ENHANCING THE ELECTRICAL PERFORMANCE OF ORGANIC FIELD-EFFECT TRANSISTORS THROUGH INTERFACE ENGINEERING

BY

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Dedication

To Alexis,
My wife and best friend for life!

Partners in Family,
Teammates in Soccer,
Companions in Adventure.
Acknowledgements

My experience as a student at Wake Forest University and as a resident of the city of Winston-Salem, NC would not have been as productive, educational, or enjoyable without the presence and support from a number of people and organizations. I worked hard to maintain a strong diversity between school and outside experiences and in doing so the past five years have been amazing.

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Jeremy William Ward
August 2015
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CHAPTER 1

INTRODUCTION

This chapter was published as Jeremy W. Ward, Zachary A. Lamport, and Oana D. Jurchescu ChemPhysChem, DOI: 10.1002/ cphc.201402757 (2015), and is adapted and reprinted with permission (License Number: 3605560738854, John Wiley and Sons Publishing).
1.1 Progress in Electronics Beyond Silicon

Progress in the technologies addressing the constantly evolving demands of consumers, driven by the development of new materials and processing techniques, has opened the door to an array of new opportunities. The field of organic electronics has emerged as a viable technology to meet very diverse consumer needs due to the synthetic versatility and the processing flexibility of carbon-based compounds. One of the vital components necessary for emerging technologies is the organic field-effect transistor (OFET). OFETs can become active components within active-matrix organic light-emitting diode (AMOLED) displays, electronic paper, smart bandaging and biological sensors, radio frequency identification tags (RFID), textiles, etc.\cite{1,2} While of prime interest for technology, organic materials also raise interesting questions in terms of fundamental science. Native to most organic systems is the presence of weak van der Waals interactions resulting in narrow electronic bandwidths, strong interactions between charge carriers and the lattice, high susceptibility to defect formation and strong dependence on the processes taking place at interfaces with contacts and dielectrics. The nature of charge transport remains unclear and significant effort is aimed towards elucidating the microscopic and macroscopic parameters affecting it. This knowledge is critical in further improving the performance of organic devices.\cite{3,4}

The electrical properties of organic materials range from insulating to superconducting, with the majority having semiconducting character.\cite{5} The figure of merit for the organic semiconductors (OSCs) is the charge carrier mobility $\mu$, which defines the charge velocity in a given electric field. This parameter is very complex, depending strongly on the materials’ purity and degree of structural order,\cite{6} but can also depend on the environmental conditions such as temperature,\cite{7} and the details of the measurement such as electric field strength.\cite{8} While, in principle, all organic semiconductors could exhibit both $p$-type (hole) and $n$-type (electron) conduction, provided that the electrodes can facilitate injection, most OSCs showed predominantly hole conduction. Recently, several electron-conducting materials with good environmental and operational stability were developed. Figure 1 shows the highest reported mobilities for different classes of materials through time and was adapted and updated from ref. [4]. The largest currently reported mobilities for solution-processed semiconductors are: 43 \text{cm}^2\text{V}^{-1}\text{s}^{-1} (small-molecule $p$-channel, blue),\cite{9} 11 \text{cm}^2\text{V}^{-1}\text{s}^{-1} (small-molecule $n$-channel, violet),\cite{10} 10.5 \text{cm}^2\text{V}^{-1}\text{s}^{-1} (polymer $p$-channel, green),\cite{11} and 7 \text{cm}^2\text{V}^{-1}\text{s}^{-1} (polymer $n$-channel, maroon).\cite{12} Similarly, for vacuum-processed OSCs the largest reported mobilities are 23 \text{cm}^2\text{V}^{-1}\text{s}^{-1} ($p$-channel, red)\cite{13} and 10 \text{cm}^2\text{V}^{-1}\text{s}^{-1} ($n$-channel, black).\cite{14} Note that the best $n$-type performance was achieved in ambipolar transistors.\cite{12,14} Several recent reports,
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however, suggest that some of these values may be overestimated owing to the fact that standard mobility extraction models were used in conjunction with non-ideal current-voltage characteristics in the corresponding devices.[15, 16] Nevertheless, the significant increase in the electrical performance with time for each class is clear, and this is a result of the development of new materials and device structures.

Single crystals provide an effective platform for the investigation of the intrinsic properties of materials, and while they generally offer the best performance achievable by a certain compound because of their high purity and minimal defect density, they are not capable of facilitating high-throughput, low cost, and market-ready devices.[17, 18] Thin films, on the other hand, are compatible with large-area and fast-deposition methods, but typically exhibit a lower degree of order, resulting in inferior electronic performance. For this reason, developing and implementing fabrication methods that allow better control of the organic film quality and uniformity are of key importance. Thus, in addition to progress with material design, intense effort is also dedicated to designing novel device structures which take advantage of the unique fabrication opportunities offered by organic compounds and allow processing at amiable conditions on flexible substrates through large-area-compatible fabrication techniques, without compromising material performance.

All field-effect transistor devices included the same functional layers, depicted in Figure 2, consisting of a gate electrode (black), semiconductor (orange), source and drain electrodes (gold)
to inject charges into the semiconductor layer, and an insulating gate dielectric (grey). Depending on the order by which each of these layers is deposited onto a substrate (blue), four different structures can be achieved, summarized in Figure 2. Most devices included in this work will focus on the structure similar to the one presented in Figure 2d, as we exploit the ability to treat the source/drain electrodes of this structure prior to the semiconductor deposition.

The fabrication of organic thin-film transistors (OTFTs) made entirely using solution-based techniques is of particular interest because of the simple processing since, in general, most of a product's final price stems from the steps required to fabricate it, not from the direct cost of the materials used. This chapter also outlines the current state of the field of solution-processed organic thin-film transistors, with an emphasis on the simplicity of processing. In Section 1.2 we discuss the development of materials that form the electronically active layers in OFETs. In Section 1.3 we focus on the device design and fabrication while providing several examples of techniques used to take full advantage of the versatility offered by the organic compounds.

Figure 2 Schematic representation of the possible field-effect transistor geometries. Labels of S and D denote the source and drain electrodes, respectively. The structures are denoted as (a) Top-gate, top-contact (TGBC); (b) Bottom-gate, top-contact (BGTC); (c) Top-gate, bottom-contact (TGB); (d) Bottom-gate, bottom-contact (BGC).
1.2 Development of Materials for OTFTs

The list of organic materials currently available for the fabrication of optoelectronic devices has grown substantially in recent decades. Their rich electronic properties allow their use as conductors, semiconductors, and insulators in a variety of device architectures. Manufacturing processes taking advantage of a material’s solubility include inkjet printing,\(^\text{19–21}\) spray deposition,\(^\text{22–25}\) and roll-to-roll processing,\(^\text{26, 27}\) among others, but require deposition from inks, which presents challenges related to the control of morphology and uniformity. Specific approaches to address these challenges are discussed in Section 1.3.1.

In addition to the materials needed for the construction of the OFET structure, materials such as self-assembled monolayers (SAMs), additives, orthogonal solvents, etc. are often used in the fabrication and manufacturing process to create optimal semiconductor film morphology and texture,\(^\text{28–32}\) good injection, improved environmental stability, or film patterning.

1.2.1 Organic Semiconductors

Available OSCs are composed of two classes of materials: small molecules and polymers. Each class, in turn, is divided into three categories: \(p\)-type, \(n\)-type, and ambipolar. The tendency of a material to conduct positive charge carriers (hole, \(p\)-type) or negative charge carriers (electron, \(n\)-type) is dependent upon both the choice of semiconductor and electrode material. The energy-level diagram presented in Figure 3 depicts the pathway for charge carriers in \(p\)-type (left) and \(n\)-type (right) transistors. While the injection of charges from the electrode into either the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the semiconductor is, in principle, possible, most OSCs operate in unipolar mode. This implies that the charge injection of one carrier type is often more efficient because of a lower energetic barrier and, thus, determines the type of device operation.

Here, our discussion will be limited to small-molecule OSCs; for a review on polymeric semiconductors, please refer to refs. [33–35]. Since the first reports of vacuum deposited \(p\)-type small-molecule OSCs by Kudo \textit{et al.} in 1984, the field-effect mobility has shown great improvements from \(\sim1.5 \times 10^{-5} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) \(^\text{36}\) to greater than \(10 \text{cm}^2\text{V}^{-1}\text{s}^{-1}\), as we will detail below. The onset of solution-processable small-molecule OSCs was realized in 1999 by Herwig and Müllen as a multi-step process of depositing a pentacene precursor and subsequently converting the film into an active pentacene layer through heating from 130 to 200 °C.\(^\text{17}\) Since then, the
availability of \( p \)-type solution-processable small-molecule OSC materials has expanded significantly, and \( n \)-type OSCs were also developed. The chemical structures and typical mobilities of a few notable compounds are summarized in Table I.

\textbf{p-Type Small-Molecule Organic Semiconductors}

In the late 1990’s, Anthony \textit{et al.} synthesized, for the first time, triisopropylsilylethynyl pentacene (TIPS Pn).\cite{38, 39} The addition of substituent groups to the pentacene backbone made the acene soluble in common organic solvents, allowing for low-cost solution deposition of this compound, shown in Table I. In subsequent years, this quickly became a benchmark material, and devices based on it were fabricated using methods such as spin coating, both traditional and off-centered,\cite{19, 31, 40} drop casting,\cite{31, 41} solution shearing,\cite{42} FLUENCE,\cite{43} electrospray deposition,\cite{44} and inkjet printing.\cite{45} Different modifications of the silylethynyl-functionlized acenes have subsequently been used to fine-tune crystal packing and enhance electrical properties.\cite{46, 50} In parallel, this synthetic platform has been extended to produce an entire set of acene and hetero-acene \( p \)-type semiconductors with varying substituent groups,\cite{24, 38, 51, 55} for example, the fluorinated triethylsilyl-substituted anthradithiophene (diF-TES ADT),\cite{24, 56} triethylgermyl-substituted anthradithiophene (diF-TEG ADT),\cite{57} and difluoro-(tri-sec-butylsilyl ethynyl)
Table 1 Small-molecule organic semiconductors exhibiting high electrical performance when processed from solution-methods. Examples of $p$-type and $n$-type compounds discussed in this review are provided and references can be found throughout the text.

<table>
<thead>
<tr>
<th>Class</th>
<th>Structure of Benchmark Performance Compounds</th>
</tr>
</thead>
</table>
| $p$-type      | ![Diagram](image)
| Functionalized Acenes | ![Diagram](image) |
| Thienoacenes | ![Diagram](image) |
| $n$-type      | ![Diagram](image) |
| Functionalized Acenes | ![Diagram](image) |
| Perylene Diimides | ![Diagram](image) |

The nature and size of the substituent group affects both the film texture and the crystalline packing of the semiconductor and therefore alters the material’s performance. Additionally, Goetz et al. reported on the effect of increasing the backbone length of partially-fluorinated, stable, soluble heteroacenes. An increase in backbone length yielded a more favorable crystalline packing and higher mobility: 1.8 cm$^2$V$^{-1}$s$^{-1}$ for tri-sec-butylsilylthiophen pentacenedithiophene (diF-TSBS ADT), compared to $2 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ in diF-TSBS ADT.

Other classes of soluble OSC materials have also shown excellent electronic performance. For example, alkylated derivatives of [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) exhibit good solubility and efficient charge transport properties. Specifically, the compound 2,7-dioctyl[1]benzo-thieno[3,2-b][1]benzothiophene (C$_8$-BTBT) has shown excellent electrical performance when deposited by a wide range of solution-based methods, such as spin-casting, directional crystallization, and inkjet printing. Minemawari et al. used anti-solvent crystallization in conjunction with inkjet printing to produce OFETs exhibiting average mobilities of 16.4 cm$^2$V$^{-1}$s$^{-1}$, with a maximum mobility of 31.3 cm$^2$V$^{-1}$s$^{-1}$, six times greater than previous results and more than an order of magnitude greater than its first application in solution-processed OFETs. Utilizing a new technique called off-center spin-coating, Yuan et al. achieved a field-effect mobility of 43 cm$^2$V$^{-1}$s$^{-1}$ from a blend of C$_8$-BTBT and polystyrene. Additional
thienoacene-based organic semiconductors, derivatives of BTBT or \( \pi \)-extended versions thereof, have recently become the subject of intense study and the reader is directed to the excellent summary included in the work by Takimiya et al.\(^6^4\) Of particular interest is the compound developed in 2007, dinaphtho\[2,3-b:2',3'-f\]thieno\[3,2-b\]thiophene (DNTT)\(^6^5\) and its more recent derivatives C\(_{10}\)-DNTT\(^6^7\) and DPh-DNTT\(^6^8\) due to their high field-effect mobility and exceptional stability\(^6^9\) when incorporated in flexible, low-voltage devices.\(^7^0\)–\(^7^2\)

While these materials display auspicious electrical characteristics, there exist several drawbacks which must be addressed before their introduction into mainstream electronics. Apart from the alkylated C\(_n\)-BTBT compounds, the solubility of these materials is quite poor, limiting the possible deposition techniques.\(^6^7\), \(^7^3\) Another major impediment associated with these materials has been the elaborate synthesis steps, along which comes higher cost and lower yield, however new synthetic techniques have been developed for both symmetric and asymmetric BTBT derivatives.\(^7^4\), \(^7^5\)

**n-Type Small-Molecule Organic Semiconductors**

In parallel with the development of organic \( p \)-type materials, \( n \)-type OSCs are also necessary for integration in complementary architectures for application in logic devices.\(^7^6\)–\(^7^8\) Challenges faced during the development of \( n \)-channel materials have included low \( I_{\text{on}}/I_{\text{off}} \) ratios and large threshold voltages when characterized in ambient conditions.\(^7^9\) In the early 2000’s, Katz and co-workers developed a set of small-molecule compounds based on a naphthalenetetracarboxylic diimide that performed as \( n \)-channel FETs, however, they observed a large decrease in performance when characterizing the devices in the presence of oxygen.\(^8^0\) The inability to fabricate devices in ambient environments greatly minimizes the choice of compatible fabrication techniques and adds to the processing and manufacturing costs. From a molecular design perspective, the objective is to overcome these limitations by developing compounds with a high electron affinity and strong intermolecular orbital overlap to facilitate both ambient stability and high charge injection and transport.\(^8^1\) In 2007, Marks, Facchetti, and co-workers realized a breakthrough by developing a new class of \( n \)-channel materials based on anthracene-dicarboximides that showed comparable performance in both air and vacuum for up to 4 months of exposure to ambient air.\(^8^2\)

Similar to the development of \( p \)-type OSCs, the \( n \)-type materials have transitioned from vacuum- to solution-deposition. In 2007, N,N’-bis(2,2,3,3,4,4,4-heptafluorobutyl)-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C\(_4\)F\(_7\)) was originally reported with an electron mobility
of 0.72 cm$^2$V$^{-1}$s$^{-1}$ and showed minimal degradation after 50 days in air.$^{[83]}$ Through modifications of the semiconductor-dielectric interface using octadecylsilanes (OTS), the mobility of this compound was improved to 1.4 cm$^2$V$^{-1}$s$^{-1}$.$^{[84]}$ This work also adds the advantage of solution-based fabrication. In 2012, Qiao et al. showed that direct modification of the π-conjugated quinoidal core to include small molecules of 2-ethyl-hexyl and 2-hexyl-decyl promoted electron-only transport in diketopyrrolopyrrole (DPP)-based materials for the first time.$^{[85]}$ Synthesized at Polyera, fluorocarbon-substituted dicyano-perylene-3,4:9,10-bis(di-carboximide) (PDIF-CN$_2$) and N,N'-bis(n-octyl)-x:y, dicyano-perylene-3,4:9,10-bis(dicarboximide) (PDI$_8$-CN$_2$) compounds showed electron mobility values as high as 0.6 and 0.1 cm$^2$V$^{-1}$s$^{-1}$ with excellent ambient stability, when deposited using spin-coating and inkjet printing, respectively.$^{[86, 87]}$ Examples of compounds that exhibit n-type behavior and are displayed in Table I.$^{[88]}$ In 2009 Bao and co-workers examined a set of functionalized acenes and observed the transition from p-type to n-type OSCs through the addition of electron withdrawing groups.$^{[89]}$

### Ambipolar Small-Molecule OTFTs

Two routes towards achieving simultaneous hole and electron transport are pursued in parallel: 1) the use of p-type and n-type material blends or bi-layers and 2) the implementation of materials that exhibit ambipolar conduction when used in conjunction with an appropriate electrode and bias condition.$^{[90]}$ In 2003 Meijer et al. fabricated OFETs by blending p- and n-type polymeric semiconductors to facilitate both hole and electron conduction.$^{[78]}$ Shortly after, Rost et al. also demonstrated an ambipolar device using a bilayer of pentacene as hole-transport and N,N'-Ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C$_{13}$H$_{27}$) as electron-transport material in combination with gold and magnesium electrodes.$^{[91]}$ A hybrid design approach combined the air-stability and solubility of hole-transporting OSCs with complimentary electron-transporting characteristics found in oxide semiconductors yielding air-stable performance with hole and electron mobilities greater than 2 cm$^2$V$^{-1}$s$^{-1}$.$^{[92]}$ Another approach has been based on a co-planar bishphthalocyaninato copper.$^{[93]}$ Shi et al. designed and synthesized a copper complex with energy levels tuned to the range of an air-stable ambipolar OSC in a single material and fabricated OFETs using a quasi-Langmuir-Shäfer process for thin-film deposition, achieving electron and hole mobilities of $1.7 \times 10^{-3}$ and $2.3 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. The applications based on ambipolar FETs have expanded to include organic light-emitting transistors (OLETs). OLETs operate similarly to OFETs with the same three-electrode device structures, however, OLETs use an
electroluminescent, ambipolar semiconductor where holes injected from one electrode recombine with electrons injected from another electrode to generate photons. A background on the OLETs can be found in a 2007 review by Cicoira and Santato.\textsuperscript{[94]}

Undoubtedly, the development of new hole- and electron-conducting materials will continue to promote improvements in the performance of unipolar and ambipolar OFETs. In parallel with the semiconductor material design, the optimization of the interfaces of the OSC with the contacts and dielectrics are also important, as we will be discussed in the sections to follow.

### 1.2.2 Organic Dielectrics in OFETs

The dielectric layer influences the operating voltage of the OTFT and can affect the semiconductor film formation in the bottom-gate device geometries. One of the most ubiquitous dielectric materials in both organic and inorganic TFTs is thermally oxidized silicon (SiO\textsubscript{2}) due to the use of highly doped silicon as the substrate and subsequent gate electrode. This, however, introduces a few glaring disadvantages: a relatively high gate leakage current requiring a thick oxide layer, incompatibility with flexible and large-area electronics, and deposition techniques generally requiring the use of high temperature and vacuum. To reduce the cost of developing TFTs and increase their applications, much research has been done in the field of solution-processed polymer dielectrics.

