Organic field effect transistors fabricated using solution based aggregation and soft lithography

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Declaration of originality

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Abhimanyu Mukherjee
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Abstract

In this thesis, we present a study on thin films and organic field effect transistor (OFET) devices using solution ageing induced aggregation and soft lithography techniques. We first investigated the effect of solution ageing and film thickness of F8T2 (poly(9,9-dioctylfluorene-co-bithiophene)) spin coated from different boiling point solvents. Using the weakly interacting H-J aggregate model, we found that with solution ageing, there was an increase in J-aggregate ordering, characteristic of the beta-phase regime commonly associated with polyfluorenes. In organic transistor devices, this corresponded with a positive correlation with threshold voltage, $V_{th}$, and the Vissenberg and Matters density-of-states temperature for disorder, $T_0$.

Azeotropic binary solvent thin films of F8T2 were also investigated in regimes of extreme H and J aggregation, with the latter indicating more presence of the beta-phase was detrimental to OFET performance.

Using the soft lithographic approach, patterning of the organic semiconductor layer was achieved by applying the micro molding in capillaries (MIMIC) and solvent assisted micro molding in capillaries (SAMIM) methods. Different architectures of stamp designs and domains using Fluorolink® MD 700 perfluoropolyether (PFPE) and polydimethylsiloxane (PDMS) materials were investigated and their effects on OFET device performance are presented. We found that patterned organic semiconductor layers of both small molecules such as TIPS-pentacene (6,13-bis(triisopropysilylethynyl)pentacene), and the polymers F8T2 and P3HT (poly(3-hexylthiophene)) from a solution precursor, were capable of forming sub-micron features using optimised stamp geometries and materials at room temperature. Furthermore, we also investigated the effect of confined crystallisation of F8T2 from mono and azeotropic binary solvents in staggered top gate geometries. Using the highly hydrophobic fluoropolymer CYTOP™ as the dielectric, saturation mobilities of $>0.001 \text{ cm}^2/\text{Vs}$, threshold voltages of $V_{th} > -20 \text{ V}$, and gate leakage currents of $(|I_D/I_G| > 10^3)$ were obtained. These results for confined crystallised F8T2 OFETs are of better performance, with the mobility in particular being an order of magnitude higher than that of conventional solution processed counterparts using spin coating and drop casting deposition methods.
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### Abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ANI</td>
<td>Anisole</td>
</tr>
<tr>
<td>BGBC</td>
<td>Bottom Gate Bottom Contact</td>
</tr>
<tr>
<td>BGTC</td>
<td>Bottom Gate Top Contact</td>
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<tr>
<td>CB</td>
<td>Chlorobenzene</td>
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<td>CHF</td>
<td>Chloroform</td>
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<td>DCB</td>
<td>1,2-dichlorobenzene</td>
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<tr>
<td>DO</td>
<td>Dodecane</td>
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<tr>
<td>F8T2</td>
<td>poly(9,9-dioctylfluorene-co-bithiophene)</td>
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<tr>
<td>HEX</td>
<td>Hexane</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane</td>
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<tr>
<td>MIMIC</td>
<td>Micro molding in capillaries</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field effect transistor</td>
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<tr>
<td>OSC</td>
<td>Organic semiconductor</td>
</tr>
<tr>
<td>OTS</td>
<td>octadecyltrichlorosilane</td>
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<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PFPE</td>
<td>perfluoropolyether</td>
</tr>
<tr>
<td>PLQE/PLQY</td>
<td>Photoluminescent Quantum Efficiency/Yield</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PVP</td>
<td>Poly(4-vinylphenol)</td>
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<td>Abbreviations</td>
<td>Description</td>
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<td>---------------</td>
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<tr>
<td>SAMIM</td>
<td>Solvent assisted micromolding in capillaries</td>
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<tr>
<td>SAM</td>
<td>Self Assembled Monolayer</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon Dioxide</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
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<tr>
<td>TET</td>
<td>Tetralin</td>
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<tr>
<td>TGBC</td>
<td>Top Gate Bottom Contact</td>
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<td>TGTC</td>
<td>Top Gate Top Contact</td>
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<tr>
<td>TIPS-Pentacene</td>
<td>6,13-bis(triisopropylsilylethynyl)pentacene</td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene</td>
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<tr>
<td>UV-vis</td>
<td>Ultra violent and visible spectroscopy</td>
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Chapter 1

Introduction

Since their invention in 1947 by Bell Labs researchers, Bardeen, Brattain, and Shockley [1][2], transistors have served as the foundation of almost every modern electronic device today. On its own, it is used to simply turn on, off or amplify electrical signals. However, once used in combination with millions (or billions) of transistors [3], they form the basis of complex logic gate circuitry that allow the functioning of smartphones, computers, hand-held tablets, electric cars, medical monitoring equipment, to even sensor instruments onboard the NASA’s Parker Solar Probe that was lifted off into space to study the Sun [4]. However, there is another type of device that is fast making its way into the mainstream – and that is the Organic Field Effect Transistor (OFET). Carbon based polymers were once widely regarded as insulators, and it was not until research done by Heeger, MacDiarmid and Shirakawa in the 1970s, did the concept of conducting conjugated polymers first get introduced [5]. Soon after, Tsumura, Koezuka and Ando of Mitsubishi Electric Corporation, managed to incorporate the first organic OFET with semiconducting polythiophene in the 1980s [6]. Since then, there has been decades of multidisciplinary research conducted by academic and commercial institutions around the world on organic semiconductors, with OFETs being one class of organic devices being researched [7].

Though not considered to be a direct competitor to conventional silicon metal-oxide-semiconductor field effect transistors (MOSFETs), OFETs have the potential to fill a niche market consisting of solution processable, ultra low cost, roll-to-roll, large area, and flexible microelectronic applications [8]. Some of these applications are flat panel displays [9] [10], radio frequency identification tags (RFID) [11][12], sensors [13], flexible electronic circuits [14], photodetecting OFETs [15] [16], and low cost memory devices [17]. For most of these applications, it is essential that OFETs have high mobilities, high on/off switching ratios, low leakage currents, steep subthreshold slopes and small threshold voltages [18][19][20]. These key metrics, which quantify performance and device physics in OFETs, will be
discussed in detail in later chapters.

To date, many reports have shown charge mobilities of OFETs to exceed that of amorphous silicon (Si) thin film transistors (TFT) using a variety of fabrication techniques [21]. Mobilities as high as 23.2 cm$^2$/Vs have been recorded for p-type thin film OFETs [22], and 6 cm$^2$/Vs for n-type [23]. Mobilities for single crystal OFETs are generally much higher than thin films due to long range molecular ordering, fewer defects and trap states that would otherwise inhibit charge transport, and values as high as 40 cm$^2$/Vs have been recorded for Rubrene single crystals [24]. OFETs fabricated using vapour and vacuum deposition techniques generally exhibit higher performance due to controllable film thickness and precise patterning parameters [25] [26]. However, solution processable techniques are fast rivalling conventional techniques [27] [28] [29] [30] [31], with mobility values exceeding 10 cm$^2$/Vs; which greatly exceeds the performance of amorphous Si TFTs [32] [33]. To this date, research is still undergoing in the field to address the key challenges of achieving charge transport efficiency, ambient stability, and long-term durability in functioning devices [34].

This thesis addresses two key topics of importance:

- Effects of ageing induced solution aggregation on the electrical and optical properties in polyfluorene thin films.

- A quantitative investigation into the viability of using soft lithography techniques to pattern the organic semiconductor active layer for use in OFET devices.

Chapter 2 provides an introduction into the background and theory behind the electronic structure of organic semiconductors, charge transport models, derivations of key OFET parameters, optical absorption and emission phenomenon, H-J aggregate model, and organic semiconductors used in this thesis.

Chapter 3 details the materials and experimental methodology used to fabricate and analyse data on the optical, structural, morphological and electrical characteristics of organic semiconductor thin films and their application in transistors.

Chapter 4 investigates ageing induced solution aggregation in F8T2 polyfluorene thin films using mono solvent based solutions.

Chapter 5 extends on the work done in the previous chapter, and explores binary solvent based F8T2 polyfluorene thin films and transistors.

Chapter 6 departs from the aggregation work and explores the second research topic of soft lithography. We investigate the application of the micro molding in
capillaries (MIMIC) and solvent assisted micro molding in capillaries (SAMIM) techniques in soft lithography, with variable PFPE and PDMS stamp geometries, to pattern aligned features of F8T2, TIPS-Pentacene and P3HT in OFETs with staggered top gate geometries.

Note: The following published work is not included in this thesis:


References

Chapter 1. Introduction


Chapter 2

Background and theory

2.1 Electronic structure of $sp^2$ carbon

Let us first start with Carbon (C), which is the crucial element at the heart of organic semiconductors. In essence, organic semiconductors are $sp^2$ hybridised $\pi$ conjugated molecular systems that have alternating single (C-C) and double (C=C) bonds [1]. Carbon, a non-metal Group IV material from the periodic table, consists of 6 electrons that split into energy sub levels with the configuration $1s^22s^22p^2$. There are 4 outer valence orbitals involving the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals. This allows Carbon to hybridise into three different configurations: $sp$, $sp^2$ and $sp^3$, which allow for the formation of triple, double and single bonds respectively. In $sp^2$ hybridisation, there are 3 $sp^2$ hybrid orbitals per carbon atom that are constructed from the $2s$ and $2p_x$ orbitals. This forms $\sigma$ bonds that are constructed from the $2s$, $2p_x$, $2p_y$ orbitals, while the remaining $2p_z$ orbital forms the basis of the delocalised conjugated $\pi$ bond, and lies perpendicular to the plane [2]. Taking the example of ethylene ($C_2H_4$), a simplified illustration of the bonding is shown in Figure 2.1a.
Chapter 2. Background and theory

Figure 2.1: (a) Illustration of the $\pi$ bonding by $2p_z$ orbitals in ethylene ($C_2H_4$), (b) and energy level splitting of HOMO and LUMO frontier orbitals with increasing conjugation length. Partly adapted from Ref [1].

In $sp^2$ conjugated molecular solids, the combination and overlap of several $2p_z$ orbitals leads to either in-phase $\pi$ bonding or out-of-phase $\pi^*$ anti-bonding levels. This corresponds to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), analogous to the valence and conduction bands in inorganic semiconductors at large conjugation lengths (see Figure 2.1b). Finally, the difference between the HOMO and LUMO orbitals is defined by the optical energy gap $E_g$ [3].

Depending on the position of the HOMO and LUMO energy levels, organic semiconductors can either be p-type, n-type or both (ambipolar), with the majority carriers being holes in p-type and electrons in n-type [4]. p-type organic semiconductors have been more widely investigated than n-types due to their high mobilities, stability in air at room temperature, and convenience of compatibility with air stable source and drain electrodes suited for injection into the HOMO regimes [5][6].

2.2 Charge transport in organic semiconductors

Conventional inorganic semiconductors such as silicon and germanium consist of ordered crystalline structures that allow for the formation of well defined valence and conduction energy bands separated by a small forbidden energy gap (see Figure 2.2(a)). This is described by the well established band theory of solids in most semiconductor textbooks [7]. At zero kelvin, there are no electrons in the conduction band and the valence band is completely filled. Through thermal excitation or doping, electrons may be excited from the valence band into the conduction band
where charge transport occurs in delocalised states. The charge carrier mobility decreases with increasing temperature due to phonon scattering caused by crystal lattice vibrations and deformation.

Organic semiconductors on the other hand, are primarily made from conjugated carbon molecules with $sp^2$ hybridisation which result in amorphous or polycrystalline ordering [8]. This results in a intrinsically lower mobility several orders of magnitude lower compared to single crystalline silicon (>1000 cm$^2$/Vs) [9]. The major difference between organic and inorganic semiconductors is that the binding energy between organic molecules is much weaker than in inorganic solids; the former relying on weak van der Waal interactions, and the latter on strong covalent bonding. As a consequence, the corresponding HOMO (valence) and LUMO (conduction) bands are much smaller in organic than in inorganic semiconductors [10].

Charge transport in organic semiconductors is thought to occur due to the hopping of charges between localised states, where the mobility is phonon assisted and increases with temperature. These localised states can either arise due to the formation of self-localised polarons or disorder in the structure. The former arises due to the presence of radical cations or anions around charge carriers such as holes (electrons), which subsequently deform the organic semiconductor lattice in response to an electric field [11]. One of the major parameters governing charge transport is the amplitude of the electronic transfer integrals between adjacent molecular chains, which is strongly dependent on the molecular packing and morphology [1]. The mobility boundary between localised and delocalised charge transport is generally taken to be between 0.1 and 1 cm$^2$/Vs [12].

Band like transport at low temperatures has been reported for high purity single crystalline organic semiconductors such as rubrene [13] and pentacene [14]. However for the most part, organic semiconductors deposited using solution processing techniques consist of a high number defect states and disorder in the morphology whose HOMO and LUMO levels are approximated to a Gaussian density of states (DOS) [15]. Over the years, several models have been proposed to model the charge transport of disordered amorphous and polycrystalline organic semiconductors, of which the ones of most importance will be qualitatively discussed here.
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Figure 2.2: Density of states for (a) single crystal silicon, (b) amorphous silicon due to weak localisation, and (c) disordered organic semiconductor with broadening of the HOMO and LUMO levels approximated by a Gaussian distribution of width $2\sigma$. For (c), the tail of the Gaussian is approximated by an exponential DOS of the form $\sim A \exp(\epsilon/kT)$. Partly adapted from Ref [16].

2.2.1 Multiple trapping and release model

Horowitz and Delannoy applied the multiple trapping and release (MTR) model widely used for amorphous silicon to explain charge transport in weakly disordered organic semiconductors [17]. The MTR model is based on the assumption that most of the charge carriers injected into the organic semiconductor are initially trapped in localised density of states extending into the forbidden energy band before finally being released into the extended states via thermally activated processes (see Figure 2.2(b)). Due to the presence of these localised states, a precise forbidden energy gap is not defined, hence the mobility edge is used to separate localised and extended (delocalised) states. Since the time trapped in localised states is greater than in the extended states, the overall mobility is reduced. For a single energy level trap system, this is given by the equation

$$\mu \simeq \mu_0 \frac{N_c}{N_t} \exp \left(-\frac{E_c - E_t}{kT}\right)$$  \hspace{1cm} (2.1)

where $\mu_0$ is the mobility in the extended states, $N_c$ is the extended density of states, $N_t$ is the density in the localised states, $E_c$ is the energy at the mobility edge and $E_t$ is the energy in the localised states [12]. As can be observed in Equation 2.1, the mobility follows a power law that is proportional to the temperature. The MTR model has been used to successful model OFET characteristics where the mobility is found to be temperature and gate voltage dependent. However, its use is limited to relatively polycrystalline small molecules and polymers that approach or exceed
mobilities of 0.1 cm²/Vs [18].

2.2.2 Miller-Abrahams Model

Due to the random distribution of energy states in disordered organic semiconductors, the HOMO and LUMO bands adopt a DOS following a Gaussian distribution given by the equation

\[ g(E) = \frac{N_0}{\sqrt{2\pi}\sigma_{DOS}} \exp\left(-\frac{E^2}{2\sigma_{DOS}^2}\right) \] (2.2)

where \(N_0\) is the total density of states per unit volume and \(\sigma_{DOS}\) is the width of the distribution. When all states are localised, charge transport is said to occur by hopping between localised states. This was modelled by Miller and Abrahams in 1960 where they described the charge transport with a hopping frequency of carriers from an initial state \(\nu_i\) to a final state \(\nu_j\) as a function of energy difference between the two states \(E_i - E_j\), distance between states \(R_{ij}\), localisation length \(\alpha\) and the temperature \(T\). This is given by the equation:

\[ \nu_{ij} = \nu_0 \exp\left(-\frac{2R_{ij}}{\alpha}\right) \begin{cases} \exp\left(-\frac{E_i-E_j}{kT}\right) & \text{for } E_i < E_j \\ 1 & \text{for } E_i > E_j \end{cases} \] (2.3)

The first exponential term in Equation 2.3 represents the probability due to tunnelling, while the second exponential term is thermally activated when hopping to a final state with higher energy \(E_i < E_j\) or equal to a probability of 1 when hopping to a final state with lower energy \(E_i > E_j\).

2.2.3 Variable Range Hopping Model

However, since the Miller-Abrahams model did not account for hops over sites greater than nearest neighbour distances, this model was further extended by N.F. Mott in the Variable Range Hopping Model (VRH) [19]. Mott assumed a constant Gaussian DOS and incorporated for hopping over large distances at low activation energy or hopping over short distances with high activation energy. The VRH model predicts a mobility dependence of temperature with the equation

\[ \mu \propto \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{d+1}} \] (2.4)

where \(T_0\) is a fitting parameter inversely related to the DOS and \(d\) is the number of dimensions of the system [20].
2.2.4 Gaussian Disorder Models

The Gaussian Disorder Model (GDM) was developed by H. Bässler in the 1990s to explain the charge transport in organic semiconductors with low charge carrier density and at high electric fields (>10^5 V/cm) [21]. He assumed a charge transport via Miller-Abraham’s hopping model and found a dependence of mobility with the Gaussian energy and positional disorder, the temperature $T$ and the electrical field $F$, with an equation numerically determined by Monte-Carlo simulations:

$$\mu_{GDM} = \mu_0 \exp \left[ - \left( \frac{2\sigma}{3kT} \right)^2 \right] \exp \left\{ C \left[ \left( \frac{\sigma}{kT} \right)^2 - \Sigma^2 \right] \sqrt{F} \right\} \quad (2.5)$$

In Equation 2.5, $\mu_0$ is the mobility limit at $T \to \infty$, $C$ is an empirical constant dependent on spacing between states, $\sigma$ is the width of the Gaussian due to energetic disorder and $\Sigma$ is the width due to positional disorder.

S. V. Novikov later expanded the GDM model to incorporate the electric field dependence $F$ at low fields [22]. This formed the basis of the correlated Gaussian Disorder Model (CDM) which accounted for spatial correlations caused by randomly oriented charge-dipole interactions. This led to the empirically determined equation

$$\mu = \mu_0 \exp \left[ - \left( \frac{3\sigma}{5k_BT} \right)^2 + 0.78 \left( \left( \frac{\sigma}{k_BT} \right)^2 - 2 \right) \sqrt{\frac{eaF}{\sigma}} \right] \quad (2.6)$$

where $\sigma$ is the width of the Gaussian, $e$ is the charge constant, and $a$ is the intersite spacing [23].

2.2.5 Vissenberg-Matters Model

Vissenberg and Matters applied the Variable Range Hopping Model to describe the mobility dependence due to charge carrier density in the accumulation layer, gate voltage and temperature in amorphous disordered polymer OFETs [24]. At low charge carrier densities and temperature, they assumed an exponential DOS models the tail of the Gaussian DOS by the following equation

$$g(\epsilon) = \frac{N_t}{k_BT_0} \exp \left( \frac{\epsilon}{k_BT_0} \right) \quad (-\infty < \epsilon \leq 0) \quad (2.7)$$

where $N_t$ is the number of states per volume, $k_B$ is Boltzmann’s constant, $T_0$ is the width of the exponential distribution (see Figure 2.2(c)). Using percolation theory, they derived the following equation

$$\mu_{FET} = \frac{\sigma_0}{e} \left[ \frac{(T_0)^4 sin \left( \pi \frac{T}{T_0} \right)}{(2\alpha)^3 B_C} \right] \frac{T_0}{T} \rho(\frac{T_0}{T})^{-1} \quad (2.8)$$
where $\sigma_0$ is the conductivity unique to the organic semiconductor, $\alpha$ is the overlap parameter of electronic wavefunctions between localised states, $\rho$ is the charge carrier density, and $B_C \approx 2.8$ is a numerically determined percolation criterion in 3D amorphous systems. The Vissenberg-Matters model has been successfully used to model the current characteristics of a number of amorphous disordered OFETs involving PCBM [25], PTV [26], P3HT [26] and pentacene [24].

### 2.2.6 Unified model in low and high charge density regimes

Tanase and coworkers applied the Vissenberg-Matters and Correlated Gaussian Disorder Model to explain why hole mobility was constant at low charge carrier densities in diodes ($< 10^{16}$ cm$^{-3}$) and increased with a power law of the form $\mu \sim \rho^{2T_0}$ at high charge densities in OFETs ($> 10^{16}$ cm$^{-3}$). By empirically combining the diode and OFET mobilities, they obtained a unified model of the form

$$\mu_h(\rho, T) = \mu_h(0, T) + \mu_{VM}$$  \hspace{1cm} (2.9)$$

where $\mu_{VM}$ is the mobility from the Vissenberg-Matters model in Equation 2.8, and $\mu_h(0, T)$ is the hole mobility at low charge densities obtained from the quadratic space-charge limited (SCL) current equation [27][28]. This equation was applied successfully to model low and high densities regimes of PPV and P3HT in diodes and OFETs [26].

Recently, Campbell and coworkers applied the Vissenberg and Matters framework using the unified model developed by Tanase to investigate the charge dependence of amorphous fluorene-triarylamine copolymers [29]. Using the power law dependence component for high density regime from the Tanase Model, the follow equation was used

$$\mu_{FET} = \mu_0 \left( \frac{\rho_{FET}}{\rho_0} \right)^{\frac{2T_0}{T_0}-1}$$  \hspace{1cm} (2.10)$$

where $\rho_{FET}$ is the charge carrier density per unit volume in the accumulation channel of the OFET, $\mu_{FET}$ is the mobility, $T_0$ is the width of the exponential DOS, while $\mu_0$ and $\rho_0$ are constants.

By substituting Equation 2.10 into the standard gradual channel approximation for the drain current in the linear (lin) and saturation (sat) regimes of an ideal MOSFET (more on this later), they achieved a charge carrier density dependent mobility equation of the approximate forms

$$I_D(lin) \simeq \frac{W \mu_{lin} C_i}{L} \left( \frac{C_i}{e \Delta x \rho} \right)^m (V_G - V_{to})^{m+1} V_D$$  \hspace{1cm} (2.11)$$

11
where \( m = (T_0/T) - 1 \), \( C_i \) is the capacitance per unit area, \( L \) is the channel length, \( W \) is the channel width, \( V_G \) is the gate voltage, \( V_{to} \) is the turn-on voltage, \( V_D \) is the drain voltage, \( \rho \) is the charge carrier density, \( \mu_{lin,sat} \) is the mobility, and \( \Delta x \) is depth of the accumulation layer near the semiconductor/dielectric interface, roughly taken to be \( \sim 1 \text{ nm} \) [30]. Note that when \( m = 0 \), Equations 2.11 and 2.12 reduce to the standard gradual channel approximations (see Equations 2.18 and 2.19).

### 2.3 Organic field effect transistors

#### 2.3.1 Operating principles

OFETs in general adopt the architecture used by amorphous Si thin film transistors (TFTs) [12]. A typical OFET design consists of source, drain and gate electrodes, along with a organic semiconducting layer (OSC) and a dielectric layer. These components can be organised into either coplanar or staggered geometries [31]. Architectures consisting of the latter are generally preferred due to improved current pathways and encapsulation that allows for lower contact resistance, improved stability, and hence, improved device performance [18][31][32][33]. These geometries further split into the following common architectures as illustrated in Figure 2.3:

1. **Coplanar**
   - Bottom gate, bottom contact (BGBC)
   - Top gate, top contact (TGTC)

2. **Staggered**
   - Bottom gate, top contact (BGTC)
   - Top gate, bottom contact (TGBC)
Chapter 2. Background and theory

Figure 2.3: OFET architectures for coplanar (a) BGBC, (b) TGTC, and staggered (c) BGTC, (d) TGBG geometries (not to scale).

It is generally accepted that OFETs are gate voltage dependent ($V_G$) and operate in the accumulation regime. The injection of charge carriers at the source, drain and semiconductor interface is crucial to the operation of OFETs. Ideally, good ohmic contact and minimal contact resistance is desirable and requires the source and drain work functions to be close to the HOMO (LUMO) level of a p-type (n-type) organic semiconductor so that the potential barrier for charge injection is minimal [34] [35]. Taking the example of a p-type OFET with holes as the majority charge carriers, when a negative voltage $V_G$ is applied between the gate and source electrode, positive charges (holes) accumulate at the interface between the OSC and insulator. The situation is reversed for n-type OFETs with electrons as the majority charge carriers. The $V_G$ dependance owes from experimental observation that charge transport is dependent on charge carrier density in the conducting channel. This can be inhibited by traps localised near the band edge which have to be filled by applying a minimum threshold gate voltage $V_{th}$ before charge transport occurs between the conducting channel [36].

When a small voltage $V_D$ is applied between the source and drain electrode ($V_D < V_G - V_{th}$), current starts to flow along the conducting channel. Current flowing through the conducting channel is proportional to $V_D$, hence increasing $V_G$ increases the number of charge carriers at the interface between OSC and insulator leading to a higher drain current $I_D$. This is considered to be the linear regime (Figure 2.4a).

As $V_D$ is increased, a point is reached where charge carriers near the drain electrode are depleted leading to non-linearity of $I_D$ ($V_D = V_G - V_{th}$) (Figure 2.4b). Upon further increases of $V_D$, current finally saturates and becomes constant at $V_D > V_G - V_{th}$. This is called the saturation or pinch off regime (Figure 2.4c).
2.3.2 Key characteristic derivations

The current-voltage characteristics of the OFET are derived from the gradual channel approximation commonly applied to metal-oxide-semiconductor field effect transistors (MOSFET) as discussed earlier [12]. This approximation assumes the following:

- Upon the application of a gate voltage $V_G$, the electric field ($F$) perpendicular to the dielectric/semiconductor interface is much larger than in the parallel direction along the conducting channel between the source and drain electrodes i.e. $\partial F_y/\partial x \gg \partial F_x/\partial x$
- The channel length $L$ is much larger than the dielectric thickness $d$
- Mobility is constant along the conducting channel and independent of charge density
- Contact resistance, doping and short channel effects are ignored

Considering an infinitely small strip of length $\partial x$ in the conducting channel, a small charge $\partial q$ per unit area corresponds to the following equation

$$\partial q = C_i[V_G - V_{th} - V(x)]W\partial x$$  \hspace{1cm} (2.13)
where $C_i$ is the capacitance per unit area, $V(x)$ is the channel potential, and $W \partial x$ is the area of the strip with respect to the channel width. As current is defined as a rate of change of charge $I_D = \partial q/\partial t$, using the chain rule we get

$$I_D = \frac{\partial q}{\partial t} = \frac{\partial q}{\partial x} \frac{\partial x}{\partial t}$$

(2.14)

We can define $\partial x/\partial t$ as the mean speed of the charge carriers in the $x$ direction along the channel between source and drain, and this is related to the mobility $\mu$, electric field $F_x$ and voltage $V$ by

$$\frac{\partial x}{\partial t} = \mu F_x = \mu \frac{\partial V}{\partial x}$$

(2.15)

Substituting Equations 2.15 and 2.13 into 2.14, we get a relation for the drain current of the form

$$I_D \partial x = \mu W C_i [V_G - V_{th} - V(x)] \partial V$$

(2.16)

Integrating from the distance at source ($x = 0, V(x) = 0$) to the drain electrode ($x = L, V(x) = V_D$), we get:

$$I_D = \frac{\mu W C_i}{L} \left[ (V_D - V_{th})V_G - \frac{V_D^2}{2} \right]$$

(2.17)

Using a first order Taylor expansion of the series $f(a) + f'(a)(V_D - a)$ into the above equation, and setting $a = 0$, we get a simplified expression for the linear regime when $V_D < V_G - V_{th}$:

$$I_D(\text{lin}) = \frac{\mu W C_i}{L} (V_G - V_{th})V_D$$

(2.18)

In order to get the current in the saturation regime, we substitute $V_D = V_G - V_{th}$ into Equation 2.17:

$$I_D(\text{sat}) = \frac{\mu W C_i}{2L} (V_G - V_{th})^2$$

(2.19)

2.3.3 Parameter extraction

2.3.3.1 Field-effect mobility

In practice, the transfer characteristics are commonly used to deduce key parameters such as the mobility, threshold voltage, on/off ratio and sub threshold slope [37] (see Figure 2.5). In some cases, the contact resistance can also be extracted from the slope of the linear regime in the output characteristics, but this was not investigated in this thesis. The mobility in the linear regime from the transfer characteristics
is extracted from the slope of the linear drain current and gate voltage, hence by differentiating Equation 2.18 we get:

\[ \mu_{\text{lin}} = \frac{L}{WC_i V_D} \left( \frac{\partial I_D(\text{lin})}{\partial V_G} \right) \]  \hfill (2.20)

On the other hand, the mobility in the saturation regime is extracted from \( \sqrt{I_D(\text{sat})} \) and gate voltage, hence differentiating Equation 2.19 gives:

\[ \mu_{\text{sat}} = \frac{2L}{WC_i} \left( \frac{\partial \sqrt{I_D(\text{sat})}}{\partial V_G} \right)^2 \]  \hfill (2.21)

As explained earlier in Section 2.2, these assumptions do not perfectly explain OFET behaviour of amorphous disordered organic semiconductors as the mobility does in fact depend and vary (at different regimes) with charge carrier density and electric field. However, since the gradual channel approximation is already an established tool to report OFET metrics throughout the literature [38], we will report values of mobility in accordance with convention in this thesis.

![Figure 2.5: Illustration of OFET parameter extraction from \( \sqrt{I_D(\text{sat})} \) and \( I_D(\text{sat}) \) transfer curves in the saturation regime.](image)

**2.3.3.2 Threshold voltage**

Due to differences in the work function between the semiconductor, gate, source and drain contacts, and surface dipoles at the dielectric/semiconductor interface, flat band conditions do not occur at \( V_G = 0 \), but at a particular threshold voltage [36][39]. This threshold voltage can be estimated in two ways from the transfer...
characteristics as shown in Figure 2.5. The first method involves extracting $V_{th}$ from the $V_G$ intercept from the saturation transfer characteristics at $\sqrt{I_D(sat)} = 0$. The second method involves identifying the voltage at which a steep increase in the drain current from the magnitude of the saturation transfer plots is observed. This is identified as the turn-on voltage $V_{to}$ [40]. Both values of $V_{th}$ and $V_{to}$ will be quoted in some parts of this thesis.

