnegie Mellon University. The technique used was frequency domain thermoreflectance, FDTR, a schematic of which is shown in Figure B.5.

The results are shown in Figures B.6, B.7, B.8, B.9, B.10, and B.11. The first obvious trend is that $\sigma$ decreases while $\alpha$ increases with increasing value of $x$, confirming
Figure B.3: Schematic showing the principle of a thermoelectric measurement. The sample is placed between two electrodes that are temperature controlled. The current through the sample is forced to be zero so that the voltage across it can be measured.

that the TCNE units take charge from the FL, thereby decreasing the population of available charge carriers.

The thermal conductivity appears independent of the electrical conductivity. This can be understood through the Wiedemann-Franz Law:

\[ \frac{\lambda_e}{\sigma} = LT \]  \hspace{1cm} (B.3)

along with

\[ \lambda = \lambda_l + \lambda_e \] \hspace{1cm} (B.4)

where \( L \) is the Lorenz number, which represents the contribution of electron thermal and lattice thermal conductivities to total thermal conductivity. If a measurement of total thermal conductivity is made, then a conservative estimate of electron thermal conductivity can be made. For a 0 TCNE pellet, \( \lambda = 0.09 \, Wm^{-1}K^{-1} \) and \( \sigma = 0.5 \).
APPENDIX B. THERMOELECTRIC PROPERTIES OF A SUPERATOMIC COCRystal

Figure B.4: Apparatus for measuring the Seebeck coefficient. a.) The apparatus was built inside of a glovebox; b.) a pellet is shown sandwiched between a hot and cold plate; c.) in the original setup, a thermoelectric cooler outside of the glovebox kept the colder plate a temperature lower than the ambient temperature; d.) feedthroughs into the glovebox.

\[ S/m \]. For a value of \( L = 2.44 \times 10^{-8} \, \text{W} \Omega K^{-2} \), \( \lambda_e = 3.66 \times 10^{-6} \, \text{W}m^{-1}K^{-1} \), and \( \lambda_l = 8.999 \, \text{W}m^{-1}K^{-1} \). The electronic component of thermal conductivity is four orders of magnitude less than the lattice contribution. Therefore, any trends in thermal conductivity are most likely attributed to changes in phononic scattering. If there
Figure B.5: FDTR setup at Carnegie Mellon University for measuring thermal conductivity. Image credit: Dr. Wee Liat Ong.

were any significant contribution from $\lambda_e$, then one would expect a decrease in $\lambda$ as electrons are depleted from the FL. However, the $\lambda$ of the intercalated compounds is slightly more than the unintercalated compound.

Note that the role of C$_{60}$ in the TE properties of the SAC should not be overlooked. C$_{60}$ has a low $\lambda$ due to its large unit cell and orientational disorder above 260 K. It has been used to reduce $\lambda$ of TE materials, and as a TE material itself in its doped state. In addition, binary SACs incorporating C$_{60}$ exhibit a reduced $\lambda$. Based on single crystal X-ray diffraction data (measured by Rose Kann), it is possible that TCNE interacts with the fullerenes, thereby reducing their orientational disorder and
Included in the results are variable temperature measurements of $\sigma$ and $\alpha$ from room temperature up to 100 °C. The temperature dependence of $\sigma$ shows activated Arrhenius hopping behavior with increasing activation energies with increasing values of $x$. However, $\alpha$ changes minimally with temperature, further supporting the hopping mechanism of the superatom cocrystals.

The Seebeck coefficient changes minimally with $T$ for samples with $x = 0, 0.5, 1$, but changes significantly for the highly intercalated sample, $x = 1.5$. Generally, for lightly doped samples, $\alpha$ remains constant with $T$, but for highly doped samples $\alpha$ increases with $T$.

![Figure B.6: Seebeck coefficient measurements as a function of equivalents TCNE ($x$). The two sets of data were taken with different versions of the setup.](image)

Note the two sets of data represented in Figure B.6, with 6 months inbetween sets (and different sets of pellets). The disparities are most likely a result of the aforementinoed modifications made to the setup. The first data set was collected with the TE-cooled block and heater, neither of which were feedback controlled.
Therefore, this set was prone to higher fluctuations in the voltage readings. With the use of two digitally-controlled heaters, the fluctuations were minimized. In addition, the average pellet temperature \( \frac{T_1 + T_2}{2} \) was far less in the first set, as the cooling block temperature fell well below room temperature.

![Graph showing conductivity measurements](image)

Figure B.7: Conductivity measurements taken with 4-probe, 2-probe and Seebeck measurement apparatus as a function of equivalents TCNE. Disparities between the sets is attributed to contact resistances in the 2-probe and Seebeck setups.

In summary, the tunability of electrical, thermal and thermoelectric properties of a binary superatomic cocrystal have been demonstrated. Although the magnitudes of the power factor and \( ZT \) are not practical for applications, the results show the independent tuning of electrical and thermal conductivities. Future work will likely entail intercalating the superatom cocrystal with an electron donating intercalant, allowing for optimal power factor and \( ZT \).
Figure B.8: Room temperature power factor and $ZT$ calculated from 4-probe conductivity, Seebeck, and thermal conductivity measurements.

Figure B.9: Temperature variable Seebeck measurements for various equivalents TCNE.
Figure B.10: Temperature variable conductivity measurements for various equivalent TCNE.

Figure B.11: Temperature variable $ZT$ measurements for various equivalent TCNE.