Polymer dielectrics offer the versatility of a wide range of deposition techniques including spin coating,\textsuperscript{[95]} spray coating,\textsuperscript{[96]} inkjet printing,\textsuperscript{[97]} and dip coating.\textsuperscript{[98]} There exists a variety of insulating organic polymers that have been examined in the context of OFETs such as polyvinyl alcohol (PVA),\textsuperscript{[99]} poly(methyl methacrylate) (PMMA),\textsuperscript{[100]} benzocyclobutene-based (BCB) polymers,\textsuperscript{[101–103]} poly-4-vinylphenol (PVP),\textsuperscript{[104]} CYTOP,\textsuperscript{[105]} and other fluoropolymers.\textsuperscript{[106]} These materials have attracted substantial attention because of their outstanding film formation, high solvent resistance, flexibility, and stability. Due to the range of solvents used and the properties of this class of insulating polymers, there exists a viable choice for an incredible array of applications based on solvent orthogonality and device structures. Another advantage held by polymer dielectrics over inorganic, rigid insulators is that many exhibit fewer dangling hydroxyl groups or other charge-scattering polar end-groups which have been shown to reduce charge mobility of an organic semiconductor.\textsuperscript{[107]} An intriguing concept that gained momentum in the late 1990’s is the idea of using a monolayer of densely packed, chemically adsorbed, and self-assembled molecules as the dielectric layer in a TFT.\textsuperscript{[108–110]} Such a self-assembled monolayer (SAM) dielectric presents
its own challenges in deposition, as well as in achieving high molecular densities, but these are outweighed by the overwhelming advantages inherent when using an ultra-thin (e.g. ~2 nm), covalently bonded dielectric. Devices constructed using ultra-thin monolayer dielectrics can operate in the saturation regime at a drain-source voltage of approximately 2 V due to the greatly increased dielectric capacitance: an areal capacitance greater than 1 µF cm$^{-2}$ can be achieved,$^{[111]}$ which is two orders of magnitude higher than the value corresponding to a 200 nm SiO$_2$ dielectric (17.3 nFcm$^{-2}$). Since the first proof of concept by the Vuillaume group in 2000, significant strides have been made. In 2004, Halik et al. provided the first example of an OTFT utilizing a SAM dielectric with a field-effect mobility of 1 cm$^2$V$^{-1}$s$^{-1}$ and a sub-threshold slope of 100 mVdec$^{-1}$ at a gate-source voltage as low as -2.5 V.$^{[112]}$ Interestingly, the current density through a SAM dielectric has been shown to increase upon deposition of the organic semiconductor, prompting the search for a monolayer with a higher packing density which was achieved using a phenoxy-terminated molecule in order to increase the π-π interactions between molecules and create a pseudo second layer.$^{[109, 110]}$ They then used the phenoxy-terminated trichlorosilane monolayer on an oxygen plasma treated silicon wafer with a thermally evaporated pentacene semiconducting layer as shown in Figure 4, panels a-d. The same group expanded this work to a phosphoric acid-based SAM on an oxygen plasma-treated aluminum bottom electrode.$^{[113]}$ They demonstrated the feasibility of their system by creating an inverter using evaporated pentacene as the $p$-type semiconductor and evaporated copper hexadecafluoro-phthalocyanine (F$\text{16}$CuPc) as the $n$-type semiconductor. A recent example of SAM dielectrics used in OTFTs has shown the further applicability of such devices with solution-processable semiconductors. Liu et al. used cyclohexyl-terminated monolayers on the high-$k$ dielectric AlO$_x$/TiO$_x$ to achieve field-effect mobilities of up to 2.7 cm$^2$V$^{-1}$s$^{-1}$ for $p$-type TIPS Pn and up to 1.44 cm$^2$V$^{-1}$s$^{-1}$ for $n$-type 6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacene (TIPS-TAP) when measured in air.$^{[114]}$ Another innovative use of monolayer dielectrics involved a bifunctional SAM where one section of the monolayer functions as the semiconductor and the other segment forms a hybrid dielectric with an oxygen plasma-treated aluminum oxide layer (Figure 4, panels e-g)$^{[115]}$

### 1.2.3 Solution-Processable Electrodes

In many organic electronics applications, RF-sputtered indium tin oxide (ITO) is used as an electrode because it is highly conductive and optically transparent.$^{[116]}$ However, ITO remains a costly option due to the vacuum-processing required, as well as the limited supply and rising price.
of indium, thus, leading to a concerted effort to find a lower-cost alternative which retains similar conductivity and transparency in addition to being compatible with large-area fabrication. Solution-processed conductors offer the unique opportunity to place device electrodes inexpensively and without the use of vapor-deposited metals observed to damage the soft layers underneath.\textsuperscript{117–119} Possibly the most prevalent of these materials is poly(3,4-ethylenedioxythiophene) polymerized with poly(4-styrene-sulfonate) (PEDOT:PSS) which is used extensively in OFETs\textsuperscript{120} as well as organic photovoltaics (OPVs).\textsuperscript{120–122} This material is water soluble and relatively inexpensive, although lower conductivities have hampered its development for use in devices requiring extremely efficient charge transport.\textsuperscript{123} Fortunately, various treatments of PEDOT:PSS with solvents and acids such as dimethyl sulfoxide (DMSO),\textsuperscript{124–126} ethylene glycol,\textsuperscript{122, 127} sulfuric acid,\textsuperscript{128} zwitterions,\textsuperscript{129} ionic liquids,\textsuperscript{130} anionic surfactants\textsuperscript{131} and combinations thereof, have been shown to increase the conductivity to within an order of magnitude of that obtained using RF-sputtered ITO, while remaining transparent and flexible.\textsuperscript{132} For example, the conductivity of unmodified PEDOT:PSS is generally reported between 0.05 - 10 Scm\textsuperscript{−1}\textsuperscript{123} while treatments with ethylene glycol show an increase in the conductivity to as high as 1418 Scm\textsuperscript{−1}\textsuperscript{122} and treatments with sulfuric acid reach even higher to 3065 Scm\textsuperscript{−1}.\textsuperscript{128} Efficient solar cells can be fabricated with
power conversion efficiencies up to 13.3% due to their already high transparency and this greatly increased conductivity.\cite{133} A creative use of PEDOT:PSS was introduced by Akkerman et al. to increase the yields in molecular electronics applications.\cite{134} In order to protect against pinholes created by vapor deposited top electrodes,\cite{117,118} they devised a method using a stack consisting of a layer of gold, photo-lithographically patterned photoresist, a monolayer attached to the gold, PEDOT:PSS, and a final gold top electrode. This design allowed for the examination of large-area molecular junctions without subjecting them to the damage generally caused by metallic top electrodes. Additionally, it has been demonstrated that PEDOT:PSS is compatible with roll-to-roll processing, a prerequisite for industrial applications of organic electronics. Lim et al. implemented the method of spray deposition to fabricate PEDOT:PSS electrodes, setting the stage for its use in large-area electronics.\cite{135}

A viable alternative to PEDOT:PSS exists in the use of single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).\cite{136-140} A particularly interesting technique used arrays of CNTs in n-type OTFTs as their source and drain electrodes.\cite{141} Cicoira et al. designed titanium contacts with CNTs along the edges which resulted in improved charge injection by allowing charge carriers to more efficiently cross the Schottky barrier at the electrode-semiconductor interface. These n-type FETs using CNT contacts exhibited mobilities of $2 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ compared to $1 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ obtained using gold contacts. Random networks of CNTs can show a high optical transmittance as well as high conductivity,\cite{138,139} however in the absence of laborious separation procedures,\cite{142,143} even purified SWCNTs contain a mixture of metallic and semiconducting CNTs due to the inherent variability in structure, and the semiconducting CNTs will absorb light without contributing to the conductivity.\cite{144,145} This mixture decreases the overall conductivity of the thin film unless the layer is made considerably thicker, resulting in a decreased transparency. The costly fabrication and purification required led many researchers in pursuit of an alternative electrode material. The search for an electrode that is both highly conductive and transparent continued on to random networks of metal nanowires, generally made of silver because of their extremely high conductivity. Lee et al. demonstrated that a mesh of silver nanowires can have similar conductivity and transparency to ITO, leading to a similar power conversion efficiency in solar cells while remaining solution-processable.\cite{146} A recent result from Kang et al. introduced the method of spray coating silver nanowire films, which presents the advantage of being compatible with large-area roll-to-roll processing.\cite{147} Another system that has received considerable interest is that of organic metals based on charge-transfer (CT) complexes, which consist of co-crystals of donor and acceptor semiconductor materials.\cite{5,90,148,149} They can
form excellent electrodes, yet the poor solubility of CT complexes has prohibited their use in large-area electronics. Hiraoka et al. were able to overcome this challenge by inkjet printing the two soluble components, tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), sequentially, which then combined on the substrate to form the CT complex TTF:TCNQ. This method allows for simultaneous deposition and patterning of electrode materials by solution processing of the CT material, greatly increasing the array of practical applications.

1.3 Low-cost Manufacturing to Exploit OSC Properties

Because of the susceptibility to degradation upon exposure to heat, light and/or many chemical compounds, the use of methods developed for the inorganic materials processing is not always suitable for organic compounds. Such materials demand new approaches to achieve appropriate film texture, effective device patterning, and high quality electrodes. A large number of creative, cost-effective techniques based on rapid, simple manufacturing schemes were designed and implemented for the fabrication of organic devices. Techniques such as inkjet printing, spray deposition, solution shearing, and dip coating, among others, take advantage of the solution processability and allow film deposition at a low cost per unit volume. Separately or together, these techniques offer considerable advantage over the energy-intensive practices such as RF sputtering, thermal or electron beam evaporation, chemical vapor deposition, and atomic layer deposition which require high temperature, high vacuum, or both.

1.3.1 Texture Control

The nature of the intermolecular interactions found in organic materials allow the opportunity to modify the film structure by tuning the processing parameters, but also create many challenges to produce optimized films for efficient charge transport. In addition, in a device configuration one must consider not only the optimization of each layer, but that the inter-layer interactions at each interface play a vital role in determining device properties. Different methods were developed to modify the morphology, microstructure, and crystallinity of the OSC, with the aim of improving charge transport. One method used to tune crystalline film formation includes the use of SAMs to influence the microstructure of crystalline domains. For example, increased grain size was observed in thin films of diF-TES ADT deposited on HMDS-treated substrates, compared to untreated
SiO$_2$.\textsuperscript{[152]} The larger grains resulted in increased charge carrier mobility and reduced low-frequency noise. A more sophisticated approach involves manipulation of chemical interactions at interfaces: by taking advantage of fluorine-fluorine and sulfur-fluorine interactions at the interface of a halogenated-SAM-treated electrode and a halogenated OSC. In 2008 Gundlach \textit{et al.} demonstrated a controlled self-assembly process of the OSC molecules, in which the film microstructure can be tuned such that it is highly conductive on and in the vicinity of an OTFT electrodes whilst maintaining insulating characteristics in the region between neighboring devices.\textsuperscript{[30]} The conductive regions were realized through the growth of molecules in a purely (001) orientation, which corresponds to the molecules arranging “edge-on”, promoting charge transport in the high conductivity direction.\textsuperscript{[155]} This is in contrast to the observed mixture of (111) and (001) orientations found in the regions where such interactions were prohibited. The mechanism for this intriguing microstructure formation was elucidated by studying combinations of fluorinated SAMs and fluorinated OSCs that allow fluorine-fluorine and sulfur-fluorine interactions of varying strengths. This phenomenon was then applied for OTFT self-patterning, as discussed in Section 3.2.\textsuperscript{[28, 58]} In 2013 a similar film morphology was observed by Kymissis \textit{et al.} for an un-fluorinated OSC (TIPS-Pn) in combination with the fluorinated-SAM, pentafluorobenzenethiol (PFBT), on copper and gold electrodes, and this was described in terms of electronic coupling between the SAM and the OSC.\textsuperscript{[31]}

Polymer additives, including nucleating agents,\textsuperscript{[45]} introduced in the small-molecule OSCs solutions prior to or during film crystallization have also been shown to improve film morphology. For example, Madec \textit{et al.} investigated the evolution of the TIPS Pn film morphology, upon the introduction of polymer binders, through x-ray diffraction and electrical characterization.\textsuperscript{[154]} They observed that the mobility of TIPS Pn-based OTFTs, in combination with poly(α-methylstyrene) (PAMS), amorphous polystyrene (PS), isotactic polystyrene (iPS), and isotactic poly(α-vinyl naphthalene) (iPVN), depends on the weight fraction of the binder up to a 50% concentration. The roughness of the OSC/binder film was observed to decrease with increased binder concentration. A few years later, in 2010, Smith \textit{et al.} observed a decrease in activation energy with decreased grain size diF-TES ADT blended with poly(triarylamine) (PTAA) explained by deeper trap levels from higher angle grain boundaries or increased surface roughness.\textsuperscript{[155]}

The methods described thus far have included the chemical modification of a surface or the addition of materials to the OSC solution to alter the morphology or structure. Much success has also been found in methods that apply an external stimulus during or after the film formation. Diemer \textit{et al.} applied gentle vibration to the substrate during the solvent evaporation, which resulted
in a significant reduction of the density of traps at the OSC/dielectric interface and devices approaching the performance of single crystals of the same materials, with a mobility of \(3 \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) and subthreshold slope of 0.43 V·dec\(^{-1}\).\[^{156}\] They explored such fabrication parameters as the amplitude and frequency of vibration and determined the parameter space that yields high performance.

Diao et al. have induced a laminar flow to an OSC solution to make highly-ordered, high performance, single crystal OFETs with average mobilities of \(8.1 \pm 1.2 \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) and as high as \(11 \text{cm}^2\text{V}^{-1}\text{s}^{-1}\).\[^{43}\] They used a modified solution-shearing method with a micropillar-patterned printing blade to induce recirculation of the OSC solution to enhance the crystal growth. They attributed the success of the technique, coined FLUENCE, to the elimination of grain boundaries, improved domain alignment and a degree of crystallinity.

Post-processing treatments were also employed to improve the morphology of organic semiconductor films. For example, solvent annealing of triethylsilylethynyl anthradithiophene (TES ADT) films, has been shown to convert a poor electrically performing amorphous layer to a high performing, highly crystalline layer.\[^{157}\] Dickey et al. observed two order of magnitude increase in film mobility when it was annealed under dichloroethane or toluene vapors and they observed that the threshold voltage shifts depend on the polarity of the annealing solvent. They suggest that the solvent vapor penetrates the organic film, altering the surface potential at the OSC/dielectric interface.

### 1.3.2 OTFT Patterning

Most solution-deposition techniques yield full-surface coverage, however, incorporation of OTFTs in transistor arrays require the insulation of individual devices (e.g. thin-film patterning). Patterning is necessary in order to minimize the cross-talking between neighboring devices, which reduces the power consumption and improves the \(I_{on}/I_{off}\) ratio. Figure 5 shows a schematic and electrical characteristics for both a non-patterned (left) and patterned (right) array of devices. The patterned devices show sharper turn-on (red curves) and higher on/off ratios because of the reduced value of the off-current (see Chapter 2, Section 2.5 for a detailed description of the electrical properties). For inorganic semiconductors this is accomplished through multi-step photolithography techniques.
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that involve developing and etching using solvents. These processes, however, result in large
amounts of chemical expense and waste, use complicated alignment procedures, involve intricate
equipment and are often performed using high intensity light sources. While some of these
techniques can be modified to be compatible with organic materials, the availability of solution-
processable organic materials open opportunities for creative, simple solutions to pattern OFETs,
not accessible to their silicon counterparts. Patterning techniques compatible with organic materials
are primarily performed in one of two ways: 1) the simultaneous deposition and patterning of the
material (additive patterning) or 2) deposition followed by patterning (subtractive patterning).
Additive processes typically require fewer steps, simplifying the fabrication process and will, thus,
be the focus of this section. Successful examples include direct evaporation through a shadow
mask,\cite{158} inkjet printing,\cite{62, 159} selectively treated surfaces,\cite{20, 160} and differential microstructure.\cite{128, 30, 31, 58, 153}

Inkjet printing is a technique in which individual droplets from a nozzle merge on a substrate
to deposit and pattern a material. This method has emerged as one of the most competitive
processing techniques in part due to its low-cost, its small environmental impact and its
compatibility with large-area and flexible electronics. First introduced in the fabrication of organic

**Figure 5** Schematic representation and electrical characteristics of non-patterned (left) and
patterned (right) OTFTs.
light-emitting (OLED) devices by Sturm and co-workers in 1998\cite{161} and later developed for use in polymer-based transistors in the early 2000’s,\cite{21,159} inkjet printing methods have become a common practice in many research environments. A thorough description of the most important developments in the inkjet printing technology can be found in refs. [162] and [163] and progress related to large-area electronics is discussed in Section 3.3,\cite{162,163}

Challenges associated with inkjet printing are the relatively large limit of printing resolution due to the tendency of low viscosity inks to naturally spread on surfaces and the inability to print on hydrophobic surfaces, such as fluoropolymer dielectrics. In 2008, Someya et al. observed a 4-fold increase in mobility of pentacene-based OTFTs as the droplet size of the silver contacts was reduced from 15 pl to 1 pl volumes.\cite{164} They further improved the resolution, achieving channel lengths as small as 1 μm through tuning the applied wave-form to a conducting wire within the printing nozzle such that sub-femtoliter droplets can be produced.\cite{19}

Another viable method for patterning OTFTs implements selective surface treatments using SAMs. Lowering the surface energy in regions surrounding OTFTs through SAM treatment has provided versatile avenues to confining material to localized regions while maintaining resolutions comparable with other photolithographic techniques.\cite{160} In 2008 Jackson and co-workers selectively exposed OTS SAMs to deep UV light through shadow masks to obtain regions of hydrophobic and hydrophilic surfaces (Figure 6). The organic thin-film deposited from solution over this surface only adhered to the hydrophilic regions and thus patterning of the OTFTs and circuits was achieved. The patterned diF-TES ADT devices had FET mobilities \(-0.12 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\), on/off current ratios \(> 10^5\), and threshold voltages of \(-4\) to \(4\) V.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_6.png}
\caption{Schematic representation of the non-relief-patterning process flow used to pattern OTFTs. Reproduced with permission from ref. [160].}
\end{figure}
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The combination of surface selectivity with the use of sintered silver nanoparticles as pinning agents has produced devices having improved resolution and has made viable the opportunity of an all-solution based process. This allowed the progress from the fabrication of inkjet-printed OFETs in which at least one layer was deposited by using other techniques (thermal evaporation, spin coating, or blade coating) to all-solution processed OFETs\(^{20, 21, 165}\) and even a fully-printed organic transistor by Arias and co-workers in 2014.\(^{20}\) By combining surface energy patterned (SEP) blade coating for the electrodes and semiconductor deposition with blanket blade coating of the gate dielectric and surface tension-guided inkjet printing of the gate electrode, OTFTs of diF-TES ADT/PTAA blended films were fabricated (Figure 7). The all-printed arrays exhibited extremely high device-to-device reproducibility with a yield of 96%. In the case of a 1:1 concentration of diF-TES ADT to PTAA, devices exhibited mobilities with an average of 0.68±0.23 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and threshold voltages near -2 V.

Other additive processes for high-throughput patterning of semiconductor films have been demonstrated. Popular methods include the use of stamping techniques (e.g. PDMS stamping\(^{166}\), printing (μCP),\(^{167, 168}\) and nanotransfer printing\(^{166}\)). Generally, stamping uses an element with a surface relief to selectively apply material. The first demonstration of this technique, by Wilbur et al. in 1994, produced feature resolutions of ~1 μm and has since been proven as viable approach to the patterning of OFET components.\(^{169}\) The simplicity in the μCP method resides in the ability to create a single high-resolution master that can then be used an unlimited number of times to accurately recreate the desired pattern.