### 2.3.3.3 On/Off ratio

The on/off ratio is determined from the magnitude difference between the $I_{on}$ and $I_{off}$ states from the $\log_{10}(I_D)$ vs $V_G$ transfer plots. The off state is defined as the lowest $I_D$ just before a threshold voltage is applied to turn the device on, while the on state is defined as the highest $I_D$ at maximum $V_G$. This will be at $V_G = -60V$ in this thesis.

### 2.3.3.4 Subthreshold slope

The subthreshold slope ($SS$) is obtained from the inverse linear slope of the $\log_{10}(I_D)$ vs $V_G$ transfer plots, defined by the equation

$$SS = \frac{\partial V_G}{\partial (\log_{10}I_D)} \quad (2.22)$$

with the units in V/dec. The $SS$ gives an indication of the charge trap density in the conducting channel below the threshold voltage hence can be used as a useful metric to assess the quality of the dielectric-semiconductor interface [41]. Small values of $SS$ ($<1 \text{ V/dec}$) are preferred as it implies lower trap states and a steeper $I_D$ at the threshold voltage [42].

### 2.3.3.5 Hysteresis

The forward and reverse scans from the transfer characteristics give an indication of the hysteresis effect in OFETs which is generally noticeable from a shift in the threshold voltage $V_{th}$. Hysteresis is generally caused by trap states close to the conducting channel, polarisation of the gate dielectric and charge injection into the dielectric from the gate electrode [43]. It is a useful effect in non-volatile memory devices but unwanted in OFETs, especially if they are to be used in integrated circuits that require a stable $V_{th}$ [44].

The direction of hysteresis generally show two shifts of the $V_{th}$, and with respect to the p-type organic semiconductors used in this thesis:

- $V_{th(\text{rev})} < V_{th(\text{for})}$: is observed when there are mobile ions or polarisation effects in the dielectric causing the $V_{th}$ to decrease during the reverse scan.
• \( V_{\text{th (rev)}} > V_{\text{th (for)}} \): is observed when there are charge carrier trap states in the conducting channel causing the \( V_{\text{th}} \) to increase during the reverse scan.

2.3.3.6 Leakage current

Ideally, there should be zero current between the gate electrode and the dielectric. However in practice, there is some amount of gate leakage \( I_G \) generally indicative of either conducting pathways being induced in the dielectric via quantum tunnelling, dipoles or pinhole defects [45]. High \( I_G \) generally results in artificially high mobilities and \( V_{\text{th}} \), hence it is crucial to keep this low [46]. In this thesis, the leakage current was defined as the magnitude difference between the maximum \( I_D \) and \( I_G \) at \( V_G = -60V \). According to the IEEE standards for OFET characterisation \( I_D/I_G \) should ideally be \( > 10^2 \).

2.4 Absorption and Emission

According to the Franck-Condon Principle, as electrons are much lighter compared to the nuclei, electronic transitions are much faster compared to the time it takes for the nuclei to rearrange to the new electronic state afterwards. When a photon is absorbed by a molecule, an electron is promoted from the singlet ground state \( (S_0) \) to the first excited singlet state \( (S_1) \). In the singlet state, all electron spins are paired, and if they exist in the same energy level they have opposite spins according to the Pauli exclusion principle. Depending on the overlap of the vibrational wave functions which varies according to the molecular structure and ordering, the transition to the first vibrational energy level \( (0-1) \) is the most probable as per the illustration in Figure 2.6(a) [47]. In a highly ordered polymer or rigid molecule, the 0−0 transitions can be the strongest. Electrons in the excited states then vibrationally relax by a process called internal conversion to the 0\(^{th}\) vibrational energy level of the excited state, before finally non-radiatively or radiatively decaying to the vibrational ground state levels, with the latter leading to the emission of light via photoluminescence. Here again, the most probable vibrational transition during emission is the the 0−1 transition. If the energy of the emitted photon is lower than the absorbed photon, this results in an energy (or wavelength) difference between the 0−0 peaks of the absorption and emission spectra, called the Stokes shift [48] (see Figure 2.6(b)).
2.4.1 Excitons

Excitons play an important role in opto-electronic devices such as OLEDs and solar cells \[49\] \[50\]. When a photon is absorbed by a molecule, an electron is excited from the HOMO level to the LUMO level leaving behind a positively charged electron hole. This hole is attracted to the electron by the coulomb force forming an electrically neutral bound state called an exciton. Excitons arise from either absorption of photons or recombination of electron-hole pairs leading to photoluminescence or electroluminescence. Due to the low dielectric constants in organic compared to inorganic semiconductors, the exciton binding energy is much larger (0.1 – 1 eV) and hence tend to have a small radius comparable to the size of the molecule, called Frenkel excitons. Excitons in inorganic semiconductors are called Wannier–Mott excitons and generally have much lower binding energies \(<0.01\) eV \[51\].

2.4.2 H-J aggregation

In conjugated polymers, charge transfer occurs in two ways: intrachain and interchain transport. In intrachain transport, charge transfer occurs along the polymer backbone (also called head-to-tail packing). While for interchain transport, charge transport takes place between neighbouring polymer chains that are coupled by \(\pi - \pi\) delocalisation (called face-to-face packing). Depending on whether the \(\pi - \pi\) orbital overlap is maximum along intrachain and/or interchain ordering, the mobility can be increased. P3HT in particular has been studied extensively over the years and researchers have come to a general agreement that the mobility is greatest along the intrachain ordering rather than interchain \[52\][53][54]. Spano and coworkers developed the H-J aggregate model in order to study interchain (H-aggregates) and intrachain (J-aggregates) interactions in P3HT films from the absorption and photoluminescence (PL) spectra \[55\][56][57]. The excitonic coupling
due to intra or interchain ordering is measured by the exciton bandwidth $W$. From absorption spectra, this is determined from the ratio of the $0-0$ and $0-1$ transition peaks and is given by the equation derived by Spano and coworkers

$$\frac{A_{0-0}}{A_{0-1}} \approx \left( \frac{1 - 0.24W/E_p}{1 + 0.073W/E_p} \right)^2$$

(2.23)

where $E_p$ is the phonon energy of the $C=C$ coupling to the electronic transition and is assumed to be 0.18 eV [58]. Rearranging Equation (2.23) and solving for $W$ we get

$$W \approx \frac{E_p(1 - \sqrt{\frac{A_{0-0}}{A_{0-1}}})}{0.073 \sqrt{\frac{A_{0-0}}{A_{0-1}}} + 0.24}$$

(2.24)

From Equation (2.24) it can be seen that $\frac{A_{0-0}}{A_{0-1}}$ is inversely proportional to $W$. It is valid as long as $A_{0-0} < A_{0-1}$ (H-aggregation) otherwise $W$ would be negative. The $0-0$ transition in pure H-aggregates is suppressed (dipole forbidden) and implies a large exciton bandwidth, while for J-aggregates the exciton bandwidth is small as the $0-0$ transition is super radiative. However, since polymer films are often disordered, this can break the symmetry and hence still allow a weak $0-0$ transition in H-aggregates [56]. These transitions are illustrated in Figure 2.7 to allow the reader to visualise the process.

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**Figure 2.7:** Simplified illustration of electronic transitions between the singlet ground state $S_0$ and first excited single state $S_1$ for H and J aggregate monomer and dimer systems. A and F indicate absorption and fluorescence.

The exciton bandwidth is also inversely proportional to the conjugation length and intrachain ordering; which is also a useful measure of the degree of crystallinity. As such, the smaller the bandwidth, the higher the crystallinity and conjugation length [59][60]. As regards to the limitations of Equation (2.23), Spano and coworkers found that compared to the PL spectra, the absorption spectra is
Insensitive to variations in temperatures between 10 - 300 K [61]. A recent paper by Ehrenreich and coworkers determined that Equation (2.23) tends to incorrectly calculate the exciton bandwidth for thicknesses below 150 nm [62]. Both recommended determining the exciton bandwidth from the ratio of the $0 - 0$ and $0 - 1$ transition peaks in corresponding PL spectra. Since PL concerns the emission of light from the excited state to the ground state and is simply the reverse process of absorption, the H-J model still holds valid. As such, Chang and coworkers derived the following equation for calculating exciton bandwidth from the PL spectra

$$\frac{I_{0-0}}{I_{0-1}} \simeq \frac{\sigma^2}{2e^{-2W^2}} \left( \frac{1 - 0.24W/E_p}{1 - 0.39W/E_p} \right)^2$$

(2.25)

where $\sigma$ is the half width at $1/e$ (1/2.718) of a Gaussian distribution modelling the vibronic peaks [58][63]. Rearranging Equation (2.25) for $W$ we get an equation of the form $aW^2 + bW + c$, which can be solved by applying the standard quadratic formula $W = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$:

$$W \simeq \frac{\sqrt{2}/\sigma \sqrt{I_{0-0}/I_{0-1}} + 0.24}{E_p} - \sqrt{\frac{\sqrt{2}/\sigma \sqrt{I_{0-0}/I_{0-1}} + 0.24}{E_p}^2 + 4 \left( \frac{0.39 \sqrt{2}/\sigma \sqrt{I_{0-0}/I_{0-1}}}{E_p} \right)^2}$$

(2.26)

One advantage of using Equation (2.26) over Equation (2.24) is that $W$ does not become negative if $A_{0-0} > A_{0-1}$ when approaching the regime of J-aggregation. As a rough estimation for our calculations of $W$, we will assume $\sigma = 0.11$ eV for aggregated films of F8T2 in order to get a preliminary estimate of $W$. Although it should be noted that this number was originally determined via numerical simulations on PL spectra of aggregated films of P3HT [61].

### 2.5 Organic semiconductors used in this thesis

#### 2.5.1 F8T2

F8T2 (poly(9,9-dioctylfluorene-co-bithiophene)) is a copolymer with ambipolar charge transport and liquid crystal properties [64]. Its HOMO and LUMO levels are at 5.5 eV and 3.1 eV respectively. It is called a hairy-rod polymer because its octyl side chains extend out from the rod-like backbone [65] and this arrangement allows F8T2 to possess good stability in ambient conditions and solubility in most common organic solvents [66]. Due to its good light emitting and ambipolar charge
transport properties, it is often used to explore the device physics of both organic LEDs and transistors.

Figure 2.8: Skeletal formula for F8T2 ($C_{37}H_{44}S_2)_n$.

Since F8T2 is also capable of pure green light emission, researchers are currently investigating its use for electrically pumped polymer lasers where a combination of high emission and charge transport is required [67]. F8T2 also exhibits a thermotropic, nematic liquid crystalline phase above the liquid-crystal transition temperature of $T_k = 265^\circ$C. In this phase, the polymer chains tend to orient uniaxially in the direction defined by a rubbed polyimide alignment layer to achieve hole mobilities between 0.009 – 0.02 cm$^2$/Vs [68]. This implies that charge transport is preferred along the intrachain polymer backbone rather than interchain hopping between adjacent chains [69]. In comparison, unaligned F8T2 exhibits hole mobilities almost a magnitude lower $\sim 1 \times 10^{-4} – 0.002$ cm$^2$/Vs [70]. Alternatively, mobilities of up to 0.015 have also been achieved through SAM treatment with OTS [70]. Interestingly, there are some reports that suggest that annealing F8T2 between 150 – 280$^\circ$C tends to lower the charge carrier mobility despite increasing the highest drain current and transistor stability [71][72]. A survey of the main processing techniques used for F8T2 in the literature reveals the following maximum OFET hole mobilities: spin coating (0.02 cm$^2$/Vs) [68], drop casting ($\sim 0.0002$ cm$^2$/Vs) [70] and inkjet printing (0.02 cm$^2$/Vs) [73].

2.5.2 TIPS-pentacene

The small molecule TIPS-pentacene (6,13-bis(triisopropylsilylethynyl)pentacene) is a p-type semiconductor with a HOMO level (ionisation potential) at 5.30 eV and LUMO level (electron affinity) at 3.5 eV, meaning its majority charge carriers are holes [74]. It has bulky triisopropylsilyl functional groups at the 6 and 13 position of the pentacene molecule that disrupts edge-to-face molecular interactions and herringbone packing [75].
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Figure 2.9: Skeletal formula for TIPS-Pentacene (C_{44}H_{54}Si_{2}).

Instead, according to X-ray diffraction experiments, TIPS-pentacene crystals tend to adopt a face-to-face packing structure that increase $\pi - \pi$ orbital overlap and reduce interplanar spacing of the aromatic rings compared to that of normal pentacene [76]. This particular arrangement is said to increase the charge carrier mobility in OFETs [1]. Thermal annealing tends to also improve the mobility but only up to a certain temperature $\sim 60^\circ$C; after which cracks and defects start to develop on the TIPS-Pentacene films that inhibit charge transport [77]. TIPS-pentacene has good solubility in common organic solvents and is resistant to oxidation in ambient conditions. But it is not very photo stable under UV radiation in thin films compared to pentacene [78]. Some researchers have attempted to address this issue by substituting the C-6 and C-13 positions of pentacene by ethynyl groups thereby leading to improved solubility and photo-oxidative stability [79]. Presence of impurities also drastically affects charge transport in TIPS-Pentacene. As shown by Jurchescu and coworkers, after purifying pentacene of quinone molecules, the mobility reached values as high as 35 cm$^2$/Vs at room temperature [80]. A survey of the literature reveals that different solution processing techniques have yielded different maximum transistor hole mobilities for TIPS-pentacene over the years: spin coating (<0.2 cm$^2$/Vs) [81], drop casting (>1 cm$^2$/Vs) [82], ink-jet printing (0.24 cm$^2$/Vs) [83], zone casting (0.3 cm$^2$/Vs) [84], confined crystallisation by soft lithography (0.29 cm$^2$/Vs) [85], solution self assembly using azeotropic binary solvents (1.42 cm$^2$/Vs) [86], and solution shearing (4.6 cm$^2$/Vs) [87].

2.5.3 P3HT

P3HT (poly(3-hexylthiophene)) is a regioregular semiconducting polymer that is soluble in a wide variety of organic solvents [88]. Its HOMO and LUMO levels are at 4.9 eV and 2.7 eV respectively [64]. P3HT has 3-hexyl substituents in a thiophene ring with a high percentage of regioregular head to tail (HT) side chain arrangement which allows good $\pi - \pi$ stacking of the conjugated backbone [89].
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Figure 2.10: Skeletal formula for regioregular head-to-tail P3HT \((C_{10}H_{14}S)_n\).

High mobilities comparable to that of amorphous silicon of up to 0.3 \(\text{cm}^2/\text{Vs}\) have been recorded when the P3HT chains self organise in a lamellar like morphology in an edge-on orientation normal to the substrate [52][53][54]. P3HT is capable of ambipolar transport of both holes and electrons [90] and has found a wide number of applications in photovoltaics [91] and flexible large area OFETs [92]. Due to its very weak emissive character in thin films caused by quenching by nonemissive excimer complexes, its use in OLEDs however have been limited [93][94]. Numerous studies over the years have shown that charge transport in P3HT tends to increase with molecular ordering and crystallinity which are influenced by molecular weight [95], synthetic manipulation of the side chains [96][97], solvent boiling point [53], film thickness [98], SAM treatment [99], and annealing [54]. However, P3HT exhibits very poor stability in ambient due to doping by \(O_2\) molecules and \(H_2O\) adsorption. This greatly reduces charge carrier mobility, fluorescence, and on/off ratios which make them impractical for long term ambient usage [100][101]. Hence for this reason, P3HT devices are normally prepared and measured in inert environments such as \(N_2\) and methods such as encapsulation [102][103] or improving the molecular ordering by reducing pin hole trap states in the morphology are pursued to increase device performance and stability [104]. A survey of the literature of various processing techniques for P3HT generally shows mobility independence in transistor devices, implying that high mobilities can be achieved with any method with proper optimisation: spin coating (0.1 \(\text{cm}^2/\text{Vs}\)) [53], dip coating (0.2 \(\text{cm}^2/\text{Vs}\)) [105], drop casting (0.01 \(\text{cm}^2/\text{Vs}\)) [106], inkjet printing (0.09 \(\text{cm}^2/\text{Vs}\)) [107], gravure printing (0.04 \(\text{cm}^2/\text{Vs}\)) [108], and confined crystallisation by soft lithography (0.03 \(\text{cm}^2/\text{Vs}\)) [85].

2.6 Soft lithography

The primary microfabrication technique used in the semiconductor industry today is photolithography. However, current state-of-the art photolithography techniques employed in fabricating sub-micron devices have very high capital and operating costs coupled with extremely lengthy manufacturing times of upto several weeks; all
of which normally drive up the price of high performance processor chips being sold in the market. Furthermore, the resolution and minimum feature size obtained using photolithography is inherently limited by the wavelength of light used in accordance with the Rayleigh equation. This often requires complicated and expensive optical equipment to be developed such as the use of UV excimer lasers to overcome the diffraction limitations and achieve patterning of sub-100 nm features and below [109]. Hence there is a strong economic argument to strive towards low cost, large area nanofabrication using unconventional methods. Soft lithography is one such method which we shall be focussing our attention to in later parts of this thesis [110].

Unconventional non-photolithographic techniques for molding, embossing and printing are divided into two categories: hard and soft lithography. Hard lithography uses hard stamp molding materials such as quartz and silicon. Patterned features on hard molds are defined by reactive ion etching, chemical etching and electron beam lithography. Hard lithographic based techniques offer the distinct advantage of good conformal contact with flat substrates with minimal deformations or collapsing of the mold’s patterned relief features. Mold materials such as silicon and quartz are chemically stable to thermal and photo curing techniques of polymer materials and commonly used organic solvents. Disadvantages include its fragility, and polymer residue and particulate build up after repeated usage which may require replacement. Although researchers have managed to reuse the hard molds more than 50 times [111]. The most commonly used hard lithographic technique are thermal nanoimprint lithography (NIL) [112] and ultraviolet nanoimprint lithography (UV-NIL) [113]. Both processes involve compressing the hard master on a prepolymer film, thermally annealing above the glass transition temperature ($T_g$) or photocuring the film, and allowing nanometre sized structures to form upon mold release. Over the years, NIL techniques have found a wide variety of applications such as photonics [114], biological microfluidics [115], OLEDs [116] and OFETs [117]. A more detailed overview on hard lithographic techniques are given in the review papers by Guo, Moonen, Kooy and coworkers [118][119][120].

Unlike photolithography, soft lithography is mainly a mechanical process which involves using an elastomeric stamp with prepatterned photoresist relief structures on it to mold, emboss or print its features onto another surface by bringing it to conformal contact. The advantages of soft lithography are several, some of them being its low cost [121], rapid fabrication times [122], application on large area non-planar and flexible substrates [123], and compatibility with a wide range of organic materials used in plastic electronics; which would normally be damaged during the UV exposure and chemical etching processes involved in photolithography [110].
2.6.1 Stamp materials

The thermally curable elastomeric polymer, polydimethylsiloxane (PDMS) with the Sylgard 184® curing agent is widely used in soft lithography research due to its low cost per kg, low toxicity, optical transparency above wavelengths of 300 nm and hydrophobicity [124][125]. Other elastomeric materials used are polyurethanes [126], polyimides [127], cross-linked Novolac resins [128] and photocurable fluoropolymers such as perfluoropolyether (PFPE) [129]. Structures as low as 50 nm have been patterned using PDMS stamps [130] and sub-20 nm for PFPE stamps [131].

Despite the popularity and low cost convenience of using PDMS as the elastomeric mold material, there are a couple of drawbacks. Due to the low modulus of ∼2 MPa the patterned feature size and aspect ratio is limited, hence it is difficult to achieve resolutions below 100 nm [132]. Its surface energy is also not low enough (∼25 mN/m [129]) to achieve high fidelity, high density features [133]. Furthermore, since PDMS has to be thermally cured at fairly high temperatures of ∼100°C and above, this could result in unwanted thermal expansion, stress, and deformation of the hard master’s resist features. PDMS also tends to swell in common non-polar organic solvents such as toluene, chlorobenzene, xylene, ethanol and propanol, which makes it challenging to accurately print and emboss high resolution, high density features without deformation due to swelling occurring [134]. Attempts have been made to address the low resolution, swelling and thermal expansion issues by synthesing artificial variants of PDMS through the use of photocurable cross linkers, thereby achieving Young’s modulus as high as 9 MPa [135][136].

The class of photocurable perfluoropolyethers (PFPE) for soft lithography use is an attractive alternative. The fluoropolymer is cross linked (cured) under ultraviolet light in the presence of a curing agent to yield elastomeric stamp materials of very low surface energies (11 – 15 mN/m) [137], low toxicity [138], high hydrophobicity [139], and high Young’s modulus such as ∼4 MPa for Fomblin MD 40 PFPE [140] and 25 – 50 MPa for Fluorolink MD 700 PFPE [141]. Unlike PDMS, PFPEs are resistant to swelling in most organic solvents, which makes it an attractive choice for use in organic electronics [140]. Disadvantages of using PFPE as the stamp material are that it is somewhat brittle due to its high modulus [131][142], requires the use of an inert gas environment for the UV curing process [143], and has a very low viscosity in the range 20 – 30 cST [144], which may make it difficult to apply it in small volumes for spin coating purposes. Furthermore, the same stamp deformation and collapse phenomenon could occur if stamp feature size is not optimally chosen [137].
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2.6.2 Common procedures

In the 1990s, George M. Whitesides’ research group and coworkers established four distinct procedures for soft lithography: Replica Molding (REM) [145], Microtransfer Molding (µTM) [146], Micromolding in Capillaries (MIMIC) [147] and Solvent Assisted Micromolding in Capillaries (SAMIM) [148]. Over the years, continuous innovative advancements of these procedures have been developed in order to satisfy the growing need for complex, high fidelity and high resolution patternable features in the nanoscale. Some promising techniques are nanotransfer printing (nTP) [149], decal transfer microlithography (DTM) [150], nanoskiving [151], capillary force lithography (CFL) [152] and liquid-bridge-mediated nanotransfer molding (LB-nTM) [153]. We will provide a brief overview of some of the primary methods used in soft lithography in this section.

2.6.2.1 Replica Molding (REM)

Replica molding is normally the first step involved in stamp fabrication. As shown in Figure 2.11, the process involves fabricating a hard master (normally silicon) with patterned photoresist relief features defined by traditional photolithographic techniques. Then, a liquid elastomer is poured on to the hard master and subsequently cured. This finally leaves behind a solidified elastomer with a negative imprint of the relief features from the hard master [145]. REM’s primary advantages are that it can be used to replicate large area stamps and produce multiple copies of patterned stamp molds with consistent resolution from just one hard master, although this largely depends on the durability and chemical stability of the hard master relief features [124]. Features as low as 1.5 – 3 nm have been imprinted onto stamps via REM [154][155]. Although the smallest resolution achievable depends on the elastomer’s Young’s modulus; the theoretical lower limit being defined by the van der Waals interactions at around 0.5 nm [110]. Overall, the REM process reduces both overall cost and fabrication time for patterning elastomeric stamps for use in a wide variety of applications.
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2.6.2.2 Microcontact printing (µCP)

Microcontact printing is used to selectively pattern solutions (or inks) based on silane and thiol based self assembled monolayers (SAM) onto substrates [156]. The process itself is rather simple and illustrated in Figure 2.12. The patterned stamp mold is first coated with a SAM solution. The stamp is then brought into conformal contact to a substrate and then removed, revealing patterned SAM features as per the topography of the stamp. It was initially used to pattern SAMs on metal surfaces such as Au in order to selectively etch it [157]. Its use has also been extended to selectively grow organic semiconductor crystals such as pentacene, rubrene and C_{60} on the patterned SAM regions for OFET applications, [158] and also fabricate large area active matrix OLED displays on flexible plastic substrates [159].

Over the years, µCP has evolved into the technique known as nanotransfer printing (nTP) [160] [161]. The process of nTP is similar to µCP, except the patterned stamp material is first coated with metals such as Au and then brought into conformal contact with a substrate coated with SAMs. Upon stamp lift off and removal, the metal remains in place in the patterned regions being covalently bonded.
into place with the underlying SAM end groups [162]. nTP has the advantage of not requiring chemical etching techniques to selectively pattern metals [110] and is also capable of producing complex metallic structures over large areas in the nanoscale on a variety of substrates [163]. However, there are issues in the morphology of the patterned metal structures. Mainly, the metal films tend to crack on the stamp material from thermal expansion during the thermal evaporation procedure, leading to a more rougher surface morphology [162]. Researchers have suggested faster metal deposition rates and cooling of the stamp as potential solutions to address this issue [110][161].

2.6.2.3 Microtransfer Molding (µTM)

As shown in Figure 2.13, in µTM, the stamp is first created using the process dictated by REM. Then, a liquid prepolymer is applied on to the recesses of the stamp’s patterned features until they are filled. Excess liquid is scraped off by a separate PDMS block or blown off with a stream of N₂. The filled stamp mold is then inverted, placed into contact with a substrate and subsequently cured. After solidification of the polymer, the stamp mold is then carefully peeled off leaving behind positive patterned structures on the substrate. µTM allows rapid prototyping of microstructures over large areas and both inorganic and organic precursors have been used to pattern on a variety of substrates such as Au, Si/SiO₂ and glass [146].

Figure 2.13: Illustration of the µTM process flow: (a) application of prepolymer solution into recesses of stamp, (b) removal of excess solution, (c) conformal contact of stamp with substrate, and (d) removal of stamp.

It also has the advantage of patterning both isolated and interconnected microstructures. However, the µTM process often leaves behind a ~100 nm residue layer between the patterned structures which requires plasma etching in O₂ to remove. Over the years, µTM has also been extended by researchers to pattern structures in the nanoscale regimes, conveniently called nanotransfer molding (nTM). Researchers have used nTM to fabricate superhydrophobic surfaces [164], optical polarisers [165], active matrix OLED displays [166], and even large area OFETs with sub-100 nm patterned features of TIPS-Pentacene and Zinc Tin Oxide [153].
2.6.2.4 Micromolding in Capillaries (MIMIC)

For MIMIC, the stamp mold has to be first patterned with an interconnecting network of trenches (or capillary channels) by REM. As illustrated in Figure 2.14, the stamp is then brought into conformal contact with the substrate ensuring the capillaries have openings at either ends of the stamp: the inlet is defined as the entrance of the capillary where the solution is applied, and the outlet is an opening at the other end of the stamp to allow the solution to evaporate. Organic semiconductor solution (or a prepolymer) is then injected or directly applied into/near these capillaries allowing it to fill the channels via capillary forces. After the channels have been filled, the OSC solution is allowed to crystallise over a period of time related to the evaporation rate of the solvent used. Upon crystallisation, the stamp is then carefully peeled off from the substrate leaving behind the patterned features [147].

![Figure 2.14: Illustration of the MIMIC process flow: (a) conformal contact of patterned stamp with substrate, (b) application of organic semiconductor (OSC) solution near capillary inlets of stamp, (c) movement of solution through stamp capillaries via capillary forces, and (d) removal of stamp upon crystallisation of solution.](image)

The rate of filling depends on the surface tension and viscosity of the liquid solution, dimensions of the capillary, and the surface energy of the substrate. As such, the rate of filling can be increased if a less viscous liquid with a low surface tension is used. However, the rate of filling also decreases considerably over long capillary distances (> 1 cm) due to the viscous drag of the liquid as it advances and builds up through the capillary, hence potentially causing incomplete filling of the channels [167]. This limits its usage for large area applications. Furthermore, due to the requirement of a continuous network of capillaries to pattern and crystallise the solution, MIMIC is unfortunately incapable of patterning isolated structures [156].

2.6.2.5 Solvent Assisted Micromolding in Capillaries (SAMIM)

SAMIM is an embossing technique which uses patterned stamps fabricated by REM to imprint features on to a substrate. Depending on stamp durability and chemical resiliency, SAMIM has the distinct advantage of replicating patterned features on numerous substrates with just one mold [148]. First, a thin film is spin coated
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from a prepolymer or organic semiconductor solution on a substrate to a thickness lower than the recesses of the patterned stamp. The relief features of the patterned stamp are soaked with a solvent that will dissolve the thin film when brought into conformal contact. The thin film dissolves in the solvent and conforms to the surface topology of the stamp mold. The solvent evaporates via diffusion through the mold, or adsorption on the surface of the stamp due to the surface energy gradient between stamp and solution, thereby leaving behind patterned structures on the substrate [168]. To allow good patterning, the solvent used must ideally have a high vapour pressure and relatively high surface tension so that it evaporates quickly and does not swell the stamp material. In some cases, researchers have skipped the first step involving spin coating the thin film and instead, directly applied the organic semiconductor solution onto the substrate before proceeding to stamp conformal contact [152]. This is illustrated in Figure 2.15.

Figure 2.15: Illustration of the modified SAMIM process flow: (a) application of organic semiconductor solution on substrate, (b) conformal contact with a substrate allows the solution to fill into the recesses of the stamp, and (c) removal of stamp after crystallisation.

References

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Chapter 3

Materials and experimental techniques

3.1 Introduction

Organic field effect transistor (OFET) fabrication was carried out in an ISO Class 6 (class 1000) cleanroom at Imperial College London. The cleanroom was fitted with yellow lightning in order to minimise unwanted exposure to UV-sensitive samples such as photoresist, enabling the cleanroom to be used for photolithography. Commonly used device fabrication equipment in the cleanroom were:

- Spin coaters by Laurell technologies corporation model WS-650 MZ-23NPP / WS-650 SZ-6NPP/LITE
- Stuart digital SD160 hotplates
- IKA RCT basic magnetic stirrer
- Emitech K1050X plasma asher
- ELC500 light exposure system (electro lite corporation)
- Karl Suss Mask Aligner MJB-3
- Monobloc AB54-S weighing scales
- Decon FS-100B ultrasonicator

An MBraun MB200B glovebox with an inert N\textsubscript{2} environment was primarily used for thermal evaporation and electrical characterisation purposes. Contaminants such as H\textsubscript{2}O and O\textsubscript{2} were generally kept below 0.1 ppm inside the glovebox. Taking into the consideration of a typical OFET design, different materials had to be chosen...
separately for each component: organic semiconductor, substrate, dielectric, source, drain and gate electrodes. These were purchased from various suppliers as per availability.