Another successful patterning method developed recently is based on establishing a differential

**Figure 7** (a) Surface-energy patterned (SEP) blading coating process flow; (b) Procedure for all-printed OTFTs from SEP blade coating of the electrodes and semiconductor, blanket blade coating of the gate dielectric and surface tension-guided inkjet printing of the gate electrode; (c) Top view of final OTFT architecture. Reproduced with permission from ref. [20].
microstructure within the OSC films. As prefaced in Section 3.1, the differential microstructure is achieved through the deliberate selection of SAM-OSC systems that allows or inhibits interactions capable of templating molecular order. The high mobility regions consisting of (001) oriented molecules are present on the electrode surfaces and their immediate vicinity (10 - 50 μm).\[30\] They are surrounded by low-mobility domains of mixed (001) and (111) orientations that electrically isolate neighboring devices in OTFT arrays. This patterning technique for the OSC is a purely additive process that, in contrast to inkjet printing techniques, can generate patterned films through blanket film techniques such as spin coating. In 2012, through a combination of electrical studies and structural characterization, the mere presence of a halogenated-SAM was found to be insufficient in promoting self-patterning of the OSC. On the contrary, specific design features must be considered in the SAM-OSC combination.\[58\] Here, the OSC diF-TES ADT was paired with three mono-fluorinated benzene thiol varieties (Figure 8a) and the per-fluorinated SAM PFBT electrode treatment. Self-patterning was observed for the case of PFBT and of 4-fluorobenzenethiol (4-MFBT) and no differential microstructure formation was observed in the cases of 2-fluorobenzenethiol (2-MFBT) and 3-fluorobenzenethiol (3-MFBT). The effectiveness of this patterning technique can be seen in the evolution of the field-effect mobility as a function of device

**Figure 8** Representation of the interaction between (a) dif-TES ADT and a fluorinated-SAM treatment allowing two or more interaction pathways and (b) diF-TIPS Pn (Peri) and a mono-fluorinate-SAM treatment with only one interaction pathway. Optical micrographs of di-F TES ADT films are shown for a (c) high-mobility (PFBT-treated electrodes) and a (d) low mobility (2-MFBT-treated electrodes) device morphology. (e) Evolution of the field-effect mobility for OTFT devices fabricated untreated (black square), 2-MFBT (violet circle), 3-MFBT (blue triangle up), 4-MFBT (orange triangle down) and PFBT (red diamond) treated electrodes. Panels a-b are reproduced with permission from ref. [28]. Panels (c-e) are reproduced and modified from ref. [58] with permission from The Royal Society of Chemistry.
channel length (Figure 8e) with the onset of two distinct regimes for the PFBT and 4-MFBT treatments, which is not present for the other treatments. The relationship between fluorinated-SAM treatments and halogenated OSCs was further investigated with diF-TIPS Pn (Peri) (a 1:1 isomeric mixture of 1,8- and 1,11-difluoro 6,13-bis(triisopropylsilylthynyl) pentacene) and diF-TSBS PDT (Figure 8b).\textsuperscript{28} It was found that the presence of two or more interactions between halogen sites on the SAM or OSC molecule is necessary and sufficient to promote molecular anchoring and contact-induced crystallization. These interactions were found to be suitably strong to induce a preferred texture only when the halogen atoms originating from the OSC and from the SAM are located closer than about twice the van der Waals interaction distances, highlighting the importance of tuning molecular interactions in organic-based electronics. Patterning by differential microstructure is different from patterning by tuning surface energy in that 1) it implies the presence of a chemical interaction at interfaces and 2) it results in a continuous film, but as the molecules within this film adopt different orientations depending on the substrate treatment, the film is electrically patterned.

1.3.3 Large-Area Electronics

Organic large-area electronics can access a variety of consumer applications such as solar cells, backplanes to light-emitting displays, and sensor technologies. Applications of electronics with physical dimensions of up to tens of meters, realized through the combination of nanometer- and/or micron-sized devices implemented into functional arrays, can be made affordable for consumers by the reduced cost per unit area of organic electronics manufacturing. For example, just the cost of patterning in traditional silicon-based technologies can be as high as 3.0 $cm^{-2}$, which may not provide an economic route to producing large-area devices.\textsuperscript{47} In contrast, organic materials processing can provide avenues for fast deposition and patterning over large-areas at low cost by using fast-processing techniques compatible with the highly desired roll-to-roll (R2R) processing. Roll-to-roll processing is a method of fabricating large-area electronic devices on flexible substrates that allow for high-throughput device manufacturing. A typical R2R process requires a substrate to traverse through a series of stages that include the deposition and patterning of subsequent layers (e.g. electrodes, insulators, semiconductors). While this process is currently more common for OPVs,\textsuperscript{170} recent advancements in the development of components necessary for R2R OTFTs have been realized.\textsuperscript{20, 23, 171, 172} OTFT devices present the unique challenge of patterning
discrete layers and are therefore much more complex than their OPV counterparts. Representative techniques used for solution-processable OTFT constituents within the R2R framework include the previously discussed ink-jet printing and spray deposition. Common among spray deposition processes is the separation of a liquid into an aerosol mist composed of discrete droplets of solution. This mist is then transferred on to a substrate, which is often heated, to form a continuous film of a desired thickness. Within the field of organic electronics, three primary methods are used to create and propel this aerosolized media: 1) gas-propelled spray, 2) ultrasonic spray, and 3) electrospray deposition.[173–175]

The gas-propelled method consists of the rapid ejection of a liquid through a small orifice using a pressurized gas (i.e. Ar or N₂). This process requires a high pressure of propellant gas to ensure a fine mist and, in turn, produces a strong directional jet of aerosol spray.[176] In contrast, the ultrasonic spray technique often uses piezoelectric crystals to induce high-frequency vibrations into the bulk of a liquid which is then transferred to the air-liquid boundary.[177] This creates constant compression and decompression of the liquid and results in the creation of very small mist droplets cast into the air. Transferred using a carrier gas, the mist is then deposited onto the desired substrate. Within these two constructs, similar physical and solution parameters require optimization, however, an increased control of the droplet diameter is realized through a fine-tuning of the piezoelectric frequency, down to picoliter drop sizes.[178] While directional spray is possible with deflection of the mist using inert gases, it is not necessary. The third technique typically used to aerosolize a liquid involves applying a high voltage between the substrate and the nozzle for ejection of the liquid.[175] Once the electric field reaches a critical value for the solution, the liquid dissociates to produce droplets of the solution at which point the solvent begins to evaporate while in flight, leaving a very dense aerosol of the organic compound. The optimization of each process for electronic applications is quite complex and requires a finely tuned balance between physical deposition parameters (i.e. spraying distance, travel rate, orifice diameter, propellant media, substrate temperature, etc.) as well as solution parameters (i.e. viscosity, vapor pressure, solution concentration, etc.).

Gas-Propelled Spray Deposition

The first demonstration of gas-propelled-spray deposited organic films were realized using semiconducting polymers in OPVs by two independent results by Ishikawa et al. in 2004[179] and Mo et al. in 2005.[180] A similar technique was employed by Chan et al. to fabricate OTFT devices
from spray-deposited poly-3-hexylthiophene (P3HT) in a 6:1 chlorobenzene:1,2,3,4-tetrahydronaphthalene solution on OTS-treated gate dielectrics exhibiting mobilities as high as 0.1 cm²V⁻¹s⁻¹. As they noted, this performance was comparable to the best mobilities observed in P3HT using other preparation methods.

Azarova et al. used this method to fabricate OTFTs from a small-molecule OSC, diF-TES ADT, and obtained mobilities of 0.2 cm²V⁻¹s⁻¹ and on/off current ratios of 10⁷. This performance was realized using 20 times more dilute solution than traditional spin-casting techniques, dramatically reducing the cost per unit area in large-area manufacturing settings. More recently, Mei et al. extended this system to demonstrate the spray-deposition of triethylgermyleneethynyl-substituted anthradithiophene (diF-TEG ADT). This compound yielded record-high spray-deposited mobilities of 2.2 cm²V⁻¹s⁻¹, low threshold voltages of 0.5 V, and on/off current ratios of 10⁴.

Khim et al. fabricated spray-deposited OTFTs and complementary inverters using the p-type semiconductor region-regular P3HT and the n-type semiconductor ActiveInk N1450. High device-to-device uniformity, suggested to be due to the production of smoother films with increased solution flow rates, was observed and the recorded charge-carrier mobilities were 0.25 cm²V⁻¹s⁻¹ and 0.01 cm²V⁻¹s⁻¹, respectively. Of distinct interest is the observation of an order of magnitude increase in device mobility for ActiveInk N1450 as the flow rate increased from 0.8 to 1.6 ml min⁻¹ while the P3HT performance remained constant. The stark improvement is attributed to the increase in crystallinity of the ActiveInk compound from the slower evaporation of the solvent.

In 2013, Yu et al. fabricated flexible ammonia (NH₃) gas sensors using OTFTs fabricated from gas-propelled spray-deposited TIPS-Pn on a PMMA dielectric. X-ray diffraction was used to demonstrate the highly ordered and highly crystalline film. Multiple device characteristics showed dependencies on NH₃ concentration, however the most prevalent was a -20 V shift in threshold voltage when exposed to a 100 ppm atmosphere of NH₃. Multiple cycles of N₂ and NH₃ exposures demonstrate the favorable response and recovery characteristics of the sensors.

Ultrasonic Spray Deposition

Even though multiple ultrasonic-based spray techniques have been demonstrated for the fabrication of OPVs, only recently has the method been used for OFET fabrication. This process was first discussed by Abdellah et al. and later developed by Shao et al. They fabricated ITO bottom-gate, Au top-contact OFETs using ultrasonic-based spray deposition of
TIPS Pn and PVP as the active semiconductor and insulator, respectively. A maximum charge-carrier mobility of 0.35 cm$^2$V$^{-1}$s$^{-1}$, threshold voltage of 11.3 V, and on/off current ratio $>10^4$ on a flexible substrate was observed from tilting a substrate at a small angle of 3° to align the TIPS Pn crystals, a solution flow rate of 1.2 ml min$^{-1}$, a nozzle-to-substrate distance of 4.6 cm, and a nozzle translation of 8 mm s$^{-1}$. This performance is comparable to devices fabricated using traditional spin-coating processes, with the added ability for large-area fabrication. The PVP film exhibits low roughness due to the nature of the small droplet size produced by the ultrasonic waves.

The ability to generate very small particles within a very narrow size distribution facilitates the formation of uniform and homogeneous films, which is especially important in the fabrication of very thin dielectric layers. While the technique is typically used in polymer-based materials, the solubility, ease of purification and synthesis, and compound diversity of small-molecule organic semiconductors create incentives for further development.

**Electrospray Deposition**

The electrospray deposition (ESD) technique offers similar advantages over traditional coating methods to that of gas-propelled and ultrasonic-generated aerosols. However, the use of an electric field between the nozzle and conductive substrate facilitates small droplet creation, charged media, improved droplet-size control, and deposition efficiency due to the ability to apply the aerosol to a substrate without the use of any carrier gas.$^{[174]}$

In 2013, Onojima *et al.* fabricated bottom-contact, bottom-gate OFETs based on domains of crystalline TIPS Pn using the ESD method.$^{[44]}$ Active semiconductor films were deposited from 1,2-dichlorobenzene and acetone at a solution feed rate of 0.6 ml min$^{-1}$, a substrate temperature held at 55°/60° C, a nozzle-substrate distance of 5 cm, and an applied voltage of 13 kV between the solution and substrate. Notably, the deposition times were very fast (~1 min). Electrical characterizations include a field-effect mobility of 0.12 cm$^2$V$^{-1}$s$^{-1}$ at a drain-source voltage, $V_{DS} = -50$ V, an on/off current ratio of $10^4$, and a high threshold voltage of −17 V. Upon reduction of the bottom-contact thickness, an improved threshold voltage of −6.4 V was observed.

In 2014, Yamauchi *et al.* implemented the ESD technique for the direct wet-patterning and development of $n$-channel ZnO-based and $p$-channel TIPS Pn-based step-edge vertical-channel FETs (SVC-FETs).$^{[186]}$ This structure has been shown to achieve a submicron channel thickness.$^{[187]}$ The linear regime field-effect mobilities were $6.8 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ ($n$-channel, $V_{DS} = -10$ V) and $1.6 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ ($p$-channel, $V_{DS} = -10$ V). While this is not a demonstration of benchmark
electrical performance, the results highlight the fabrication of OFET devices from both inorganic and small-molecule organic semiconductors and the ability to directly pattern the films through electrically biasing the gate lines.

1.4 Conclusion

Organic-based FETs provide the unique opportunity to place electronics on large-area, light weight, flexible substrates at a low cost, a process that is inaccessible to most inorganic devices. In addition, the versatile chemistry of organic compounds allows for fine-structural modifications that result in a diverse assortment of usable dielectrics, semiconductors, and electrodes that can be deposited by a rich variety of deposition techniques. The solution-based techniques include, but are not limited to, doctor blading, spray coating, drop casting, and inkjet printing. While full solution-processing greatly simplifies production, the inherent disorder in the resulting films has great influence on their performance. Even so, decades of cross-discipline research in all phases of development has resulted in device efficiencies worthy of use in modern electronics applications. Investigations during the infancy of organic field-effect transistor research focused mainly on obtaining and characterizing high mobility semiconductors, however it was quickly realized that the dielectric deserved equal attention due to its far-reaching impact on the performance of a device. This led to the examination of high-k dielectrics, various polymer dielectrics, ultra-thin monolayers, as well as hybrid multi-layer dielectrics in search of a material that combines low voltage operation with low leakage currents. The research efforts dedicated to the development of organic electrodes focused on improving charge injection by reducing contact resistance in the presence of organic/organic interfaces. Materials that are readily deposited from solution, such that the entire process avoids high-vacuum environments, are of prime interest. Examples include dispersions of inorganic metals and carbon nanotubes, metallic polymers and organic charge-transfer complexes. Modern electronics generally requires device patterning on a particular substrate to reduce power consumption and signal ambiguity, whereas most approaches to organic electronics involve full-surface coverage. Organic materials allow for creative solutions to this issue including selective surface energy treatments, differential microstructures, as well as applications to large-area electronics.
1.5 Thesis Outline

This thesis is organized in the following manner:

Chapter 2 describes the solution processing and electrical characterization of organic thin-film transistors and the techniques used in this study to measure the structure of organic semiconductor films. The assembly, composition, and characterization of self-assembled monolayers on electrode surfaces is also discussed.

In Chapter 3 we emphasize the impact that structural phase transitions can have on the performance and stability of OTFTs. A temperature driven phase transition is identified for the high-mobility organic semiconductor, diF-TES ADT. This transition is studied by variable temperature electrical characterization, thermal measurements, and structure determination.

In Chapter 4 and Chapter 5 we develop relationships between halogenated self-assembled monolayers and organic semiconductors that allow us to fine tune film morphology and achieve self-patterning of OTFTs by differential microstructure. Chapter 4 is dedicated to understanding the effect that subtle changes in the self-assembled monolayer structure have on the thin-film growth, device performance, and feasibility of self-patterning. In Chapter 5 we expand these studies on a broader range of organic semiconductors and SAMs and establish design rules for efficient OTFT self-patterning.
References


References


References


CHAPTER 2

ORGANIC FIELD-EFFECT TRANSISTOR FABRICATION AND CHARACTERIZATION

2.1 Introduction

As shown in Chapter 1 (Figure 2), the architecture of an OFET requires a set of individual layers to be assembled in a specific manner to create a functioning device. While a variety of techniques used to deposit the organic semiconductor were outlined throughout Chapter 1, this chapter will serve to detail the specific techniques used to fabricate the individual layers for the devices used throughout this research project. Section 2.2 describes the methods used to fabricate an array of contacts using photolithography and electron-beam evaporation, Section 2.3 provides details about the fabrication and characterization of self-assembled monolayers, Section 2.4 describes the growth and characterization of the organic semiconducting layer, and Section 2.5 details the electrical characterization of the complete OFET devices.

2.2 Contact Fabrication by Photolithography

Independent features within an OFET can be defined using additive approaches (i.e. printing\[1\]) or subtractive techniques (i.e. stamping\[2\] or shadow masking\[3, 4\]). An approach used to define the features of the electrodes on to a substrate of n++Si with thermally oxidized SiO\(_2\) is the subtractive method of photolithography. This method, shown in Figure 1, includes the general process of coating a substrate with a layer of a photo-reactive material (photoresist) (Figure 1b) and selectively exposing regions of the film to a high-intensity light through a transparent mask containing the desired features (Figure 1c). When using a “negative” process, the features that are to eventually be contacts are realized by the opaque regions of the mask, preventing those regions from exposure. This process effectively “hardness” the regions illuminated by the light, rendering them insoluble to the liquid developer used to remove the portions hidden by the mask (Figure 1d). Upon development of the film, the contact region of the substrate now consists of voids in the photoresist regions by dissolving the remaining photoresist using a compatible solvent (Figure 1g).
Figure 1 Schematic representation of the fabrication process used to fabricate the OFET devices used in the present research. Panels (a-g) depict the photolithography and metallization processes used to pattern the device electrodes and panels (h-i) show the placement of the SAM and OSC layers, respectively.
The procedure used to fabricate the contact-patterned substrates in this research is detailed hereinafter. A 4 inch wafer of n++Si with a 200 nm thermally oxidized SiO\textsubscript{2} film was prepared using a 4 minute dehydration bake at 90 °C. Since the approach used consisted of a negative process, the NFR016D2 photoresist was spun on using a two-step process: a 1) 500 rpm sec\textsuperscript{-1} acceleration to 500 rpm for 5 seconds to spread the liquid uniformly over the substrate and a 2) 1000 rpm sec\textsuperscript{-1} acceleration to 3000 rpm for 30 sec to thin the photoresist to the desired thickness. The coated film was baked for 2 minutes at 90 °C in an oven in air prior to a 10 second exposure through a Cr-patterned quartz mask at a 13.5 mw sec\textsuperscript{-1} intensity. A final bake for 2 minutes at 90 °C in air completed the curing of the exposed photoresist. The substrate was immersed for 1 minute in MF-319 developer to remove the unexposed regions of photoresist. The developed substrate was exposed to a 45 second oxygen plasma ash at 100 W to ensure full removal of the photoresist from the unexposed regions.

In order to ensure a high quality metallization occurs, the substrate was placed in a vacuum chamber and pumped down to near or below pressures ~10\textsuperscript{-6} torr. Typically when depositing Au onto a silicon-based substrate, the use of an intermediate layer (i.e. Ti or Cr) is needed to ensure good adhesion of the Au to the substrate. In our case, we deposited 50 Å of Ti immediately followed by 600 Å of Au, both with a rate of 2 Å sec\textsuperscript{-1}. The final steps for the fabrication of the contacts included the metal lift-off through a 1-2 hour soak in a solvent such as N-Methyl-2-pyrrolidone (NMP) or acetone. This process can be expedited using elevated temperatures (~60 °C) or sonication, however this increases the risk of torn contacts that show poor edge definition.

Prior to further deposition of subsequent layers or contact treatments, the 4 inch wafer was subdivided into identical pieces (~2 cm x 2 cm) using a diamond-tipped pen. Prior to the deposition of the OSC layer, each of these test-beds were subjected to a thorough degreasing and photoresist removal process that included a 10 minute soak in acetone and then isopropanol (IPA) at 80 °C followed by a 10 minute UV-ozone exposure and a 30 second rinse with deionized (DI) water.

### 2.3 Self-Assembled Monolayers

The processing of organic compounds using solution-based techniques requires a precise control of the relationship between the surface of the underlying substrate and the composition of the liquid. One technique to impart improved wettability is through the modification of the surface using a
self-assembled monolayer (SAM). SAMs are available in a wide variety of configurations and are highly tunable to form strong, chemical, bonds with a range of surfaces. The ability for SAMs to modify pristine oxide and metal surfaces allows the tailoring of those surfaces to support improved semiconductor growth and morphology,\textsuperscript{5–10} better charge injection at the semiconductor’s interface with the electrodes,\textsuperscript{7,11–13} and the reduction of charge scattering and trapping sites at the semiconductor-dielectric interface and thus improving the charge transport characteristics of OFET devices.\textsuperscript{14} The chemical structures and names of a subset of typical SAMs used in OFET fabrication are shown in Figure 2.

2.3.1 Composition and Function of SAMs

In this work, SAMs terminated with a sulfur atoms, known as thiols, were used to promote a strong adsorption of the monolayer to the metallic surfaces during the device fabrication process, as shown in Figure 1h. The incorporation of SAMs into the research presented here served two purposes:

1) Modification of the substrate’s electronic properties at the interfaces between the device electrodes and semiconducting film to promote improved injection of charge carriers into the active layer,
2) Modification of the substrate’s surface chemistry to promote interactions between the SAM and deposited organic semiconductor.

In Chapter 3, the fluorinated pentafluorobenzethiol (PFBT), displayed in Figure 2a, was used to both shift the work function of the electrode and to create an electrode surface suitable with the growth of large, highly-ordered, and favorably oriented films for effective charge transport. This choice takes advantage of exploiting the fluorinated SAM and the fluorinated organic semiconductor to create an environment capable of facilitating interactions at their interface through halogen-halogen interactions. In Chapter 4 and Chapter 5, the nature of this interaction was further exploited through the investigation of SAMs with similar composition to PFBT presenting compounds with a reduced amount of fluorination.