3.2 Materials

3.2.1 Organic semiconductors

TIPS-Pentacene was acquired from Ossila Ltd (United Kingdom), F8T2 with a Mw $> 20,000$ g/mol was acquired from Luminescence Technology Corp (LumTec, Taiwan) and $>95\%$ regioregular (RR) P3HT with a Mw of $\sim 67,000$ g/mol was acquired from BASF (Germany). All of these were p-type organic semiconductors (OSCs) with holes as the majority charge carriers. Table 3.1 summarises a few important properties of these materials, including the ionisation potential (corresponding to the HOMO level), which are important when choosing the type of material for the source/drain electrode in order to facilitate efficient charge injection with minimal energetic barriers.

The mentioned organic semiconductors were dissolved in a variety of solvents at different concentrations depending on the purpose of application. Anhydrous solvents (with $\sim 99\%$ purity) such as isopropyl alcohol, acetone, hexane, xylene, toluene, anisole, chlorobenzene, 1,2-dichlorobenzene, tetralin and dodecane were provided by Sigma Aldrich or VWR. Deionised water was supplied by the Cleanroom. Organic semiconductors were weighed using a Monobloc AB54-S weighing scale to estimate the appropriate volume of solvent required to achieve the desired concentration. TIPS-Pentacene was dissolved in concentrations between 1 - 4 wt%, while F8T2 and P3HT were dissolved between 0.5 - 1 wt%. Solutions were generally stirred or heated until dissolution on an IKA RCT basic magnetic hotplate stirrer at 70°C for 24 hours before use.

<table>
<thead>
<tr>
<th>Material</th>
<th>Classification</th>
<th>Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>HOMO (eV)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS</td>
<td>Small molecule</td>
<td>$C_{44}H_{54}Si_2$</td>
<td>639.07</td>
<td>5.30 [1]</td>
<td>Ossila</td>
</tr>
<tr>
<td>F8T2</td>
<td>Polymer</td>
<td>$(C_{37}H_{44}S_{2})_n$</td>
<td>$&gt;20,000$</td>
<td>5.55 [2]</td>
<td>LumTec</td>
</tr>
<tr>
<td>P3HT</td>
<td>Polymer</td>
<td>$(C_{10}H_{14}S)_n$</td>
<td>$\sim 67,000$</td>
<td>4.86 [2]</td>
<td>BASF</td>
</tr>
</tbody>
</table>

Table 3.1: Organic semiconductors used and some important properties.
3.2.2 Substrates

Prefabricated n-doped silicon bottom gate, bottom contact (BGBC) OFETs with 30 nm gold (Au) source/drain electrodes treated with a high work function 10 nm indium tin oxide (ITO) adhesion layer underneath, and 230 nm SiO$_2$ dielectric were purchased from Fraunhofer IPMS (Germany). These were 15×15 mm$^2$ in size. Each chip had 16 transistors with constant channel width ($W$) of 10,000 µm and 4 identical transistors for channel lengths ($L$) 20, 10, 5 and 2.5 µm respectively (see Figure 3.1(a)).

![Figure 3.1: Optical micrograph of a stand-alone BGBC Fraunhofer IPMS OFET with $L = 20$ µm and $W = 10,000$ µm (a). Top view CAD designs of a (b) BGTC OFET with rectangular arrays of source and drain contacts with $L = 50$ µm and $W = 2000$ µm, (c) and TGB-C OFET with $L = 50$ µm and $W = 2000$ µm.]

n-doped (phosphorus) silicon (Si) wafers with thickness 500 – 550 µm, orientation $< 100 >$, resistivity 0.007 – 0.03 Ωcm, and a pre-grown 230 nm SiO$_2$ dielectric were purchased from Mi-Net Ltd (United Kingdom). These were mainly used for bottom gate, top contact (BGTC) OFET architectures with rectangular source and drain contacts with $L = 50$ µm and $W = 2000$ µm (see Figure 3.1(b)). This was done so that during thermal evaporation of the contacts, the large area would maximise the chances of depositing on top of patterned organic semiconductors using soft lithography (See Chapter 6)

Plain glass substrates with 1.1 mm thickness were purchased from Luminescence Technology Corp and were used in top gate bottom contact (TGB-C) OFET architectures with $L = 50$ µm and $W = 2000$ µm (see Figure 3.1(c)).

3.2.3 Dielectrics

Aside from the inorganic SiO$_2$ dielectric, two polymer dielectrics were used: Poly(4-vinylphenol) (PVP) and the hydrophobic perfluorinated polymer CYTOP$^\text{TM}$ in TGB-C architectures. PVP with a Mw $\sim$25,000 g/mol was acquired from Sigma-Aldrich (United Kingdom). CYTOP version CTL-809M was acquired from Asahi Glass Co. (Japan).
PVP was dissolved in isopropyl alcohol (IPA) at a concentration of 8 wt% and rigorously stirred at 800 rpm on a IKA RCT basic magnetic hotplate stirrer at 70°C for 24 hours before use. No post-annealing of PVP films was attempted. CYTOP on the other hand, was used as provided and was thermally cross-linked at 120°C for 10 mins in ambient. Spin coaters by Laurell technologies corporation model WS-650 MZ-23NPP / WS-650 SZ-6NPP/LITE were used to deposit thin films. Both PVP and CYTOP were spin coated in two steps: one initial ramp up step at 500 rpm for 10 seconds in order to spread the solution around the substrate, and a final step between 500 – 4000 rpm for 60 seconds. 2D film thickness and root mean squared (RMS) surface roughness for at least 3–4 repeat films were measured using Tencor Instruments Alphastep 200 and/or Bruker Dektak XT profilometers in ambient. Table 3.2 displays relevant properties for the dielectrics used.

Table 3.2: Dielectrics used and important properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Classification</th>
<th>Dielectric constant ($\varepsilon_r$)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Inorganic</td>
<td>3.9</td>
<td>Fraunhofer IPS, Mi-Net</td>
</tr>
<tr>
<td>PVP</td>
<td>Organic</td>
<td>3.6 - 5.7 [3][4][5]</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>CYTOP$^\text{TM}$</td>
<td>Organic</td>
<td>2.1 - 2.2 [6][7][8]</td>
<td>Asahi Glass Co.</td>
</tr>
</tbody>
</table>

3.2.4 Gate, Source and Drain Electrodes

When Si substrates were used for BGBC and BGTC devices, the n-doped Si layer was directly used as the conductive gate electrode. Gold (Au) pellets (1/8” diameter × 1/8” long, 99.99% purity) and Chromium (Cr) plated tungsten rods (2” long × 0.050” diameter, 99.9% purity) were purchased from Kurt J. Lesker Ltd (United Kingdom). Aluminium (Al) pellets (1/8” diameter × 1/8” long, 99.99% purity) were readily available in the glovebox for public use and were also obtained from Kurt J. Lesker Ltd. These were deposited using thermal evaporation through custom made shadow mask design which patterned gate, source, drain and/or capacitor electrodes. Au was used due to its high work function (∼5 eV [9][2]) and compatibility with p-type organic semiconductors used in this thesis. A 1.5 nm Cr layer was used as an adhesion layer on glass substrates before Au deposition for TGBC devices. Al was evaporated as contacts for capacitor structures for impedance measurement.
3.2.5 Curable polymers

For stamps prepared using soft lithography, two curable polymers were used: Poly(dimethylsiloxane) (PDMS) and Solvay Solexis Fluorolink® MD 700 bifunctional perfluoropolyether-urethane methacrylate (PFPE). PDMS was obtained in a standard DOW Corning® Sylgard® 184 kit from Univar Specialty Consumables (United Kingdom). Fluorolink® MD 700 PFPE was purchased from Acota Ltd (United Kingdom). The photocuring agent for PFPE, 2-Hydroxy-2-methylpropiophenone (Darocur 1173), was purchased separately from Sigma-Aldrich.

3.2.6 Photoresists

MicroChem SU-8 2002, SU-8 2005 negative photoresists and SU-8 developer were supplied by A-Gas Electronic Materials Ltd (United Kingdom). The positive photoresist Microposit™ S1813 G2 and MF-26A developer was used as provided by the Imperial College’s Cleanroom facility. These photoresists were mainly used to fabricate hard master templates for soft lithography.

3.2.7 Self-Assembled Monolayers (SAMs)

Where appropriate, SAMs were used in order to modify and lower the surface energy and/or work function of materials. Hexamethyldisilazane (HMDS) (C₆H₁₉NSi₂) and octadecyltrichlorosilane (OTS) (C₁₈H₃₇Cl₃Si) were purchased from Sigma-Aldrich. OTS and HMDS were used to lower the surface energy of Si/SiO₂ and/or glass substrates.

3.2.8 Summary of materials

In conclusion, all materials used in this thesis are summarised in Table 3.3.
### Table 3.3: Summary of materials used in this thesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Use</th>
<th>Preparation method</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS-Pentacene</td>
<td>OSC</td>
<td>Soft lithography</td>
<td>Ossila</td>
</tr>
<tr>
<td>F8T2</td>
<td>OSC</td>
<td>Spin coating, soft lithography</td>
<td>LumTec</td>
</tr>
<tr>
<td>P3HT</td>
<td>OSC</td>
<td>Spin coating, soft lithography</td>
<td>BASF</td>
</tr>
<tr>
<td>Si with 230 nm SiO₂</td>
<td>substrate, dielectric, gate</td>
<td>Used as provided</td>
<td>Mi-Net, Fraunhofer IPMS</td>
</tr>
<tr>
<td>Glass (20x20x)</td>
<td>substrate</td>
<td>Used as provided</td>
<td>LumTec</td>
</tr>
<tr>
<td>PVP</td>
<td>dielectric</td>
<td>spin coating</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>CYTOP™</td>
<td>dielectric</td>
<td>spin coating</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>gate, source, drain ...</td>
<td>thermal evaporation</td>
<td>Kurt J. Lesker</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>adhesion layer</td>
<td>thermal evaporation</td>
<td>Kurt J. Lesker</td>
</tr>
<tr>
<td>Aluminium (Al)</td>
<td>capacitor contacts</td>
<td>thermal evaporation</td>
<td>Kurt J. Lesker</td>
</tr>
<tr>
<td>HMDS</td>
<td>SAMs</td>
<td>spin coating</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>OTS</td>
<td>SAMs</td>
<td>solution immersion</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>DOW Corning® Sylgard®</td>
<td>patterned stamp mold</td>
<td>thermal curing</td>
<td>Univar Speciality Consumables</td>
</tr>
<tr>
<td>184 PDMS kit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorolink® MD 700</td>
<td>patterned stamp mold</td>
<td>UV curing</td>
<td>Acota Ltd</td>
</tr>
<tr>
<td>PFPE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Darocur 1173</td>
<td>curing agent</td>
<td>Used as provided</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>SU-8 2002/2005</td>
<td>negative photoresist</td>
<td>photolithography</td>
<td>A-Gas Electronic Materials</td>
</tr>
<tr>
<td>SU-8 developer</td>
<td>negative developer</td>
<td>photolithography</td>
<td>A-Gas Electronic Materials</td>
</tr>
<tr>
<td>S1813 G2</td>
<td>positive photoresist</td>
<td>photolithography</td>
<td>Cleanroom</td>
</tr>
<tr>
<td>MF-26A</td>
<td>positive developer</td>
<td>photolithography</td>
<td>Cleanroom</td>
</tr>
</tbody>
</table>
3.3 Methods

3.3.1 Transistor characterisation

An Agilent B2902A Parameter analyser unit was used for DC characterisation of OFET devices in an MBraun MB200B glovebox with an inert \( N_2 \) environment (\( H_2O < 0.1 \) ppm and \( O_2 < 0.1 \) ppm). Probe tips were either 1 mm diameter gold or copper needles which were fabricated inhouse and were connected to the source measure unit (SMU) sockets of the Agilent B2902A via triaxial cabling. The source electrode was connected to ground in the low force SMU, while the gate and drain electrodes were connected to high force SMUs where a voltage bias could be applied. The Quick IV Measurement software package supplied by the Agilent B2902A unit was used to acquire and collect the data measured. During measurement, the source electrode was kept at \( V_S = 0 \) V and the drain (to source) current \( I_D \) and gate (to source) current \( I_G \) were recorded simultaneously. Figure 3.2 displays an illustration of the experimental setup.

**Figure 3.2:** Experimental setup of the B2902 parameter analyser to measure OFET characteristics.

Output characteristics were measured by sweeping the drain (to source) voltage \( V_D \) from 20 V to -60 V in steps of -3.33 V at constant gate (to source) voltage \( V_G \) from 0 to -60 V in steps of -10 V. Transfer characteristics were measured by taking forward and reverse scans of the current by sweeping the gate voltage \( V_G \) from 20 V to -60 V (and -60 V to 20 V) in steps of -3.33 V at constant drain voltages \( V_D \) of -10 V and -60 V, which corresponded to the set linear and saturation regimes respectively for all the OFETs measured in this thesis.

Parameters such as mobility, threshold voltage, on/off ratio, subthreshold slope,
hysteresis, drain current, and leakage current were extracted from the transfer characteristics based on the equations and procedures described in Chapter 2.3.3, and reported according to the IEEE Standard Test Methods for the Characterization of Organic Transistors and Materials [10].

### 3.3.1.1 Modelling of transistor characteristics

Equations 2.11 and 2.12 from Chapter 2.2.6 were used to fit the linear and saturation regimes of OFET transfer characteristics. Non-linear least squares fitting was performed using the Gauss-Newton algorithm [11], and the modelling routine involved two main steps:

1. Determination of $T_0$ at room temperature $T = 300K$ by fitting to Equation 2.11 for $m$, $\rho$ and $V_{le}(lin)$ using the $\mu_{lin}$ determined from the linear regime of the experimental transfer characteristics at $V_D = -10V$.

2. Determination of $\mu_{sat}$ by using the results obtained from the linear fits as constants, fitted to Equation 2.12 for the saturation regime at $V_D = -60V$.

Sample code of the implementation is provided in Appendix C.

### 3.3.2 Photoluminescence Quantum Efficiency

![Figure 3.3](image-url)

**Figure 3.3:** Setup for measuring PLQE using an integrating sphere with (a) no sample, (b) unaligned sample, and (c) aligned sample facing the excitation beam.

As illustrated in Figure 3.3, PLQE was measured using an integrating sphere attached to the sample compartment position of a Jobin Yvon Horiba FluoroMax-3 spectrofluorometer. The method described by de Mello and coworkers [12] was followed to estimate PLQE by measuring the area under the emission spectra, which gave an estimate of the total number of absorbed and emitted photons. This involved three main steps:
a) **No sample**: Measurement of the maximum peak intensity at excitation wavelength $x$ between $x - 50$ nm $< x < x + 50$ nm with no sample in the integrating sphere.

b) **Unaligned sample**: Measurement of the PL intensity between wavelengths $x - 50$ nm to 700 nm with the sample not in line with the excitation beam and placed at the bottom of the integrating sphere.

c) **Aligned sample**: Measurement of the PL intensity between wavelengths $x - 50$ nm to 700 nm with the sample aligned facing the excitation beam inside the integrating sphere.

The external PLQE $\eta$ can be approximated using the following equation:

$$\eta = \frac{\text{photon intensity emitted}}{\text{photon intensity absorbed}}$$

(3.1)

From Figure 3.3(b) for the unaligned sample, a fraction $\mu$ of laser light scattered from the sphere wall is absorbed by the sample. For the aligned sample in Figure 3.3(c), the laser strikes the sample first, and then a fraction $A$ of this light is absorbed by the sample. Consequently, a fraction $(1 - A)$ will either be transmitted or reflected. de Mello then assumed that the area under the emission intensity profile at the excitation peak wavelength was proportional to the amount of unabsorbed light $L$ ($L_a$, $L_b$ and $L_c$ respectively for no sample, unaligned and aligned samples), and the area under the emission profiles due to the sample was proportional to the amount of emitted light $P$ ($P_a$, $P_b$ and $P_c$ respectively for no sample, unaligned and aligned samples). Assuming an absorption coefficient following $A = (1 - \frac{L_c}{L_b})$, de Mello subsequently derived the follow equation for the PLQE $\eta$:

$$\eta = \frac{P_c - (1 - A)P_b}{L_aA}$$

(3.2)

Areas under the emission profile were integrated using the trapezium rule in Python 3.6.

### 3.3.3 Contact angle and surface energy

Contact angle and surface energy measurements were taken using a Kruss DSA100 Goniometer. Static water contact angles were measured by depositing 2–5 $\mu$L sessile drops on a solid surface which involved a variety of surfaces such glass, SiO$_2$, SAM treated surfaces and elastomeric polymers such as PDMS and PFPE. The sessile drop measurement was illuminated from one side and a camera on the opposite side captured the image which can be analysed real time or statically with the Kruss DSA software. After establishing a baseline of the droplet with respect to the surface,
the contact angle was deduced using the fitting tools provided by the DSA software [13]:

- **Circle method** involves fitting the droplet to a segment of a circle. This was applied for contact angles up to 20°

- **Tangent method** involves fitting a polynomial equation directly at the three phase contact point. This was applied for contact angles above 20°

![Figure 3.4: Illustration of sessile drop (a) and pendant drop (b) measurement.](image)

For the sessile drop, contact angle $\theta_c$, surface energies between solid-liquid $\gamma_{SL}$, solid-vapour $\gamma_{SV}$ and liquid-vapour $\gamma_{LV}$ are shown following Young’s equation [14]. For the pendant drop, $d_s$ is an arbitrary selected plane on the drop taken as a distance from the base of the droplet equal to the equatorial diameter $d_e$.

The surface energy of various solid surfaces were determined by measuring the contact angle of two or three reference liquids with known overall, dispersive and polar components of the surface tension: deionised water ($\gamma_L = 72.8$ mN/m, $\gamma_D = 26.4$ mN/m, $\gamma_P = 46.4$ mN/m), diiodomethane ($\gamma_L = 50.8$ mN/m, $\gamma_D = 50.8$ mN/m, $\gamma_P = 0$ mN/m) and ethylene glycol ($\gamma_L = 47.7$ mN/m, $\gamma_D = 26.4$ mN/m, $\gamma_P = 21.3$ mN/m) [15][16][17]. The equation developed by Owens, Wendt, Rabel and Kaelble (OWRK) was used to fit the data to a linear equation using the DSA software

$$\frac{\gamma_L(1 + \cos \theta)}{2 \sqrt{\gamma_D^P}} = \sqrt{\gamma_S^P} \left( \sqrt{\frac{\gamma_L^P}{\gamma_D^P}} + \sqrt{\frac{\gamma_S^D}{\gamma_D^D}} \right)$$

where the slope $\sqrt{\gamma_S^P}$ and intercept $\sqrt{\gamma_S^D}$ can be used to calculate the polar and dispersive components of the solid surface free energy respectively [18][19]. The dispersive component accounts for non-site specific van der waal interactions between a surface with applied liquids, while the polar component accounts for dipole-dipole interactions due to different electronegativities in the molecules between a surface.
with applied liquids [14][20]. Finally, we can use the following equation to deduce the total solid surface energy $\gamma_S$ of the sample:

$$\gamma_S = \gamma_S^D + \gamma_S^P$$

(3.4)

On the other hand, the surface tension of liquids had to be calculated in two steps. The first step involved determining the overall liquid surface tension $\gamma_L$ via pendant drop analysis which was calculated automatically by the DSA software on a hanging droplet from a needle with diameter 1.85 mm using the Young-Laplace equation

$$\gamma_L = \frac{g d_e^2 \Delta \rho}{B}$$

(3.5)

where $\gamma_L$ is the total liquid surface tension, $g$ is the acceleration due to gravity, $\Delta \rho$ is the difference in density between air and the liquid, $d_e$ is the equatorial diameter of the droplet, and $B$ is a droplet shape parameter that is numerically determined. $B$ is related to the shape of the pendant droplet by $S$, defined as $S = \frac{d_s}{d_e}$ where $d_s$ is an arbitrary selected plane on the droplet taken as a distance from the base of the droplet equal to the equatorial diameter $d_e$ (see Figure 3.4) [21].

The second step involved measuring the liquid’s contact angle on a poly(tetrafluoroethylene) (PTFE) surface. PTFE is assumed to have a total surface energy of 18 – 22 mJ/m$^2$ with a near zero polar component [22][23]. Hence by equating $\gamma_S^P = 0$ and rearranging Equation 3.3 we get

$$\gamma_L^D = \left(\frac{\gamma_L \cos \theta_{PTFE} + 1}{2\sqrt{\gamma_S^D}}\right)^2$$

(3.6)

where $\theta_{PTFE}$ is the contact angle of the liquid on the PTFE surface. The polar liquid surface tension component $\gamma_L^P$ can be deduced by rearranging Equation 3.4. PTFE blocks were sonicated in IPA and deionised water for 2 mins, O$_2$ plasma ashed at 50 W for 2 mins and dehydrated on a hotplate at 120°C for 5 mins before use.

By converting Equation 3.3 into cylindrical polar coordinates with $\gamma_L^D = R \cos \phi$ and $\gamma_L^P = R \sin \phi$, the wettability envelope of solid surfaces at different contact angles $\theta$ can be calculated using the equation:

$$R = \frac{4 \left[ \sqrt{\gamma_S^D} \cos \phi + \sqrt{\gamma_S^P} \sin \phi \right]^2}{(1 + \sin 2\phi)(1 + \cos \theta)^2}$$

(3.7)

For complete wetting at $\theta = 0$, Equation 3.7 simplifies to:

$$R(\phi) = \frac{\left[ \sqrt{\gamma_S^D} \cos \phi + \sqrt{\gamma_S^P} \sin \phi \right]^2}{1 + \sin 2\phi}$$

(3.8)
3.3.4 Impedance spectroscopy

Aluminium (Al) parallel plate capacitors were made on glass substrates $20 \times 20 \text{ mm}^2$ in size using the following process flow:

- Evaporation of rectangular array of Al contacts on glass substrates
- Spin coating of the dielectric
- Curing or annealing of the dielectric
- Evaporation of rectangular array of Al contacts perpendicular to the previous layer

![Figure 3.5: Schematic of Al capacitors in the (a) side view, and (b) top view.](image)

The capacitance and dielectric constant of unknown dielectric materials were measured using a Solartron 1260 Impedance/Gain-Phase Analyser in a glovebox with an inert $N_2$ environment. This was connected via triaxial cabling to the same probe station used for OFETs except only two probe tips were used for applying an AC current and measuring the capacitance/impedance respectively. The gate probe was connected to the input terminal of the Solartron 1260 ($INPUT I (100 \text{ mV max})$ and $INPUT VI LO$ sockets), while the source probe was connected to the output terminal ($GEN OUTPUT 0.4\text{ V PEAK}$ and $INPUT VI HI$ sockets). The SMART software package supplied by Solartron was used to initialise the parameters for capacitor measurement. The capacitance $C$ and impedance $Z$ for both real and imaginary parts were measured at an alternating current (AC) level of 100 mV by sweeping the frequency from 1 MHz to 100 Hz, with step sizes of 5 – 10 points/decade and integration time of 0.5 – 1 seconds. The capacitance per unit area $C_i$ in $F/cm^2$ units was calculated at a fixed frequency depending on the dielectric by using the following equation

$$C_i = \frac{1}{A2\pi fZ''} \quad (3.9)$$
where $A$ is the area of the parallel plate capacitor, $f$ is the frequency and $Z''$ is the imaginary component of the total impedance in the circuit. For an ideal capacitor, the impedance will have a phase angle of $-90^\circ$ hence this was plotted against frequency in order to verify whether capacitance was being measured [24]. The phase angle of the capacitor is given by

$$\phi = \tan^{-1}(Z''/Z')$$  \hspace{1cm} (3.10)

where the real component $Z'$ is the resistance in the circuit due to any intrinsic resistors, and the imaginary component $Z''$ is the resistance due to the opposition of current flow in the capacitor (the reactance).

Upon the deduction of the capacitance, the dielectric $\varepsilon_r$ was then deduced using the standard equation for parallel plate capacitance

$$C_i = \frac{\varepsilon_0 \varepsilon_r}{d}$$  \hspace{1cm} (3.11)

where $\varepsilon_0 = 8.85 \times 10^{-12} \text{F/m}$ and is the permittivity of free space and $d$ is the thickness of the dielectric.

### 3.3.5 Grazing Incidence Wide Angle X-ray Scattering

Grazing incidence wide angle x-ray scattering (GIWAXS) is a useful tool in probing the molecular packing structure of amorphous and crystalline organic semiconductors [25][26]. Thin films are poor scatterers of X-rays due to disorder and finite quantity of available scattering planes which results in weak diffraction peaks using conventional X-ray diffractometers [27]. Hence synchrotron sources are used to probe diffraction over a larger angular range and at higher resolution [28]. Figure 3.6 displays a basic setup of the GIWAXS measurement. A monochromatic X-ray beam is directed at very small incident angle onto a sample. This beam is then diffracted at various sets of planes defined by the unit cell of the sample. The momentum transfer (scattering vector) due to these various diffracted planes $q$ is then detected on a 2D detector. The intensity of the scattering sites depends on the electron density at the planes where the x-rays are being diffracted. Information such as lattice constants, lamellar and $\pi-\pi$ stacking distances and molecular orientation (indicating degree of crystallinity) can be deduced from the GIWAXS data [29][30].
Figure 3.6: Setup for measuring GIWAXS where $k_i$ and $k_f$ are the incident and scattered beams respectively, $\alpha$ and $\beta$ are the incident and scattered beam angles, $2\theta$ is the angle of the diffracted beam, and $q$ is the scattering vector in the $y$ and $z$ directions. Partly adapted from Ref [31].

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) of samples were investigated by Warren Stevenson (University of Sheffield) on station I16 of the Diamond Light Source in the United Kingdom. The samples were positioned on the surface of a custom-made six circle goniometer. A helium filled flight tube was positioned between the sample and a Pilatus 2M Dectris area detector to reduce background scattering due to air. The incident photon energy was set at 14 keV and measurements were taken at room temperature.

3.4 Experimental processes

3.4.1 Substrate preparation

Before any experimental processes were carried out, Si and/or glass substrates were always thoroughly cleaned before fabrication in order to minimise surface contaminants. The standard cleaning protocols generally involved rigorous ultrasonication in acetone, IPA and deionised water baths for 5 mins each. The substrates were then placed on a hotplate for dehydration at 120°C for 10 mins. After this, the substrates were placed in an Emitech K1050X plasma asher where $O_2$ plasma was applied at 80 W for 2 mins with a 20 second $O_2$ pumping time before ionisation. This was the final cleaning step before device fabrication unless SAM treatment was applied afterwards.
3.4.2 Optical microscopy

A Zeiss Axioplan Microscope was used to observe non-polarised and polarised optical micrographs at 2.5 – 50X magnification. The ProgRes capturePro 2.8.8 software was used to capture and analyse the micrographs. Polarised microscopy was used to identify anisotropic materials that exhibited birefringent light scattering. This shows up as a colour contrast with respect to a dark background that is characteristic of crystalline structures. Isotropic materials however show no contrast and appear dark.

3.4.3 Surface profilometry

Film thickness and roughness were measured using Tencor Instruments Alphastep 200 and Bruker Dektak XT profilometers. Where applicable, scratches were made on the surface of the film using a sharp needle before the substrate was placed on the profilometer loading stage. Distances between 100 – 2000 µm were measured with scan speeds of 10 – 200 µm/s. Due to minor inclinations of the substrate on the loading stage, the final thickness profile was levelled to zero with respect to flat scans before outputting the data.

3.4.4 Atomic force microscopy (AFM)

Surface topography of thin films were conducted using a Bruker Dimension Icon AFM. The AFM data was acquired by Muhammad Kamaludin (University College London). This AFM had a standard silicon cantilever and all measurements were taken in tapping mode with the settings: force constant ∼40 N/m, resonant frequency ∼300 kHz and an AFM tip radius of ∼8 nm (as per the manufacturer). Scans were taken over an area of 2×2 µm² on the surface of the thin film, which corresponded to a resolution of 128×128 pixels². The scan speed was set at 0.750 Hz which was 3 µm/s for each line. The open source software package Gwyddion was used to analyse and edit AFM images.

3.4.5 Absorption spectroscopy

A Shimadzu UV-2550 spectrophotometer with a 50 W halogen and deuterium lamp source was used to perform ultra violet and visible (UV-vis) absorption spectroscopy in the wavelength range 190 – 900 nm. A beam of light from the halogen or deuterium light source is collimated through a monochromator so that one wavelength at a time could reach the detector and its intensity is measured as a function of wavelength. The Shimadzu UV-2550 is a double beam instrument, hence the light was split in two before reaching the sample and reference. The Shimadzu
UVProbe software was used to control the parameters of the spectrophotometer and collect and store the data measured.

Before operation, a baseline measurement was first taken over a defined range of wavelength in order to ensure the absorbance was zero with no samples in position. Thin films spin coated onto glass substrates (20×20 mm$^2$) were then placed in the sample chamber and sealed shut in the dark from outside and background sources of light. The absorbance was measured between wavelengths 300 nm – 700 nm at a wavelength bandwidth of 1 nm (spectral slit width), and collected and stored using the Shimadzu UVProbe software. Measurements were always conducted with respect to a reference sample (a clean glass slide) which was automatically subtracted from the absorbance measured for the thin film sample.

3.4.6 Photoluminescence spectroscopy

A Jobin Yvon Horiba FluoroMax-3 spectrofluorometer was used to measure photoluminescence spectra (PL) and photoluminescence quantum efficiency (PLQE). According to the manufacturer’s handbook, a continuous light source generated from a 150 W ozone free xenon arc lamp is first illuminated through an excitation monochromator which selects a band of wavelengths that are directed onto a sample for excitation purposes. Upon excitation of the sample, photoluminescence is generated over a band of wavelengths which are then directed into a second emission monochromator which selects one wavelength at a time to observe at the signal detector. The DataMax software package was used to initialise the parameters of the FluoroMax-3 and measure and collect the data received from the detector.

Photoluminescence data was measured in increments of 2 nm with an integration time of 0.1 s. The excitation wavelength was chosen from the wavelength recorded at maximum absorption from UV-vis spectra, which varied depending on the organic semiconductor used. Slit widths were kept between 1 – 2 nm for PL and PLQE measurements and adjusted accordingly to keep the raw signal level <$4 \times 10^6$ cps (counts per second) to avoid oversaturation (and damage) of the detector. Samples were positioned at an angle of 15° with respect to the direction of the excitation beam in order to acquire reasonable PL intensity. The PL spectra was recorded between wavelengths $x + 10$ nm to 700 nm, where $x$ is the excitation wavelength of the sample.

3.4.7 Spin coating

Spin coating is a widely used procedure in the field of organic electronics as well as in the microelectronics industry for the application of photoresists. It involves the deposition of solution on a static horizontal disc which is then subsequently
rotated at high angular velocity. Centrifugal forces acting on the rotating solution combined with evaporation of the solvent causes most of the solution to be ejected from the disc leaving behind a uniform thin film. As such, the main advantage of this process is that it allows direct control of the film thickness and coating of large areas depending on initial parameters such as spin speed, acceleration and spinning time. The main disadvantage of it being the excessive waste of the solution in order to achieve the desired thickness. Conditions such as solvent boiling point, solution concentration, type of semiconductor used, surface energy and temperature also affect the final thickness and morphology of the spin coated film [32].

Figure 3.7: Setup of the spin coater for thin film deposition.

Spin coaters by Laurell technologies corporation model WS-650 MZ-23NPP / WS-650 SZ-6NPP/LITE were used in the cleanroom. An illustration of the spin coater setup is shown in Figure 3.7. The substrate was first placed on a chuck and held in place by low vacuum. Between 50 – 100 µL solution was applied using a pipette for 15×15 mm$^2$ substrates and 100 – 250 µL for 20×20 mm$^2$ substrates. Acceleration was generally kept constant at 1000 – 2000 rpm/s, while spin speeds and time were varied depending on the purpose.

Organic semiconductor solutions were generally spin coated in a single spin speed step between 500 – 4000 rpm for 30 – 60 seconds. Photoresists, SAMs and dielectrics were spin coated using two stages: one initial ramp up stage at low spin speed, generally around 300 – 500 rpm for 5 – 10 seconds in order to spread the solution around the substrate, and a final stage of 1000 – 4000 rpm for 30 – 60 seconds to reduce the thickness to the desired size. After each spin coating procedure, the interior of the spin coater was always thoroughly cleaned using acetone soaked wipes in order to prevent residual solution contamination on new substrates. The relation between angular velocity (spin speed) and thickness generally follows a
power law, and was calibrated for each solution used in order to achieve reproducible thicknesses.

### 3.4.8 Thermal evaporation

An MBraun MB200B glovebox (under N\textsubscript{2} environment) with a built in thermal evaporator was used for depositing metals. The process involves resistively heating a material at high vacuum until its vapour pressure exceeds the background pressure of the material in the chamber, causing it to evaporate and condense on cooler surfaces such as a shadow mask plate holding the samples directly above it. The high vacuum is required for three reasons:

- Reduce the concentration of O\textsubscript{2} and other gases which may react with the sample
- Allows materials with low vapour pressure to evaporate easily
- The mean free path is increased between the evaporated material to the sample minimising deflection

Custom made aluminium shadow mask designs (20×20 mm\textsuperscript{2} in size) for gate, source, drain or capacitor electrodes were designed using AutoCAD and fabricated by Steve Cussell and David Bowler from the Mechanical Workshop department at Imperial College London. These were placed onto a shadow mask plate with 3×3 square slots 20×20 mm\textsuperscript{2} in size. Metals were secured into place in either tungsten crucible boats (for pellets) or directly for rods between two electrodes in the evaporator. The evaporator was then evacuated to high vacuum at around 10\textsuperscript{-6} mbar which took 30 mins – 1 hour to achieve. The current was then increased slowly up to a certain limit in order to control the rate of evaporation depending on the metal used. For the evaporation of Au source and drain electrodes onto Si/SiO\textsubscript{2} and glass substrates, a Cr adhesion layer had to be evaporated first due to poor adhesion of Au with the substrates. A rate of 0.1 Å/s was used to achieve a 1.5 nm thick Cr layer. After which a rate of 0.01 Å/s was used to evaporate Au up to a thickness of 10 nm and then increased to 0.2 Å/s to achieve a final Au thickness of 50 nm. In a similar manner, 50 nm Au gate electrodes were evaporated for top gate OFETs. For Al capacitor contacts, the current was increased slowly until a rate of 0.5 – 1 Å/s was reached and a final Al thickness of 50 nm was achieved. Shadowing effects were observed at shadow mask resolutions <50 μm during the evaporation of Au and Cr where one would overlap the other. Due to this intrinsic limitation with shadow mask based evaporation, distances between two contacts were kept at or above 50 μm in order to minimise undesired shorting between metal contacts.
3.4.9 Calibration of polymer dielectrics

The dielectric is crucial to the operation of a field effect transistor. Since the capacitance per unit area is proportional to the charge in the accumulation layer and therefore the drain current, it is intuitive to increase it in order to achieve high performance OFETs. However, it is not such a simple matter since key interfacial features such as surface roughness, surface energy, surface polarity, surface hydrophobicity and dielectric constant (i.e. relative permittivity $\varepsilon_r$ or $k$) have also been found to greatly affect aspects of an OFET’s performance such as the mobility, threshold voltage, leakage current, on/off ratio, and subthreshold slope [33]. Several review papers already exist covering many different dielectrics and SAMs which the reader can consult for further information [34][35][36][37].

The polymer dielectrics PVP and CYTOP were mainly used for top gate devices in this thesis. The capacitance of a prefabricated 230 nm SiO$_2$ dielectric sandwiched between a top Au contact and bottom n-doped Si gate contact was first measured as a baseline to calibrate the Solartron 1260 setup before measuring the PVP and CYTOP dielectrics. The effective capacitance $C_i$ at 100 Hz was calculated to be $1.48 \times 10^{-8}$ F/cm$^2$ using the equation $C_i = \frac{1}{\pi f Z''}$ with a measured capacitor plate area of 0.01 cm$^2$. The relative permittivity was subsequently calculated from the standard equation for parallel plate capacitance, with an average value of $\varepsilon_r = 3.84 \pm 0.05$. This value was very close to the experimentally accepted value of 3.9 for the relative permittivity of SiO$_2$ [38], indicating our setup for measuring the capacitance and relative permittivity was a success.

![Figure 3.8: Capacitance and phase angle ($\phi$) dependence on frequency of a 230 nm thick SiO$_2$ dielectric between 100 – 1 MHz. The blue triangles represent the capacitance while the red circles represent the phase angle. The connecting lines serve as a guide to the eye.](image-url)

Figure 3.8(a) shows the dependence of effective capacitance and relative
permittivity at different PVP thicknesses at 10 kHz, while Figure 3.9(b) shows the capacitance and phase dependence with frequency of a 700 nm PVP film. The phase angle initially started at >-90° at 1 MHz before stabilising at -90° from about <100 kHz, with a stable capacitance slightly lower than $10^{-8}$ F/cm². However, at frequencies <1 kHz, the phase angle increasingly became positive indicating a resistive component possibly caused by slow polarisation of hydroxyl groups (-OH groups) in the PVP film at mid-low frequencies [39][40][4]. Hence at a frequency of 10 kHz, the relative permittivity $\varepsilon_r$ was calculated to be 6.28 ± 0.11. Using $\varepsilon_r = 6.3$ and a dielectric thickness of 700 nm, the effective capacitance was calculated to be $7.96 \times 10^{-9}$ F/cm².

Values for the PVP relative permittivity have varied depending on cross-linking temperature, time and curing agent used, with $\varepsilon_r$ between 3.6 – 5.7 being measured by researchers [35][4][41][3]. Since we used the PVP film as is and did not cross-link it in order to avoid annealing of the underlying organic semiconductor in top-gate OFETs for our studies, our estimate for the relative permittivity was somewhat higher than reported values [42].

![Figure 3.9](image_url)

**Figure 3.9:** (a) Variation of capacitance and relative permittivity with the dielectric thickness of PVP at a fixed frequency of 10 kHz. (b) Capacitance and phase angle ($\phi$) dependence on frequency of a 700 nm thick spin coated PVP-IPA-8WT% dielectric between 100 Hz - 1 MHz. The blue triangles represent the capacitance while the red circles represent the phase angle. Zoomed inset in (b) shows variation of capacitance and phase angle between $10^3$ - $10^6$ Hz.

Similarly, CYTOP™ was another polymer dielectric used. It is an amorphous fluoropolymer that is reported to possess excellent hydroxyl free (hydrophobic) properties and good resistivity at high gate voltages that has lead to applications in low voltage, high performance OFETs [35][40][8]. Figure 3.10 (a) shows the effective capacitance and relative permittivity with CYTOP film thickness at 10 kHz and Figure 3.10 (b) shows the capacitance and phase angle dependence with frequency for a 700 nm film. The capacitance was taken at 10 kHz because at frequencies < 10 kHz the phase angle was positive, indicating a considerable resistive component.
at mid-low frequencies in the film. Hence at 10 kHz, the relative permittivity of CYTOP was calculated to be $3.73 \pm 0.01$, which at a 700 nm thickness gave us a capacitance of $4.68 \times 10^{-9} \text{ F/cm}^2$.

Our estimate for the CYTOP relative permittivity was higher than reported values ($\varepsilon_r \approx 2.1 - 2.2$) as curing times of up to a few hours were used in the reports [6][8][7].

![Figure 3.10](image)

**Figure 3.10:** (a) Variation of capacitance and relative permittivity with the dielectric thickness of CYTOP at a fixed frequency of 10 kHz. (b) Capacitance and phase angle ($\phi$) dependence on frequency of a 700 nm thick spin coated CYTOP dielectric between 100 Hz - 1 MHz. The blue triangles represent the capacitance while the red circles represent the phase angle. Zoomed inset in (b) shows variation of capacitance and phase angle between $10^3$ – $10^6$ Hz.

### 3.4.10 Surface tension of solvents

**Table 3.4:** Surface tension $\gamma_L$ of some common organic solvents used in this thesis with respective dispersive $\gamma_L^D$ and polar $\gamma_L^P$ components.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_L$ (mN/m)</th>
<th>$\gamma_L^D$ (mN/m)</th>
<th>$\gamma_L^P$ (mN/m)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.80</td>
<td>21.80</td>
<td>51.00</td>
<td>[17]</td>
</tr>
<tr>
<td>Hexane</td>
<td>18.40</td>
<td>18.40</td>
<td>0.00</td>
<td>[43]</td>
</tr>
<tr>
<td>Toluene</td>
<td>28.50</td>
<td>27.18</td>
<td>1.32</td>
<td>[17]</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>33.60</td>
<td>32.37</td>
<td>1.23</td>
<td>[17]</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>25.37</td>
<td>18.44</td>
<td>6.93</td>
<td>Measured</td>
</tr>
<tr>
<td>Tetralin</td>
<td>37.30</td>
<td>37.20</td>
<td>0.10</td>
<td>Measured</td>
</tr>
</tbody>
</table>

Table 3.4 summarises the total, dispersive and polar surface tension of some common solvents used in this thesis. The surface tension of 1,2-dichlorobenzene (DCB) and tetralin (TET) were determined using pendant drop analysis as we could not find values for the dispersive $\gamma_L^D$ and polar $\gamma_L^P$ components in the literature. A needle diameter of 1.85 mm was used for pendant droplets of DCB and TET.
The total liquid surface tension $\gamma^D_L$ was first determined using the KRUSS DSA100 software and were 25.4 mN/m for DCB and 37.3 mN/m for TET. In order to determine the surface tension due to dispersive and polar components, the contact angle of these liquids were measured on a polytetrafluoroethylene (PTFE) block surface.

Contact angles of $54.0 \pm 2.1^\circ$ and $57.7 \pm 2.1^\circ$ were measured for DCB and TET respectively on PTFE. Using the known solid surface energy values $\gamma_S = 22$ mN/m and $\gamma_P^S = 0$ mN/m for PTFE [17], we calculated $\gamma^D_L = 18.4$ mN/m, $\gamma^P_L = 6.9$ mN/m for DCB, and $\gamma^D_L = 37.2$ mN/m, $\gamma^P_L = 0.1$ mN/m for TET.

The total surface free tension for DCB appears to be underestimated as values of 36.7 mN/m and 37.0 mN/m have been recorded by others [44] [45]. On the other hand, for TET, our measured total surface free tension was slightly higher compared to the value of 35.3 mN/m in the literature [46].

The effect of solvent polarity on the surface tension measurement is assumed to have affected the result. Since TET is less polar than DCB due to its lower dielectric constant (2.77 [47]) compared to DCB (9.93 [48]), we assume the high dielectric constant for DCB might be the reason why the surface tension was underestimated considerably. We found that PTFE had a tendency of getting charged and attracting polar liquids such as water as can be seen in Figure 3.11. Hence this might have resulted in lower or higher than expected contact angle and surface tension components for DCB and TET droplets measured.

3.4.11 Self Assembled Monolayer treatment

Self assembled monolayers are commonly used in organic electronics for wide variety of applications such as surface energy modification and tuning of wetting properties
ultra thin dielectrics for use in high capacitive transistors [50], and work function modification of the metal electrodes in order to ease charge injection between the HOMO (or LUMO levels) of an organic semiconductor [51][52].

Figure 3.12: Illustration of removal of -OH groups from a Si/SiO$_2$ surface with an arbitrary self assembled monolayer.

SAMs often consist of a headgroup (–SiX$_3$) which forms the chemical bond on the surface atoms of a substrate via hydrolysis, an alkyl chain (–(CH$_2$)$_n$–) which assists in the ordering of the molecular structure, and a surface group (–R) which can be functionalised with different chemical groups in order to tune wetting and interfacial properties [53]. This is depicted in Figure 3.12. As such, there are generally four steps involved during SAM formation on SiO$_2$ surfaces:

1. Physisorption of the silane molecules with the hydroxyl (–OH) groups on the SiO$_2$
2. Hydrolysis of the silane head groups in the presence of an adsorbed water layer on the surface forming highly polar –Si(OH)$_3$ molecules
3. Formation of covalent bonds between the –Si(OH)$_3$ and –OH groups on the SiO$_2$ surface
4. After a certain period of time, a well ordered monolayer of the SAM is formed on the SiO$_2$ surface by self assembly

In this thesis, where applicable we used hexamethyldisilazane (HMDS) (C$_6$H$_{19}$NSi$_2$) and octadecyltrichlorosilane (OTS) (C$_{18}$H$_{37}$Cl$_3$Si) to treat Si/SiO$_2$ and/or glass substrates.

For HMDS application, a substrate was first placed on a spin coater chuck and coated with approximately 250 $\mu$L of HMDS and allowed to pool for 1 minute. Spin coating was then carried out at 4000 rpm for 30 seconds (acceleration: 1000 rpm/s). After which, the substrate was sonicated in ethanol for 2 mins before finally
annealing at 150°C for 10 mins in ambient. For OTS application, substrates were
immersed in a 1 mM solution of OTS in 25 mL of Toluene for 15 mins in ambient.
After which it was sonicated in Toluene for 30 mins in order to remove excess layers
of OTS before finally annealing at 150°C for 10 mins in ambient. It was observed
that a large number of substrates (up to 8) could be SAM treated with the OTS
solution immersion method compared to just a single substrate at a time with the
HMDS spin coating method.

3.4.12 Photolithography

The process of photolithography involves exposing a UV sensitive material (the
photoresist) with a constant intensity of UV radiation through an optically
transparent photomask with patterned opaque features. Photolithography was
mainly used to pattern permanent photoresist features onto silicon substrates to
act as hard master templates for soft lithographic molds. A Karl Suss Mask
Aligner MJB-3 was used for photolithography. Photomasks were designed using
the AutoCAD software package and fabricated by JD Photo Data on 4×4 inches²
soda lime bases with chromium patterned features.

Initially, S1813 G2 positive resists were used to fabricate the master templates
but it was found that it was easily susceptible to mechanical deformation upon just
minor use. Hence SU-8 2002 and 2005 negative resists were used for the majority of
the soft lithographic work due to their robust durability.

A 0.2 μm PTFE filter was always fitted to disposable plastic syringes in
order to minimise the development of air bubbles in the deposited photoresist.
The photolithography process flow involved several steps where the photoresists,
developers, exposure and development times were adjustable parameters that had
to be carefully calibrated and optimised for reproducibility [54]. A brief overview of
this process was as follows:

1. Cleaning of substrates
2. Application of SAM treatment (optional)
3. Spin coating of photoresist on substrates
4. Soft bake annealing of substrates
5. Exposure to UV radiation
6. Post exposure annealing
7. Development to remove unexposed features
8. Rinsing in DI water or IPA
9. Post-development annealing
10. Plasma ashing at a low power output to remove residual undeveloped resists
11. Application of SAM treatment to ease lift off of cured stamps via soft lithography

3.4.13 Soft lithography

Soft lithography involves fabricating micro and nano metre sized structures using a flexible elastomeric stamps. In this thesis, two methods of soft lithographic deposition of the organic semiconductor layer were investigated: Micro Molding in Capillaries (MIMIC) and Solvent Assisted Micromolding (SAMIM). SU-8 is a commonly used epoxy based negative photoresist in microtechnology and micro-electro mechanical systems (MEMS) for structural and mold material applications, especially in soft lithography [55]. First developed by IBM in 1996 [56], it is mechanically and chemically stable [54], and its sensitivity to ultraviolet radiation allows it to be integrated into photolithographic patterning. Hard master SU-8 templates on silicon substrates for MIMIC and SAMIM process flows were first fabricated. Two grades of SU-8 photoresist were used to achieve different thicknesses. We used SU-8 2002 to pattern down to a thickness of $\sim 2 \mu m$ and with SU-8 2005, a thickness of $\sim 8 \mu m$. The reason why we choose such large thicknesses is because attempts in fabricating master templates in the nanometre regime were largely unsuccessful (see Appendix B.1).

We used a process flow similar to the one developed by Pinto and coworkers [57] with some modifications to the UV curing time, baking temperature and development time due to the varying viscosities of the SU-8 used. SAM treatment was applied to finished silicon resist masters in order to reduce the surface energy and ease the removal of stamp molds after the curing process. Standard cleaning procedures in IPA, DI water and plasma ashing were used to clean the silicon substrates before use.

3.4.13.1 Process flow for SU-8 2002 masters

The method for achieving $\sim 2 \mu m$ thick SU-8 2002 resist was as follows:

- Two stage spin coating of SU-8 2002: 500 rpm for 10 seconds (acceleration: 100 rpm/s) followed by 3000 rpm for 30 seconds (acceleration: 300 rpm/s)
- Soft bake annealing at 65°C and 95°C for 1 min each respectively
- 10 second exposure time at 10 mW UV radiation (100 mJ/cm\(^2\) dosage)
- Post exposure annealing at 65\(^\circ\)C and 95\(^\circ\)C for 1 min each respectively
- Development in SU-8 developer for 60 seconds with minor stirring
- Rinsing in IPA and drying with a stream of N\(_2\)
- Plasma ashing at 40 W for 1 min to descum residual resist
- Hard bake anneal at 150\(^\circ\)C for 5 min
- SAM treatment of masters in 1 mM OTS/Toluene solution

An average was taken over 3 patterned features and we obtained a resist thickness of 1.90 ± 0.00 \(\mu\)m and RMS of 0.008 ± 0.001 \(\mu\)m, indicating highly smooth and uniform surfaces with SU-8 2002.

### 3.4.13.2 Process flow for SU-8 2005 masters

The method for achieving ∼8 \(\mu\)m thick SU-8 2002 resist features was as follows:

- Two stage spin coating of SU-8 2002: 500 rpm for 10 seconds (acceleration: 100 rpm/s) followed by 1000 rpm for 30 seconds (acceleration: 300 rpm/s)
- Soft bake annealing at 65\(^\circ\)C for 5 mins and 95\(^\circ\)C for 7 mins respectively
- 15 second exposure time at 10 mW UV radiation (150 mJ/cm\(^2\) dosage)
- Post exposure annealing at 65\(^\circ\)C for 2 mins and 95\(^\circ\)C for 4 mins respectively
- Development in SU-8 developer for 1.5 - 2.5 mins with minor stirring
- Rinsing in IPA and drying with a stream of N\(_2\)
- Plasma ashing at 40 W for 1 min to descum residual resist
- Hard bake anneal at 150\(^\circ\)C for 5 min
- SAM treatment of masters in 1 mM OTS/Toluene solution

An average was taken over 3 patterned features and we obtained a resist thickness of 8.34 ± 0.02 \(\mu\)m and RMS of 0.009 ± 0.003 \(\mu\)m, indicating highly smooth and uniform surfaces with SU-8 2005.
Chapter 3. Materials and experimental techniques

3.4.13.3 Process flow for elastomeric stamps

For the development of PDMS stamps, viscous PDMS solution was directly poured in a 20 mL glass vial and rigorously stirred with Sylgard 184 curing agent in a 10:1 (weight/weight) ratio. The mixture was then placed in a vacuum desiccator for 1 hour to remove trapped air bubbles. Approximately 1 mL of PDMS was poured onto Si hard masters with SU-8 resist structures and cured on a hotplate at 150°C between 20 – 30 mins in ambient, and then allowed to cool to room temperature before use.

For the PFPE stamps, Darocur 1173 curing agent was dissolved in PFPE at 1 wt% and 4 wt% concentrations and stirred on a magnetic stirrer at 1200 rpm at 70°C for 24 hours. Approximately 10 - 30 µL of PFPE solution was pipetted onto Si masters with SU-8 resist features. UV curing of the PFPE mixture was done inside an ELC-500 light exposure system with a constant UV intensity of 30 mW/cm² in a N₂ environment.

Upon preparation of the stamp molds, they were applied onto clean Si/SiO₂ or glass substrates following the MIMIC and SAMIM procedures described in Chapter 2.6.2.

3.5 Uncertainty analysis

As each device took some amount of time to design and fabricate, a small number of repeats in the range of 3 – 6 were conducted where appropriate. With this sample size, the experimental uncertainty was determined at the 80% and 95% confidence intervals using the Student’s t-distribution. Assuming measured samples were normally distributed, the confidence interval yields an upper and lower margin of error of which we can be 80 - 95% confident that the true population mean would lie in the region. This is given by the equation:

\[ \bar{X} \pm t_{\alpha/2} \frac{s}{\sqrt{n}} \]  

where \( \bar{X} \) is the sample mean, \( s \) is the sample standard deviation, \( n \) is the sample size, and \( t_{\alpha/2} \) is the t-statistic value from the area of tails in the t-distribution with \( n - 1 \) degrees of freedom. \( \alpha \) is the confidence interval in decimal form (also known as the confidence level).

In cases where a non-linear model was compared to experimental data (such as the case for the Tanese, Vissenberg-Matters disorder model), confidence interval bands were constructed at the 95% level. The confidence interval is the region where there is a 95% probability that the true line of best would explain the experimental data. This is given by the equation.
\[ Y_{FIT} \pm t_{\alpha/2} SE \sqrt{1/n + \frac{(X - \bar{X})^2}{SS_{xx}}} \]  

(3.13)

where \( SE \) is the standard error of the modelled fit to the experimental data and \( SS_{xx} \) is the sum of squared errors of the independent variable \( X \) \[58\].

References


Chapter 3. Materials and experimental techniques


Chapter 3. Materials and experimental techniques


Chapter 4

Study of beta-phase aggregation in aged F8T2 thin films

The effects of solution ageing induced aggregation of the polyfluorene, F8T2, were investigated in this chapter. We found that solution ageing induces the beta-phase state of the F8T2 polymer chains in the form of J aggregation intrachain ordering according to the H and J aggregate model by Spano and coworkers, and this was also compared to changes in the photoluminescent quantum efficiency. In bottom gate OFET devices, p-type charge carrier mobilities differed by almost an order of magnitude between H and J aggregated films, with the former giving high mean mobilities in the order of $>10^{-4}$ cm$^2$/Vs, and threshold voltages $>-10$ V. Contrary to previous reports, annealing was found to decrease overall OFET performance when there was an increase in J aggregation, indicating that the beta-phase may be detrimental to device performance in some cases. Using the Vissenberg and Matters model for charge transport in disordered amorphous organic semiconductor systems, we also found a correlation with increasing J-aggregation, threshold voltage and the $T_0$ disorder with increasing beta-phase.
4.1 Introduction

Organic semiconductors based on polyfluorene conjugated polymers have attracted considerable academic and industrial interest over the years owing to their usage in organic field effect transistors [1], organic light-emitting and phototransistors [2][3], organic light emitting diodes [4] and even organic photovoltaics [5]. Through the use of various solution processing techniques such as spin coating [6], inkjet printing [7][8], roll-to-roll gravure printing [9] and nanoimprint lithography [10] low cost large area electronics are increasingly turning out to be a reality [11][12]. Polyfluorenes are particularly desirable for OLED applications because its class of conjugated polymers can emit colours spanning the entire visible range with high efficiency and low operating voltage [13]. However, some reports suggest that polyfluorenes are prone to degradation by oxidation and aggregate formation in solution which tends to reduce exciton recombination thereby lowering the efficiency in devices such as OLEDs and OPVs [14][15][16][17]. In inkjet, screen, and gravure printing processes, changes in viscosity due to solution aggregation could result in poor quality films in devices and potential clogging of the printing mechanisms [18][19]. Hence to realise large scale electronics, issues such as electronic and photophysical stability due to ageing induced aggregated solutions of organic semiconductors will need to be addressed.

In the late 1990s, Grell and Bradley reported the existence of a beta-phase of the dioctyl substituted polyfluorene known as poly(9,9-dioctyfluorene) (PFO). A distinctive red shifted peak in the absorption spectra and a reduced stokes shift with respect to PL spectra was observed upon thermal treatment via slow cooling or exposure to poor dissolving solvents subsequent to film deposition [20][21]. This change was coined as being in an “aggregated” state, and was attributed to a structural change of the PFO polymer chains, which indicated increased intrachain ordering, a planar zigzag structure and an extended conjugation length [22]. This was in contrast to traditional spin coated films which resulted in a predominantly amorphous and disordered phase (also known as the alpha-phase) [13]. Since then, the beta-phases of a variety of polyfluorenes have been investigated by preparing deposited films with varying concentration [23], molecular weight [24], varying alkyl side chain additives [25], binary solvents [26], solvent vapor annealing [27] and solvent ageing [28]. The beta-phase in polyfluorenes is particularly desired due to its enhanced charge carrier mobilities and high PLQE which are essential in applications relating to efficient and stable OLED and lasers [29][30][31].

The technique of solution ageing induced aggregation has been investigated by researchers to control the degree of intra and interchain interactions, morphology, and the electronic and photophysical properties of different conjugated polymers.
Work by Nguyen and coworkers showed that conjugated polymers of MEH-PPV in chlorobenzene tended to have higher photoluminescent quantum efficiencies (PLQE) than in THF due to increased aggregation in the latter. In chlorobenzene, MEH-PPV tended to unfold and maximise the favourable $\pi-\pi$ interactions (interchain interactions) between the polymer and the solvent, while in THF it tended to coil tightly minimizing the number of aromatic repeating chains in the most extended conformation. Due to increased torsional defects along the backbone in an aggregated solution involving THF, this yielded lower PL efficiencies [32].

The PLQE has also been shown to be affected by solution aggregation by using polymers with different side chain lengths [33]. Polyfluorene compounds with bulky side chains gave much higher PLQE than those with smaller side chains. Explanations for this quenching effect are that these smaller side chains facilitate denser packing of the polymer chains leading to an increased degree of $\pi-\pi$ electron stacking, defect sites, and thereby fewer excitonic recombination sites for photoluminescence [33][34].

In this chapter, we investigate the effect of ageing induced solution aggregation of poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) thin films prepared from different solvents and concentrations. Previous studies of F8T2 have examined its ambient stability to oxygen doping [35], solubility in a wide range of organic solvents [36][37], low voltage bulk heterojunction solar cell applications with PCBM blends [38], and charge carrier mobility enhancement with its highly aligned morphology in its nematic liquid crystalline phase [1][39].

In particular we study the absorption and PL spectra and conduct exciton bandwidth analyses to quantify the beta-phase aggregation, and compare it to the PLQE and charge carrier mobilities in OFETs in order to ascertain relationships. Recently, there have been some reports that suggest that annealing F8T2 between 150 – 280°C tends to lower the charge carrier mobility despite increasing the highest drain current and OFET stability [3][40]. We will also investigate why this is so through the use of spectroscopy and GIWAXS XRD measurements. Selected OFET transfer characteristics are fitted as per the equations derived by Campbell and coworkers who used the Tanase, Vissenberg and Matters model for charge transport in amorphous, glassy disordered organic semiconductors [41][42][43].

*Note:* Throughout this chapter and subsequent ones, “aged solutions”, “aged films” and “aged devices” all refer to measurements of the *deposited* thin films from the solutions. In no part of the analyses were any measurements taken directly from the solutions themselves.
4.2 Experimental method

Samples in this chapter were prepared from F8T2 with a $M_w > 20,000$ g/mol and dissolved in solvents such as Toluene (TOL), Chlorobenzene (CB), 1,2-dichlorobenzene (DCB) with varying concentrations of 0.125, 0.25, 0.5, 1 and 2 wt%. These solutions were stirred or heated until dissolution on a magnetic hotplate stirrer at 70°C for 24 hours. Depending on application, freshly prepared solutions were immediately used on the same day for characterisation and device fabrication purposes (labelled as FRESH or I in this thesis). While aged solutions were stored in dark and ambient conditions for a period of 7 days before use (labelled as AGED or II). Thin films were spin coated at 1500 and 4000 rpm for 30 s. Where appropriate, F8T2 thin films were thermally annealed in N$_2$ above the liquid-crystal transition temperature at 280°C for 30 mins, and allowed to slowly cool to room temperature before use.