The wetting properties of the SAM-modified surfaces were macroscopically investigated using goniometry (Section 2.3.2) and the modification of the electronic nature of the modified surface were characterized using Kelvin Probe measurements (Section 2.3.3).

### 2.3.2 Growth and Characterization of SAMs

The treatment of substrates using self-assembled monolayers is typically accomplished by either vapor deposition (in vacuum or ambient) or by immersion in a solution. In this study, all electrode treatments were performed from a 30 - 50 mM solution of the SAM material diluted in high purity ethanol. A 3 ml solution was placed in the bottom of a small beaker (~5 ml) followed by the submersion of the cleaned substrate containing Au-patterned electrodes. After a 30 minute treatment, the substrate was removed and thoroughly rinsed with and/or sonicated in ethanol to ensure full removal of the remaining bulk layers not covalently bonded to the substrate. Using this approach, the timescale of SAM adsorption is dependent on the size of the SAM molecule and can range from ~10 minutes to ~2 days.\(^{[15]}\)

We have performed goniometry using a Rame Hart Model 200 Standard Contact Angle Goniometer and image analysis using the DROPimage Standard software suite.\(^{[16]}\) All goniometry experiments were performed using the static sessile drop method in which a small, constant, volume of a DI water was gently deposited on the substrate under test. A bright, diffuse, light was shone through the droplet and the stage was translated relative to the ccd camera so that its silhouette was visible on an image of high contrast. Figure 3 shows a representative image used in this analysis with a water droplet on untreated, cleaned, Au surface on the left and an Au surfaced treated in a
solution of 30 mM PFBT on the right. The high fluorination of the monolayer promotes a shift in the hydrophobic nature of the substrate. The impact that a SAM treatment has on a surface was studied by characterizing multiple substrates to gain an understanding of the reproducibility of the treatment method and characterizing multiple spots per substrate to reveal the spatial uniformity of the treated substrate.

2.3.3 Interface Energetics and Electrical Characterization of SAMs

A key component that must be considered upon the selection of a SAM for modifying a device’s electrode stems from the ability of SAMs that exhibit a dipolar nature to shift the energetics of the electrode, schematically represented in Figure 4. Ensuring a proper alignment between the HOMO/LUMO of an organic semiconductor and the work function of the electrode surface is vital to improving and maintaining efficient charge transport in a device. A misalignment creates an energetic “injection” barrier that charge carriers must overcome prior to being involved in effective charge transport through the OSC.

A SAM based on alkanethiols or their perfluorinated counterparts adsorbed onto a metal electrode can be represented as a stacked bilayer of two dipolar layers. One constituent of the total dipole is due to that formed by the metal-sulfur (M-S) interaction and the other is from the composition of the monolayer itself. In the case of a non-fluorinated alkanethiol SAM, the dipole contribution of the metal-sulfur interaction exceeds that of the SAM itself and thus, a smaller, negative, shift in the work function of the electrode is observed relative to the fluorinated variety. The change in the electrode’s work function can be determined from

\[ \Delta W_F = -N \left[ \frac{\mu_{\perp \text{SAM}}}{\varepsilon_0 K_{\text{SAM}}} + \frac{\mu_{\perp \text{M-S}}}{\varepsilon_0 K_{\text{M-S}}} \right] \]  

(2.1)

where \( N \) is the grafting density of the monolayer, \( \mu_{\perp \text{M-S}} \) and \( \mu_{\perp \text{SAM}} \) are the components of the
SAM’s dipole moment and the effective metal-sulfur dipole moment perpendicular to the surface, respectively, $\varepsilon_0$ is the permittivity of free space, and $\kappa_{\text{SAM}}$ and $\kappa_{\text{M-S}}$ represent the dielectric constants of the SAM and metal-sulfur interaction, respectively.

Two primary methods to determine the work function of either a pure metal electrode surface or a modified electrode surface are through using either ultraviolet photoemission spectroscopy (UPS) or Kelvin Probe measurements. Using a UPS method requires the use of a high-vacuum environment whereas a Kelvin Probe approach can be done in ambient conditions.$^{[17, 18]}$ As such, since the majority of the processing of organic materials in this work was accomplished in ambient conditions, we have chosen the Kelvin Probe method to be more appropriate in mapping the charge-injection picture of our systems.

We have performed the Kelvin Probe measurements using TREK Model 325 Electrostatic Voltmeter, calibrated using freshly cleaved highly ordered pyrolytic graphite (HOPG). A schematic of the probe and surface under test is shown in Figure 5. After the instrument was zeroed using the HOPG standard, the SAM-treated Au substrate was placed on a grounded metallic stage, capable precise translation along the vertical axis. The surface under test was brought within one to two millimetres of the probe head, making sure the two surfaces did not come in physical contact. Due to the sensitivity of the measurement to static charge in the surround area, the probe head setup was placed in a grounded Faraday cage. The contact potential difference between the surface under test
and probe surface \((V_{\text{sample}} - V_{\text{probe}})\), as measured, was used to determine the absolute work function using

\[
WF = -e\left(-(V_{\text{sample}} - V_{\text{probe}})\right) + \phi_{\text{HOPG}}
\]  \(2.2\)

where ‘e’ is the electron charge, \(V_{\text{sample}}\) is the signal from sample, \(V_{\text{probe}}\) is the signal from the HOPG and \(WF_{\text{HOPG}} = 4.48\) eV is the work function of HOPG.\([19]\)

2.4 Organic Semiconductors

2.4.1 Growth and Film Morphology of OSC Layers

The methods used to deposit the organic semiconducting films include both techniques intended to fabricate discrete devices, such as physical vapor transport\([20-22]\) and inkjet printing processes,\([25-27,1,28]\) as well as those intended to create more continuous films such as spin casting,\([6,7,21,29-32]\) doctor
Chapter 2. OFET Fabrication and Characterization

blading,$^{33-35}$ and drop casting.$^{13,31}$ As is briefly outlined in Figure 6 for a few representative deposition techniques, each method presents advantages and disadvantages related to the device performance and rate of throughput of fabrication. Along the top axis, “slow” refers to a process that requires a long (~days) to perform the crystal growth process while “fast” denotes a much quicker process (~seconds). The bottom axis refers, generally, to the relative expected electrical performance of the organic semiconductor crystals grown when in an OFET devices. The primary method used throughout this research is that of spin coating. This process is most frequently used to create very uniform thin films on geometrically flat surfaces. After the substrate is mounted, a typical deposition process includes four phases: 1) dispensing of a liquid onto the substrate, 2) rotational acceleration of the substrate to a low speed to facilitate the uniform spreading of the liquid, 3) further acceleration to a very high rotational velocity to thin the film to the desired thickness through spinning fluid off the substrate using the outward centrifugal force, and 4) evaporation of the remaining solvent through a constant rotation of the stage for an extended period of time. The parameters used in each of the steps are dependent on the properties of the liquid (i.e. viscosity) as well as the desired thickness of the resulting film.

The organic semiconductor films deposited for the OFET fabrication that is presented in the following chapters typically included the deposition of ~300 μl of 1-2% by wt. organic semiconductor dissolved in an organic solvent (i.e. chlorobenzene) onto a 2 cm x 2 cm substrate adhered by vacuum to the stage of the spin coater. The stage is accelerated at a rate of 100-333 rpm sec$^{-1}$ to a maximum spinning speed of 1000 rpm. In most spin coating processes, the magnitude of the acceleration is less vital to the resulting film formation, however in processes intended to allow

---

**Figure 6** Schematic illustration of a few representative techniques used for the deposition of the organic semiconductor layer within OFET fabrication. From left to right: Physical vapor transport, Solvent assisted deposition, Drop casting, Spin casting. General trends related to the time required for film/crystal formation and electrical performance are depicted above and below the arrow, respectively.
the interaction between the organic semiconductor and the chemically modified substrates, we found that a small acceleration is necessary. Solvent evaporation continues for an additional 80 seconds of rotation to ensure its full removal. Since the devices fabricated here were bottom-gate, bottom-contact devices, following the deposition of the OSC, structural and electrical characterization was conducted, as discussed in Sections 2.4.2 and 2.4.3. This process creates an environment suitable for the investigation of interactions between organic semiconductor and device surfaces, however it does not facilitate a high-throughput technique to take advantage of the unique applications of OFETs.

2.4.2 Structural Characterization of OSC Layers

The structure and function of a thin film are intimately related, thus a good control of the electrical performance requires a thorough understanding of the structure of the film and its impact on charge transport. In this work, we will use x-ray scattering techniques to investigate the structural characteristics of the semiconductor layer performed as a function of temperature, surface treatments, and spatial location within a device. X-ray diffraction (XRD) techniques are appropriate for our purpose for two main reasons: 1) the wavelength of x-rays are on the same length scale as the interatomic distances in the materials of interest (0.15 – 4.0 nm) and 2) under appropriate procedures, x-ray scattering techniques are non-destructive to the sample or device under test.\[^{36}\]

Depending on the information that is to be extracted from the XRD experiment, there exist many approaches to choose from (i.e. single crystal diffraction, powder diffraction, x-ray reflectometry (XRR), grazing incidence x-ray diffraction, etc.). However, the basic principles are similar, regardless of the method, and they will be discussed conceptually here. For a more detailed discussion and mathematical derivation of these principles see \textit{X-Ray Diffraction} by B.E. Warren\[^{37}\] and \textit{Thin Film Analysis by X-Ray Scattering} by Mario Birkholz.\[^{36}\]

An X-ray scattering process used throughout this work includes the following steps: 1) the production of X-rays, either from a synchrotron source or a Cu radiation source in the lab, 2) the shaping and directing of the source X-rays towards the sample under test, and 3) the interaction (i.e. scattering) of the incident waves with the lattice planes of the crystalline solid. When interacting with the lattice, those waves whose path lengths have been altered by an integer \(n\) multiple of the incident X-ray’s wavelength \(\lambda\) will interfere constructively and remain in phase. This condition for constructive interference leads to the Bragg relationship between the lattice spacing of the solid and the incident wavelength of the X-rays, given by:
where $d$ is the interplanar spacing between two adjacent planes of a crystal lattice and $\theta$ is the angle of the incident x-rays. As the X-rays are scattered from the lattice, a diffraction pattern is measured by the detector. Based on the intensity and location of the detected X-rays incident on the detector, the structural properties and film characteristics can be obtained.

In Chapter 3, we explored the structural changes induced to the small-molecule diF-TES ADT using temperature-dependent powder X-ray diffraction. In Chapter 4 we explore the structural changes within blanket films of diF-TES ADT deposited on SAM-treated electrodes using the grazing incidence x-ray diffraction (GIXD) technique. In Chapter 5, we use the microbeam grazing incidence wide angle X-ray scattering (μGIWAXS) to investigate the structure of organic semiconductor films on components within an actual device.

### 2.5 Electrical Characterization of OTFTs

The OFET consists of only a few necessary components (see Chapter 1, Figure 2) and the quality of and relationship between them play a vital role into the overall performance, and thus the feasibility of the device being used for certain applications. A typical set of figures of merit are used to determine and communicate the electrical performance of an OFET. The methods used throughout this thesis to determine the field-effect mobility ($\mu$), threshold voltage ($V_T$), sub-threshold slope ($S$), and on/off current ratios ($I_{on}/I_{off}$) are discussed below. In this section we also present the algorithm used for the calculation of contact resistance and contact work function. This section serves as a discussion of the electrical characterization techniques used throughout the present research.

#### 2.5.1 Figures of Merit of OFETs

Organic field-effect transistors operate by the principles described below. When a gate voltage that is greater than the threshold voltage is applied, either holes (negative $V_{GS}$) or electrons (positive $V_{GS}$) from the organic semiconductor accumulate at its interface with the gate insulator and the device operates in accumulation mode. While in this mode, the source and drain electrodes allow access to the mobile charges.
The operation of a FET consists of two regimes, identified in Figure 7b. A device is in the linear regime of operation when $V_{DS} \ll |V_{GS} - V_T|$. Here, the device acts as a gate voltage controlled variable resistor with the source-to-drain current following

$$I_D = \frac{W}{L} \mu C_i \left(V_{GS} - V_T - \frac{V_{DS}}{2}\right)V_{DS}$$

(2.4)

where $W$ and $L$ are the width and length of the FET channel, respectively, $\mu$ is the charge carrier mobility, and $C_i$ is the areal capacitance of the gate insulator.

As the drain voltage increases, a space charge forms, limiting further increase in the drain current and this is denoted as the pinch-off point. Beyond that point, the device operates within the saturation regime and the drain current follows

$$I_D = \frac{W}{2L} \mu C_i (V_{GS} - V_T)^2$$

(2.5)

The models discussed above follow from the long channel silicon FET model developed by Van de Wiele.\[^{38}\] The remainder of the section details the extraction of useful parameters from typical device transfer and transport characteristics.

### Off-Current

The first stage of a typical cycling of an OFET device for determining device properties begins in the devices’ off-state. In this stage, the device is biased with a $V_{GS}$ such that a very small, often negligible, drain current ($I_D$) is observed. A very low current in this regime is desired so that minimal power is used when the device is supposed to be inactive. In the present research, the device’s off-current ($I_{off}$) is defined as the minimum $I_D$ measured and is denoted in Figure 7a.

### Subthreshold Slope

The subthreshold slope is used to characterize the subthreshold swing of a device prior to becoming active and is determined using

$$S = \frac{\partial V_{GS}}{\partial (\log I_D)}$$

(2.6)

The subthreshold swing quantifies the speed with which the device turns, where a better device is identified by a smaller value, and is typically reported in units of mV dec\(^{-1}\). Equation (2.6) represents the inverse slope of the log ($I_D$) versus $V_{GS}$ curve and is typically determined from the
maximum slope of that curve. Fundamentally, the best room temperature value for the subthreshold slope is 60 mV dec⁻¹.[39]

**Threshold-Voltage**

As the \( V_{GS} \) in a device is increased, it transitions from its off-state to one in which the channel is active. The threshold voltage (\( V_T \)) occurs upon the accumulation of charges at the interface of the OSC with the gate dielectric and is observed by an appreciable increase in \( I_D \). In the present research, the threshold voltage is determined by extrapolating the linear portion of the \( \sqrt{I_D} \) versus \( V_{GS} \) curve to the axis with \( V_{GS} \), as shown in Figure 7a. A threshold voltage near zero is ideal, resulting in an efficient amount of power required to maintain a device in its off-state.

**Field-Effect Mobility**

After the channel of an OFET becomes active, charge carriers move from the source electrode, through the semiconducting channel, and into the drain electrode. The effectiveness and rate of this movement is most commonly discussed in terms of the device’s field-effect mobility (\( \mu \)) and is typically reported in units of cm²V⁻¹s⁻¹. The drift velocity of a charge carrier in an electric field is related by its mobility through

\[
\dot{v} = \mu E
\]  

(2.7)
and can be experimentally determined from the FET IV characteristics. Solving Equations (2.4) and (2.5) for \( \mu \), we can use the slopes of the \( I_D \) versus \( V_{GS} \) curve in the linear regime and the \( \sqrt{I_D} \) versus \( V_{GS} \) curve in the saturation regime with the following expressions:

\[(\text{Linear Regime}) \quad \mu_{\text{lin}} = \frac{L}{C_i W} \frac{\partial I_D}{\partial V_{GS}} \]  \hspace{1cm} (2.8)

\[(\text{Saturation Regime}) \quad \mu_{\text{sat}} = \frac{2L}{C_i W} \left( \frac{\partial \sqrt{I_D}}{\partial V_{GS}} \right)^2 \]  \hspace{1cm} (2.9)

While this model assumes ideal behaviors that satisfy Equations (2.4) or (2.5), not all OFET devices exhibit this behavior. Realistically, factors such as a high contact resistance at the interface of the device’s electrode and organic semiconductor can create non-ideal behavior in the current-voltage characteristics.\(^{15,40}\) In this research, the mobility was extracted using the most linear portion of the transfer characteristics. We note that the experimental interpretation of mobility can be greatly enhanced by selectively choosing only a few points that can often originate from noise regions of device operation. To avoid this, in this research we developed a LabVIEW-based analysis platform that helped to remove much of the subjectivity in extracting the mobility through automating the analysis of the measured data. All measurements use a minimum of a five points to determine the slope by first choosing the set of lines possessing the highest degree of linearity from which the maximum value was chosen.

**On/Off Current Ratio**

After the region in which the \( I_D \) greatly increasing, a final region observed in a typical \( V_{GS} \) sweep is one where the drain current begins to saturate and is identified in Figure 7a. Here, the maximum \( I_D \) is measured. We define this maximum drain current as the on-current \( (I_{on}) \). A measure of the contrast between a transistor’s on- and off-states is the ratio between \( I_{on} \) and \( I_{off} \).

**2.5.2 Contact Resistance**

The resistance that a charge-carrier experiences as it transfers from the electrode to the semiconductor is defined as the contact resistance \( (R_c) \). The method used in the present research for extracting this figure of merit is the gated-transmission line method (Gated-TLM).\(^{47}\) In this
formalism, the resistance in a device is modeled as a series of three resistors (Figure 8a), two for the contributions of the contact resistance at each electrode and one for the contribution from the resistance within the channel. For a set of devices, the total device resistance for each \( V_{\text{GS}} \) sweep is given by

\[
R_{\text{on}} = \frac{\partial V_{\text{DS}}}{\partial I_{\text{D}}} \quad (2.10)
\]

and is determined in the linear regime of device operation, as shown in Figure 8c. Since the overall resistance of the device depends on the length of the channel, the evolution of the total resistance as a function of channel length is determined and is displayed in Figure 8d. Modeling the overall resistance of a transistor device to include contributions from both the semiconductor channel and the injection of charge carriers into the channel we have:

\[
R_{\text{on}} = R_{\text{ch}}(L) + R_{\text{c}} \quad (2.11)
\]

where \( R_{\text{c}} \) is the contact resistance. As \( L \) approaches zero, all the resistance of the device now

---

**Figure 8** Circuit diagrams depicting the (a) contact and channel resistance for channel lengths greater than zero and (b) contact resistance as \( L \rightarrow 0 \). Representative transport characteristics (c) and evolution of the total device resistance with channel length (d) used in the contact resistance analysis.
 originates at the electrode-semiconductor interface, thus the contact resistance (Figure 8b). Extrapolating the evolution of $R_{\text{on}}$ versus $L$ to $L = 0$, we determine the contact resistance of the device. As the channel length decreases, so too does the contribution of the channel resistance term in Equation (2.11). Therefore, the total resistance for devices with short channel lengths is realized by a greater fraction of $R_c$ relative to the $R_{\text{ch}}$. Since $R_c$ is dependent on the device width, and often the applied $V_{\text{GS}}$, a common representation is the evolution of the width-normalized $R_c$ as a function of $V_{\text{GS}}$, shown in Chapter 5. While typically $R_c$ decreases with increasing $V_{\text{GS}}$ due to the reduction of the injection barrier between the charge carrier and the metal electrode as the Fermi level shifts,\cite{42,43} we observed $V_{\text{GS}}$-independent $R_c$, similar to that observed by Smith et. al.\cite{18} The origins for these observations are currently under investigation.
References


References


[16] F. K. Hansen, DROPimage Standard (rame-hart)


The use of organic semiconductors in high-performance organic field-effect transistors requires a thorough understanding of the effects that processing conditions, thermal and bias-stress history have on device operation. Here, we evaluate the temperature dependence of the electrical properties of transistors fabricated with 2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (dif-FTES ADT), a material that has attracted much attention recently due to its exceptional electrical properties. We discovered a phase transition at $T = 205$ K and discuss its implications on device performance and stability. We examined the impact of this low-temperature phase transition on the thermodynamic, electrical, and structural properties of both single crystals and thin films of this material. Our results show that while the changes to the crystal structure are reversible, the induced thermal stress yields irreversible degradation of the devices.
3.1 Introduction