Surface profilometry, optical micrography, absorption, photoluminescence spectroscopy, and transistor characterisation were conducted as per the protocols described in Chapter 3. For collaborative work, raw data for Atomic Force Microscopy (AFM) were obtained at University College London by Muhammad Kamaludin, while Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) data were obtained at Diamond Light Source by Warren D. Stevenson.

4.3 Ageing due to solvent and concentration effects

4.3.1 Surface morphology

In order to investigate the effect of solvent and concentration effects on aggregation, we dissolved F8T2 in toluene (TOL), chlorobenzene (CB) and 1,2-dichlorobenzene (DCB) in concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%. Thin films were spin coated at a fixed spin speed of 1500 rpm for 30 s. Figures 4.1 and 4.2 show the respective optical micrographs for fresh (I) and 7 day aged (II) F8T2 thin films.
Figure 4.1: Optical micrographs of fresh (I) F8T2 thin films prepared from TOL, CB and DCB solvents at concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%. Rows from left to right indicating the variation in film morphology with increasing concentration. Columns from top to bottom indicate the solvent used.

Figure 4.2: Optical micrographs of 7 day aged (II) F8T2 thin films prepared from TOL, CB and DCB solvents at concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%. Rows from left to right indicating the variation in film morphology with increasing concentration. Columns from top to bottom indicate the solvent used.

At first glance, we can see from Figure 4.1 that fresh films of F8T2 showed an increase in film quality with increase in concentration. Curls and streaks in the film began to develop at higher concentrations for F8T2-TOL-I and F8T2-DCB-I films, whereas for F8T2-CB-I films not much variation in the film morphology was observed. In contrast for aged films, Figure 4.2 showed considerable changes in the morphology. F8T2-TOL-II solutions in particular precipitated solid aggregates after 7 days ageing hence showed little or no film coverage at concentrations <0.5
wt%, while at concentrations greater than that yielded very poor film quality. F8T2-CB-II showed an increased deposition of aggregated particulates on the film at concentrations >1.0 wt%. Precipitation of F8T2-DCB-II solutions was less severe and showed little or no aggregated particulates in the film. Film thicknesses and root mean squared (RMS) roughness values were also measured and are shown in Table 4.1. Film thicknesses measured at concentrations <0.5 wt% were unreliable and noisy hence were not included. Film thickness for F8T2-TOL-II could also not be measured as little or no films were present at concentrations <1.0 wt%. In general, the film thickness was observed to increase with concentration as expected. For F8T2-TOL-II, very large particulates were deposited with thicknesses measured in the region of several dozen microns. An increase in the surface roughness for all concentrations and solvents was observed after deposition from aged solutions. Taking the 1.0 wt% concentration as an example, for F8T2-TOL, an increase of upto 50 times in the RMS was measured after ageing; although it should be noted that this value is relatively meaningless since strictly speaking these were not thin films any more. For F8T2-CB on the other hand, the RMS increased by approximately 4 times from 0.8 nm and 3.8 nm, indicating a noticeable change to the morphology. Whereas for F8T2-DCB, there was little to no change in the RMS after solution ageing.

**Table 4.1**: Film thickness and RMS roughness values for fresh and 7 day aged F8T2 films in TOL, CB and DCB solutions, spin coated at 1500 rpm for 30s. Values are quoted to 1 d.p.)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc (wt%)</th>
<th>Ageing</th>
<th>Thickness (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
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<tr>
<td>TOL</td>
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<td>Fresh</td>
<td>21</td>
<td>1.1</td>
</tr>
<tr>
<td>TOL</td>
<td>1.0</td>
<td>Fresh</td>
<td>54</td>
<td>1.1</td>
</tr>
<tr>
<td>TOL</td>
<td>2.0</td>
<td>Fresh</td>
<td>162</td>
<td>4.1</td>
</tr>
<tr>
<td>CB</td>
<td>0.5</td>
<td>Fresh</td>
<td>28</td>
<td>0.7</td>
</tr>
<tr>
<td>CB</td>
<td>1.0</td>
<td>Fresh</td>
<td>50</td>
<td>0.8</td>
</tr>
<tr>
<td>CB</td>
<td>2.0</td>
<td>Fresh</td>
<td>141</td>
<td>1.2</td>
</tr>
<tr>
<td>DCB</td>
<td>0.5</td>
<td>Fresh</td>
<td>17</td>
<td>1.7</td>
</tr>
<tr>
<td>DCB</td>
<td>1.0</td>
<td>Fresh</td>
<td>31</td>
<td>1.2</td>
</tr>
<tr>
<td>DCB</td>
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<td>Fresh</td>
<td>112</td>
<td>0.7</td>
</tr>
<tr>
<td>TOL</td>
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<td>Aged</td>
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</tr>
<tr>
<td>TOL</td>
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<td>Aged</td>
<td>23949</td>
<td>3414</td>
</tr>
<tr>
<td>CB</td>
<td>0.5</td>
<td>Aged</td>
<td>38</td>
<td>5.0</td>
</tr>
<tr>
<td>CB</td>
<td>1.0</td>
<td>Aged</td>
<td>38</td>
<td>3.8</td>
</tr>
<tr>
<td>CB</td>
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<td>Aged</td>
<td>127</td>
<td>5.1</td>
</tr>
<tr>
<td>DCB</td>
<td>0.5</td>
<td>Aged</td>
<td>17</td>
<td>1.8</td>
</tr>
<tr>
<td>DCB</td>
<td>1.0</td>
<td>Aged</td>
<td>32</td>
<td>1.2</td>
</tr>
<tr>
<td>DCB</td>
<td>2.0</td>
<td>Aged</td>
<td>95</td>
<td>1.7</td>
</tr>
</tbody>
</table>
4.3.2 Optical spectroscopy

We next examined the UV-vis and PL spectra of fresh and 7 day aged F8T2 solutions in TOL, CB and DCB with varying concentration. For all fresh (I) solutions, a gradual reduction of the 0−0 peak at ~485 nm was observed with increased concentration in both UV-vis and PL spectra in Figures 4.3 and 4.5. A blue shift of the wavelength was also observed with increasing concentration in fresh UV-vis spectra, which corresponded to a red shift in the PL spectra. For aged (II) solutions, we observed no noticeable change in the UV-vis 0−0 peaks for TOL in Figure 4.4. However the PL spectra in Figure 4.6 showed a 0−0 peak reduction for aged TOL, CB and DCB solutions. This reduction could be perhaps due to self absorption effects within the layers of thicker films produced at high concentrations. For aged TOL, the wavelength position at 0−0 was at 480 nm for 0.125 wt%, which appear to be a blue shift from 485 nm in the UV-vis spectra for fresh solutions in Figure 4.3. Aged TOL also showed a slight red shift with increasing concentration owing to its precipitation in the solvent after ageing. A similar blue shift in the UV-vis spectra was observed for aged CB and DCB. Upon increasing concentration, a further blue shift in the wavelength was also observed, which corresponded to a red shift in the PL spectra.

![Figure 4.3: Normalised UV-vis spectra of fresh (I) F8T2 thin films in TOL, CB and DCB solutions with varying concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%.]
Figure 4.4: Normalised UV-vis spectra of 7 day aged (II) F8T2 thin films in TOL, CB and DCB solutions with varying concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%.

Figure 4.5: Normalised PL spectra taken at an excitation wavelength of 450 nm for fresh (I) F8T2 thin films in TOL, CB and DCB solutions with varying concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%.

Figure 4.6: Normalised PL spectra taken at an excitation wavelength of 450 nm for 7 day aged (II) F8T2 thin films in TOL, CB and DCB solutions with varying concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%.

These changes in the $0 - 0$ and $0 - 1$ peaks from the normalised UV-vis and PL spectra were used to determine the exciton bandwidth using the H-J aggregate model.
developed by Spano, Chang and coworkers [44][45][46]. The exciton bandwidth is a useful measure of the degree of crystallinity as it is inversely proportional to the conjugation length and intrachain ordering. It also gives us an idea of the degree of interchain (H-aggregates) and intrachain (J-aggregates) ordering, with the latter indicative of the characteristic beta-phase. Hence, the smaller the exciton bandwidth, the higher the crystallinity (J-aggregate intrachain ordering) and conjugation length. [47][48]. Figure 4.7 shows the exciton bandwidth calculated at different concentrations, ageing and solvents for both UV-vis and PL spectra. Due to lack of $W$ data for F8T2 in the literature, our values of the $W$ could not be compared, hence should be taken as a rough estimate rather than an absolute measure as explained earlier in Chapter 2.4.2. The exciton bandwidth calculated from the UV-vis in Figures 4.7 (a) – (c), showed considerable variation and even negative values, especially for DCB, with increasing concentration and solvent type. As the film thicknesses measured according to Table 4.1 were well below < 150 nm, these anomalous variations of the $W$ from the UV-vis spectra are in accordance with the observations made by Ehrenreich and coworkers before [49]. Due to the tendency of $W$ yielding negative values with UV-vis data, we will mainly calculate it using the PL data from this point onwards in the thesis.
Figure 4.7: Exciton bandwidth (W) calculated from the $0 - 0 / 0 - 1$ peak ratios from the UV-vis (a)–(c) and PL spectra (d)–(f) for fresh and 7 day aged F8T2 thin films in TOL, CB and DCB in concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%. The solid coloured lines are a guide to the eye.

The exciton bandwidth calculated from PL spectra certainly gave much clearer trends, as can be seen in Figures 4.7 (d) – (f). For fresh solutions, a general increase in the exciton bandwidth with concentration indicated a decrease in the crystallinity, conjugation length and increase in H aggregate ordering. However, it should be noted that some part of the increase in the $W$ could have also been due to the effects of self absorption at thicker films (with higher concentrations). At a concentration of 2 wt%, fresh CB had the highest exciton bandwidth at $\sim 190$ meV, while DCB had the lowest exciton bandwidth at $\sim 175$ meV, indicating the latter was more crystalline with J-aggregate ordering due to its higher boiling point (TOL = 110$^{\circ}$C, CB = 131$^{\circ}$C, DCB = 180$^{\circ}$C). This is in accordance with the general understanding that organic semiconductors deposited from higher boiling point solvents tend to result in more crystalline ordering [50].

For aged solutions, we observed an increase of the exciton bandwidth for TOL solutions that was much higher than its fresh counterpart, owning to the disordered nature of the precipitation in the solvent upon ageing. In contrast, aged CB and
DCB solutions showed reduced exciton bandwidths compared to the fresh spectra. At 2 wt%, the exciton bandwidth decreased from 190 meV to 185 meV for CB, and 175 meV to 160 meV for DCB. This reduction in exciton bandwidth indicates the ageing the solutions slightly increased the intrachain ordering and conjugation length. However, since the 0 – 0 peak value did not exceed that of the 0 – 1 peak value in the aged UV-vis and PL spectra in Figures 4.4 and 4.6, we assume that the solutions were still in a H aggregate regime with a weak mixture of J aggregates.

![Figure 4.8](image)

**Figure 4.8:** Photoluminescence Quantum Efficiency (PLQE) of fresh I (a) and 7 day aged II (b) F8T2 thin films in TOL, CB and DCB in concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%. The connecting lines are a guide to the eye.

We also studied the variation of the photoluminescence quantum efficiency (PLQE) with respect to solution ageing, solvent type and concentration. The uncertainty was calculated to the 80% confidence interval using the Student’s t-distribution due to very large deviations of the PLQE at lower concentrations. A general increase in the mean PLQE was observed with increasing concentration for all solvents in Figure 4.8(a). High quantum yields generally are indicative of the absence of quenching effects due to aggregation and increased intermolecular packing which inhibit exciton recombination sites [51][52]. Hence this ties up to the UV-vis and PL spectra results earlier which showed a gradual decrease in the 0 – 0 peak indicative of decreased intrachain J-aggregate ordering and conjugation length. At 1 wt%, fresh DCB had the highest PLQE at 23.3%, followed by TOL (22.0%) and CB (15.7%). The PLQE tended to saturate within the error bars at a higher concentration of 2 wt%. By plotting the PLQE against the exciton bandwidth for the fresh solutions we observed a positive correlation, with the PLQE increasing with exciton bandwidth in Figure 4.9(a). This is a surprising result because emission intensity and efficiency is thought to be correlated with increasing π conjugation length, and hence lower exciton bandwidth [44][53]. Hence this implies that the F8T2 polymer chains are coiled and packed in an orientation favourable for increased excitonic recombination sites for efficient emission at higher concentrated
Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films

fresh solutions. In contrast, solution ageing largely quenched the PLQE in Figure 4.8(b), and saturated in the region between PLQEs of 10 – 15% with increasing concentration. The PLQE still appeared to increase with exciton bandwidth for aged CB and DCB in Figure 4.9(b), although for aged TOL the PLQE tended to saturate at ∼10%.

Figure 4.9: Comparison plots of the Exciton bandwidth (W) calculated from the PL spectra and the PLQE of fresh I (a) and 7 day aged II (b) F8T2 thin films in TOL, CB and DCB in concentrations of 0.125, 0.25, 0.5, 1.0 and 2.0 wt%.

4.3.3 Transistor analysis

In order to investigate the effect of solution ageing, solvent and concentration on charge carrier mobility, we fabricated bottom gate, bottom contact (BGBC) OFETs with a 230 nm SiO₂ dielectric. Thin films were spin coated at a constant speed of 1500 rpm for 30 s. OFET measurements were taken for minimum and maximum concentrations of 0.125 and 1 wt% respectively. Mean values were taken over 4 OFETs for each condition: spin speed, concentration, and solvent type, resulting in a total of 48 devices measured.

Figures 4.10(a) and (b) display important performance metrics for fresh and aged OFETs using different concentrations and solvents. Analysing the data for the 0.125 wt% concentration, mean mobility and drain current showed a gradual decrease with increasing boiling point of the solvent for OFETs prepared from fresh solutions. In contrast, the mean subthreshold slope and hysteresis showed a gradual increase. Upon preparing of films with aged solutions, with the exception of TOL, an increase in the mean mobility, drain current and threshold voltage was observed in all cases with respect to the devices prepared from fresh solutions. With the exception of CB, changes in the threshold voltage were not statistically significant for TOL and CB due to the overlap of the error bars, although large variation were observed. The on/off ratio remained in the region between $10^3 – 10^5$, and the subthreshold slope was between -20 – -10 V for most devices due to overlapping of
errors.

In contrast, OFETs with 1 wt% concentration showed more significant trends between solvent type. Mean mobilities were a magnitude higher than 0.125 wt% OFETs and clear changes between fresh and aged devices were observed, with the mobility increasing with solvent boiling point after preparation from aged solutions. The threshold voltage also showed an increase between solvent type, however between ageing type, the differences were not statistically significant due to overlapping error bars, with the only exception being for aged DCB. Other metrics such as on/off, subthreshold slope and hysteresis did not show any significant trends between solvent and ageing type, with the exception of aged DCB, which showed a significant increase in on/off by an order of magnitude from $10^4$ to $10^5$. Characteristic output and transfer plots of the best performing devices for each concentration regime are exhibited in Figure 4.11. A maximum mobility of $2.6 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -29 V and on/off ratio of $8 \times 10^5$ was recorded at a concentration of 1 wt% for aged DCB OFETs.

In light of these results, with the exception of aged TOL OFETs, ageing appears to increase the mean mobility, threshold voltage and drain current of CB and DCB F8T2 BGBC OFETs. The increase in mobility for CB and DCB corresponds with a reduced exciton bandwidth and PLQE as can be seen in Table 4.2. The general increase in threshold voltage with solution aggregation implies that these aggregates acted as charge carrier traps in the conducting channel or at the contacts. Similar observations have been found for other polymers such as P3HT where solution ageing and aggregation improved OFET mobility, although a general decrease in threshold voltage with aggregation was observed instead [54][55][56].
Table 4.2: Comparison of mean saturation mobility $\mu_{\text{sat}}$, threshold voltage $V_{\text{th}}$, exciton bandwidth ($W$) and PLQE with variable concentration and solvent type of fresh and 7 day aged F8T2 BGBC OFETs with 230 nm SiO$_2$ dielectric. F8T2 thin films are spin coated at 1500 rpm for 30s. The mean was taken over 3 – 4 unique OFET devices separately, with constant $L = 10\mu m$ and $W = 10,000\mu m$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc (wt%)</th>
<th>Ageing</th>
<th>$\mu_{\text{sat}}$ (cm$^2$/Vs)</th>
<th>$V_{\text{th}}$ (V)</th>
<th>$W$ (meV)</th>
<th>PLQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOL</td>
<td>0.125</td>
<td>Fresh</td>
<td>$3.9 \times 10^{-5}$</td>
<td>-9.0</td>
<td>138</td>
<td>7.3</td>
</tr>
<tr>
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<td>Aged</td>
<td>$1.1 \times 10^{-6}$</td>
<td>-12.7</td>
<td>149</td>
<td>7.2</td>
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<td>177</td>
<td>22.0</td>
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<td>TOL</td>
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<td>Aged</td>
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<td>-9.5</td>
<td>194</td>
<td>10.5</td>
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<tr>
<td>CB</td>
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<td>$3.6 \times 10^{-6}$</td>
<td>-7.4</td>
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<td>1.3</td>
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<td>146</td>
<td>1.4</td>
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</tbody>
</table>
Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films

Figure 4.10: Comparison of the mean saturation mobility ($\mu_{\text{sat}}$), threshold voltage $V_{\text{th}}$, on/off ratio, subthreshold slope (SS), hysteresis and max drain current ($I_{D,max}$) from the transfer characteristics of fresh and 7 day aged BGBC F8T2 OFETs in TOL, CB and DCB solutions with concentrations 0.125 (a) and 1.0 wt% (b). Thin films were spin coated at 1500 rpm, 30s. Error bars were calculated at the 80% confidence interval using the standard error between 3–4 repeated measurements separately. The on/off ratio is displayed in a box and whisker plot as the margin of errors often yielded negative values. Channel lengths and widths were 10 $\mu$m and 10,000 $\mu$m ($W/L = 1000$) respectively.
Figure 4.11: Comparison of output and transfer (shown left to right) characteristics of selected fresh and 7 day aged BGBC F8T2 OFETs in 0.125 and 1.0 wt% TOL (a)–(b), CB (c)–(d) and DCB (e)–(f) solution. Films were spin coated at 1500 rpm, 30s. The output drain currents displayed are at a gate voltage of \( V_G = -60 \) V and the transfer drain current is displayed in a logarithmic scale at a drain voltage of \( V_D = -60 \) V. Channel lengths and widths were 10 \( \mu \)m and 10,000 \( \mu \)m (\( W/L = 1000 \)) respectively.
4.4 Effect of spin speed on aged films in different solvents

4.4.1 Surface morphology

Based on the consistency of the results obtained for 1 wt% solutions in the previous section, we next investigated the effect of spin speed on aged F8T2 films in TOL, CB and DCB at a fixed concentration of 1 wt%. This was done in order to investigate whether varying film thickness for a given concentration affected the degree of aggregation after solution ageing. Film thickness was controlled by spin coating at a slow spin speed of 1500 rpm and a fast spin speed of 4000 rpm for 30s. Figures 4.12 and 4.13 display optical micrographs of the changes observed in the film morphology with spin speed. The fresh films did not show any distinctive variation with increase in spin speed, however noticeable changes began to appear for aged films. For aged TOL, the particulates of F8T2 still precipitated after ageing, however at 4000 rpm, there was a higher density of precipitated clusters than compared to 1500 rpm. For aged CB, minor tears started appearing for 4000 rpm films. However for aged DCB, distinctive changes in the film morphology was not observed.

![Optical micrographs of fresh (I) 1 wt% F8T2 thin films in TOL, CB and DCB spin coated at 1500 and 4000 rpm. Rows from left to right show micrographs with increase in spin speed. Columns from top to bottom show micrographs with change in solvent. Note: the colour change from green to orange/brown reflect use of a different coloured filter during observation and do not indicate a change in the morphology.](image)

Figure 4.12: Optical micrographs of fresh (I) 1 wt% F8T2 thin films in TOL, CB and DCB spin coated at 1500 and 4000 rpm. Rows from left to right show micrographs with increase in spin speed. Columns from top to bottom show micrographs with change in solvent. Note: the colour change from green to orange/brown reflect use of a different coloured filter during observation and do not indicate a change in the morphology.
Figure 4.13: Optical micrographs of 7 day aged (II) 1 wt% F8T2 thin films in TOL, CB and DCB spin coated at 1500 and 4000 rpm for 30 s. Rows from left to right show micrographs with increase in spin speed. Columns from top to bottom show micrographs with change in solvent. Note: the colour change from green to orange/brown reflect use of a different coloured filter during observation and do not indicate a change in the morphology.

Figure 4.14: AFM scans of fresh and 7 day aged 1 wt% F8T2 films in TOL, CB and DCB spin coated at a fixed speed of 4000 rpm for 30s. Rows from left to right show fresh and aged scans. Columns from top to bottom show scans with change in solvent.

Figure 4.14 displays AFM images of fresh and aged films in TOL, CB and DCB taken at 4000 rpm. Grain sizes were measured to be 80 – 90 nm and 500 – 1000
nm for fresh and aged TOL. For CB, they were 50 – 100 nm and 60 – 200 nm for fresh and aged films, while for DCB they were 100 – 150 nm and 200 – 400 nm respectively. The RMS roughness was also determined directly from the AFM measurements. For TOL: the RMS roughness increased from 0.48 nm to 241 nm upon ageing. For CB: the RMS increased from 0.80 nm to 0.99 nm. And finally for DCB: the RMS increased from 0.75 nm to 1.24 nm. Reliable AFM measurements could not be taken for aged TOL due to precipitation in the solution after ageing. For CB films, the AFM scan for fresh films appeared to be more uniform than aged. This was probably due to minor tears observed in the optical micrographs for aged CB films at 4000 rpm in Figure 4.13. For DCB films, the aged films showed an increased density of features $>$6 nm compared to fresh films indicating some degree of ordering or aggregation in this particular section.

### 4.4.2 Optical spectroscopy

We next examined the normalised UV-vis and PL spectra of these 1500 and 4000 rpm films in order to understand their optical characteristics. A general increase in the $0-0$ peak indicative of increased conjugation length and ordering was observed with solution ageing and spin coating speed in both the UV-vis and PL spectra for TOL, CB and DCB in Figures 4.15 and 4.16. This was a surprising trend as one would have expected less ordering in the films with a faster spin speed due to faster evaporation/drying rate of the solvent [57][58]. For DCB films, the variation of the $0-0$ peak with spin coating speed and ageing from the UV-vis spectra was minor, however the variation showed up clearly in its corresponding PL spectra. The maximum intensity for the $0-1$ transition peak was at $\sim$460 nm for the UV-vis spectra and $\sim$540 nm for the PL spectra. With the exception of TOL films, we did not observe any changes in the $0-1$ peak position wavelength by solution ageing or varying the spin coating speed for CB and DCB.

![Figure 4.15: Normalised UV-vis spectra of fresh (I) and 7 day aged (II) 1500 and 4000 rpm films of F8T2 in 1 wt% TOL, CB and DCB solutions.](image-url)
Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films

Figure 4.16: Normalised PL spectra taken at an excitation wavelength of 450 nm for fresh (I) and 7 day aged (II) 1500 and 4000 rpm films of F8T2 in 1 wt% TOL, CB and DCB solutions.

![PL Spectra](image)

Figure 4.17: Comparison of photoluminescence quantum efficiency (PLQE) for fresh (I) and 7 day aged (II) 1500 and 4000 rpm spin coated films of F8T2 in 1 wt% TOL, CB and DCB solutions. Error bars were determined at the 80% confidence interval from the standard error of 3 repeated PLQE measurements.

![PLQE Comparison](image)

The PLQE of fresh and aged 1500 and 4000 rpm films were also measured. The PLQE decreased for all solvents at 4000 rpm for fresh films in Figure 4.17(a). Fresh DCB films showed the greatest variation with its PLQE falling from roughly 23% to 15% with increasing spin speed, and CB films showing the least variation well within the error bars. Considering the aged films in Figure 4.17(b), the PLQE fell for all solvents at 1500 rpm compared to the fresh films. However at 4000 rpm, the PLQE increased for aged TOL and CB films from 11% to 15% and 12% to 20% respectively. On the other hand, the PLQE decreased for aged DCB films from 15% to 9%.
4.4.3 Transistor Analysis

4.4.3.1 Bottom Gate OFETs

Fresh and aged films spin coated at 1500 and 4000 rpm were then investigated in BGBC OFET devices with a 230 nm SiO$_2$ dielectric. Mean values were taken over 4 OFETs for each condition: spin speed, ageing, and solvent type, resulting in a total of 48 devices measured. As the data concerned here uses the results determined for the analysis of fresh and aged 1 wt% F8T2 films at 1500 rpm in Section 4.3, their relevance will only be briefly mentioned here.

Figure 4.19 summarises various performance metrics of the OFETs tested. Characteristic output and transfer plots of selected devices for each concentration regime are also exhibited in Figure 4.20. Similar to what was observed in Figure 4.10(b) in Section 4.3 for 1500 rpm films, ageing increased the mean threshold
voltages, SS and hysteresis. Interestingly, the mean mobility decreased for aged TOL and CB 4000 rpm films when compared to the 1500 rpm films in Figure 4.10(b), but increased for the aged DCB 4000 rpm films. The best device was fabricated from aged DCB 4000 rpm films and had a maximum saturation mobility of $5.2 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -26 V, leakage current magnitude of $|I_D/I_G| > 10^2$ and on/off ratio of $2 \times 10^5$. These performance metrics were the highest amongst the solvents and BGBC OFET architecture compared so far.

A clear relationship between mean mobility, threshold voltage and solvent boiling point was not observed, although DCB devices generally appeared to have higher mean mobilities and threshold voltages compared to TOL and CB. Hysteresis seemed to be a consistent problem in all devices regardless of solvent type, and were increased upon preparation of the films from aged solutions. Table 4.3 shows the comparison of mobility, threshold voltage, exciton bandwidth and PLQE for 1500 and 4000 rpm films. However in this case, the exciton bandwidth did not show a clear trend with respect to PLQE or mobility for 4000 rpm films as it did for 1500 rpm films in Table 4.2, Section 4.3.

Table 4.3: Comparison of mean saturation mobility $\mu_{sat}$, threshold voltage $V_{th}$, exciton bandwidth ($W$) and PLQE for 1500 and 4000 rpm spin coated of fresh and 7 day aged 1 wt% F8T2 BGBC OFETs with 230 nm SiO$_2$ dielectric. The mean was taken over 3 – 4 OFET devices with constant $L = 10\mu m$ and $W = 10,000 \mu m$. 

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Spin speed (rpm)</th>
<th>Ageing</th>
<th>$\mu_{sat}$ (cm$^2$/Vs)</th>
<th>$V_{th}$ (V)</th>
<th>$W$ (meV)</th>
<th>PLQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOL</td>
<td>1500</td>
<td>Fresh</td>
<td>$8.6 \times 10^{-5}$</td>
<td>-7.6</td>
<td>177</td>
<td>22.0</td>
</tr>
<tr>
<td>TOL</td>
<td>1500</td>
<td>Aged</td>
<td>$1.0 \times 10^{-5}$</td>
<td>-9.5</td>
<td>194</td>
<td>10.5</td>
</tr>
<tr>
<td>CB</td>
<td>1500</td>
<td>Fresh</td>
<td>$1.1 \times 10^{-5}$</td>
<td>-18.7</td>
<td>190</td>
<td>15.7</td>
</tr>
<tr>
<td>CB</td>
<td>1500</td>
<td>Aged</td>
<td>$3.2 \times 10^{-5}$</td>
<td>-18.2</td>
<td>166</td>
<td>11.3</td>
</tr>
<tr>
<td>DCB</td>
<td>1500</td>
<td>Fresh</td>
<td>$1.0 \times 10^{-5}$</td>
<td>-18.0</td>
<td>173</td>
<td>23.3</td>
</tr>
<tr>
<td>DCB</td>
<td>1500</td>
<td>Aged</td>
<td>$1.7 \times 10^{-4}$</td>
<td>-28.3</td>
<td>168</td>
<td>14.7</td>
</tr>
<tr>
<td>TOL</td>
<td>4000</td>
<td>Fresh</td>
<td>$1.3 \times 10^{-4}$</td>
<td>-13.0</td>
<td>166</td>
<td>15.3</td>
</tr>
<tr>
<td>TOL</td>
<td>4000</td>
<td>Aged</td>
<td>$1.5 \times 10^{-5}$</td>
<td>-13.8</td>
<td>211</td>
<td>14.8</td>
</tr>
<tr>
<td>CB</td>
<td>4000</td>
<td>Fresh</td>
<td>$8.3 \times 10^{-5}$</td>
<td>-11.1</td>
<td>167</td>
<td>14.8</td>
</tr>
<tr>
<td>CB</td>
<td>4000</td>
<td>Aged</td>
<td>$2.1 \times 10^{-5}$</td>
<td>-12.3</td>
<td>164</td>
<td>19.3</td>
</tr>
<tr>
<td>DCB</td>
<td>4000</td>
<td>Fresh</td>
<td>$1.1 \times 10^{-4}$</td>
<td>-16.1</td>
<td>157</td>
<td>14.1</td>
</tr>
<tr>
<td>DCB</td>
<td>4000</td>
<td>Aged</td>
<td>$3.7 \times 10^{-4}$</td>
<td>-25.4</td>
<td>158</td>
<td>9.4</td>
</tr>
</tbody>
</table>
Figure 4.19: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(\text{max})$ from the transfer characteristics of fresh and 7 day aged BGBC F8T2 OFETs in 1.0 wt% concentrations of TOL, CB and DCB solutions. Thin films are spin coated at 4000 rpm, 30s. Error bars were calculated at the 80% confidence interval using the standard error of 3–4 repeated measurements. Channel lengths and widths used were 10 µm and 10,000 µm ($W/L = 1000$) respectively.
Figure 4.20: Comparison of output and transfer characteristics (shown left to right) of selected fresh and 7 day aged BGBC F8T2 OFETs in 1.0 wt% TOL (a)–(b), CB (c)–(d) and DCB (e)–(f) solutions spin coated at 1500 and 4000 rpm. The output drain currents displayed are at a gate voltage of $V_G = -60\, \text{V}$ and the transfer drain current is displayed in a logarithmic scale at a drain voltage of $V_D = -60\, \text{V}$. Channel lengths and widths used were $10\, \mu\text{m}$ and $10,000\, \mu\text{m}$ ($W/L = 1000$) respectively.
4.4.3.2 Top Gate OFETs

In order to verify that the ageing effect on OFET performance and morphology of spin coated thin films from different solvents was not unique to bottom gate devices, we also investigated top gate bottom contact (TGBC) devices with a 700 nm spin coated PVP dielectric. Due to time and resource issues, we examined the effect of ageing on F8T2-1WT% thin films in TOL, CB and DCB spin coated at 4000 rpm TGBC devices only. Table 4.4 displays the yield of the devices measured. A total of 42 TGBC devices were fabricated and analysed with acceptable yields obtained for fresh films of TOL and CB. Poor yields were obtained for aged TOL and CB devices due to high gate leakage currents and shorting during operation caused by the poor film quality and high surface roughness (see Section 4.4.1). In comparison, aged DCB devices gave a much higher yield of working devices than its fresh counterpart.