Soluble small-molecule organic semiconductors exhibit excellent electrical performance when crystallized by a variety of techniques; these include ink-jet printing,[1, 2] polymer blends,[3, 4] solution shearing,[5] vibration assisted crystallization (VAC),[6] and spray deposition.[7–10] Charge transport in these materials is strongly dependent on the crystal packing motif, which is dictated by the molecular structure: very subtle modifications in the chemistry of the compound yield significant changes in the electronic couplings[11, 12] and device performance.[3, 6, 10, 13–15] In addition, such systems are susceptible to variations in crystalline structure upon processing. The existence of more than one possible crystal structure for a compound is referred to as polymorphism, a phenomenon that is quite common in molecular crystals given the weak nature of the intermolecular interactions that are characteristic to such systems.[5, 16–28] With 5,11-Bis(triethylsilylethynyl) anthradithiophene (TES ADT), for example, the solvent type used during film deposition affects its crystalline structure and morphology, and alters its field-effect mobility by over one order of magnitude.[29] In the same material, polymorphism can be driven by post-processing steps such as solvent annealing,[30] or by sweeping the temperature.[31] The fluorinated version of the aforementioned compound, 2,8- difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TES ADT), also exhibits temperature-dependent polymorphism.[32] In this system an enantiotropic phase transition was reported near room temperature, which affected its electrical properties, and the observed changes were completely reversible. In the present study, we explore the properties of this material over a broader temperature range and discover the presence of another structural phase transition present at $T = 205$ K. This transition is completely reversible in terms of crystalline structure, but it yields irreversible deterioration of the electrical performance in organic thin-film transistors (OTFTs) fabricated from this material. The transition was studied using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and OTFT measurements. This study provides a complete phase diagram of the phases present in diF-TES ADT in the temperature range 120 - 350 K and their effect on charge transport and device stability.
3.2 Experimental

3.2.1 Calorimetric and Structural Characterization of the OSC

DSC measurements were performed in hermetically sealed aluminum pans at a scanning rate of 20 K/min using a Q2000 TA Instruments differential scanning calorimeter. Multiple heat/cool sweeps were performed over the 180 – 350 K temperature range. Temperature-dependent XRD was carried out in order to elucidate the structural changes within the material as it passed through the phase transitions. Single crystal XRD measurements were not successful as the crystal routinely cracked or shattered upon cooling below 280 K, preventing the collection of sufficient data to determine the crystalline structure at temperatures below the 205 K transition. We were, however, able to gain qualitative information about the low-temperature phase by performing powder XRD. Powder diffraction was acquired on a Bruker D8 DaVinci diffractometer with Cu-Kα radiation and a liquid nitrogen-cooled low-temperature stage fitted with a Be hemispherical enclosure. The source beam was conditioned using a 0.1 mm lateral slit and 2.5° Soller slits. The reflected beam was conditioned with a 0.6 mm lateral slit, 2.5° Soller slits and a Ni filter to remove Kβ contributions. The powder was lightly mechanically ground and sifted using a fine mesh filter screen to ensure an even coating on a zero-background Si substrate. After initial measurements were taken at room temperature \( T = 294 \) K, the powder was sequentially cooled to \( T = 200 \) K then \( T = 150 \) K, and finally returned to \( T = 294 \) K, all at a rate of 5 K min\(^{-1}\). Scan data set was collected at each temperature for the range \( 10° < 2θ < 40° \).

3.2.2 Field-Effect Transistor Fabrication and Characterization

The device studies were carried out using bottom-gate, bottom-contact field-effect transistor (FET) structures with heavily doped n++Si as the gate electrode and 200 nm SiO\(_2\) gate dielectric. The source and drain contacts were defined by photolithography and lift-off, with Ti (5 nm)/Au (45 nm) deposited using e-beam evaporation. The substrates were cleaned with hot acetone and hot isopropanol followed by UV-ozone exposure and an ethanol rinse. A self-assembled monolayer (SAM) treatment was performed on the electrodes by soaking the substrate in a 30 mM room-temperature bath of pentafluorobenzenethiol (PFBT) (Sigma Aldrich) for 30 minutes followed by a 5 minute sonication in ethanol. The organic semiconductor was spin-coated from a 1.2 wt. % chlorobenzene (Sigma Aldrich) solution at 1000 rpm. As-prepared devices were placed in vacuum
for at least 24 hours prior to measurement to ensure full solvent removal. Electrical characterization was carried out during cooling, followed by heating using an Agilent 4155C Semiconductor Parameter Analyzer in combination with LakeShore cryogenic probestation. The heating/cooling rates were 5 K min\(^{-1}\) to prevent film cracking.

### 3.3 Results and Discussions

Figure 1 depicts the DSC results obtained for a typical diF-TES ADT sample. Two peaks can be clearly distinguished, denoting the presence of two distinct transitions separated by a \(\Delta T = 90\) K interval. The known room-temperature phase transition manifests itself as a peak at \(T = 294\) K, characterized by a latent heat of \(\Delta H = 1.8\) kJ mol\(^{-1}\), in agreement with previous reports.\(^{[32]}\) Further cooling shows an additional peak at \(T = 205\) K, with latent heat twice as large at \(\Delta H = 3.6\) kJ mol\(^{-1}\). Both transitions appear to be enantiotropic in nature. For the remainder of this article, the individual phases will be denoted from warmest to coolest as \(\alpha\), \(\beta\), and \(\gamma\). Slight shifts in the peak positions are observed during the heating segments of the DSC, but the temperature interval between the two peaks remains constant.

The devices operate as \(p\)-type FETs, and in Figure 2a we present a typical device characteristics in the saturation regime (\(V_{DS} = -40\) V). We extracted the mobility \(\mu\) from the slope of the square root of the drain current (\(I_D\)) vs the gate voltage (\(V_{GS}\)) using the current-voltage relationship:

\[
I_D = \frac{W}{2L} \mu C_i (V_{GS} - V_T)^2 \tag{3.1}
\]
Chapter 3. Structural Phase Transitions in Organic Semiconductors

where \( W \) and \( L \) are the channel width and length, respectively, \( C_i \) is the gate oxide capacitance per unit area, and \( V_T \) is the threshold voltage. The plot in Figure 2a corresponds to measurements taken at \( T = 295 \, \text{K} \) and representative transfer characteristics at different temperatures are displayed in Figure 3 for the saturation regime. The evolution of the FET mobility, as characterized in the saturation regime of operation, versus temperature is shown in Figure 2b. We measured more than 15 devices, and all showed similar behavior. This plot shows several inflection points at temperatures that coincide with peak locations in the DSC measurements. For this reason, we attribute them to the phase transitions. A similar trend was observed in data extracted from linear regime (Figure 4), however to minimize the effects due to the contacts and to more effectively access the intrinsic properties of the material, our discussion will be limited to the saturation regime characterization. The change in the slope of the \( \mu \) vs. \( T \) plot begins at \( T = 294 \, \text{K} \), marking the transition from the \( \alpha \)-phase into a region where the \( \alpha \)- and \( \beta \)-phases co-exist, in agreement with previous results.\(^{[32]}\) In the temperature range \( 220 \, \text{K} < T < 275 \, \text{K} \) the mobility varies monotonically with temperature and the film consists of pure \( \beta \)-phase. Upon further cooling, the onset of a region in which the mobility increases is observed. This marks a phase-coexistence region between the

![Figure 2](a) Typical current-voltage characteristics for a device in the saturation regime of operation (\( V_{DS} = -40 \, \text{V} \)), taken at \( T = 295 \, \text{K} \). This device has a geometry of \( W = 1000 \, \mu \text{m} \) and \( L = 15 \, \mu \text{m} \). The inset displays the schematic of the device that was used. (b) Evolution of the saturation field-effect mobility (\( \mu \)) with temperature. The inflection points correspond to the structural phase transitions. Individual phases are identified by \( \alpha \), \( \beta \), and \( \gamma \). The inset shows representative slopes used in the activation energy calculation.
β- and γ-phases, with the β-phase gradually being converted into the higher mobility γ-phase. At $T < 175$ K the film consists of a single phase, i.e. the γ-phase. Small differences in the transition temperatures between the DSC and electrical measurements are due to the differences in the grain

![Saturation Regime Characteristics](image)

**Figure 3** (a-c) Output characteristics of a device with $L/W = 15/1000$ and dielectric thickness of 200 nm in the saturation regime, $V_{DS} = -40$ V. The data is taken at $T = 300$ K ($\alpha$ – polymorph, red), $T = 250$ K ($\beta$ – polymorph, black) and $T = 150$ K ($\gamma$ – polymorph, blue).

![Linear Mobility vs Temperature](image)

**Figure 4** Device linear mobility as a function of temperature. Vertical dotted lines denote the phase transitions as observed in DSC and saturation regime mobility.
size between the organic semiconductor powder used in the DSC measurements and the thin-films used in the OFET characterization. Other causes for peak shifting in DSC measurements are variations in heating and cooling rates and the total mass of the sample, though the peak onset remains the same. In addition, the width of the transition windows varied slightly between measurements on different samples, which is typical for transitions that proceed via a nucleation and growth mechanism.\textsuperscript{[33]}

Each of the three phases exhibit activated behavior in the evolution of the mobility with temperature, as observed in Figure 2. We extracted the activation energies $E_A$ for the temperature zones where only pure phases are present (see inset in Figure 2) using the Arrhenius relationship given by:

$$
\mu = \mu_0 e^{-E_A/(k_BT)}
$$  \hspace{1cm} (3.2)

where $\mu_0$ is the trap-free mobility and $k_B$ is the Boltzmann constant. The corresponding values for each phase are $E_A(\alpha) = 20$ meV, $E_A(\beta) = 115$ meV, and $E_A(\gamma) = 40$ meV. The electrical properties are completely reversible when the system contains $\alpha$ and/or $\beta$ polymorphs, but they cannot be recovered upon heating once the devices reach the $\gamma$-phase, as the mobility drops irreversibly (Figure 5). This result can be better understood upon a closer look at Figure 6, which shows pictures of a diF-TES ADT single crystal while passing through the two transition points. The high temperature transition ($\alpha$- to $\beta$-phases) does not induce any notable optical changes within the crystal (Figure 3a-b), but as the crystal transitions into the $\gamma$-phase, it changes color from red to a

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5.png}
\caption{Device saturation mobility as a function of temperature for a full temperature cycle. Cycle include one cooling step (black) and one heating step (red).}
\end{figure}
pale pink, exhibits cracking, and in some cases shatters completely. This behavior suggests that in spite of the fact that the 205 K transition is enantiotropic in nature, as pointed out by our DSC measurements, the mechanical stress associated with this transformation induces irreversible damage to the crystal. This explains the degradation in our transistor measurements and highlights the detrimental effect of such transition in the reliability of devices made on this material when measured at low temperatures. The $\beta$ to $\gamma$ transition is thus very different than the one observed near room temperature, which resulted in minor, reversible changes in the electrical characteristics.$^{[32]}$ Encouragingly, the characteristic transition temperature is well below the device operating temperatures, and while the transition degrades the device performance, it does not pose a threat for the operation of diF-TES ADT OTFTs in opto-electronic applications. This is unlike the case of 6,13-bis(triisopropylsilylethynyl) pentacene, where such dramatic transitions occur slightly above room temperature, yielding film cracking and irreversible performance degradation.$^{[34,35]}$

Because the single crystals cracked when cooled into the $\gamma$-phase, we were not able to determine the crystal structure of the new polymorph. Nevertheless, our temperature-dependent powder XRD
measurements (Figure 7) clearly show that the transition observed at low temperature is structural in nature, and that the phase transformation occurs gradually, with the β and γ polymorphs co-existing over a temperature interval that vary slightly from sample to sample. The two room-temperature measurements taken before (red) and after (not shown) the cooling are very similar, confirming the fact that the transition is reversible. Measurements taken near the transition temperature (150 K and 200 K) exhibit noticeably different patterns beyond simple shifts in the peak positions; which are also significantly different from those observed near room temperature. Based on the mobility data presented in Figure 2, the spectrum taken at $T = 200 \text{ K}$ corresponds to a phase-coexistence region between β and γ polymorphs, while at $T = 150 \text{ K}$, a single phase (γ) is present.

The observed changes in the device mobility reported in Figure 2 have two possible origins. First, the intrinsic material mobility varies as a result of the different molecular packing characteristic to each of the three polymorphs, promoting different electronic structures.\textsuperscript{[11]} Second, the changes in the crystalline packing at the surface of the electrode occurring when the system undergoes the transition cause shifts in the position of the highest occupied molecular orbital (HOMO) level of the semiconductor. This alters the Schottky barrier at the injecting contact, and thus the contact resistance. We have shown that a shift of $\sim 0.2 \text{ eV}$ in HOMO is obtained by transitioning from a pure (001) to a mixed (111):(001) orientation with respect to the surface, with
no changes in the crystalline structure. This resulted in variation of the contact resistance ($R_c$) by more than two orders of magnitude\[36\]. It is therefore expected that similar or greater shifts will occur in the case of polymorph transition. To investigate the effect of the structural phase transition on the contact resistance of our OTFTs, we analyzed it as a function of temperature using the gated transmission line method (TLM), as described in Chapter 2. For a set of devices of different channel lengths and fixed widths we measured the total device resistance in the linear regime of operation using

$$R_{on} = \frac{\partial I_D}{\partial V_{DS}}, \quad (3.3)$$

where $R_{on} = 2R_c + R_{ch}$\[37\]. Plotting the values of $R_{on}$ as a function of channel length for each gate-source voltage $V_{GS}$ and extrapolating the total resistance to $L = 0$ allowed us to extract the contact resistance of the FET (see the inset in Figure 8a). In Figure 8a we show the evolution of $R_c$ as a function of temperature for $V_{GS} = -20$ V. Typical output curves used for these calculations are shown in Figure 8b. The increase in the contact resistance with decreasing temperature is typical for OFETs and is observed as more pronounced deviations from linearity in the low $V_{DS}$ region.

**Figure 8** (a) Evolution of the contact resistance with temperature for $V_{GS} = -20$ V. The inflections indicate the impact that structural changes in the semiconducting material have on the injection of charges between the SAM-treated device electrodes and diF-TES ADT. In the inset, representative curves for the total device resistance as a function of channel length is shown for several gate voltages. (b) Output characteristics of the same device characterized in the $\alpha$-phase ($T = 300$ K), $\beta$-phase ($T = 220$ K), and $\gamma$-phase ($T = 120$ K).
(Figure 8b). Systems in which the semiconductor undergoes no phase transition exhibit an exponential dependence of $R_c$ on temperature. Nevertheless, in our measurements we also observe an inflection point of the $R_c$ vs. $T$ curve as a result of the conversion of the $\beta$ to $\gamma$ polymorphs, in agreement with our hypothesis that the changes in the crystal packing induce shifts in the HOMO level. Studies are ongoing to describe in detail the impact of the transition on the band structure of diF-TES ADT.

### 3.4 Conclusions

In conclusion, we have shown that (2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene) undergoes a low-temperature phase transformation at $T = 205$ K. We discovered a new phase, which we define as the $\gamma$ polymorph. This phase exhibits higher mobility in OTFTs, in spite of the significantly higher contact resistance that results from an unfavourable shift in the HOMO level. The phase transition is completely reversible in XRD and DSC measurements, but once the system undergoes the changes, the device performance cannot be recovered. We believe this effect results from the strain induced in the crystal upon the molecular rearrangement, which yields cracks within the film. Our results provide a complete picture of the structure-property relationships as a function of temperature in a high performance organic semiconductor, and highlight the impact that fine adjustments in crystalline packing can have on the overall device performance and operational stability.
References


CHAPTER 4

TAILORED INTERFACES FOR SELF-PATTERNING

ORGANIC THIN-FILM TRANSISTORS

Patterning organic thin-film transistors (OTFTs) is critical in achieving high electronic performance and low power consumption. We report on a high-yield, low-complexity patterning method based on exploiting the strong tendency of halogen-substituted organic semiconductors to crystallize along chemically tailored interfaces. We demonstrate that the organic semiconductor molecules self-align on the contacts, when the halogen-halogen interaction is allowed by the chemical structures and conformations of the self-assembled monolayer and organic semiconductor. The ordered films exhibit high mobilities and constrain the current paths. The regions surrounding the devices, where the interaction is inhibited, consist of randomly oriented molecules, exhibiting high-resistivity and electrically insulating neighboring devices. To identify the role of F-F interactions in the development of crystalline order, we investigate OTFTs fabricated on mono-fluorinated benzene thiol treated contacts, which allows us to isolate the interactions between the F originating from the organic semiconductor and the F in each position on the benzene ring of the thiol, and to selectively study the role of each interaction. Combining the results obtained from quantitative grazing incidence x-ray diffraction and Kelvin probe measurements, we show that the surface treatments induce structural changes in the films, but also alter the injection picture as a result of work function shifts that they introduce. We show that both effects yield variations in the field-effect transistor characteristics, and we are able to tune the field-effect mobility more than two orders of magnitude in the same material.

This work was published as J. W. Ward, M. A. Loth, R. J. Kline, M. Coll, C. Ocal, J. E. Anthony, and O. D Jurchescu, Journal of Materials Chemistry 22, 190487 (2012) – Reproduced by permission of The Royal Society of Chemistry and part of this work was published as R. Li, J. W. Ward, D.-M. Smilgies, J. E. Anthony, O. D. Jurchescu, and A. Amassian, Advanced Materials 24, 5553 (2012), reprinted with permission (License Number: 3605560123653, John Wiley and Sons). For the Advanced Material manuscript, JWW fabricated the devices, collected and analyzed the electrical data and assisted with structural data acquisition and analysis.
4.1 Introduction

The performance of organic electronic devices is rapidly increasing, but their use in low-cost, large-area applications is hindered by insufficient device performance and poor reproducibility. Efforts addressing these issues are focused towards the development of new materials,\cite{1-4} improving structural order,\cite{5,6} and patterning thin-films to reduce the crosstalk between neighboring devices.\cite{7-9} Unfortunately, photolithography techniques developed for patterning inorganic semiconductors are not compatible with organic semiconductors, as they damage the organic materials due to the high energy of the patterning beams, or by the chemicals needed for the processing.\cite{10-12} Several approaches have been taken towards non-destructive patterning of organic films. They include direct evaporation of organic semiconductors through shadow masks,\cite{13} ink-jet printing,\cite{14} screen printing,\cite{15} lithographic stamping,\cite{16,17} selective removal of organic layer by UV exposure,\cite{18} and thin-film processing using orthogonal solvents.\cite{10} Unfortunately, most of these methods consist of elaborate processing steps, which can be a barrier for low-cost mass production of organic electronics.

Recently, self-patterning of organic thin-film transistors (OTFTs) was achieved by exploiting the ordering of organic semiconductors driven by interactions at interfaces.\cite{19} The observed patterning was a result of the formation of a differential microstructure driven by the presence of the pentafluorobenzenethiol (PFBT) self-assembled monolayer (SAM) on the surface of the contacts and its absence on the dielectric surface. The microstructure consisted of ordered domains of high conductivity on the contacts surrounded by poorly ordered-highly resistive domains, that electrically insulate neighboring devices.\cite{20} In this study, we uncover the mechanism responsible for the observed film formation. This knowledge is indispensable for the practical control of patterning OTFTs by differential microstructure, as well as for its implementation in complicated device architectures. We propose that the halogen-halogen (F-F) interactions between the F atom of the SAM and the F atom present in the backbone of the organic semiconductor diF-TES ADT (2,8-difluoro-5,11-bis(triethylsilylthynyl) anthradithiophene) is a strong interaction capable of controlling the orientation of the organic semiconductor molecules (Figure 1a). Exploiting F-F interactions has been previously used as a powerful tool in crystal engineering, allowing for rapid and enhanced crystallization.\cite{21,22} We believe this interaction can also promote molecular assembly at the surface of contacts and/or dielectrics. Additionally, we show that halogen-sulfur interactions can play an important role in the development of crystalline order (Figure 1a).\cite{22} Validation of the
proposed mechanism may allow the combination of synthetic diversity in molecular design with device processing to achieve a general and powerful route for low-cost, high-throughput patterning of OTFTs.