Table 4.4: TGBC device success rate for fresh (I) and aged (II) TOL, CB and DCB F8T2-1WT% films spin coated at 4000 rpm with a 700 nm PVP dielectric. Device success rate considers OFETs that did not short upon operation and have $|I_D/I_G| > 1$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ageing</th>
<th>Total measured</th>
<th>Device success rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOL I</td>
<td></td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>TOL II</td>
<td></td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>CB I</td>
<td></td>
<td>6</td>
<td>67</td>
</tr>
<tr>
<td>CB II</td>
<td></td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>DCB I</td>
<td></td>
<td>8</td>
<td>38</td>
</tr>
<tr>
<td>DCB II</td>
<td></td>
<td>7</td>
<td>57</td>
</tr>
</tbody>
</table>

Due to the poor yield obtained with aged OFETs of TOL and CB, the output drain current for fresh films was much higher than aged films. The high gate leakage in aged films lead to poor on/off ratios and high turn on voltages as can be seen in Figure 4.21. Examining the DCB OFETs on the other hand, the output drain current of the fresh and aged films did not vary significantly with respect to each other. Even the turn on voltage and on/off ratios did not vary significantly in the transfer characteristics.

Analysing the OFET performance metrics in Figure 4.21, we noticed a slight increase in mobility and on/off ratio for aged DCB OFETs. The results obtained for fresh and aged films in TGBC architectures showed similar trends with ageing compared to those obtained for BGBC architectures in Figure 4.19 earlier. Interestingly, a solvent boiling point dependent mobility and threshold voltage was not observed for TGBC OFETs. As can be seen in Figure 4.21, there was hardly any variation in the $\mu_{sat}$ ($\sim 1 \times 10^{-3}$ cm²/Vs), $V_{th}$ ($\sim 5$V) and other parameters in the fresh films of TOL, CB and DCB.
The best OFET obtained for TOL was with fresh films which had a $\mu_{\text{sat}}$ of $1.5 \times 10^{-3}$ cm$^2$/Vs, $V_{th}$ of -7 V and on/off ratio of $2 \times 10^5$. For CB OFETs, again fresh films had the best performance with a $\mu_{\text{sat}}$ of $1.4 \times 10^{-3}$ cm$^2$/Vs, $V_{th}$ of -7 V and on/off ratio of $2 \times 10^5$. For DCB OFETs on the other hand, we obtained higher performance with aged films, which had a $\mu_{\text{sat}}$ of $2.2 \times 10^{-3}$ cm$^2$/Vs, $V_{th}$ of -16 V and on/off ratio of $3 \times 10^5$.

These results were much higher than those obtained with BGBC OFETs with a thinner dielectric. Most notably, very minimal hysteresis was observed in TGBC devices compared to BGBC devices. However, this is to be expected because top gate architectures generally possess larger injection areas which allow favourable injection paths leading to lower contact resistances than compared to bottom gate architectures [59][60]. The highest mobility obtained for aged DCB OFETs was an order of a magnitude lower to the highest F8T2 mobility recorded to date ($\sim 0.02$ cm$^2$/Vs) by Sirringhaus and coworkers who also used a similar top-gate PVP architecture [1]. However, it should be noted that they aligned the F8T2 chains parallel to the source and drain electrodes with a rubbed polyimide alignment layer and used a much thinner PVP dielectric (300 nm).
Figure 4.21: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(max)$ from the transfer characteristics of fresh and 7 day aged TGBG F8T2 OFETs with a 700 nm PVP dielectric. Thin films were spin coated at 4000 rpm, 30s with 1.0 wt% TOL, CB and DCB solutions. Error bars were calculated at the 80% confidence interval from the standard error of 3–4 repeated measurements. Channel lengths and widths used were 50 $\mu$m and 2000 $\mu$m ($W/L = 40$) respectively.
Figure 4.22: Comparison of selected output and transfer characteristics of fresh and 7 day aged TGBC F8T2-1WT% OFETs with 4000 rpm spin coated films of TOL (a)–(b), CB (c)–(d) and DCB (e)–(f). A 700 nm spin coated film of PVP was used as the dielectric. The channel lengths and widths used were 50 μm and 2000 μm (W/L = 40) respectively. Shaded regions represent the area between the paths of the minimum and maximum forward scan drain current measured from the sample size for each condition.
4.4.4 Modelling of aged F8T2 OFETs with varying solvent and spin speed

Selected BGBC OFET transfer characteristics for 1500 and 4000 rpm spin coated 1 wt% F8T2 films in TOL, CB and DCB were fitted as per the equations derived by Campbell and coworkers who used the Tanase, Vissenberg and Matters model for charge transport in amorphous, glassy disordered organic semiconductors [41][42][43]. Using the modelling routine described in Chapter 3.3.1.1, fits for the $\rho$, $V_{to}$, $m$ and $\mu_{sat}$ were initially obtained for the linear regime at $V_D = -10V$. The Vissenberg and Matters exponential DOS distribution characteristic temperature $T_0$ was then calculated from $m = T_0/T - 1$, where $T = 300$ K at room temperature. The values obtained from the linear regime fits were kept constant and subsequently fitted for the saturation regime at $V_D = -60V$ to obtain an estimate for the saturation mobility $\mu_{sat}$. Table 4.5 displays the fit parameters for fresh and aged 1500 and 4000 rpm films.
**Table 4.5:** V&M modelling fit parameters for 1500 and 4000 rpm spin coated films of fresh (I) and 7 day aged (II) 1 wt% F8T2 BGBC OFETs with 230 nm SiO$_2$ dielectric at $T = 300K$. Channel length and widths used were $L = 10\mu m$ and $W = 10,000\mu m$ respectively.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Spin speed (rpm)</th>
<th>Ageing</th>
<th>$\mu_{lin}$</th>
<th>$\mu_{sat}$</th>
<th>$V_{th}$</th>
<th>$V_{to}$</th>
<th>$\rho$</th>
<th>$m$</th>
<th>$\mu_{sat}$</th>
<th>$T_0$</th>
<th>$\mu_{sat}$ fit variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOL</td>
<td>1500</td>
<td>I</td>
<td>$6.0 \times 10^{-5}$</td>
<td>$9.5 \times 10^{-5}$</td>
<td>-9.6</td>
<td>-6.2</td>
<td>$6.0 \times 10^{19}$</td>
<td>0.60</td>
<td>$1.3 \times 10^{-4}$</td>
<td>479</td>
<td>41</td>
</tr>
<tr>
<td>TOL</td>
<td>1500</td>
<td>II</td>
<td>$7.1 \times 10^{-6}$</td>
<td>$9.9 \times 10^{-6}$</td>
<td>-5.0</td>
<td>-4.7</td>
<td>$4.1 \times 10^{19}$</td>
<td>1.06</td>
<td>$1.7 \times 10^{-5}$</td>
<td>618</td>
<td>72</td>
</tr>
<tr>
<td>CB</td>
<td>1500</td>
<td>I</td>
<td>$4.6 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>-19.2</td>
<td>-11.3</td>
<td>$4.5 \times 10^{19}$</td>
<td>1.47</td>
<td>$1.6 \times 10^{-5}$</td>
<td>741</td>
<td>54</td>
</tr>
<tr>
<td>CB</td>
<td>1500</td>
<td>II</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$3.2 \times 10^{-5}$</td>
<td>-14.4</td>
<td>-8.6</td>
<td>$4.3 \times 10^{19}$</td>
<td>1.36</td>
<td>$4.9 \times 10^{-5}$</td>
<td>709</td>
<td>55</td>
</tr>
<tr>
<td>DCB</td>
<td>1500</td>
<td>I</td>
<td>$7.0 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>-19.8</td>
<td>-11.2</td>
<td>$4.4 \times 10^{19}$</td>
<td>1.50</td>
<td>$1.7 \times 10^{-5}$</td>
<td>749</td>
<td>55</td>
</tr>
<tr>
<td>DCB</td>
<td>1500</td>
<td>II</td>
<td>$9.8 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>-20.9</td>
<td>-9.8</td>
<td>$5.9 \times 10^{19}$</td>
<td>0.69</td>
<td>$1.9 \times 10^{-4}$</td>
<td>508</td>
<td>34</td>
</tr>
<tr>
<td>TOL</td>
<td>4000</td>
<td>I</td>
<td>$8.2 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>-13.5</td>
<td>-7.5</td>
<td>$6.2 \times 10^{19}$</td>
<td>0.47</td>
<td>$1.6 \times 10^{-4}$</td>
<td>441</td>
<td>18</td>
</tr>
<tr>
<td>TOL</td>
<td>4000</td>
<td>II</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$1.9 \times 10^{-5}$</td>
<td>-14.4</td>
<td>-3.9</td>
<td>$5.0 \times 10^{19}$</td>
<td>1.50</td>
<td>$2.6 \times 10^{-5}$</td>
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<td>37</td>
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<td>CB</td>
<td>4000</td>
<td>I</td>
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<td>$1.1 \times 10^{-4}$</td>
<td>-9.8</td>
<td>-6.4</td>
<td>$5.3 \times 10^{19}$</td>
<td>0.47</td>
<td>$1.4 \times 10^{-4}$</td>
<td>441</td>
<td>25</td>
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<tr>
<td>CB</td>
<td>4000</td>
<td>II</td>
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<td>$2.1 \times 10^{-5}$</td>
<td>-12.0</td>
<td>-6.9</td>
<td>$4.9 \times 10^{19}$</td>
<td>0.89</td>
<td>$2.9 \times 10^{-5}$</td>
<td>566</td>
<td>37</td>
</tr>
<tr>
<td>DCB</td>
<td>4000</td>
<td>I</td>
<td>$6.5 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>-16.6</td>
<td>-8.5</td>
<td>$6.0 \times 10^{19}$</td>
<td>0.64</td>
<td>$1.6 \times 10^{-4}$</td>
<td>493</td>
<td>25</td>
</tr>
<tr>
<td>DCB</td>
<td>4000</td>
<td>II</td>
<td>$2.4 \times 10^{-4}$</td>
<td>$4.1 \times 10^{-4}$</td>
<td>-20.7</td>
<td>-9.6</td>
<td>$6.7 \times 10^{19}$</td>
<td>0.69</td>
<td>$4.8 \times 10^{-4}$</td>
<td>506</td>
<td>17</td>
</tr>
</tbody>
</table>
Figures 4.23 and 4.24 show the model fits for 1500 and 4000 rpm films respectively. As shown in Figures 4.23 and 4.24 for fresh and aged the 1500 and 4000 rpm films, very good fits were obtained within the 95% confidence interval bands. However, poor fits was obtained for aged DCB films and aged 4000 rpm TOL films, possibly caused by poor film formation and trap states, leading to unexpected non-ideal behaviour. Interestingly, the fitted turn on voltage $V_{to}$ was consistently smaller than the experimentally extracted threshold voltage $V_{th}$ for the same devices in Table 4.3. As previously mentioned in Chapter 2.3.3, the turn on voltage $V_{to}$ is defined as the gate voltage at which there is no band bending in the organic semiconductor. $V_{to}$ is ideally 0 V if there are no fixed charges at the semiconductor and dielectric interface [61]. Hence despite the reduction in $V_{to}$, the non-zero values possibly indicates the presence of deep trap states and other polarising factors at the organic semiconductor and dielectric interfaces for all devices measured [62].

The fitted parameters for carrier density per unit volume were generally obtained in the region of $> 1 \times 10^{19}cm^{-3}$, which is in agreement with previous reports involving polyfluorene OFETs [42][63]. The variation of $T_0$ with solution ageing showed different trends with respect to the spin coating speed. For 1500 rpm films there was no particular trend, but $T_0$ was observed to increase with ageing for 4000 rpm films for all solvent types, indicating increased disorder for charge transport. Interestingly, this corresponded with a slight increase in the fitted $\mu_{sat}$ along with an increase of the $V_{to}$.

Despite obtaining very good fits for most devices, the fitted values for the $\mu_{sat}$ were in general overestimated by several percent. This perhaps indicates that the experimentally deduced $\mu_{sat}$ from the slope of the saturation transfer characteristics were consistently underestimated. This is characteristic of organic transistors, as the current does not immediately increase rapidly at the threshold voltage compared to standard silicon transistors due to the presence of trap states, hence there is some ambiguity in deciding the best location to draw the line of best fits for the linear slopes [64][65].
Figure 4.23: Model fits to the experimental transfer characteristics of 1500 rpm spin coated films of TOL (a)–(b), CB (c)–(d) and DCB (e)–(f). Fitted parameters are given in Table 4.5. Plots from left to the right show fresh and 7 day ageing: (a), (c) and (e) are fresh films, while (b), (d) and (f) are aged films. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data.
Figure 4.24: Model fits to the experimental transfer characteristics of 4000 rpm spin coated films of TOL (a)–(b), CB (c)–(d) and DCB (e)–(f). Fitted parameters are given in Table 4.5. Plots from left to the right show fresh and 7 day ageing: (a), (c) and (e) are fresh films, while (b), (d) and (f) are aged films. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data.
4.5 Effect of annealing on aged F8T2-CB films

4.5.1 Surface morphology

We next turn our attention to annealed films of fresh and aged F8T2 in 1 wt% CB solutions. F8T2 is known to possess a thermotropic, nematic liquid crystalline phase when annealed above 265°C. According to X-ray diffraction studies, F8T2 in the nematic crystalline phase have their polymer backbones lie in the plane of the substrate (face to face packing), and this generally results in enhanced charge transport characteristics [1][66]. In this section, F8T2 thin films films were annealed in N₂ above the liquid-crystal transition temperature at 280°C for 30 mins, and then allowed to slowly cool to room temperature before use. Figure 4.25 shows AFM scans of the fresh and aged F8T2-CB films spin coated at 4000 rpm. An mean film thickness of 34 nm was obtained for fresh F8T2-CB films and 27 nm for aged films spin coated 4000 rpm.

We can see from the AFM scans that there were distinctive changes to the morphology in annealed films. For annealed fresh F8T2-CB films, we observed a high density clustering of uniform regions with >15 nm thickness, compared to fresh films with no annealing. Annealed grain sizes were measured to be 200 – 350 nm in size, much larger than fresh non-annealed CB films in Section 4.4.1. In aged annealed films on the other hand, the clustering was interrupted with scattered regions of feature heights <6 nm and variable grain sizes between 60 – 200 nm. An RMS roughness of 0.80 nm and 0.99 nm was obtained for fresh and aged F8T2-CB films with no annealing. Upon annealing, the RMS of these films increased to 2.77 nm and 2.41 nm for fresh and aged films respectively.

![AFM scans of non-annealed (NA) and annealed (A) films of fresh and 7 day aged F8T2-CB-1WT% solutions spin coated at 4000 rpm, 30s.](image)

**Figure 4.25:** AFM scans of non-annealed (NA) and annealed (A) films of fresh and 7 day aged F8T2-CB-1WT% solutions spin coated at 4000 rpm, 30s.
### 4.5.2 Optical spectroscopy

In Figures 4.26(a) and (b), the normalised UV-vis spectra of no annealing/annealed F8T2-CB-1wt% films are displayed at 1500 rpm and 4000 rpm annealing. The 1500 rpm films were 50 nm in thickness while the 4000 rpm films had a thickness of 35 nm. A small redshift was observed at the $0 - 0$ peak wavelength upon annealing. For fresh 1500 rpm films, the $0 - 0$ peak wavelength increased from 483 nm to 488 nm, and for the 4000 rpm films the wavelength increased from 485 nm to 490 nm upon annealing. A similar red shift was observed for the $0 - 1$ peak. Similarly, from the corresponding normalised PL spectra in Figures 4.27(a) and (b), the $0 - 0$ peak wavelength increased from 511 nm to 515 nm for fresh 1500 rpm films, and 510 nm to 512 nm for fresh 4000 films upon annealing.

![Figure 4.26](image-a.png)  
**Figure 4.26:** Normalised UV-vis spectra of non-annealed (a) and annealed (b) films of fresh and 7 day aged F8T2-CB-1WT% solutions spin coated at 1500 and 4000 rpm.

![Figure 4.27](image-b.png)  
**Figure 4.27:** Normalised PL spectra taken at an excitation wavelength of 450 nm for non-annealed (a) and annealed (b) films of fresh and 7 day aged F8T2-CB-1WT% solutions spin coated at 1500 and 4000 rpm.
From both the UV-vis and PL spectra, we observed a gradual restoration of the $0 - 0$ transition peak indicating an increase in the molecular ordering characteristic with J-aggregate intrachain ordering after annealing. Using the $0 - 0$ and $0 - 1$ peak ratios from the PL spectra, we analysed the exciton bandwidth with respect to the spin coating speed for fresh and aged F8T2-CB films with and without annealing in Figure 4.28.

A decrease in the exciton bandwidth was observed after annealing for the PL spectra estimated exciton bandwidth. We can see for fresh 1500 rpm films that the exciton bandwidth decreased from 192 meV to 159 meV after annealing. For fresh 4000 rpm films it decreased from 167 meV to 160 meV, a much smaller decrease compared to the 1500 rpm films. Examining the aged 1500 rpm films, the exciton bandwidth decreased from 166 meV to 156 meV, and for 4000 rpm films it decreased from 164 meV to 160 meV. Interestingly, the relative decrease in exciton bandwidth upon annealing the aged films was much smaller than compared to annealing the fresh films. Hardly any change in the exciton bandwidth was observed for both annealed fresh and aged 4000 rpm films. This possibly indicates that ageing induced some degree of J-aggregate ordering to the films prior to annealing hence resulting in very little or no changes in the exciton bandwidth. In some reports, researchers have found that annealing temperatures of $>100$ °C tended to suppress the $\beta$ phase formation in polyfluorenes such as PFO. Hence this can perhaps explain why very little change in the exciton bandwidth was observed for annealed devices of F8T2 [67][68].

![Figure 4.28](image)

Figure 4.28: Exciton bandwidth (W) calculated from the $0 - 0/0 - 1$ peak ratios from PL spectra for non-annealed (NA) and annealed (A) films of fresh and 7 day aged F8T2-CB-1WT% solutions spin coated at 1500 and 4000 rpm.

In Figures 4.29(a) and (b) we analysed the effect of annealing on the PLQE on fresh and aged F8T2-CB films. For fresh films in Figure 4.29(a), we noticed an increase in the PLQE from 11% to 27% for 1500 rpm films, and 15% to 22% for 4000 rpm films. Similarly for the aged films, we saw an increase in the PLQE from 11%
to 15% for 1500 rpm films, and 19% to 40% for 4000 rpm films. This is a surprising result because this increase in PLQE upon annealing corresponds with a decrease in the exciton bandwidth. This is an inverse relationship compared to what was observed in Figure 4.9 in Section 4.4 and seems to suggest that annealing removes quenching effects in the disordered amorphous thin films resulting in a restoration of the PLQE.

![Figure 4.29: Comparison of photoluminescence quantum efficiency (PLQE) with non-annealed (NA) and annealed (A) films of fresh (I) and 7 day aged (II) F8T2-CB-1WT% solutions spin coated at 1500 and 4000 rpm. Error bars are deduced at the 80% confidence interval for 3 repeated measurements.](image)

### 4.5.3 GIWAXS

In order to get an idea of the packing and orientation within the F8T2-CB films, Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) measurements were taken. Figures 4.30(a)–(b) show GIWAXS of fresh and 7 day aged F8T2-CB films prior to annealing, and Figures 4.30(c)–(d) show the effects of annealing at 280°C for 30 min and quenching to room temperature. As can be seen in Figures 4.30(a) and (b), there are no sharp Bragg reflections, indicating that there was no long range structural order in either the fresh or aged non-annealed F8T2-CB films. The lack of long range order in the non-annealed films indicates either two possibilities: the films were amorphous, or the films contained small, misaligned domains of nematic-like liquid crystalline order. Only the outer diffuse ring was visible and was estimated to have a d-spacing of 4.1 Å which corresponded to either the (001) or (004) reflection peaks indicating the intermolecular $\pi-\pi$ spacing between the F8T2 chains according to the literature [69].
Figures 4.30: GIWAXS plots of fresh and aged non-annealed (a)–(b), and fresh and aged annealed (280°C, 30 min) (c)–(d) F8T2-CB-1WT% films spin coated at 4000 rpm. The grid lines on the pictures are a consequence of using the Pilatus detector hence were unavoidable.

Figures 4.30(c) and (d) on the other hand started to show sharp Bragg reflections, indicating early development of a crystalline structure for both fresh and aged F8T2-CB films after annealing. The presence of the inner diffuse ring attributes to the (100) reflection with a measured d-spacing of 15.9 Å. The d-spacing estimated for (100) was slightly lower than the literature value of 16 Å and is thought to correspond to the distance between layers of separate F8T2 chains which pack in a plane perpendicular to their longitudinal axes arising from the segregation between main chain backbones and aggregated alkyl side chains [70][37]. Other faint diffuse rings observed in the GIWAXS spectra could have formed due to incomplete side-chain crystallization [71], although unfortunately they could not be attributed to any specific reflection peaks.

In annealed films, the fact that the Bragg reflections appear as sharp spots or very narrow arcs, signifies that the crystallites were well oriented, i.e. grown in approximately the same direction. However the presence of the outer diffuse ring indicates that some parts of the film were still amorphous. These GIWAXS results relate back to the increase in the 0–0 peak and hence J aggregate intrachain ordering/crystallinity identified earlier in Section 4.5.2 with annealed CB films.
4.5.4 Transistor Analysis

Bottom gate, bottom contact (BGBC) OFETs with a 230 nm SiO$_2$ dielectric were fabricated to investigate the charge transport characteristics for fresh and aged annealed films of F8T2-CB-1WT% at different spin speeds of 1500 and 4000 rpm. The channel length and width used for the OFETs were kept constant at 10 µm and 10,000 µm ($W/L = 1000$) respectively. Mean film thicknesses obtained for fresh and aged 1500 rpm films were 49 nm and 52 nm respectively, while for 4000 rpm films they were 34 nm and 27 nm respectively. Averages of the OFET characteristics were taken over 4 repeats for each condition: spin speed, ageing, and annealing, resulting in a total of 32 devices measured.

Figure 4.31 show the key performance metrics of the F8T2-CB OFETs with ageing, annealing and variation in spin speed. Output and transfer characteristics for best performing devices are shown in Figure 4.32. For the 1500 rpm films, annealing showed a slight enhancement of the mean mobility for fresh films. No significant change was observed for aged films due to the overlapping of the error bars. The opposite effect was observed for the films spin coated at 4000 rpm, where both annealing and ageing tended to reduce the mean mobility. Changes in $V_{th}$ and $SS$ due to ageing on the other hand, were not statistically significant, although annealing did increase it in general. A noticeable reduction in the on/off ratios for aged and annealed films of F8T2-CB were observed for both thin film regimes.

There is some ambiguity in the literature regarding the effects of annealing on the performance of F8T2 devices. For example, some papers have shown that annealing above $T_G$ tends to result in higher mobilities and low threshold voltages [1][37][72]. While some have instead observed lower mobilities and higher threshold voltages with annealing [3]. Our results seem to agree with the latter for 4000 rpm films as indeed there is a clear trend of increasing threshold voltage with annealing. However, due to the overlapping of the error bars, we cannot say there is a significant difference between fresh and aged devices. In contrast, the mean saturation mobility increased with annealing for fresh 1500 rpm films as can be seen in Figure 4.32(a). In this case, the annealed 1500 rpm films of fresh F8T2-CB gave the highest $\mu_{sat}$ of $3.2 \times 10^{-5}$ cm$^2$/Vs, $V_{th}$ of -16 V and an on/off ratio of $2 \times 10^4$.

Why annealing a fresh (aged) thin film spin coated at a slow spin speed of 1500 rpm gave a much higher (lower) mobility than its non-annealed counterpart, whereas annealing a fresh (aged) thin film spin coated at a high spin speed of 4000 rpm showed a complete opposite trend is unclear. According to Richards and coworkers who also used F8T2, a film thickness less than the source and drain contact thickness tends to result in higher contact resistances due to incomplete step coverage at the contact edge [59]. Since the source and drain contacts in our BGBC OFETs had
a total thickness of 40 nm (30 nm Au + 10 nm ITO), we should have expected a higher contact resistance and hence much lower mobility with the fresh 34 nm 4000 rpm films. But this was not the case as they gave a much higher OFET performance than the 51 nm thick films obtained at 1500 rpm. Based on these results, we can see that in general, the effect of annealing on $\mu_{sat}$ and $V_{th}$ for F8T2-CB-1WT% OFETs appears to show a dependence on film thickness and ageing. Similar trends and results were also observed in annealed and aged F8T2-CB top gate OFETs, and these are provided in Appendix A.1.

**Table 4.6:** Comparison of mean saturation mobility $\mu_{sat}$, threshold voltage $V_{th}$, exciton bandwidth ($W$) and PLQE for annealed 1500 and 4000 rpm spin coated of fresh and 7 day aged 1 wt% F8T2 BGBC OFETs with 230 nm SiO$_2$ dielectric. Annealing was carried out at 280°C for 30 mins in N$_2$. The mean is taken over 3 – 4 OFET devices with constant $L = 10\mu$m and $W = 10,000\mu$m. In the table, no annealing = NA and annealing = A.

<table>
<thead>
<tr>
<th>Spin speed (rpm)</th>
<th>Annealing</th>
<th>Ageing</th>
<th>$\mu_{sat}$ (cm$^2$/Vs)</th>
<th>$V_{th}$ (V)</th>
<th>$W$ (meV)</th>
<th>PLQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>NA</td>
<td>Fresh</td>
<td>$1.0\times10^{-5}$</td>
<td>-17.9</td>
<td>192</td>
<td>10.9</td>
</tr>
<tr>
<td>1500</td>
<td>NA</td>
<td>Aged</td>
<td>$2.8\times10^{-5}$</td>
<td>-17.3</td>
<td>166</td>
<td>11.3</td>
</tr>
<tr>
<td>1500</td>
<td>A</td>
<td>Fresh</td>
<td>$2.8\times10^{-5}$</td>
<td>-16.7</td>
<td>159</td>
<td>26.7</td>
</tr>
<tr>
<td>1500</td>
<td>A</td>
<td>Aged</td>
<td>$1.8\times10^{-5}$</td>
<td>-19.6</td>
<td>156</td>
<td>15.4</td>
</tr>
<tr>
<td>4000</td>
<td>NA</td>
<td>Fresh</td>
<td>$9.1\times10^{-5}$</td>
<td>-10.4</td>
<td>167</td>
<td>14.8</td>
</tr>
<tr>
<td>4000</td>
<td>NA</td>
<td>Aged</td>
<td>$1.9\times10^{-5}$</td>
<td>-11.8</td>
<td>164</td>
<td>19.3</td>
</tr>
<tr>
<td>4000</td>
<td>A</td>
<td>Fresh</td>
<td>$4.5\times10^{-5}$</td>
<td>-14.8</td>
<td>160</td>
<td>22.0</td>
</tr>
<tr>
<td>4000</td>
<td>A</td>
<td>Aged</td>
<td>$3.2\times10^{-5}$</td>
<td>-16.4</td>
<td>160</td>
<td>40.8</td>
</tr>
</tbody>
</table>
Figure 4.31: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(max)$ from the transfer characteristics of non-annealed (NA) and annealed (A) fresh and 7 day aged BGBC F8T2-CB-1WT% OFETs spin coated at 1500 (a) and 4000 rpm (b). Error bars were calculated at the 80% confidence interval using the standard error between 3–4 repeated measurements. Channel lengths and widths used were 10 $\mu$m and 10,000 $\mu$m ($W/L = 1000$) respectively.
Figure 4.32: Comparison of selected output and transfer characteristics for fresh and aged F8T2-CB-1WT% BGBC OFETs with 230 nm SiO$_2$ dielectric with and without annealing at 280°C for 1500 rpm films (a)–(b), and 4000 rpm films (c)–(d). Channel length and width used for the OFETs were 10 µm and 10,000 µm (W/L = 1000) respectively.

4.5.5 Modelling of aged annealed OFETs

In order to estimate the Vissenberg and Matters exponential DOS distribution characteristic temperature $T_0$, we fit the transfer characteristics of selected non-annealed/annealed BGBC F8T2-CB-1WT% OFETs spin coated at 1500 and 4000 rpm with fresh and 7 day aged films. Table 4.7 displays the fitting parameters. The fitting parameters obtained previously in Table 4.5 in Section 4.4 for non-annealed 1500 and 4000 rpm spin coated films of F8T2-CB-1WT% are repeated in the same table for comparison purposes. A charge carrier density in the region of $\sim 1 \times 10^{19}$ cm$^{-3}$ was obtained for both 1500 and 4000 rpm films.