To identify the role of F-F interactions in the development of crystalline order, we study the mono-fluorinated benzene thiols (MFBTs): 2-Fluorobenzenethiol (2-MFBT), 3-Fluorobenzenethiol (3-MFBT), and 4-Fluorobenzenethiol (4-MFBT) (molecular structures presented in Figure 1b). The use of these fluorinated SAMs (F-SAMs) allows us to isolate the interactions between the F originating from the organic semiconductor and the F in each position on the benzene ring of the F-SAM molecule, and to selectively study the role of each interaction.

To investigate the effect of the F-SAMs on the diF-TES ADT device properties, we characterize the organic thin-films deposited on each treatment using field-effect transistor (FET) measurements, optical microscopy, and grazing incidence X-ray diffraction (GIXD). Our results
Figure 2 Images used to measure the H₂O angle are shown. The four treated Au surfaces all exhibit similar wetting characteristics when compared to cleaned Au or SiO₂.

demonstrate that the location of the terminating fluorine atom within the structure of the SAM plays a critical role in the development of order within the organic film. More subtly, when the F atoms of the SAM and the semiconductor molecule are in close proximity, the strong interaction between them induces a preferred orientation of the organic semiconductor, which results in a high electrical mobility. We show that charge transport in OTFTs with F-SAM modified electrodes results from an interplay between film microstructure and work-function shifts. Exploring these effects allows us to achieve patterning by differential microstructure induced on selectively chemically modified surfaces.

4.2 Experimental

4.2.1 SAM Fabrication and Characterization

SAM solutions were prepared by dissolving the self-assembled monolayers (Sigma Aldrich) in ethanol (Sigma Aldrich). The SAM treatments were performed by soaking the substrate in a 30mM room-temperature solution for 30 minutes followed by a 5 minute sonication in an ethanol bath and a thorough ethanol rinse. The monolayer quality was characterized using the static sessile drop method with de-ionized water. The contact angles were measured using a Ramé-Hart Model 200 Contact Angle Goniometer and calculated using DROPimage Standard. The measurements were conducted at room temperature in air and are displayed in Figure 2.

Work function measurements of the SAM modified contacts were evaluated as described in
Chapter 4. Tailored Interfaces for Self-Patterning OTFTs

Section 2.3.3. All samples were stored in air for about 12 hours to allow for full solvent removal and film stabilization. PM-IRRAS measurements confirm that even longer air exposure does not produce degradation of the SAMs used in this study.

Polarized Modulated-Infrared Reflection Absorption Spectroscopy (PM-IRRAS) studies, used to evaluate the quality of the F-SAMs, were performed with an IR-Spectrometer Vertex 70 from Bruker equipped with a Polarization Modulation Accessory (PMA 50 unit) and a mercury cadmium telluride (MCT) detector (700 - 4000 cm\(^{-1}\)).\(^{[24]}\) SAMs and neat spectra were measured with a resolution of 4 cm\(^{-1}\) and an incidence angle of 75º by averaging 350 interferograms. Fluorinated monolayers, 2-MFBT, 3-MFBT, 4-MFBT and PFBT, self-assembled on Au substrates were investigated. Neat spectra of the four different molecules were also collected within 2 minutes of 2 \(\mu\)l deposition of molecules on a clean Au and Si substrate.

4.2.2 Field-Effect Transistor Fabrication and Characterization

The device studies were carried out using bottom contact FETs on highly doped Si gate contact, with a 200 nm thermally grown SiO\(_2\) gate dielectric. The source and drain contacts were defined by photolithography and deposited by e-beam evaporation (5 nm Ti/ 45 nm Au). We cleaned the substrates with hot acetone and isopropanol, followed by a UV-ozone and de-ionized water rinse. The SAM treatments were performed as described above. The organic semiconductor was synthesized at University of Kentucky\(^{[25]}\) and spin-coated from a hot (55 °C) chlorobenzene solution (Sigma Aldrich) (1.2% wt.) at 1000 rpm spinning speed. As-prepared devices were placed in vacuum for 24 hours to ensure full solvent removal and electrically characterized using an Agilent 4155C Semiconductor parameter analyzer.\(^{[24]}\)

4.2.3 Structural Characterization of the Organic Semiconductors

Two complementary structural characterization techniques were used in this study. The \(\mu\)GIWAXS technique was performed on a typical device structure (with patterned gold contacts on a SiO\(_2\) substrate) that provided structural information within a spatial resolution of 10 \(\mu\)m, allowing for a 2-D structural mapping of devices. The second was GIXD performed on diF-TES ADT films deposited on gold substrates that replicated the electrode region of the transistors for treatment scenario, as well as on untreated gold. These sets of data gave quantitative information about the structure of the films.

The \(\mu\)GIWAXS was performed at the Cornell High Energy Synchrotron Source. This
technique, with its ability to resolve microstructural features on the micron-scale, allowed us to map a 7 × 7 array of 1 × 1 cm² OFETs of a variety of channel lengths. This work was first-of-its kind in its ability to perform structural characterization on actual devices and to spatially-resolve heterogeneous micro-domains within the films. This insight is relevant as it allows us to locate different structural features within the transistor channels, and to identify microstructural bottlenecks to charge transport. In Figure 3, the μGIWAXS setup is shown. An intense X-ray beam was focused onto the substrate, which was an actual FET, at an incidence angle of 2° by an X-ray focusing capillary, producing a X-ray beam with a footprint of 10 μm in the z direction and 610 μm in the y direction, as verified using a polished cadmium tungstate crystal at grazing incidence as a fluorescent screen in lieu of the sample. An alignment procedure allowed us to collocate the marker in the optical micrograph with the center (in x and y) of the x-ray microbeam. The spatial resolution of the 10 μm microbeam enabled spatially-resolved measurements of the organic semiconductor on the Au electrode, in the channel area between the two electrodes, and on the oxide away from the electrodes. All three regions were located on the same OFET device.

**Figure 3** Schematic of the μGIWAXS beam scanning a bottom contact device structure. Top left: typical scattering mapping in the region off the contacts. Top right: footprint of the microbeam (scale bar = 100 μm).
GIXD was performed at beam line 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). The samples were in a He-enclosed chamber to reduce air scattering and beam damage. The incidence angle for grazing-incidence measurements was 0.12°. The data was collected using a 2D image plate detector and is corrected for the polarization and the fixed incidence angle. Pole figures were constructed using a combination of the grazing-incidence diffraction and a local specular measurement as described by Baker et al. The local specular measurement involved rocking the sample incident angle ±0.4° about the Bragg angle of the (001) peak during the exposure. To calculate the orientation fractions, the integration of the pole figures must include the change in solid angle as a function of χ. For samples with isotropic in-plane orientation, the total population of crystals at a given azimuthal tilt goes up with sin χ while the pole figure measures a constant solid angle. As a result, the pole figures substantially under-represent the crystal population at large azimuthal tilts.

4.3 Results and Discussion

Polarization Modulation Infrared Reflections Adsorption Spectroscopy (PM-IIRRAS) measurements carried out on the Au substrates with each of the SAM treatment indicates preferential orientation of the organic monolayers. Figure 4 shows the IR spectra of the four SAMs and neat fluorinated molecules (a) 2-MFBT, (b) 3-MFBT, (c) 4-MFBT and (d) PFBT. In the four neat spectra, three different groups of vibrations can be identified. The benzene ring compounds commonly exhibit several bands in the region 1600 - 1400 cm⁻¹ attributed to C-C aromatic stretching modes. Another group of vibrational bands appear in the range of 1300 - 1000 cm⁻¹ and are assigned to C-H bending and C-F stretching modes. Finally, out-of-plane bending vibrations are observed below 1000 cm⁻¹. The SAMs' spectra show a reduced number of vibrational bands compared to neat molecules as a consequence of the IR surface selection rule (i.e. IR band with transition dipole moment (TDM) oriented parallel to the metal surface are absent). Therefore, preferential observation of some vibrational modes denotes a degree of molecular order in the monolayer. The peaks observed at 1600 - 1500 cm⁻¹ are attributed to modes with a TDM along the S-aromatic ring axis, thus, a molecular geometry lying 100% parallel to the substrate surface is ruled out for the 3-MFBT, 4-MFBT and PFBT. Interestingly, 2-MFBT SAMs show peak shift frequency compared to 2-MFBT neat spectra that is not observed in the other 3 SAMs. This is likely attributed to a higher degree of molecular tilting. IR studies on fluorinated
benzenethiols are rather limited but differences in molecular arrangement for substituted benzenethiols on a metal surface have been also identified by other techniques.\cite{35} For example, STM imaging studies on \textit{para} and \textit{ortho}-substituted halo benzenes identify significant differences in molecular packing and ordering of these two molecules. Lower surface coverage and a more inclined arrangement have been identified for the \textit{ortho}-substituted molecules attributed to complex combination of interaction energies (i.e. dipole-dipole, S-F, quadrupole).\cite{36}\cite{37}\cite{38} Preferential orientation close to tangential has been reported for \textit{para}-halosubstitued benzene rings and PFBT, in agreement with our results.\cite{35,36,37,38} Out-of-plane vibrations (associated dipole moment perpendicular to the phenyl ring) are extremely useful for quantitative orientational analysis;\cite{39} however, in our SAM samples they could not be unambiguously identified (900 - 700 cm\(^{-1}\)) because they appear near to the detector cutoff and this spectral region becomes unreliable. Consequently, in this work we keep orientational analysis qualitative. Based on our IR results and the STM data available in the literature,\cite{35,40} we estimated a tilt angle range from the surface normal of 40° - 70° for the 3-MFBT, 4-MFBT and PFBT and 80° - 90° for 2-MFBT. This is consistent with previous studies on

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure_4}
\caption{PM-IRRAS of fluorinated SAMs and the corresponding neat spectra of (a) 2-MFBT, (b) 3-MFBT, (c) 4-MFBT and (d) PFBT.}
\end{figure}
substituted benzenethiols and results from the steric hindrance and the intermolecular interactions between the aromatic rings.\cite{38, 40} More accurate orientational analysis is impeded by the difficulty to unambiguously identify out-of-plane vibrations in the SAM’s PM-IRRAS spectra.\cite{30}

Optical micrographs taken on the FETs fabricated on bottom contacts chemically modified with the SAMs of interest are presented in Figure 5. In Figure 5a we present the case of untreated contacts, for comparison. This film consists of very fine grains and only a few distinguishable features. Figure 5(b-c), corresponding to the 2-MFBT and 3-MFBT, respectively, show a gradual increase in the grain size. Note that in all these cases the morphology of the film on the contact region is comparable to that observed on the oxide region of the FET. On the contrary, the devices presented in Figure 5(d-e), fabricated on contacts chemically tailored with 4-MFBT and PFBT, respectively, exhibit very different crystal habits, consisting of large grains on the contacts, protruding into transistor channel, and fine grains in the middle of the channel. Figure 5f is a schematic representation of the differential microstructure present on the source-drain contact regions and the oxide regions.

We believe the changes observed in the film features originate from the different F-F interactions that each of the F-SAMs provide, and are not a result of the modifications in surface energies, as reported in the case of other SAMs.\cite{41, 42} This is supported by our goniometry measurements (Figure 2), which show that the water contact angles are similar for all treatments.
The static water contact angle ($\theta_{H2O}$) values are summarized in Table I at the end of the chapter; for comparison, the water contact angle of pristine SiO$_2$ is lower than 5°. This result confirms that, in this case, the surface energy following SAM treatment does not play a dominant role in determining the structure of the organic semiconductor film, and the observed effects arise from interactions between the semiconductor and the F-SAM.

The $\mu$GIWAXS measurements allowed us to obtain spatially-resolved microstructural information from real devices non-destructively and non-invasively. Compared with existing microscopic methods, such as scanning transmission X-ray microscopy (STXM)\[^{45, 46}\] and Raman microscopy,\[^{47, 48}\] both of which are indirect and highly localized $\mu$GIWAXS provides direct and quantitative microstructural information, including lattice constants, grain size, orientation distributions and polymorphism averaged along the entire channel width of a working OFET device. $\mu$GIWAXS confirmed that the diF-TES ADT film consists of purely (001) oriented molecules on PFBT treated Au electrodes, with diffuse scattering just above the attenuator in Figure 3. The film also maintained the same, pure, (001) orientation within the channel for short channel devices (Figure 6a), however, in the regions away from the electrodes both (001) and (111) orientations co-exist.
In Figure 6 we map the microstructure across a device with a channel length of 20 μm and across a device with a channel length of 80 μm. We show a side view of the each of these device structures in the top panel, a polarized optical micrograph of a portion of the device in the middle, and the bottom graphs are (top) the integrated intensity map of the diffraction peaks associated to Au, <001> and <111> and (bottom) the out-of-plane lamellar crystal size and angular full-width at half max (FWHM) determined from the (001) Bragg sheet of <001>-textured crystal. In Figure 6a, for \( L = 20 \) μm, large grains with a pure (100) orientation are shown to extend through the channel of the device, while in Figure 6b, for \( L = 20 \) μm, while those grains extend deep into the channel, they terminate before they reach the adjacent electrode. The Au (111) intensity maps help to discern the channel from the buried electrodes, making it possible to distinguish the microstructure of diF-TES ADT in the channel and on the electrodes. By following the integrated intensity of the (001) peaks and the sum of the (121 and (122) diffraction peak intensity associated to the <111> texture, we find that the <001> texture is present everywhere, whereas the <111> texture appears only in the middle of the channel where there was no PFBT treatment present. The (001) oriented film extends nearly 25 μm away from the treated contacts, thus allowing a bridge between the contacts in devices with smaller channel lengths.

GIXD allows us to determine the quantitative structural details of the films, and to establish the mechanism of the formation of this unique microstructure. Figures 7(a-e) show the 2D-GIXD measurements taken on diF-TES ADT films spin coated onto untreated Au substrates and substrates containing each of the four treatments. These substrates replicate the film morphology on the electrode region of the transistor structure. All films exhibit signatures of high crystallinity, but a careful inspection points to the fact that the molecular orientations within the films are quite different. Films deposited on PFBT and 4-MFBT treated Au (Figure 7d-e) display similar structural features, with all crystallites preferentially orientated along the (001) crystallographic direction. In this orientation, the molecular backbones are aligned “edge-on”, meaning perpendicular to the surface, as depicted in Figure 7f, left. This allows for large \( \pi-\pi \) overlap in the direction of charge transport, supporting high charge carrier mobility. The films deposited on untreated Au, 2-MFBT and 3-MFBT (Figure 7a-c) exhibit richer diffraction features. Here, we identify the peaks denoting (001) orientation, as well as additional ones distinguished by red ovals. The latter peaks can be indexed to (111) orientation of the same crystal structure where the molecules lay “face-down” on the substrate (Figure 7f, right).\(^{43}\) The films containing mixed orientations exhibit low mobility and high current noise.\(^{44}\) By using the pole figure comparing the relative intensity of the (001) peak as a function of the polar angle, \( \chi \) (Figure 8), we extract quantitative information about the (001)
orientation distribution in each film. The full-width half-maximum (FWHM) of the (001) orientation is about 2° and the FWHM of the (111) orientation is about 8°. For films deposited on untreated Au, we found that 66% of the crystals have a nominal (001) orientation relative to the substrate. The (001) content for films deposited on treated Au is determined to be 55% for 2-MFBT, 94% for 3-MFBT, ≈100% for 4-MFBT, and ≈100% for PFBT. These findings clearly indicate that the films on 4-MFBT and PFBT treated contacts are similar and contain 100% (001) crystals, while films on untreated, 2-MFBT and 3-MFBT treated contacts contain a mixture of (111) and (001) crystals in various ratios. The observed structural features for the untreated and PFBT treated films are in agreement with those reported earlier by Kline et al.\textsuperscript{[20]} Introduction of mono-fluorinated SAMs in this study, with the fluorine atom located in specific positions, allowed us to selectively investigate the effect of each F, and to develop a thorough description of the mechanism responsible for the development of the crystalline order.

The different content of (001) phase detected for the three MFBTs, while having similar surface wettability, supports our hypothesis that the F-F interactions between the SAM and the organic
semiconductor are responsible for the observed microstructure. The different location of the F atom within the F-SAM either allows a geometrically favorable interaction with the F termination of the organic semiconductor’s backbone, or frustrates this interaction. If either the SAM or the organic semiconductor does not contain an F atom in their structure, or if this atom is not located in a position suitable for interaction, self-patterning by differential microstructure cannot occur. This hypothesis is further supported by the work of Kymissis et al, who examined the effects of PFBT treatment on un-halogenated materials and concluded that no significant interactions occur between the two species.\[49\]

Within this scenario, the highest degree of structural order, with 100% (001) phase, measured in the case of films deposited on 4-MFBT, is a result of the fact that here the F-F interactions are permitted by the close vicinity between the F in position 4 on the benzene ring and the F of the organic semiconductor. The identical structure of the diF-TES ADT thin-films on 4-MFBT and PFBT treated Au suggests that the dominant F-F interaction between the SAM and the fluorinated semiconductor occurs at the F located in position 4 on the thiol benzene ring also in the case of the PFBT SAM (Figure 1a). The films deposited on 3-MFBT treated Au accommodate a smaller fraction of (001) oriented crystals, but still considerably higher compared to untreated Au. This may result from the fact that the fluorine located in position 3 within this SAM is geometrically

**Figure 8** GIXD full pole figure comparing relative intensities of a (001) peak for each treatment case.
suitable to only facilitate a weak F-F interaction compared to the previous case, but a F-S interaction between the fluorinated SAM and the sulfur on the semiconductor is not excluded, and is under investigation. Additionally, unlike the case of PFBT or 4-MFBT, where due to symmetry the molecular dipole is always pointing in the same direction, here the F-SAM will present a surface where the dipoles are pointing in random directions. Since the F may be in either position 3 or 5 of the benzene ring, regular crystal growth may be disrupted. The films deposited on 2-MFBT treated Au present a small content of (001) orientation, similar to the untreated case, because the fluorine atom is located in a position that cannot promote any interaction with the fluorinated semiconductor. In the absence of these F-F interactions, the first organic semiconductor layer is not anchored to an edge-on configuration, and cannot template the arrangement of the following layers in an ordered fashion. While these observations clearly mark the importance of F-F interactions in assisting the self-patterning process, the nature of these interactions is still under investigation.

The electrical response of the TFTs fabricated on Au electrodes modified with the F-SAMs investigated in this study is in agreement with the structural differences induced by these treatments. In Figure 9a we show typical current-voltage characteristics: the evolution of the drain current versus gate-to-source voltage \( I_D \) versus \( V_{GS} \) for a PFBT treated device biased in the
saturation regime (source-drain voltage, $V_{DS} = -40 \text{ V}$). The curve on the left axis represents $\sqrt{I_D}$ versus $V_{GS}$ and was used to calculate the saturation mobility ($\mu_{\text{sat}}$) using the following expression:

$$
\mu_{\text{sat}} = \frac{2L}{W C_1} \left( \frac{\partial \sqrt{I_D}}{\partial V_{GS}} \right)^2
$$

where $C_1 = 17.3 \text{ nF cm}^2$ is the geometrical capacitance of the dielectric.

In Figure 9b we plot the field-effect mobilities for devices fabricated on each contact treatment. The measured mobilities span almost three orders of magnitude, from $5.5 \times 10^{-3} \ (\pm 7.4 \times 10^{-4}) \ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for untreated contacts (black), to $3.0 \times 10^{-1} \ (\pm 5.2 \times 10^{-2}) \ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the PFBT treated contacts (red). Devices fabricated on MFBTs lay in between these values, and mobility increases from $1.6 \times 10^{-2} \ (\pm 1.5 \times 10^{-3}) \ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the 2-MFBT (purple), to $3.8 \times 10^{-2} \ (\pm 7.7 \times 10^{-3}) \ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the 3-MFBT (blue), and $1.8 \times 10^{-1} \ (\pm 5.5 \times 10^{-3}) \ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for the 4-MFBT (orange). The averages are obtained over at least 10 devices. While these dramatic differences in the electrical properties of the same material, promoted by varying the F-SAM treatment, are a result of both the different grain-size environment and the molecular orientation induced by the F-F interactions, the polar nature of the F-SAM molecules at the surface of the Au contacts also results in a shift in the work function of the electrodes and modifies the injection

**Figure 10** The work function evolution throughout time as measured by Kelvin probe. The breaks in the signal represent the grounding of the detector during the movement to a different spot on the sample.
Figure 10 shows the work function of the 2-MFBT (Purple), 3-MFBT (Blue), and 4-MFBT (Orange) treated Au substrates. Uniformity between spots suggests a uniform SAM film on Au, while the consistency through time points to a stable electrode work function in the presence of the F-SAM treatments. Our clean Au exhibits a work function $W_{FAu}=4.91$ eV, in agreement with the results reported from UPS studies.\cite{50-52} The measured shifts in the electrode work-function as a result of SAM treatment are reported in Table I and plotted in Figure 11. The reported values are averages obtained over 15 measurements. The 2-MFBT treatment results in a negligible shift from $\phi_{Au}$ as the dipole moment vector is likely parallel to the surface. The presence of the fluorine atom farther from the Au surface accommodates an increased surface normal component to the dipole, and for this reason, the 3-MFBT treated Au shows a greater shift in work function, $\Delta WF_{3-MFBT} = +0.07$ eV. For the cases where the greatest component of the dipole moment is normal to the electrode surface, 4-MFBT and PFBT treated Au, the shift in work function increases further to: $\Delta WF_{4-MFBT} = +0.43$ eV and $\Delta WF_{PFBT} = +0.39$ eV. The increase in electrode work-function as a result of F-SAM treatment allows for a reduction in the parasitic contact resistance, as resulting from our estimations using the gated transmission line method.\cite{53} The contact resistance for each electrode configuration is shown in Figure 12.

To complete the injection picture, we estimated the position of the HOMO level of the organic semiconductor using Kelvin Probe. It was shown with other molecular systems that the position of the HOMO and LUMO levels depends on molecular orientation.\cite{54} Indeed, our films consisting of
pure (001) oriented crystals are shifted with approximately 0.14 eV in the position of the HOMO level when compared to the films of the mixture of (111) + (001). While the measured shifts are accurate representations of the differences in the HOMO level locations for the two types of films, their absolute values should be regarded as estimates, as the Kelvin probe measurements yield the chemical potential of the organic semiconductor, which is slightly shifted with respect to its HOMO. Nevertheless, the fact that our films containing mixed orientations have a HOMO of 5.08 eV, in agreement with the results obtained from ultraviolet photoemission spectroscopy combined with inverse photoelectron spectroscopy (UPS/IPES) by Anthopoulos et al, on films grown on indium tin oxide (ITO), which likely were composed of a mixture of the two orientations, point to the fact that our measurements give a good estimation of HOMO level. On the contrary, for the films containing 100% (001) molecular orientation, we determine a HOMO of 4.94 eV, combining the results from GXID and Kelvin Probe measurements, we can now complete the charge injection and transport picture. The different situations are presented in Figure 11, where the work functions of the electrodes are represented following the same color scheme used for Figure 9 and the gray shaded area represents the valence band of the organic semiconductor, where hole-injection occurs. The left panel represents the injection from untreated contacts, 2-MFBT and 3-MFBT treated
contacts into the film composed of the (111) + (001) mixture. Here, the hole-injection barriers range from 0.17 eV for untreated Au to 0.18 eV for the 2-MFBT treated Au and 0.10 eV for the 3-MFBT treated Au. The low injection barriers suggest that the transport in our devices is not contact-limited. This is in agreement with the decrease in mobility with increasing the channel length (Figure 13), a trend consistent with a grain-boundary limited charge transport. The increase in the mobility values presented in Figure 9b from untreated Au, to 2-MFBT, and 3-MFBT treated electrodes arise from the cooperating effects of reducing the density of grain boundaries and increasing the content of (001) phase. The right panel represents the injection from the 4-MFBT and PFBT treated electrodes, which are shifted to higher work functions because of the stronger dipole within the SAM. Here, the organic semiconductor films presents pure (001) orientation and a lower HOMO level. As a result, the energetic barrier vanishes, allowing for efficient hole-injection. The edge-on molecular orientation further allows efficient charge transport and as a result the measured mobilities are the highest.

Figure 13a presents the evolution of the mobility against the transistor channel length for TFTs with various surface treatments and demonstrates the efficiency of the proposed self-patterning
technique. While for all treatments the mobility decreases with increasing channel length, a few unique features can be distinguished for each of them. In PFBT (red diamond) and 4-MFBT (orange triangle down) treated devices, the similar mobilities agree well with the structural and injection data. These devices exhibit two distinct regimes that can be distinguished by a dramatic change in the rate at which the mobility decreases as the channel length increases, located at $L = 50 \mu m$. At short channel lengths, large grains consisting of the (001) molecular orientation, which is preferential to charge transport and the fast crystal growth direction, extend from the contacts to span the full length of the transistor channel, in agreement with the μGIWAXS measurements shown in Figure 6a. Here, the most favorable charge injection and transport scenario applies (Figure 11, right). For TFTs with larger source-drain separation ($L > 50 \mu m$) an optically visible break in large grains is observed (Figure 13b), and this film consists of a mixture of (001) and (111) orientations, as suggested by Figure 6a. As the F-SAM does not attach to the SiO$_2$ surface, and thus the F-F interaction is not present here, the film in the middle of the channel consists of fine grains of mixed orientations, similar to the case of untreated Au. While the injection corresponds to the right panel of Figure 11, the charge transport in the channel region of the transistor is a combination of competing effects arising from the presence of large and small grains, as well as the mixed molecular orientations in the film within the channel. The poorly ordered regions of high resistivity present in the case of 4-MFBT and PFBT Au both the middle of the channel for long-channel devices and the regions surrounding all devices, provide electrical insulation between neighboring transistors. Self-patterning has occurred as a result of the formation of the different microstructure on the contacts versus their vicinity. On the contrary, when the F-F interactions are inhibited, due to lack of proximity between the F atoms, or when the F-SAM is not present, self-patterning is not successful (Figure 13c). This is the case of devices fabricated on 3-MFBT (blue triangle up), 2-
MFBT (purple circle), and the untreated devices (black square), where a lower mobility is measured, as expected from the presence of mixed orientations and the larger injection barriers (Figure 11, left). The mobility decreases monotonically with increasing channel length. In these cases, on average, there are fewer large grains present on either the contact or oxide regions of the transistor structure.

The effectiveness of our patterning technique is also reflected in the values of the on/off ratios measured for each treatment (data for $L = 5 \, \mu m$ is included in Table I). A clear increase from $\sim 10^4$ in the case of untreated devices to $\sim 10^7$ in 4-MFBT and PFBT OTFTs supports our scenario of F-F interactions inducing self-patterning by differential microstructure. Our results clearly mark the fact that when the F atoms of a SAM and organic molecule are in close proximity, an exploitable interaction occurs between them. This interaction is the governing factor in initiating a template structure for molecular orientation. Once the first layer is formed, the film adopts the same morphology throughout its thickness.

We suspect that the F-F interactions are weaker than the intermolecular interactions within the crystals, and the proposed scenario can only occur if the intrinsic crystalline packing of a material allows such an arrangement. For example, in difluoro-(tri-sec-butylsilyl ethynyl) anthradithiophene (diF-TSBS ADT), a material with similar chemical structure, but which adopts a sandwich-herringbone packing, the F-F interactions are not sufficiently strong to induce a co-facial packing in OTFTs fabricated on F-SAM treated contacts. This is reflected in similar electrical and structural properties for the case of PFBT treated and untreated contacts (Figure 14).
Chapter 4. Tailored Interfaces for Self-Patterning OTFTs

4.4 Conclusions

Differential microstructure allowing self-patterning of organic thin-film transistors proceeds via F-F interactions, when the halogen interactions are allowed by the chemical structures and conformations of the SAM and organic molecule. The patterning we observe as a result of F-SAM induced differential microstructure is fundamentally different than the patterning resulting from tuning the hydrophobicity of the contacts and oxide regions. The size obtained for the high mobility domains (up to 50 µm, reproducibly demonstrated) meets the requirements of most applications, and is thus technologically relevant. Smaller device size can be easily defined by controlling the source-drain separation on the substrate using conventional photolithography. Our results provide insights for the rational design of novel molecular structures targeted towards low temperature patterning in the presence of SAMs.

Figure 14 GIXD on films of diF-TSBS ADT on a) PFBT treated Au and b) Untreated Au. c) Evolution of mobility with channel length for diF-TSBS ADT bottom contact devices fabricated on PFBT treated contacts (black square) and untreated (red circle) contacts.
References


[24] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement
by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.


Understanding the interactions at interfaces between the materials constituting consecutive layers within organic thin-film transistors (OTFTs) is vital in optimizing charge injection and transport, tuning thin-film microstructure and designing new materials. Here, we explore the influence of the interactions at the interface between a halogenated organic semiconductor (OSC) thin film and a halogenated self-assembled monolayer on the formation of the crystalline texture directly affecting the performance of OTFTs. By correlating the results from microbeam grazing incidence wide angle scattering (µGIWAXS) measurements of structure and texture with OTFT characteristics, we find that two or more interaction paths between the terminating atoms of the semiconductor and the halogenated surface are vital to templating a highly-ordered morphology in the first layer. These interactions are effective when the separating distance is lower than 2.5 $d_w$, where $d_w$ represents the van der Waals distance. We demonstrate the ability to modulate charge carrier transport by several orders of magnitude by promoting “edge-on” versus “face-on” molecular orientation and crystallographic textures in OSCs. We find that the “edge-on” self-assembly of molecules forms uniform, (001) lamellar-textured crystallites which promote high charge carrier mobility, and that charge transport suffers as the fraction of the “face-on” oriented crystallites increases.
5.1 Introduction

Solution processable OSCs promise to allow mass-production of electronic devices at a low-cost, on flexible substrates such as plastics, paper and even on human skin.\textsuperscript{11-5} The unique properties of such materials enable new paradigms for device manufacturing that go beyond the limitations of their a-Si:H counterpart and significantly reduce the cost and complexity of processing. For example, it has been shown that high performance organic single crystal and thin-film devices can be simultaneously deposited and patterned using ink-jet printing,\textsuperscript{6, 7} and that both the OSC and dielectric layers can be deposited in a one-step process by controlling their phase-separation from the mixed solution.\textsuperscript{8, 9} In these demonstrations, the relationship between the OSC and its interfaces within the device was successfully exploited to achieve the desired morphology. However, there is little insight into the roles of molecular design and interfacial interactions on molecular self-assembly in the context of heterogeneous nucleation at the solution-solid interface.\textsuperscript{10} A recent development in this area is the successful use of fluorine-fluorine (F-F) interactions between the conjugated molecule and the surface to control crystallization and engineer film ordering.\textsuperscript{11-15} Fluorine-terminated OSCs can exhibit a differential microstructure when deposited on surfaces selectively treated with fluorinated self-assembled monolayers (F-SAM): the formation of crystalline domains consisting of (001)-textured lamellar sheets of molecules, with in-plane $\pi$-stacking capable of effectively transporting charges in the plane of the semiconductor-dielectric interface, only occurs on and in the vicinity of regions where the F-F interactions are present. The surrounding regions exhibit a mixture of crystalline textures, which inhibit effective carrier transport, slowing it down by several orders of magnitude. The interface-driven growth behavior yields improved device performance by self-patterning the organic thin-film transistors (OTFTs) over an array of electrodes.\textsuperscript{13, 14} Our earlier investigations identified the role that the F-F interactions between the F-SAM and a fluorinated OSC have on the development of the crystalline order within the organic film and evaluated their strength with respect to the van der Waals intermolecular interactions.\textsuperscript{12} However, the generality and the limitations of OTFT microstructural patterning via F-F interactions are not known. This insight is deemed crucial for the rational design of novel molecular structures coupled with surface treatments to enable high performance bottom-contact OTFT devices. The identification of appropriate combinations of interfacial layers and OSCs can also assist in the development of cost-effective, bottom-up self-patterning procedures for organic electronic structures. We have therefore designed a series of experiments based on several
combinations of F-SAMs and halogenated-OSCs to investigate F-F and F-S interactions.

Displayed in Figure 1 is the chemical structure of the OSCs we employed in this study: (a) diF-TES ADT (2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene) referred to as ADT, (b) diF-TIPS Pn (a 1:1 isomeric mixture of 1,8- and 1,11-difluoro 6,13-bis(triisopropylsilylethynyl) pentacene) referred to as Pn, and (c) diF-TSBS PDT (2,10-difluoro-5,13-bis(tri-sec-butylsilylethynyl) pentadithiophene) referred to as PDT. Each of the above molecules crystallizes into lamellae with in-plane 2D-brickwork packing motif, which is necessary to achieve an “edge-on” co-facial packing within the OSC layer favoring 2D in-plane charge transport. The packing motif is crucial, as we have previously shown the interactions between the F-semiconductor and F-SAM are not sufficiently strong to modify the growth pattern of other packing motifs.\[12, 16, 17\] The ADT and PDT promote both F-F and F-S interactions with the F-SAM, while the Pn only allows the F-F interactions. This chemical difference offers us an experimental platform for the investigation of a secondary interaction, F-S, that was suggested to impact the microstructure within the organic films.\[18\] The length of the heteroacene backbone and its orientation with respect to the surface normal affect the distance between interacting terminal atoms and provide different interaction strengths for each of the three cases. The two F-SAMs, pentafluorobenzenethiol (PFBT) and 4-fluorobenzenethiol (4-MFBT), allow either one (4-MFBT) or multiple (PFBT) F-F interaction opportunities.

By correlating the crystalline texture from microbeam grazing incidence wide angle x-ray scattering (μGIWAXS) with electrical properties derived from OTFT measurements, we find that two conditions are necessary for successfully establishing the differential microstructure which
promotes self-patterning and high electronic performance. First, at least two anchoring points must be established. These atoms originating from either the semiconductor or the F-SAM can connect with molecular moieties within the consecutive layer via F-F and/or F-S interactions. We believe this bonding, once established, can prevent any molecular twist in the first layer of the organic film and thus promotes the formation of a highly ordered templating layer. Second, when the separation between the interacting atoms is larger than about twice the sum of their van der Waals radii, the F-F and F-S interactions are too weak to dictate the polycrystalline texture within the film.

5.2 Experimental

5.2.1 Self-Assembled Monolayer Treatment

SAM treatment solutions were prepared by dissolving the respective molecules in ethanol (Sigma Aldrich). The treatment consisted of soaking the substrate for 30 minutes in a 30 mM room-temperature solution followed by a 5 minute sonication in an ethanol bath for removal of the bulk layers. The substrates were then rinsed with ethanol and dried using a stream of N₂ gas.

5.2.2 Field-Effect Transistor Fabrication and Characterization

The device characterization was carried out using bottom contact OTFT structures on a highly doped Si gate electrode with a 200 nm thermally grown SiO₂ gate dielectric. The source and drain contacts (5 nm Ti/45 nm Au) were defined by optical photolithography and deposited by e-beam evaporation. The substrates were cleaned in hot acetone and isopropanol, followed by a 10 minute UV-ozone exposure, ethanol rinse, and N₂ drying. The SAM layers were subsequently applied, as described in Chapter 2. The OSCs were dissolved in a 1.2 wt.% solution in high purity chlorobenzene (Sigma Aldrich).

The warm (55 °C) solution was spin cast onto the substrates at a 1000 rpm spinning speed and the obtained films were placed in a vacuum oven at room-temperature for 24 hours to ensure full solvent removal. The devices were electrically characterized in a nitrogen environment using an Agilent 4155C Semiconductor parameter analyzer.

5.2.3 Structural Characterization of the Organic Semiconductor

The μGIWAXS measurements were performed at D1-line, Cornell High Energy Synchrotron Source (CHESS) at Cornell University. The X-ray beam with a wavelength of 1.155 Å and a wide bandpass (1.47%) was focused into a 10 x 10 μm² spot using a single-bounce X-ray focusing
capillary positioned on a V groove. The samples were placed on the focal point of the capillary (35 mm away from the capillary tip) and an incidence angle of 2° was chosen to ensure the beam footprint did not extend beyond the channel width of individual OTFTs. An optical microscope was located vertically on top of the sample and was used to monitor the beam and sample locations using a positionally calibrated crosshair. A square beam attenuator was placed between the sample and the detector to weaken 5 times of the intense (001) Bragg sheet in the (001) texture, thus allowing longer integration times for other diffraction peaks without saturating the detector. A Medoptics CCD detector located 98 mm from the sample holder was used with an exposure time of 30 sec and a lateral sample scan step of 2 μm to collect μGIWAXS maps of each device according to a mapping procedure previously developed elsewhere.  

5.3 Results and Discussion

5.3.1 Structural Characterization

We have utilized μGIWAXS mapping, a method previously developed to map the microstructural heterogeneities of the OSC within OTFTs,[21] to determine the preferred microstructure and texture of the OSC on top of the untreated and F-SAM-treated Au electrodes and within the channel of the transistor, as shown in Figures 2 and 3. The treated Au surfaces maintain uniform, monolayer coverage for both F-SAMs, in agreement with our previous Polarized Modulated-Infrared Reflection Absorption Spectroscopy (PM-IRRAS), goniometric and Kelvin probe measurements (see Chapter 4). As expected, all organic thin films were found to be highly crystalline. In the absence of a surface treatment, the crystalline texture of the semiconductor thin film consisted of a mixture of “edge-on” and “face-on”-oriented crystallites on the electrode and in the channel. However, the microstructure on the F-SAM-treated electrodes consisted of either purely “edge-on” oriented crystallites or of a mixture of orientations in various relative intensities (quantities), depending upon the choice of F-SAM, molecule and combination thereof, as will be discussed below. Note that for all three molecules, the “edge-on” molecular orientation presents the (001) texture, with the a-b plane and the π-stacking in the plane of the substrate, favoring good in-plane charge transport. On the contrary, the “face-on” orientation is geometrically ineffective for in-plane charge transport in OTFTs, present in the (111) texture of diF-TES ADT and (101) texture of diF-TIPS Pn and diF-TSBS PDT, respectively, as shown in Figure 3d-e. Mixtures of these two
orientations also suffer from lower mobility, depending upon the relative amount of “face-on” oriented crystallites in the film. Thus, self-patterning by differential microstructure is successful when the regions containing a pure (001) texture are present on the F-SAM-treated Au electrode and extend to its immediate vicinity (up to tens of microns) to completely cover the critical channel of the OTFT, and they are surrounded by regions consisting of a mixture of orientations. As all the molecules studied herein crystallized in mixed orientations on the oxide regions located far from the electrodes, we will focus our comparison to the structural development directly on top of the F-
SAM-treated Au electrodes. In Figure 2, we show representative µGIWAXS patterns for each semiconductor on the electrode regions of the device. Based on such scans on all material-SAM combinations (Figure 3), we have estimated the fraction of “edge-on” and “face-on” crystallite orientations across the entire device.\(^{[22]}\)

In Figure 4a, we plotted the fraction of “edge-on” oriented crystallites for each combination of molecule/F-SAM. A summary of the film texture for each molecule-F-SAM combination is also summarized in Table I and details about the determination of the fraction of “edge-on” orientation are provided in Table I. As expected, all the materials in question adopt a mixed orientation on untreated Au electrodes (black). In cases of the Pn and ADT molecules, the “face-on” orientation of crystallites is fully inhibited in thin films formed on PFBT/Au electrodes (blue). However, unlike ADT, Pn forms into a mixture of orientations when deposited on 4-MFBT/Au (red), despite the presence of the F-F interaction, suggesting that there is a threshold of minimum number of halogen bonds to influence molecular orientation and crystallographic texture. One F-F anchor, as in the case of Pn on 4-MFBT/Au, does not appear to be sufficiently strong to impede the growth of the “face-on” orientation. In the cases of Pn on PFBT and ADT on 4-MFBT or PFBT, there are multiple halogen bonding opportunities, in the forms of F-F and/or F-S (Figures 4b, c), with the F/S atoms originating either from the SAM or the semiconductor. Such interactions can establish several active halogen bonds, obstructing molecular conformational changes and possibly anchoring the molecule onto the fluorinated surface in an orientation that favors growth of \(<001>\)-textured lamellar crystallites. The formation of 100% “edge-on” orientation of Pn crystallites on PFBT/Au suggests that two bonding opportunities are sufficient, here in the form of F-F interactions (Figure 4c), to successfully achieve a pure preferential orientation of the molecules at the surface of the treated electrodes. The single F-F path in the Pn/4-MFBT case, possibly together with “surface

<table>
<thead>
<tr>
<th>Material</th>
<th>PFBT Orientation</th>
<th>4-MFBT Orientation</th>
<th>Untreated Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>diF-TES ADT</td>
<td>(001)</td>
<td>(001)</td>
<td>(001) &amp; (111)</td>
</tr>
<tr>
<td>diF-TIPS Pn (Peri)</td>
<td>(001)</td>
<td>(001) &amp; (101)</td>
<td>(001) &amp; (101)</td>
</tr>
<tr>
<td>diF-TSBS PDT</td>
<td>(001) &amp; (111)</td>
<td>(001) &amp; (101)</td>
<td>(001) &amp; (101)</td>
</tr>
</tbody>
</table>

**Table I** Summary of crystalline orientations detected by µGIWAXS of different F-SAM-OSC combinations.
“templating” provided by the aromatic SAM, encourages a higher content of “edge-on” crystallite orientation in Pn films on 4-MFBT/Au (28 ± 4.3%) compared to the case of untreated

Figure 3 (a–c) Structural maps of bottom-contact OTFTs determined from μGIWAXS analysis, including gold electrodes (top panels) and fractions of “edge-on” (blue) and “face-on” (red) orientations on PFBT/Au, 4-MFBT/Au, and untreated (UT) Au (lower panels) for (a) ADT, (b) PDT, and (c) Pn. (d–f) Schematic representations the <001> and <111> molecular orientation for ADT (d), Pn (e) and PDT (f).
Au (10 ± 1.1%), but it is not sufficiently strong to promote the formation of a purely (001)-textured film, similar to the case of other OSC-SAM combinations.\textsuperscript{[23, 24]}

We now explore whether the formation of the pure (001) texture can be generalized for molecular systems containing F and S terminating atoms and deposited on an F-SAM surface. We performed similar measurements using PDT (Figure 1c), a molecule with a longer backbone, oriented at an 8.4° angle with respect to the surface normal. We found that in PDT, the presence of F-SAMs cannot suppress the formation of the (101) textured “face-on” orientation, even when several F-F and F-S anchors are afforded by the respective SAM and semiconductor molecular structures (Figure 4b). To understand these results we inspected in more detail the possible interactions at the F-SAM-OSC interface.