Figures 4.33 and 4.34 display the model fits for 1500 and 4000 rpm films respectively. Good fits were obtained for both experimental linear and saturation regimes within the 95% confidence interval bands. For 1500 rpm spin coated films, the $T_0$ calculated decreased from 658 K to 512 K after annealing for fresh films, and 709 K to 664 K for aged films. On the other hand, the 4000 rpm spin coated films showed an increase in the $T_0$ from 441 K to 510 K for fresh films, and 566 K to 592 K for aged films upon annealing. In all cases, there was a clear trend where an increase...
in the $T_0$ disorder lead to an increase in the $V_{to}$. These estimations of $T_0$ also seem to agree with our previous analysis in Section 4.5.4, where upon annealing thicker films of fresh F8T2 resulted in enhanced charge carrier mobility, whereas for fresh thin films, the mobility decreased.
### Table 4.7: V&M modelling fit parameters for annealed (A) and non-annealed (NA) 1500 and 4000 rpm spin coated films of fresh (I) and 7 day aged (II) F8T2-CB-1WT% BGBC OFETs with 230 nm SiO$_2$ dielectric at $T = 300K$. Annealing was carried out at 280°C for 30 mins in N$_2$. Channel length and widths used were $L = 10\mu m$ and $W = 10,000\mu m$ respectively.

<table>
<thead>
<tr>
<th>Solvent Spin speed (rpm)</th>
<th>Ageing</th>
<th>$\mu_{\text{lin}}$</th>
<th>$\mu_{\text{sat}}$</th>
<th>$V_{\text{th}}$</th>
<th>$V_{\text{to}}$</th>
<th>$\rho$</th>
<th>$m$</th>
<th>$\mu_{\text{sat}}$</th>
<th>$T_0$</th>
<th>$\mu_{\text{sat}}$ fit variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 NA</td>
<td>I</td>
<td>$4.9 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>-15.4</td>
<td>-8.8</td>
<td>4.7 $\times 10^{19}$</td>
<td>1.19</td>
<td>1.6 $\times 10^{-5}$</td>
<td>658</td>
<td>49</td>
</tr>
<tr>
<td>1500 NA</td>
<td>II</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$3.2 \times 10^{-5}$</td>
<td>-14.4</td>
<td>-8.6</td>
<td>4.3 $\times 10^{19}$</td>
<td>1.36</td>
<td>4.9 $\times 10^{-5}$</td>
<td>709</td>
<td>55</td>
</tr>
<tr>
<td>1500 A</td>
<td>I</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$3.2 \times 10^{-5}$</td>
<td>-16.3</td>
<td>-8.8</td>
<td>5.7 $\times 10^{19}$</td>
<td>0.71</td>
<td>3.8 $\times 10^{-5}$</td>
<td>512</td>
<td>18</td>
</tr>
<tr>
<td>1500 A</td>
<td>II</td>
<td>$8.1 \times 10^{-6}$</td>
<td>$2.1 \times 10^{-5}$</td>
<td>-20.1</td>
<td>-10.4</td>
<td>4.8 $\times 10^{19}$</td>
<td>1.21</td>
<td>2.8 $\times 10^{-5}$</td>
<td>664</td>
<td>34</td>
</tr>
<tr>
<td>4000 NA</td>
<td>I</td>
<td>$6.0 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>-9.8</td>
<td>-6.4</td>
<td>5.3 $\times 10^{19}$</td>
<td>0.47</td>
<td>1.4 $\times 10^{-4}$</td>
<td>441</td>
<td>25</td>
</tr>
<tr>
<td>4000 NA</td>
<td>II</td>
<td>$8.2 \times 10^{-6}$</td>
<td>$1.9 \times 10^{-5}$</td>
<td>-12.9</td>
<td>-8.0</td>
<td>4.6 $\times 10^{19}$</td>
<td>0.96</td>
<td>2.6 $\times 10^{-5}$</td>
<td>588</td>
<td>38</td>
</tr>
<tr>
<td>4000 A</td>
<td>I</td>
<td>$2.0 \times 10^{-5}$</td>
<td>$4.9 \times 10^{-5}$</td>
<td>-15.4</td>
<td>-8.5</td>
<td>5.6 $\times 10^{19}$</td>
<td>0.70</td>
<td>6.0 $\times 10^{-5}$</td>
<td>510</td>
<td>22</td>
</tr>
<tr>
<td>4000 A</td>
<td>II</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$3.3 \times 10^{-5}$</td>
<td>-16.3</td>
<td>-9.0</td>
<td>4.9 $\times 10^{19}$</td>
<td>0.97</td>
<td>4.5 $\times 10^{-5}$</td>
<td>592</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 4.33: Model fits to the experimental transfer characteristics for fresh/aged (left to right) non-annealed/annealed (top to bottom) 1500 rpm spin coated films of F8T2-CB-1WT%. Fitted parameters are given in Table 4.7. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data.
Figure 4.34: Model fits to the experimental transfer characteristics for fresh/aged (left to right) non-annealed/annealed (top to bottom) 4000 rpm spin coated films of F8T2-CB-1WT%. Fitted parameters are given in Table 4.7. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data.
4.6 Conclusions

In this chapter, we investigated the beta-phase aggregation effect in F8T2 using solution ageing techniques with different boiling point solvents, concentrations, spin speeds and annealing. Using the H-J aggregation model developed by Spano and coworkers, in Section 4.3 we found that F8T2 predominantly prefers an H-aggregate orientation (interchain ordering) with films prepared from fresh solutions. Ageing the solutions induced a small degree of J-aggregate intrachain ordering proportional to concentration and solvent boiling type, corresponding to the beta-phase of F8T2. This was confirmed with exciton bandwidth analysis from the PL spectra. It was also found that the PLQE was slightly dependent on the exciton bandwidth, with a higher PLQE observed at larger exciton bandwidths.

In Section 4.4 we found that films of CB and DCB prepared from aged solutions spin coated at 1500 rpm generally gave enhanced saturation mobilities and on/off ratios compared to thin films prepared from fresh solutions. Although an increase in the threshold voltage was also observed, the decrease in the Vissenberg and Matters DOS distribution characteristic temperature $T_0$ generally indicated a decrease in disorder in the charge transport characteristics. Ageing the 4000 rpm films of TOL and CB on the other hand reduced OFET performance and increased the $V_{th}$ correlating with an increase in the $T_0$. The opposite was observed for DCB films, as ageing instead improved its OFET performance characteristics. We also observed the same ageing effect trends with top-gate architectures. Mobilities in the bottom-gate configuration were generally $> 1 \times 10^{-4}$ cm$^2$/Vs with on/off ratios in the region of $10^4 - 10^5$. While mobilities and on/off ratios in the top-gate configuration were generally a magnitude higher due to improved F8T2 morphology at the top interface than in the buried interface in bottom gate devices.

Finally, in Section 4.5 we observed an increase in the J-aggregation with annealing. Based on GIWAXS analysis, non-annealed fresh and aged F8T2-CB films were mainly amorphous and did not possess long range structure order compared to annealed films. In OFET devices, we found that annealing thicker films of fresh F8T2 spin coated at 1500 rpm generally tended to decrease the $T_0$ disorder resulting in enhanced saturation mobilities, whereas for thin films (4000 rpm) the disorder was increased thereby reducing the mobility. Interestingly, the opposite was observed for films prepared from aged solutions as the mobility decreased upon annealing aged 1500 rpm films, while it increased for aged 4000 rpm films. However in general, we found that annealing tended to increase the threshold voltages for both 1500 and 4000 rpm films regardless of ageing, and this was quantified with an increase in the $T_0$ disorder.
Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films

References


Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films


Chapter 4. Study of beta-phase aggregation in aged F8T2 thin films


Chapter 5

Beta-phase in F8T2 films from azeotropic binary solutions

The formation of the beta-phase was investigated with changes in concentration, spin speed, and annealing in the previous chapter. The beta-phase was mainly prominent in films prepared from high boiling point solvents such as 1,2-dichlorobenzene, however this came at the cost of higher threshold voltages and $T_0$ disorder. Furthermore, it may be impractical to rely on solvents with very low vapour pressures for industrial processes that demand high throughput and low operating voltages. With these challenges in mind, we shifted our attention to using azeotropic binary solutions to study the beta-phase of F8T2. Using mainly chlorobenzene as the primary solvent due to its relatively high vapour pressure, along with hexane and tetralin as the secondary poor solvents, we found certain regimes where the beta-phase was detrimental to OFET performance in terms of mobility, threshold voltage and on/off ratios. Quantitative analysis using the H-J aggregate and Vissenberg-Matters models were again employed to provide deeper insight.
5.1 Introduction

Common solution processing techniques for crystalline organic semiconductor deposition such as spin coating, dip coating and drop casting result in thin films that are polycrystalline or semicrystalline in nature. Compared to single crystalline morphologies, these generally have an increased number of defects and disorder which result in trap states that reduce charge carrier mobility [1][2]. The degree of crystallinity can be increased through the use of solvents with higher boiling points and vapour pressure [3]. Recently, researchers have used azeotropic binary solvent mixtures (also called the solvent exchange method) to achieve highly crystalline growth. This has resulted in improved charge carrier mobilities in OFET devices much higher than that of single solvent solutions [4][5].

An azeotropic solution is a mixture of two different liquids with different properties and has a constant boiling point depending on the volume fraction of the solvents. Good crystal growth has been achieved by using a mixture of polar and nonpolar solvents with one having a high or low boiling point. The nonpolar solvent used is generally the one which dissolves the organic semiconductor very well compared to the polar solvent where it is insoluble and forms aggregates. By this approach the π−π interactions for good crystalline growth are enhanced when the solute has minimum interaction with the bad solvent. This gradient in surface tension between the two solvents induces ordered aggregation or crystallisation of the nuclei via self assembly [6]. In some cases, binary solvent mixtures with a higher fraction of polar solvent have achieved good crystal growth [5][7], while in other cases the reverse has been applied to achieve a similar degree of success [8].

There are some reports on using binary solvent mixtures involving polyfluorenes. For example, Knaapila and coworkers used poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) and poly[9,9-dioctylfluorene-2,7-diyl] (PFO or PF8) in order to induce crystallisation with toluene:methyl cyclohexane mixtures [9]. In other instances, efficient white light emission in OLEDs was achieved by Liu and coworkers using WPF05 in chlorobenzene:toluene mixtures [10], whereas Lu and coworkers achieved efficient green light emission with poly(diphenylmethylenefluorene) (PDPMF) in binary solutions of dichloromethane (CH₂Cl₂) and boron trifluoride diethyl etherate (BFEE) [11].

As per our knowledge to date, there is currently no research in the literature regarding investigation into the beta-phase of F8T2 binary solutions. Hence, following on from the results and analysis from Chapter 4, we will study the ageing induced aggregation effect in binary solutions in this chapter. We will primarily focus on the study of hexane and tetralin in chlorobenzene binary solvent mixtures.
We will carry out systematic analyses to study the morphology, optical spectroscopy, GIWAXS, modelling and performance in fresh and aged OFET devices using F8T2 binary solutions.

5.2 Experimental method

Binary solvent mixtures of F8T2 were prepared from a chlorobenzene (CB) primary solvent with hexane (HEX), toluene (TOL), anisole (ANI), tetralin (TET) and/or dodecane (DO) secondary solvents in a 1:1 volume/volume (v/v) ratio at 1 wt% concentrations. These solutions were stirred or heated until dissolution on an IKA RCT basic magnetic hotplate stirrer at 70°C for 24 hours. Depending on application, freshly prepared solutions were immediately used on the same day for characterisation and device fabrication purposes (labelled as FRESH or I). While aged solutions were stored in dark and ambient conditions for a period of 7 days before use (labelled as AGED or II). The experimental techniques and procedures used in this chapter largely follows what was previously described in Chapter 4. As before, data for Atomic force microscopy was acquired at University College London by Muhammad Kamaludin, and data for Grazing incidence wide angle x-ray scattering were acquired at Diamond Light Source by Warren D. Stevenson.

5.3 Evaluation of secondary solvents for F8T2-CB binary solutions

As observed in Chapter 4, chlorobenzene (CB) was found to be a generally good solvent for F8T2 to study the effects of ageing. Furthermore F8T2 thin films from CB solutions generally dried instantaneously, whereas from higher boiling solvents such as 1,2-dichlorobenzene (DCB), drying took several hours. Binary solutions with 1,2-dichlorobenzene were briefly studied for comparison purposes, but since they do not fit the overall narrative of this chapter, these results are displayed in Appendix A.2.

In order to obtain a bad solvent counterpart with chlorobenzene, we prepared 1 wt% binary solvent mixtures in low and high boiling solvents such as hexane (b.p = 68.0°C), toluene (b.p = 110.6°C), anisole (b.p = 155.5°C), tetralin (b.p = 207.0°C) and dodecane (b.p = 216.3°C) in a volume/volume (v/v) ratio of 1:1. Thin films were spin coated at 1500 rpm for 30 s and analysed using optical spectroscopy.

Figures 5.1(a) and (b) show the normalised UV-vis and PL spectra of the binary solvent mixtures. From the UV-vis spectra, we observed a redshift of the 0−0 and 0−1 vibration peak wavelengths and increase in the 0−0 peak intensity proportional
to the solvent boiling used.

![Graphs showing absorbance and PL spectra](image)

**Figure 5.1:** Normalised UV-vis (a) and PL spectra (b) of F8T2 thin films from 1 wt% CB, HEX-CB, TOL-CB, ANI-CB, TET-CB and DO-CB binary solvent mixtures in 1:1 ratios.

A general increase in the $0^-0$ peak at 510 nm, and also a decrease in the $0^-2$ peak at 580 nm was observed in the PL spectra in Figure 5.1, indicating increase in J-aggregation with increasing boiling point. Using plain mono solvent F8T2-CB as a baseline, which had $0^-0$ and $0^-1$ peak wavelengths at 483 nm and 456 nm from the UV-vis spectra and 511 nm and 542 nm from the PL spectra, HEX-CB binary mixtures exhibited a slight redshift at the $0^-0$ and $0^-1$ peak wavelengths of 484 nm and 456 nm from the UV-vis spectra, and a slight blue shift at 510 nm and 539 nm from the PL spectra. The lack of a $0^-0$ peak intensity in relation to the $0^-1$ peak indicated a predominately H-aggregate interchain ordering for HEX-CB. For the higher boiling point secondary solvent, TET-CB binary mixtures showed considerable redshifted $0^-0$ and $0^-1$ peak positions at 494 nm and 462 nm from the UV-vis spectra and a minor blue shift at 511 nm and 540 nm from the PL spectra. The increase in the $0^-0$ peak intensity here indicated an increase in the J-aggregate intrachain ordering. We faced some difficulty in obtaining a thin film spin coated from dodecane binary solvent as upon spin coating it took between 2 – 3 days for the thin film to dry due to its very high boiling point and vapour pressure. Hence we did not observe any change of its wavelengths from the UV-vis spectra. However, in the corresponding PL spectra, DO-CB showed a blue shift at 506 nm and 539 nm and a considerable increase in the $0^-0$ peak intensity in relation with CB films indicating more J-aggregate intrachain ordering than TET-CB.
Due to very minor and inconsistent changes observed in the peak absorptions in Figure 5.1, exciton bandwidth (W) analysis based on the H-J aggregate model developed by Spano, Chang and coworkers [12][13][14] was applied using the 0 − 0/0 − 1 peak ratios. The exciton bandwidth was observed to decrease with increase in solvent boiling point from the PL calculations. A general decrease in the exciton bandwidth was observed with solvent boiling point for all the secondary solvents tested. The exciton bandwidth values calculated in increasing order of boiling point were 169 meV (HEX-CB), 158 meV (TOL-CB), 162 meV (ANI-CB), 155 meV (TET-CB) and 139 meV (DO-CB). The exciton bandwidth for mono solvent 1 wt% CB films was calculated earlier in Table 4.2 in Chapter 4 and had a value of ∼190 meV. Hence we can see that binary solvent mixtures with CB reduced the exciton bandwidth overall.

We also examined the change in photoluminescence quantum efficiency with respect to the secondary solvent used in Figure 5.3. The PLQE of mono solvent F8T2 solutions with CB was estimated earlier to be 15.7% in Chapter 4. In relation to CB, the PLQE estimated for binary mixtures were 13.6% (HEX-CB), 14.6% (TOL-CB), 16.1% (ANI-CB), 12.3% (TET-CB) and 6.9% (DO-CB). Comparing with the exciton bandwidth calculated in Figure 5.2(b), the PLQE increased for HEX, TOL and ANI whereas the exciton bandwidth decreased. However we noticed some variation in the PLQE for these solvents but they were within the standard deviation error bars estimated in Figure 5.3. For ANI, TET and DO, the PLQE subsequently decreased along with a decrease in exciton bandwidth. This indicated that increase in the beta-phase formation was detrimental to PLQE in binary solvent thin films.
Chapter 5. Beta-phase in F8T2 films from azeotropic binary solutions

Figure 5.3: PLQE of F8T2 thin films from 1 wt% HEX-CB, TOL-CB, ANI-CB, TET-CB and DO-CB binary solvent mixtures in 1:1 ratios. Uncertainties are quoted to 80% confidence.

5.4 Effect of film thickness on aged F8T2-CB binary solutions

5.4.1 Surface morphology

Based on the results and analysis in Section 5.3 we decided to pick secondary solvents that gave two extremes of H and J aggregation. These were 1 wt% binary solvent mixtures of F8T2 in HEX-CB (1:1) and TET-CB (1:1) respectively. Optical micrographs were taken for fresh and 7 day aged binary solvent mixtures of HEX-CB and TET-CB spin coated at 1500 and 4000 rpm for 30 s. Film thickness and root mean squared roughness values measured using a 2D Dektak profilometer are given in Table 5.1.

Table 5.1: Film thickness and RMS roughness values for fresh (I) and 7 day aged (II) HEX-CB (1:1) and TET-CB (1:1) thin films.

<table>
<thead>
<tr>
<th>Binary Solvent</th>
<th>Spin speed (rpm)</th>
<th>Ageing</th>
<th>Thickness (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-CB</td>
<td>1500</td>
<td>I</td>
<td>36</td>
<td>1.0</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>1500</td>
<td>II</td>
<td>36</td>
<td>1.0</td>
</tr>
<tr>
<td>TET-CB</td>
<td>1500</td>
<td>I</td>
<td>58</td>
<td>7.5</td>
</tr>
<tr>
<td>TET-CB</td>
<td>1500</td>
<td>II</td>
<td>55</td>
<td>10.3</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>4000</td>
<td>I</td>
<td>31</td>
<td>0.9</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>4000</td>
<td>II</td>
<td>22</td>
<td>2.2</td>
</tr>
<tr>
<td>TET-CB</td>
<td>4000</td>
<td>I</td>
<td>13</td>
<td>0.8</td>
</tr>
<tr>
<td>TET-CB</td>
<td>4000</td>
<td>II</td>
<td>12</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Interestingly, spin coating fresh HEX-CB at 1500 rpm gave smooth films in Figure 5.4, while at 4000 rpm minor aggregates of F8T2 started to be deposited.
in the film due to its poor solubility in the hexane solvent. This however, did not appear to affect the thickness or RMS. Spin coating aged HEX-CB at 1500 rpm gave large aggregates of approximately 37 µm in size in the film, while at 4000 rpm the size of these aggregates were reduced to 5 µm. On the other hand, there were slight blemishes and streaks in TET-CB films spin coated at 1500 rpm in Figure 5.5. The same morphology was observed at 4000 rpm. Upon ageing TET-CB, there were large aggregates 74 µm in size in the 1500 rpm film, which were reduced to 22 µm in the 4000 rpm films.

**Figure 5.4:** Optical micrographs of fresh (I) HEX-CB (1:1) and TET-CB (1:1) thin films. Columns from left to right display change in spin speed, while rows from top to bottom display change in binary solvent. Note: Colour changes from green to brown/orange are due to varying optical filters and do not indicate changes to thin film morphology.

Upon observation under cross polarisers in Figure 5.6, the streaks in both fresh and aged TET-CB films showed optical birefringence aligned radially outward from
the centre in the direction of the spin coating rotations. As per the analysis from the UV-vis and PL spectra earlier in Figures 5.2(a) and 5.2(b) which showed enhanced $0-0$ peak intensities relative the $0-1$ peak, these streaks in TET-CB films possibly indicate regions of anisotropic crystallinity that rotated the incoming light when observed under the polariser. However it should be noted that due to the poor dissolving qualities of the TET-CB solution, these aligned features were sedimentary particulates of F8T2. Indeed, as we shall discuss shortly in the AFM section, as TET-CB films exhibited very large thicknesses and RMS. HEX-CB films on the other hand did not show any optical birefringence and appeared dark indicating possibly an isotropic film.

![Figure 5.6: Selected polarised optical micrographs of HEX-CB (a) and TET-CB (b) thin films.](image)

From the atomic force microscopy (AFM) scans of HEX-CB and TET-CB films shown in Figure 5.7, the RMS roughness for fresh and aged HEX-CB were 0.34 nm and 0.40 nm indicating very smooth films, while for TET-CB they increased to 5.17 nm and 13.30 nm indicating rougher films. Grain sizes of 60 – 120 nm were measured for fresh HEX-CB films, and 50 – 100 nm for aged films. For TET-CB films, grain sizes increased to 150 – 400 nm for fresh films, and 300 – 800 nm for aged films. Comparing the thickness and RMS estimated from the 2D Dektak profilometry in Table 5.1 to the AFM results, the Dektak measurements were considerably underestimated for TET-CB films. This confirms the suspicion that these TET-CB films mainly consisted of sedimented F8T2 particulates, leading to irregular raised and depressed regions and streaks in its morphology. This is shown in the AFM scans in Figure 5.7 as for fresh TET-CB films, there were many clusters of depressed regions $< 10$ nm and raised regions $> 25$ nm across the film morphology. For aged TET-CB films, large pockets of depressed regions $< 20$ nm and streaks of raised regions $> 50$ nm started to appear in the morphology.
5.4.2 Optical spectroscopy

In Figures 5.8(a) and (b) we display the UV-vis and PL spectra of fresh and 7 day aged HEX-CB thin films spin coated at 1500 and 4000 rpm. An increase in the $0-0$ peak intensity was observed with ageing and spin speed indicating a gradual increase in J-aggregates. However, since the intensity of $0-0 < 0-1$, HEX-CB films were still predominantly in the H-aggregate regime. For 1500 rpm films, both fresh and aged films had $0-0$ and $0-1$ peak wavelengths at 483 nm and 456 nm in the UV-vis spectra, and 511 nm and 540 nm in the PL spectra. Upon spin coating at 4000 rpm, a redshift was observed for both fresh and aged films with the new wavelength positions being at 485 nm and 458 nm in the UV-vis spectra, and a very small blue shift at 510 nm and 539 nm in the corresponding PL spectra.
Figure 5.8: Normalised UV-vis (a) and PL spectra (b) of fresh and 7 day aged HEX-CB (1:1) thin films spin coated at different spin speeds.

Comparing the HEX-CB spectra with TET-CB, stronger $0-0$ peak intensities were observed, increasing with spin speed. A redshift was observed for fresh 1500 rpm films at wavelengths 495 nm and 462 nm in the UV-vis spectra in Figure 5.9(a). The wavelengths were unchanged in the PL spectra in Figure 5.9(b) and were 511 nm and 540 nm, similar to that of HEX-CB. Ageing 1500 rpm TET-CB films induced a small blue shift of the $0-0$ peak shifting it to 493 nm in the UV-vis spectra, while the rest remaining unchanged in comparison to the fresh wavelengths. For 4000 rpm films, the blue shift was more pronounced at the $0-0$ peak at 489 nm, while the $0-1$ peak remained at 462 nm. In the PL spectra, the $0-0$ peak saw a very small blue shift at 510 nm, while the $0-1$ peak remained at 540 nm. Ageing 4000 rpm films however induced a redshift of the $0-0$ peak to 493 nm and the $0-1$ peak to 463 nm in the UV-vis spectra, while the wavelengths remained unchanged for the PL spectra.

Figure 5.9: Normalised UV-vis (a) and PL spectra (b) of fresh and 7 day aged TET-CB (1:1) thin films spin coated at different spin speeds.
The changes in the peak absorption from the UV and PL spectra were not statistically significant due to very minor changes observed. Hence the exciton bandwidth was calculated using the ratio of the $0 - 0$ and $0 - 1$ peak intensities from the PL spectra in Figure 5.10. Clearer trends were observed and the exciton bandwidth decreased upon ageing and increase spin speed for HEX-CB from PL estimations.

TET-CB showed a more pronounced decrease in exciton bandwidth with respect to ageing and spin speed than compared to HEX-CB. For fresh HEX-CB films, a minor decrease in the exciton bandwidth from 168 meV to 161 meV was observed upon increasing spin speed. While for aged HEX-CB films, the exciton bandwidth decreased in relation to the fresh films, but showed a minor decrease from 161 meV to 158 meV with an increase in spin speed. On the other hand, fresh TET-CB films showed a more pronounced decrease in the exciton bandwidth from 155 meV to 147 meV with increase in spin speed. In contrast, for aged TET-CB films, the decrease in exciton bandwidth from 150 meV to 148 meV with spin speed was minor relative to the fresh films. This increase in intrachain ordering with ageing and faster spin speed (due to increased evaporation/drying rate) of the solvent was a similar trend to what was observed previously in Chapter 4.4.2 for F8T2 films spin coated from mono solvent TOL, CB and DCB at different spin speeds.

Figure 5.10: Exciton bandwidth calculations from the $0 - 0/0 - 1$ peak ratios from the PL spectra for fresh and aged HEX-CB (a) and TET-CB (b) thin films spin coated at different spin speeds.

Figures 5.11(a) and (b) display the change in PLQE with ageing and spin speed for HEX-CB and TET-CB binary solvent mixtures. Interestingly, we observed an increase in the PLQE with ageing for both fresh and aged films of HEX-CB and TET-CB. This seems to suggest that aggregation is beneficial in these binary systems resulting in less degree of exciton quenching sites. As can be seen in Figure 5.11(a), the PLQE for 1500 rpm films increased from 13.6% to 26.9% upon ageing for HEX-CB, and in 4000 rpm films the increase was from 17.1% and 24.0%. Similarly
for TET-CB in Figure 5.11(b), the PLQE increased from 12.3% to 20.4% upon ageing 1500 rpm films, and 12.0% to 19.3% upon ageing 4000 rpm films. This increase in PLQE with ageing corresponded with decreases in the exciton bandwidth when comparing to Figure 5.10. However, since the HEX-CB and TET-CB binary solvent mixtures were two different systems, we observed a higher PLQE at higher exciton bandwidths when comparing the two, with HEX-CB films generally having higher PLQE and exciton bandwidth than TET-CB.

Figure 5.11: PLQE of fresh and aged HEX-CB (a) and TET-CB (b) thin films spin coated at different spin speeds. Uncertainties are quoted to 80% confidence.

5.4.3 GIWAXS

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) measurements were taken for fresh and aged HEX-CB and TET-CB films spin coated at 4000 rpm. Figure 5.12 shows GIWAXS of fresh and 7 day aged HEX-CB films (a)–(b), and TET-CB films (c)–(d). Both classes of binary solvent films were found to be amorphous lacking any long range structural order due to no prominent reflections peaks at the center, which is generally considered as a litmus test for crystallinity [15][16][17]. Only a prominent dark outer diffuse ring was observed which had a d-spacing of 4.1 Å corresponding to either the (001) or (004) reflection peaks indicating the intermolecular $\pi - \pi$ spacing between the F8T2 chains according to the literature [18]. The lack of any structural order in TET-CB films was especially surprising considering they had shown optical birefringence under cross polarisers in Figure 5.6 earlier. This possibly indicates that TET-CB films had some regions of orientational ordering rather than long range crystalline structural order.
5.4.4 Transistor Analysis

5.4.4.1 Bottom Gate OFETs

In order to test transistor performance of HEX-CB and TET-CB binary solutions, BGBC OFETs with a 230 nm SiO$_2$ dielectric were fabricated. Figures 5.14(a) and (b) display the best output and transfer characteristics of 3 – 4 separate devices measured for fresh and 7 day aged HEX-CB thin films spin coated at 1500 and 4000 rpm. At both spin speeds, ageing reduced the output drain current by roughly 4 times in 1500 rpm and 2 times in 4000 rpm films. In its corresponding transfer characteristics, the turn on voltage $V_{to}$ was generally $>-20$ V, although ageing tended to result in a decrease in the on/off ratio and increase in the $V_{th}$. Fresh HEX-CB films spin coated at 4000 rpm gave the best performance for this binary solvent mixture, with a $\mu_{sat}$ of $2.6 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -7.3 V and on/off ratio of $3.1 \times 10^4$. This gave a slightly higher performance compared to plain F8T2-CB-1WT% films in Chapter 4.4.3, which gave a maximum $\mu_{sat}$ of $1.2 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -10.1 V and an on/off ratio of $1.3 \times 10^4$. However, examining the performance metrics in detail in Figure 5.13, HEX-CB OFETs gave mobilities a magnitude higher than plain CB films along with a drain current that was at least 3 times larger. Despite ageing slightly reducing the performance in HEX-CB OFETs, mean mobilities and on/off were at least one or two magnitudes higher than aged mono solvent F8T2-CB.
TET-CB OFETs on the other hand exhibited considerable degraded performance compared to both plain CB and HEX-CB OFETs on average. We suspect that spin coating from tetralin, which is a high boiling point solvent (207 °C), gave rise to poor film formation due to the slow evaporation rate. This perhaps lead to scattered sites of film aggregation on the substrate with high RMS as seen earlier in Figure 5.7. This might have resulted as charge carrier trap sites thereby reducing overall performance of these devices.

The highest output drain current for TET-CB in Figure 5.15(a) was a magnitude lower than even the worst HEX-CB OFET in Figure 5.14(a). Examining the transfer characteristics in Figure 5.15(b), TET-CB OFETs in general also had very large turn on voltages < -20 V and hysteresis, with aged OFETs further increasing the $V_{to}$ and reducing on/off ratio. Interestingly, ageing 1500 rpm films of TET-CB gave mobilities a magnitude higher than that of fresh TET-CB films, while the opposite trend was observed for ageing 4000 rpm films in Figure 5.13. Fresh TET-CB films spin coated at 4000 rpm gave the best performance, with a maximum $\mu_{sat}$ of $4.9 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -30.0 V and an on/off ratio of $1.8 \times 10^5$ (see Figure 5.15). The mobility and on/off ratio of this device was higher than the best HEX-CB OFET analysed earlier, although the $V_{th}$ and hysteresis of TET-CB was much higher, making them impractical for low voltage operation.