Figure 4 (a) Relative “edge-on” oriented content for ADT, PDT and Pn deposited on PFBT (Blue), 4-MFBT (Red) and untreated substrates (Black). (b) Schematic illustrating the relationship between the OSC and the F-SAM for the cases when both F-F and F-S bonding present and (c) only F-F bonds are present.
5.3.2 Interface Interactions Analysis

In Figure 5, we present a schematic view of the molecular orientation with respect to the substrate for a (001)-textured crystal viewed along the b-axis. The backbone orientation relative to the a-b plane is similar for each molecule and the angle with the substrate is provided in Table II. The crystal structure was analyzed using CrystalMaker software.\textsuperscript{[125]} We define the F-F and F-S separations, $d_{F-F}$ and $d_{F-S}$, as the distances between the F or S termination of the OSC molecule to the F termination of the SAM, which corresponds to a plane through the highest point of the F-SAM layer. This assumption is valid for both SAMs, as their orientations with respect to the surface normal are similar, with the aromatic ring slightly tilted with respect to the surface normal and the F-atom pointing upwards.\textsuperscript{[12]} The distances for each compound are provided in Table II. By correlating the estimated F-F and F-S separation distances with the experimental results provided in Figures 2, 3 and 4, the current study provides a lower limit for the $d_{F-F}$ and $d_{F-S}$ for which the interaction is strong enough to promote long range order and inhibit the formation of the “face-on” oriented crystallites. We find that when the separation distance is $1.75\cdot d_w$ or less, where $d_w$ is the sum of the respective van der Waals radii, the formation of a pure “edge-on” orientation is observed for all cases explored herein.\textsuperscript{[126]} This condition is achieved in the case of ADT and Pn molecules. In PDT the F-F and F-S interactions are weak as a result of relatively large separation induced by the backbone orientation ($\sim 2.5\cdot d_w$). As a result, while the formation of (001)-oriented crystallites is observed, the presence of the F-SAM does not inhibit the formation of the “face-on” oriented crystallites. These results indicate the upper limit for the interaction distance lies within the range $1.75\cdot d_w < d_{F-F/S} < 2.5\cdot d_w$.

\begin{itemize}
\item Figure 5: Schematic drawing of the relationship between the OSCs, composed of a molecular backbone and substituent groups (SG) and the F-SAM.
\end{itemize}
Chapter 5. Rational Design of OSC for Texture Control and Self-Patterning

5.3.3 Electrical Characterization

Organic thin-film transistor measurements were performed as a means to investigate the impact of the film’s microstructure and texture on the effectiveness of charge transport. In Figure 6, we show plots of the FET current-voltage characteristics: the evolution of the drain current versus the gate-source voltage ($\sqrt{I_D}$ versus $V_{GS}$) for representative devices of ADT (Figure 6a), Pn (Figure 6b) and PDT (Figure 6c) biased in the saturation regime (source-drain voltage, $V_{DS} = -40$ V). The graphs in Figure 6 correspond to untreated contacts (black), 4-MFBT (red), and PFBT treated (blue) electrodes, respectively. For all devices the channel lengths are sufficiently short that when the halogen interactions are effective, the crystallization induced from the electrodes into the channel inhibits the formation of “face-on” oriented crystallites. The slope of the curves presented in Figure 6 yielded the field-effect mobility ($\mu$) using the following relation:

$$\mu = \frac{2L}{W C_1} \alpha \left(\frac{\sqrt{I_D}}{V_{GS}}\right)^2$$

where $C_1 = 17.3$ nF cm$^2$ is the geometrical capacitance of the dielectric and $L$ and $W$ are the channel length and width, respectively. The reported averages were calculated based on the results obtained on at least 5 devices. Devices fabricated on ADT films deposited on PFBT and 4-MFBT treated electrodes showed high currents and produced similar mobilities of $\mu_{PFBT/Au} = (1.23 \pm 0.09) \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ and $\mu_{MFBT/Au} = (9.7 \pm 1.2) \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. Films deposited on untreated electrodes exhibited nearly two orders of magnitude poorer performance, with $\mu_{Au} = (1.8 \pm 0.5) \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. The lower mobility is a result of higher injection barrier at the metal/OSC interface in the absence of the F-SAM, and due to the presence of the mixed molecular orientations, with the “face-on” (111)-oriented crystallites hindering in-plane charge transport and intergrain transport.

<table>
<thead>
<tr>
<th>Material</th>
<th>Angle</th>
<th>$d_{F-F}$ (Å)</th>
<th>$d_{F-S}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>diF-TES ADT</td>
<td>26.7</td>
<td>5.13</td>
<td>5.13</td>
</tr>
<tr>
<td>diF-TIPS Pn (Peri)</td>
<td>2.5</td>
<td>4.49</td>
<td>-</td>
</tr>
<tr>
<td>diF-TSBS PDT</td>
<td>8.4</td>
<td>8.25</td>
<td>7.63</td>
</tr>
</tbody>
</table>

Table II Comparison of molecular backbone-to-substrate angle and relative molecule-to-SAM distances.
due to large crystallographic misorientation.\cite{12} The evolution of the drain current versus the drain-source voltage for each semiconductor-treatment pair at various gate-to-source voltages are shown in Figure 7.

Measurements performed on devices fabricated using Pn films also echo the differences determined in our structural studies: the OTFTs fabricated on PFBT-treated electrodes showed the
highest mobility with $\mu_{\text{PFBT/Au}} = (2.1\pm0.2)\times10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, owing to a pure “edge-on” molecular orientation obtained in the presence of favorable F-F interactions. Pn-based devices on 4-MFBT-treated electrodes and on untreated electrodes showed progressively decreasing performances due to the decrease in the amount of <001>-textured crystallites phase content (Figure 3b). The resulting
values for mobilities are $\mu_{4\text{-MFBT/Au}} = (7.6\pm0.4)\times10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ and $\mu_{\text{Au}} = (9\pm8)\times10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$ for devices based on 4-MFBT-treated and untreated electrodes, respectively.

When the separation distance between the semiconducting molecule and the F-SAM is too large to promote halogen-halogen interactions, such as in the PDT case, then $\mu$GIWAXS shows a mixture of orientations on all electrodes and OTFT devices also yield similar electrical properties for all types of electrodes. The characteristic mobilities measured for PDT films are: $\mu_{\text{PFBT/Au}} = (1.8\pm0.4)\times10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$, $\mu_{4\text{-MFBT/Au}} = (1.1\pm0.3)\times10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$, and $\mu_{\text{Au}} = (8.0\pm0.7)\times10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. The slightly higher mobilities obtained on PFBT/Au and 4-MFBT/Au are a result of the lower injection barrier created by the work function shift of the F-SAM-treated electrode.[12] Nevertheless, these values are significantly lower than the one reported for PDT OTFTs deposited by solvent-assisted crystallization (SAC), where a pure (001) oriented film, characterized by $\mu = 1.5$ cm$^2$V$^{-1}$s$^{-1}$ was obtained because of the slow nature of this crystallization process.[25] The lower mobility in our thin-films is thus limited by injection into the (001)+(111) phase and not by the transport through the (001) phase present in the channel (Figure 3).

5.4 Conclusions

In summary, we investigated the role of interfacial halogenation of the substrate on mediating texture formation and self-patterning of polycrystalline OSC films and the resulting effects on charge transport properties in OTFTs. We demonstrate that OSCs can either allow or inhibit texture selection based on whether or not F-F and/or F-S interactions are present at the F-SAM/semiconductor interface. We report that the presence of two or more interaction opportunities between F and F/S species per SAM or per OSC molecule are required to promote molecular anchoring, which can promote the formation of high in-plane mobility textures of the OSC. The halogen interactions are found to be sufficiently strong to mediate texture only when the halogen atoms on the molecule and the SAM are located closer than about twice the respective van der Waals interaction distances. When these conditions are satisfied, the organic film exhibits a high degree of texture purity, with crystallites oriented with the (001) plane parallel to the surface and effective in-plane $\pi$-stacking, resulting in high mobility devices. This study has provided rare insight directly linking the surface chemistry of the electrode, the terminating atom of the OSC molecules, the resulting film microstructure and the performance of OTFT devices. This
information is vital to enabling the rational design of OSCs and demonstrates the importance of considering both the molecule and surface chemistry.
References


**Figure A1** Front cover for *Advanced Materials*, 24 (2012), related to manuscript: “Direct Structural Mapping of Organic Field-Effect Transistors Reveals Bottlenecks to Carrier Transport” by R. Li, J. W. Ward, D.-M. Smilgies, J. E. Anthony, O. D. Jurchescu and A. Amassian in *Advanced Materials*, 24, 5553 (2012). Cover was designed and produced by the Amassian Research Group at the King Abdullah University of Science and Technology.
Figure A3 Inside front cover for ChemPhysChem, 16 (6) (2015), related to manuscript “Versatile Organic Transistors Realized from Solution Processing” by Jeremy W. Ward, Zachary A. Lamport, and Oana D.
Recent decades have been witness to a fast transition into an era consumed with technology. Ranging from large displays that can now curve to optimize a viewer’s experience to those small enough to be worn on one’s wrist, the diversity of applications is constantly challenged by consumer demands. A common thread among all applications is the field-effect transistor (FET); a small electrical switch that can control the current flow. First proposed in a patent by Julius Lilienfeld in 1930 and later prepared by Dawon Kahng and Martin Atalla in 1959, the most common material used in FETs today, from display to processor technologies, is silicon. Materials used in silicon-based electronics have now begun to be complemented by, and in some case replaced by, organic-based (i.e. carbon-based) materials. Due to weaker interactions between the molecules of organic materials, these compounds can be dissolved into a liquid to form an ink. This ink can be deposited into a film by using low-cost, low-thermal budget methods such as roll-to-roll printing and spray-processing, thus significantly increasing the manufacturing versatility over the brittle silicon-based materials. Organic field-effect transistors (OFETs) fabricated from solution-based methods create pathways to fabricating electronic applications that are: flexible, transparent, large-area, low-power consuming, and/or even wearable. Since the first OFET based on a soluble semiconductor was developed by Koezuka in 1987, much progress has been made in designing new materials, creating new device structures, and developing new fabrication methods, improving the electronic performance of devices by nearly six orders of magnitude (or 1,000,000 times). Even in the presence of such great improvement, the adoption of organic electronic devices in industrial manufacturing is challenged by the following limitations:
#1. The environmental stability of the organic semiconductors;
#2. The low device performance and high operating voltages;
#3. Insufficient understanding about the relation between organic semiconductor processing, microstructure and its electrical properties.

Through my doctoral research, I addressed these problems, as detailed below:

*Challenge #1* was addressed in Chapter 3. We discovered a solid-solid phase-transition at 205 K in a commonly used organic semiconductor. We investigated the conditions under which the transition occurred and the implications it had on the thin-film structure and electrical performance. We found that when the material was in a powder form, the transition was completely reversible; however, once it was confined to a substrate, in a form of a thin layer, the film cracked upon passing through the transition point and its electrical properties suffered. This finding contains important information for this material since it clarifies its response to thermal changes and the stability of this material. With respect to the consideration for potential commercial manufacturing, since this transition occurs at very low temperatures, it does not impact the devices’ operation in consumer applications.

*Challenge #2* and *Challenge #3* are addressed concurrently through Chapters 4 and 5 by exploring methods to connect molecular design and processing in order to improve the field-effect mobility of OTFTs fabricated from organic semiconductors. The approach adopted in this work is through inducing organic thin-film transistor patterning to electrically segregate individual devices within an array. In the current electronics industry, the semiconductor films are patterned using multistep processes that involve harsh chemicals and intense light sources, which are incompatible with organic materials. In 2008 Gundlach et al. discovered a technique that took advantage of the chemical structure of the organic semiconductor and its relationship to the surface on which it was deposited. They demonstrated that by treating the surfaces of the OFET electrodes with a halogenated (i.e. Fluorine) self-assembled monolayer, they could coerce the semiconductor molecules in these regions to form a highly conductive film. Patterning was realized since the film not in contact with the treated-metal surface was a poorly conducting film, thus preventing charges from leaking to neighboring devices. This technique faced challenges when being transferred to other materials or treatments as the underlying phenomena was not well understood.
First, by implementing three similar treatments on the metal surfaces and then selectively choosing other halogenated organic semiconductors, we discovered key components of the treatment and semiconductor composition that facilitate this type of film growth. We identified the role of interactions between the fluorine atom on the treatment molecule and the fluorine atom residing on the organic semiconductor. Specifically, we discovered that these interactions are effective only when the distance between the interacting atoms within the semiconductor and the treatment is less than 2.5 times the characteristic bonding length of the halogen atoms involved. The development of a deeper understanding into the interplay between organic semiconductors and the surfaces onto which they are placed helps to guide synthetic chemists in making new, high-performance semiconductors and creates guidelines for device patterning, which are important for device design.

Throughout the thesis, we addressed Challenge #3 by exploring how different processing parameters, such as the details of the spinning recipe, interface engineering, or post-deposition treatments alter the structure of the organic semiconductor film. As the film morphology is intimately related to its electrical properties, we followed these changes in FET measurements. By establishing a processing – structure – properties feed-back loop, we gained a great control over the properties of the resulting devices and consequently improved their performance.
List of Publications

1. **Quantitative Analysis of the Density of Trap States at the Semiconductor-Dielectric Interface in Organic Field-Effect Transistors**
   Peter J. Diemer, Zachary A. Lamport, Yaochuan Mei, Jeremy W. Ward, Katelyn P. Goetz, Wei Li, Marcia M. Payne, Martin Guthold, John E. Anthony, and O. D. Jurchescu
   *Applied Physics Letters* (In Revisions)

2. **Low-Voltage Polymer/Small-Molecule Blend Organic Thin-Film Transistors and Circuits Fabricated via Spray Deposition**

3. *† Versatile Organic Transistors by Solution Processing*
   J. W. Ward, Z. A. Lamport and O. D. Jurchescu
   *ChemPhysChem*, 16 (6), 1118 (2015)

4. **Freezing-in Orientational Disorder Induces Crossover from Thermally-activated to Temperature-independent Transport in Organic Semiconductors**
   *Nature Communications* 5, 5642 (2014)

5. **Low-Temperature Phase Transitions in a Soluble Oligoacene and Their Effects on Device Performance and Stability**

   *Advanced Functional Materials* 24 (32), 5052 (2014)

7. † **Electronics Beyond Silicon**
   J. W. Ward and O. D. Jurchescu
   *Circuit Cellar* 278, 80 (2013)

8. *Direct Structural Mapping of Organic Field-Effect Transistors Reveals Bottlenecks to Carrier Transport*
   R. Li, J. W. Ward, D-M. Smilgies, J. E. Anthony, O. D. Jurchescu and A. Amassian
   *Advanced Materials* 24, 5553 (2012)

* Cover Article
† Invited Article
9. **Tailored Interfaces for Self-Patterning Organic Thin-Film Transistors**


   Journal of Materials Chemistry 22 (36), 19047 (2012)

10. **Synthesis and Charge Transport Studies of Stable, Soluble Hexacenes**


    Chemical Communications 48, 8261 (2012)

11. **Effect of Acene Length on Electronic Properties in 5-, 6-, and 7-Ringed Heteroacenes**


    Advanced Materials 23, 3698 (2011)

12. **Variation of the Side Chain Branch Position Leads to Vastly Improved Molecular Weight and OPV Performance in 4,8-dialkoxybenzo[1,2-b:4,5-b']dithiophene/2,1,3-benzothiadiazole Copolymers**


    Journal of Nanotechnology 572329 (2011)
List of Presentations

1. *Low-Temperature Structural Phase Transistion in a Soluble Oligoacene and Its Effect on Charge Transport*
   American Physical Society March Meeting
   Oral Presentation in Denver, CO (2014)

2. *Tailored Interfaces for Self-Patterning Organic Thin-Film Transistors*
   WFU Physics Colloquium
   Invited Talk in Winston-Salem, NC (2014)

3. *Tailored Interfaces for Self-Patterning Organic Thin-Film Transistors*
   Materials Research Society Spring Meeting
   Oral Presentation in San Francisco, CA (2013)

4. *Tailored Interfaces for Self-Patterning Organic Thin-Film Transistors*
   Wake Forest University Graduate Student & Postdoc Research Day
   Poster Presentation in Winston-Salem, NC (2013)
   Award: *1st Runner-Up*

5. *Tuning the Microstructure and Electronic Performance in Organic Thin-Film Transistors Using Chemical Modifications at Interfaces*
   International Semiconductor Device Research Symposium
   Oral Presentation in College Park, MD (2011)
   Award: *Best Student Oral Presentation Award*

6. *From Nano to Micro-Scale Control of Crystalline Order in Small-Molecule Organic Semiconductor Films*
   North Carolina Nanotechnology Commercialization Conference
   Poster Presentation in Charlotte, NC (2011)

7. *From Nano to Micro-Scale Control of Crystalline Order in Small-Molecule Organic Semiconductors*
   Electronic Materials Conference
   Oral Presentation in Santa Barbara, CA (2011)

8. *From Nano to Micro-Scale Control of Crystalline Order in Small-Molecule Organic Semiconductors*
   Wake Forest University Graduate Student & Postdoc Research Day
   Poster Presentation in Winston-Salem, NC (2011)
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Curriculum Vitae

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