Based on the surface morphology and optical spectroscopy analysis of HEX-CB and TET-CB films earlier, it was found that HEX-CB films exhibited a predominantly H-aggregate orientation (interchain ordering) with a high exciton bandwidth, while TET-CB films showed J-aggregate ordering (intrachain ordering) with a low exciton bandwidth. The latter showed optical birefringence under cross polarisers indicating regions of orientational crystallinity due to aggregate particulates forming non-continuous films. Hence it seems that F8T2 binary solvents that exhibited a weakly developed beta-phase (H-aggregation), generally possessed enhanced charge carrier mobilities and operating voltages $V_{th} > -10$ V. Selected mean OFET performances for 4000 rpm films were compared with the exciton bandwidth and PLQE and are summarised in Table 5.2. A corresponding decrease in mobility resulted in an increase in PLQE, which seems to agree with previous reports on polymers where $\pi - \pi$ overlap interactions which are favourable for charge transport is detrimental for luminescence due to exciton quenching [19].
Table 5.2: Comparison of mean saturation mobility $\mu_{\text{sat}}$, threshold voltage $V_{\text{th}}$, on/off ratio, exciton bandwidth (EBW) and PLQE of selected fresh and 7 day aged BGBC OFETs with a 230 nm SiO$_2$ dielectric and 1 wt% F8T2 in CB, HEX-CB (1:1) and TET-CB (1:1) thin films spin coated at 4000 rpm. The mean was taken over 3 – 4 separate OFET devices with constant $L = 10\,\mu m$ and $W = 10,000\,\mu m$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ageing</th>
<th>$\mu_{\text{sat}}$ (cm$^2$/Vs)</th>
<th>$V_{\text{th}}$ (V)</th>
<th>On/Off</th>
<th>EBW (meV)</th>
<th>PLQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>I</td>
<td>$8.3\times10^{-5}$</td>
<td>-11.1</td>
<td>$6.0\times10^4$</td>
<td>167</td>
<td>14.8</td>
</tr>
<tr>
<td>CB</td>
<td>II</td>
<td>$2.1\times10^{-5}$</td>
<td>-12.3</td>
<td>$4.2\times10^3$</td>
<td>164</td>
<td>19.3</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>I</td>
<td>$2.5\times10^{-4}$</td>
<td>-8.7</td>
<td>$2.3\times10^4$</td>
<td>161</td>
<td>17.1</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>II</td>
<td>$1.7\times10^{-4}$</td>
<td>-15.2</td>
<td>$1.1\times10^5$</td>
<td>158</td>
<td>24.0</td>
</tr>
<tr>
<td>TET-CB</td>
<td>I</td>
<td>$2.0\times10^{-4}$</td>
<td>-30.1</td>
<td>$1.1\times10^5$</td>
<td>147</td>
<td>12.0</td>
</tr>
<tr>
<td>TET-CB</td>
<td>II</td>
<td>$5.9\times10^{-5}$</td>
<td>-31.6</td>
<td>$4.1\times10^4$</td>
<td>148</td>
<td>19.3</td>
</tr>
</tbody>
</table>
Figure 5.13: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(max)$ from the transfer characteristics of fresh and 7 day aged BGBC OFETs with 1 wt% F8T2 in CB, HEX-CB (1:1) and TET-CB (1:1) thin films spin coated at 1500 rpm (a) and 4000 rpm (b). Error bars were calculated at the 80% confidence interval from the standard error between 3–4 repeated measurements. The on/off ratio is displayed in a box and whisker plot as the standard deviation errors gave large variations over several magnitudes. The channel lengths ($L$) and widths ($W$) were 10 $\mu$m and 10,000 $\mu$m ($W/L = 1000$) respectively.
5.4.4.2 Top Gate OFETs

In order to observe whether ageing induced aggregation affected binary solvent films in top gate devices in a similar way, we fabricated TGBC OFETs with a 700 nm PVP dielectric. A total of 30 devices were fabricated but a number of them either shorted or either had high leakage currents with $|I_D/I_G| < 1$. As can be seen in Table 5.3, device success rates for fresh and 7 day aged HEX-CB films were 43% and 80%, while for TET-CB films they were 22% and 33%.
Table 5.3: TGBC device success rate for fresh (I) and aged (II) F8T2-1WT% HEX-CB (1:1) and TET-CB (1:1) thin films spin coated at 4000 rpm with a 700 nm PVP dielectric. Device success rate considers OFETs that did not short upon operation and have \(|I_D/I_G|>1\).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ageing</th>
<th>Total measured</th>
<th>Device success rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-CB</td>
<td>I</td>
<td>7</td>
<td>43</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>II</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>TET-CB</td>
<td>I</td>
<td>9</td>
<td>22</td>
</tr>
<tr>
<td>TET-CB</td>
<td>II</td>
<td>9</td>
<td>33</td>
</tr>
</tbody>
</table>

Selected output and transfer characteristics of these binary solvent OFETs are displayed in Figures 5.17(a) and (b) and are also compared with mono solvent F8T2-CB characteristics. Compared to F8T2-CB, the mean performance of HEX-CB and TET-CB OFETs were lower. We noticed that upon ageing HEX-CB films, the drain current increased by an order of magnitude from \(10^{-8}\) A to \(10^{-7}\) A. This corresponded to a decrease in the \(V_{to}\) and an increase in on/off ratio in the transfer characteristics. Examining the breakdown of the OFET performance metrics in Figure 5.16, upon ageing HEX-CB films, significant changes were observed for most metrics. The mean \(\mu_{sat}\) increased by an order of magnitude to \(\sim1\times10^{-3}\), \(V_{th}\) decreased from -23 V to -13 V, hysteresis reduced from -15 V to -7 V and the on/off ratio increased by an order of magnitude to \(10^4\). This is in contrast with BGBC 4000 rpm HEX-CB OFETs earlier where we found that ageing instead reduced mobility and increased the \(V_{th}\) (see Table 5.2). We assume this peculiar enhancement with ageing could perhaps be due to improved face to face ordering of F8T2 in aged HEX-CB binary solvent films that are favourable for charge transport [17]. Although due to the generally low yield obtained with fresh HEX-CB top gate devices, it is difficult to ascertain statistical significance. The best TGBC OFET out of the batch was with aged HEX-CB had a \(\mu_{sat}\) of \(1.5\times10^{-3}\) cm²/Vs, \(V_{th}\) of -13.7 V, and on/off ratio of \(1.3\times10^4\) (see Figure 5.17).

The characteristics for TET-CB films on the other hand were very poor and displayed high \(V_{to}\) and hysteresis, and low on/off ratios <\(10^3\). Although not visible in Figure 5.17, the drain current was \(\sim10^{-8}\) A for fresh films, and \(\sim10^{-9}\) A for aged films of TET-CB. Compared to HEX-CB, mean \(\mu_{sat}\) for TET-CB were two magnitudes lower for fresh films and aged films. Ageing further degraded mobility and increased \(V_{th}\). These trends for TET-CB seem consistent with those obtained for BGBC TET-CB devices earlier in Figure 5.13.
Figure 5.16: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(max)$ from the transfer characteristics of fresh and 7 day aged TGBC OFETs with 1 wt% F8T2 in CB, HEX-CB (1:1) and TET-CB (1:1) thin films spin coated at 4000 rpm. Error bars were calculated at the 80% confidence interval from the standard error between 3–4 repeated measurements. The channel lengths ($L$) and widths ($W$) were 50 $\mu$m and 2000 $\mu$m ($W/L = 40$) respectively.
Chapter 5. Beta-phase in F8T2 films from azeotropic binary solutions

5.4.5 OFET modelling

Selected BGBC OFET transfer characteristics for 1500 and 4000 rpm spin coated films of 1 wt% F8T2 HEX-CB (1:1) and TET-CB (1:1) binary solutions were fitted to Equation 2.11 and Equation 2.12 derived by Campbell and coworkers who used the Tanase, Vissenberg and Matters model for charge transport in amorphous, glassy disordered organic semiconductors [20][21][22]. Fitting parameters are displayed in Table 5.4. The parameters determined for mono solvent F8T2-CB solutions earlier in Chapter 4 are repeated here for convenience. Charge carrier densities were generally in the region of $\sim 1 \times 10^{19}$ cm$^{-3}$ for both HEX-CB and TET-CB films. Based on the results in Table 5.4, we observed a charge density dependent relationship with the saturation mobility $\mu_{\text{sat}}$, turn on voltage $V_{\text{to}}$, and the exponential DOS characteristic temperature $T_0$ for both fresh and aged HEX-CB and TET-CB.

Figure 5.18(a)–(b) displays the model fits for 1500 rpm films, and (c)–(d) for 4000 rpm films for HEX-CB binary solvent OFETs. Good fits within the 95% confidence interval bands were obtained for both 1500 and 4000 rpm films. Estimated $\mu_{\text{sat}}$ from the fits compared to the experimentally deduced $\mu_{\text{sat}}$ from the slope of the transfer characteristics were consistently larger, and reasons for this was given previously in Chapter 4.4.4. Analysing the width of the exponential DOS $T_0$ for HEX-CB films, we observed an increase from 524 K to 806 K after ageing 1500 rpm films. The $T_0$ decreased considerably for fresh HEX-CB 4000 rpm films to 356 K, but increased to 588 K after ageing. These values of $T_0$ were much lower than mono solvent F8T2-CB solutions which correlate with a decrease in trap densities and hence increased charge carrier mobility.

Observing the fits to the TET-CB films in Figure 5.19, good fits were obtained
for 1500 fresh rpm films. However, considerable deviations in the fits were observed
upon ageing and in thinner 4000 rpm films. $T_0$ for TET-CB was much higher than
HEX-CB in general which translated to lower mobilities and higher $V_{to}$. For 1500
rpm films, $T_0$ decreased from 1927 K to 412 K upon ageing which correlated with a
decrease in $V_{to}(lin)$ from -19.7 V to -7.5 V. Most notable was the additional increase
in the threshold voltage in the saturation regime from the data in the plots, which
the model could not capture accurately. These large non-ideal deviations could have
occurred due to poor film formation, hence increased trap states, when the film was
formed with the high boiling point secondary solvent, tetralin. Overall, the values
obtained for $T_0$ agree with the mean mobility and threshold voltage trends observed
in previous sections for HEX-CB and TET-CB binary solutions.
Table 5.4: V&M modelling fit parameters of fresh and 7 day aged BGBC OFETs 1 wt% F8T2 in CB, HEX-CB (1:1) and TET-CB (1:1) binary solutions spin coated at 1500 and 4000 rpm. Channel length and widths used were $L = 10\mu m$ and $W = 10,000\mu m$ respectively.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Spin speed (rpm)</th>
<th>Ageing</th>
<th>$\mu_{\text{lin}}$ ($cm^2/Vs$)</th>
<th>$\mu_{\text{sat}}$ ($cm^2/Vs$)</th>
<th>$V_{th}$ (V)</th>
<th>$V_{to}$ (V)</th>
<th>$\rho$ ($cm^{-3}$)</th>
<th>$m$</th>
<th>$\mu_{\text{sat}}$ ($cm^2/Vs$)</th>
<th>$T_0$ (K)</th>
<th>$\mu_{\text{sat}}$ fit variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB 1500</td>
<td>I</td>
<td>4.9×10$^{-6}$</td>
<td>1.1×10$^{-5}$</td>
<td>-15.4</td>
<td>8.8</td>
<td>4.7×10$^{19}$</td>
<td>1.19</td>
<td>1.6×10$^{-5}$</td>
<td>658</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>CB 1500</td>
<td>II</td>
<td>1.3×10$^{-5}$</td>
<td>3.2×10$^{-5}$</td>
<td>-14.4</td>
<td>8.6</td>
<td>4.3×10$^{19}$</td>
<td>1.36</td>
<td>4.9×10$^{-5}$</td>
<td>709</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>HEX-CB 1500</td>
<td>I</td>
<td>9.1×10$^{-5}$</td>
<td>1.5×10$^{-4}$</td>
<td>-13.6</td>
<td>8.3</td>
<td>5.0×10$^{19}$</td>
<td>0.75</td>
<td>2.1×10$^{-4}$</td>
<td>524</td>
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<tr>
<td>HEX-CB 1500</td>
<td>II</td>
<td>1.6×10$^{-5}$</td>
<td>7.4×10$^{-5}$</td>
<td>-18.5</td>
<td>10.3</td>
<td>4.2×10$^{19}$</td>
<td>1.69</td>
<td>1.1×10$^{-4}$</td>
<td>806</td>
<td>49</td>
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</tr>
<tr>
<td>TET-CB 1500</td>
<td>I</td>
<td>1.2×10$^{-6}$</td>
<td>1.0×10$^{-6}$</td>
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<td>6.2×10$^{-6}$</td>
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<td>509</td>
<td></td>
</tr>
<tr>
<td>TET-CB 1500</td>
<td>II</td>
<td>1.4×10$^{-5}$</td>
<td>5.7×10$^{-5}$</td>
<td>-18.9</td>
<td>7.5</td>
<td>7.6×10$^{19}$</td>
<td>0.37</td>
<td>7.8×10$^{-5}$</td>
<td>412</td>
<td>37</td>
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</tr>
<tr>
<td>CB 4000</td>
<td>I</td>
<td>6.0×10$^{-5}$</td>
<td>1.1×10$^{-4}$</td>
<td>-9.8</td>
<td>-6.4</td>
<td>5.3×10$^{19}$</td>
<td>0.47</td>
<td>1.4×10$^{-4}$</td>
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<tr>
<td>CB 4000</td>
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<td>1.9×10$^{-5}$</td>
<td>-12.9</td>
<td>-8.0</td>
<td>4.6×10$^{19}$</td>
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<td>2.6×10$^{-5}$</td>
<td>588</td>
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<tr>
<td>HEX-CB 4000</td>
<td>I</td>
<td>1.5×10$^{-4}$</td>
<td>2.6×10$^{-4}$</td>
<td>-7.3</td>
<td>-5.7</td>
<td>7.0×10$^{19}$</td>
<td>0.19</td>
<td>3.0×10$^{-4}$</td>
<td>356</td>
<td>14</td>
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</tr>
<tr>
<td>HEX-CB 4000</td>
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<td>7.9×10$^{-5}$</td>
<td>1.7×10$^{-4}$</td>
<td>-14.5</td>
<td>-8.9</td>
<td>4.6×10$^{19}$</td>
<td>0.96</td>
<td>2.4×10$^{-4}$</td>
<td>589</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>TET-CB 4000</td>
<td>I</td>
<td>6.1×10$^{-5}$</td>
<td>2.2×10$^{-4}$</td>
<td>-22.0</td>
<td>-8.5</td>
<td>8.0×10$^{19}$</td>
<td>0.52</td>
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<td>457</td>
<td>11</td>
<td></td>
</tr>
<tr>
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<td>5.2×10$^{-5}$</td>
<td>-23.9</td>
<td>-10.6</td>
<td>6.0×10$^{19}$</td>
<td>0.86</td>
<td>8.5×10$^{-5}$</td>
<td>558</td>
<td>62</td>
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</tbody>
</table>
Figure 5.18: Model fits to the experimental transfer characteristics of fresh and 7 day aged BGBC OFETs of F8T2-1WT% HEX-CB (1:1) thin films spin coated at 1500 rpm (a)–(b) and 4000 rpm (c)–(d). Fitted parameters are given in Table 5.4. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data. Plots from left to the right show fresh and 7 day ageing: (a) and (c) are fresh films, while (b) and (d) are aged films.
Figure 5.19: Model fits to the experimental transfer characteristics of fresh and 7 day aged BGBC OFETs of F8T2-1WT% TET-CB (1:1) binary solutions spin coated at 1500 rpm (a)–(b) and 4000 rpm (c)–(d). Fitted parameters are given in Table 5.4. Dashed lines show 95% confidence interval bands of the modelled fit to the experimental data. Plots from left to the right show fresh and 7 day ageing: (a) and (c) are fresh films, while (b) and (d) are aged films.

5.5 Conclusions

In this chapter, the ageing induced aggregation effect of F8T2 binary solutions in hexane (HEX) and tetralin (TET) were investigated. Based on our analysis of binary solvents with F8T2-CB in Section 5.3, we chose hexane and tetralin as the secondary solvents as they represented two extremes of H and J aggregate ordering for us to study. In Section 5.4, in relation to plain CB films (167 meV and 164 meV for fresh and aged), the exciton bandwidth from the PL spectra decreased for HEX-CB (161 meV and 158 meV for fresh and aged) and TET-CB (147 meV and 148 meV for fresh and aged) films, with the latter showing the greatest reduction. We also observed that ageing increased the overall PLQE compared to mono solvent F8T2-CB, with a maximum of 24.0% being recorded for aged HEX-CB films. GIWAXS analysis further confirmed the amorphous nature of both fresh and aged HEX and TET
Chapter 5. Beta-phase in F8T2 films from azeotropic binary solutions

binary solvent mixtures.

In BGBC OFET devices, higher performance was generally achieved with thinner films. HEX-CB films gave mean $\mu_{sat}$ in the region of $10^{-4}$ cm$^2$/Vs, low $V_{th} < -10$ V and high on/off ratios $10^4$–$10^5$ in the bottom gate configuration, much higher than those recorded for mono solvent F8T2-CB films. Ageing tended to reduce overall performance, however the results were still better than aged mono solvent F8T2-CB films. In the top gate architecture on the other hand, ageing tended to increase the overall $\mu_{sat}$ and decrease the $V_{th}$, compared to aged mono solvent F8T2-CB films. TET-CB OFETs on the other hand generally performed much poorly, indicating J-aggregate ordering was not favourable for charge transport. Performance was slightly improved in the top gate architecture although considerably high hysteresis, leakage currents and threshold voltages was still observed.

The ageing of F8T2-DCB binary solvents with hexane and tetralin were also briefly investigated towards the end. In comparison to plain DCB films (157 meV and 158 meV for fresh and aged), HEX-DCB films tended to increase exciton bandwidths (172 meV and 167 meV for fresh and aged) while TET-DCB films decreased them (145 meV and 147 meV for fresh and aged). Compared to CB binary films, the PLQE for DCB binary films were at least halved. We observed a general tendency of predominate J-aggregate intrachain ordering with both HEX-DCB and TET-DCB films, with the latter showing the greatest. In BGBC devices, mobilities were at least 2 – 3 times higher than CB binary OFETs along with high on/off ratios $\sim 10^5$, although they also had high hysteresis and high $V_{th} > -20$ V. Ageing did not have considerable effects on the OFET performance with HEX-DCB films. TET-DCB OFETs on the other hand failed to perform in the bottom gate architecture, although in the top gate architecture it started to show some degree of OFET characteristics restored albeit with considerably high hysteresis and threshold voltages $> -30$ V.

A general trend with increasing $V_{th}$ and J-aggregate head-to-tail ordering was observed for both CB (and DCB, see Appendix A.2) binary systems. This beta-phase regime of aggregation for F8T2 is both detrimental to PL efficiency (with some exceptions when ageing is applied) and charge transport. Hence careful examination must be taken regarding the regime of aggregation of F8T2 when selecting for the appropriate application in OFET and/or OLED devices.

References

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Chapter 6

Soft lithographic patterning and transistor devices

Despite possessing impressive ambipolar and emissive properties in ambient, poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) has achieved relatively little attention using soft lithography techniques. Here we present fabrication of top gate field effect transistors, with the F8T2 layer patterned using soft lithographic techniques such as micro molding in capillaries (MIMIC) and solvent assisted micro molding in capillaries (SAMIM). A Fluorolink® MD 700 perfluoropolyether (PFPE) stamp with 100 µm wide capillary arrays was used in conjunction with 1,2-dichlorobenzene (mono) and hexane:1,2-dichlorobenzene (binary) azeotropic solvents to achieve crystallised thicknesses in the sub-micron regime. Proof of concept F8T2 OFETs with an amorphous fluoropolymer CYTOP™ dielectric are presented, exhibiting low gate leakage currents (∼10⁻¹⁰ A), low hysteresis and relatively high saturation mobilities in the region of >10⁻³ cm²/Vs, which are about an order of magnitude higher than those reported for drop cast and spin coated techniques.
Chapter 6. Soft lithographic patterning and transistor devices

6.1 Introduction

Since the first demonstration of fabricating micron and nanometre structures using elastomeric stamp molds by George M. Whitesides’ research group during the 1990s, soft lithography has received a tremendous amount of academic interest over the past several years [1]. The technique has been used to fabricate a wide variety of devices such as inorganic [2] and organic transistors [3], OLEDs [4], lab-on-chip microfluidics for biological and medical applications [5][6][7], sensors [8] and organic solar cells [9][10].

Micro molding in capillaries (MIMIC) is a soft lithographic technique which crystallises solutions confined inside capillary channels of an elastomeric stamp mold. MIMIC has been used to fabricate devices such as MOSFETs [2], optical waveguides [11][12], polymer light emitting diodes [13][14], source/drain electrodes [15], and OFETs [16]. Within the last few years, Zhenan Bao and coworkers have fabricated OFETs by inducing confined crystallisation of P3HT, TIPS-Pentacene and C_{60} in the capillary channels defined by MIMIC. Although the reported mobilities were much higher than that of spin coated values, the patterned crystals themselves were randomly shaped in the capillaries, highlighting some of the difficulties in crystallising organic semiconductors in confined spaces with the MIMIC process [17].

On the other hand, due to its ability to pattern both isolated and interconnected structures, the technique of solvent assisted micromolding in capillaries (SAMIM) has found a wide variety of applications in photonics such as the fabrication of polymer lasers [18], OLEDs [16], P3HT/PCBM solar cells [19] and TES-ADT OFETs [20]. Triethylsilyl ethynyl anthradithiophene (TES-ADT) is a small molecule in the latter reference, which implies that SAMIM’s patterning capabilities also extends to small molecule organic semiconductors. Over the years, researchers have also managed to incorporate the SAMIM and nanoimprint lithography (NIL) techniques into novel processes such as Capillary Force Lithography (CFL) [21] to achieve well defined, highly ordered patterned features upon stamp removal [22].

In this chapter we develop SU-8 master templates on smooth silicon substrates by soft lithography. A fabrication process is presented for developing Fluorolink® MD 700 PFPE and poly(dimethylsiloxane) (PDMS) stamp materials with micron sized relief structures. We attempt to optimise crystal growth of F8T2, TIPS-Pentacene and P3HT semiconductors in stamp channels using the MIMIC and SAMIM process flows. In order to examine the electrical characterisation of these patterned structures, OFETs with staggered geometries are fabricated. Towards the end, we investigate soft lithographic patterning and OFET application of azeotropic binary solutions of F8T2 that applies some of the research done previously in Chapter 5.
6.2 Experimental Method

Fluorolink® PFPE and PDMS elastomeric stamps were fabricated on SU-8 2002 and 2005 silicon master templates for the MIMIC and SAMIM processes. F8T2, TIPS-Pentacene and >95% regioregular (RR) P3HT were dissolved in anhydrous solvents of Toluene (TOL), Chlorobenzene (CB) and/or 1,2-dichlorobenzene (DCB) at concentrations between 0.25 – 2 wt% and were stirred or heated until dissolution at 70°C for 24 hours. In MIMIC, both PFPE and PDMS stamps were used, and approximately 5 – 10 µL of solution was pipetted near the entrance of the capillary channel inlets for crystallisation. In SAMIM, approximately 20 – 50 µL solution was pipetted on to a clean silicon substrate before lightly compressing a PDMS stamp to induce crystallisation inside the stamp recesses. Crystallisation for both MIMIC and SAMIM process flows were allowed to take place over a period of 24 hours in ambient room temperature conditions before stamp removal. No post-annealing of the substrates was attempted. Standard optical, surface and OFET electrical characterisation were carried out as per the protocols defined in Chapter 3.

6.3 Development of SU-8 masters and elastomeric stamps

6.3.1 Quality control of SU-8 masters

Figure 6.1 displays optical micrographs of some of the common resist features observed at low development times (a), over exposure to UV-radiation (b), and delamination during the development process (c). After some trial and error, resist features to those shown in Figure 6.1(d) were frequently obtained during rapid prototyping of the master templates.

For the MIMIM and SAMIM process flows that will be discussed in the next chapter, we prepared SU-8 master templates with thicknesses ~2 µm and ~8 µm. For MIMIC, rectangular SU-8 capillaries were designed like those displayed in Figure 6.2(a), with the capillary width varying between 100 µm and 2000 µm. For SAMIM, SU-8 features were designed like in Figure 6.2(b), with rectangular shapes 100 µm in width and 1000 µm in length.

6.3.2 Stamp development

The concentration of D1173 curing agent and UV curing time was optimised for MD 700 PFPE stamps. Longer curing times were generally required due to the incomplete inert environment inside the ELC-500 chamber. Taking into
consideration of the dimensions of our ELC-500 chamber, N₂ gas was pumped at a rate of 8 L/min for 10 mins until a N₂ concentration of 99.3% was achieved. Using a rough backhand calculation, the O₂ concentration was estimated to be $\sim 6 \times 10^3$ ppm, hence longer curing times and higher concentrations of D1173 curing agent were necessary as the generation of O₂ free radicals in UV would have disrupted and slowed down the curing process.

Figures 6.3(a) and (b) displays the change in water contact angle on PFPE and surface energy with respect to curing time using 1 wt% and 4 wt% concentrations of D1173. In order to verify that PFPE was successfully cured, optical micrographs of simple scratch tests on the surface were also taken at different curing times as shown in Figures 6.5 and 6.6. We observed that PFPE cured faster with the 4 wt% concentration as the contact angle increased and saturated at values $>100^\circ$ more rapidly at shorter curing times and no visible scratches were observed indicating good polymerisation. Hence we decided to go with an optimal curing time of 5 mins.
as this obtained us a very high contact angle of $\sim 116^\circ$ (see Figure 6.4(b)) and a total surface energy of 7.4 mN/m. The root mean squared (RMS) roughness for PFPE was measured to be $1.68 \pm 0.29$ nm over 6 repeats.

Figure 6.4: Water contact angles on PDMS $\sim 110^\circ$ (a) and PFPE $\sim 116^\circ$ (b) using a KRUSS DSA100 Goniometer.
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Figure 6.5: Scratch tests on the surface of PFPE with 1 wt% D1173 curing agent photocured at 0.2 (a), 0.5 (b), 1.0 (c), 3.0 (d), 5.0 (e) and 9.0 (f) mins.

Figure 6.6: Scratch tests on the surface of PFPE with 4 wt% D1173 curing agent photocured at 0.2 (a), 0.5 (b), 1.0 (c), 3.0 (d), 5.0 (e) and 9.0 (f) mins.

No optimisation was required for curing PDMS as its process flow is well established in the literature [23]. A quick water contact angle check gave us a value of $\sim110^\circ$ as can be seen in Figure 6.4(a). The dispersive and polar components of the surface energy for PFPE and PDMS were also calculated: $\gamma_S = 7.4 \text{ mN/m}$, $\gamma_D = 5.6 \text{ mN/m}$, $\gamma_P = 1.8 \text{ mN/m}$ for PFPE, and $\gamma_S = 22.8 \text{ mN/m}$, $\gamma_D = 21.7 \text{ mN/m}$, $\gamma_P = 1.1 \text{ mN/m}$ for PDMS. Since these surface energy components were determined
using only two reference liquids at the time, deionised water and ethylene glycol, our estimation for the total surface energy for PFPE was somewhat off from the literature value of 15 mN/m \[^{[24]}\], while for PDMS the total surface energy was very close to the values 20 – 30 mN/m recorded \[^{[25]}\][^{[26]}\]. The RMS roughness for PDMS was measured to be 1.95 ± 0.11 nm over 6 repeats.

Figure 6.7: Simulated wetting envelopes for PFPE (a) and PDMS (b) at contact angles $\theta_C = 0^\circ$, 45$^\circ$ and 90$^\circ$. (Please note difference in scales between the plots.)

Wetting envelopes at contact angles $\theta_C = 0^\circ$, 45$^\circ$ and 90$^\circ$ were simulated for PFPE and PDMS and are shown in Figures 6.7(a) and (b). Referring to the surface tension components given in Chapter 3.4.10, only a few solvents such as water, hexane and chlorobenzene would have partially wetted PFPE at contact angles between 45$^\circ$ – 90$^\circ$. For PDMS on the hand, an increased number of solvents such as water, hexane, toluene, chlorobenzene, 1,2-dichlorobenzene and tetralin would have partially wetted the surface at contact angles between 45$^\circ$ – 90$^\circ$.

Swelling experiments of PFPE and PDMS were carried out in common organic solvents such as chloroform (CHF), hexane (HEX), toluene (TOL), chlorobenzene (CB), xylene (XYL) and 1,2-dichlorobenzene (DCB). Small blocks of PFPE and PDMS were cut, and their masses were measured before placing in separate glass vials filled with solvent. Their masses were measured again after 24 hours in order to calculate the change in mass to give us an idea of the percentage of swelling. Figure 6.8 shows the swelling of PFPE and PDMS in different boiling solvents.

PFPE did not swell in most organic solvents except in CHF where swelling was ~8.3%). Small decreases in the final measured mass in the range 0.0007 – 0.002 g were observed when weighing PFPE swelled in the other solvents, although this could be attributed to minor vibrational fluctuations with the weighing scales.

PDMS on the hand swelled considerably in all solvents, with a slight inverse relationship observed between swelling and solvent boiling point. The highest degree
of swelling was observed in CHF at \( \sim 211\% \), and the lowest swelling was in DCB at \( \sim 64\% \).

Based on the surface energy, wetting envelopes and swelling experiment results, we chose 1,2-dichlorobenzene as the solvent to dissolve organic semiconductors as it was most compatible with both PFPE and PDMS. DCB was also found to evaporate completely within 24 hours in ambient during MIMIC and SAMIM application, compared to other higher boiling solvents such as tetralin or dodecane which would take several days.

### 6.3.3 Stamp stability during adhesion and removal

Due to the low surface energy and adhesion of the stamp with respect to the substrate, the stamp should ideally replicate the design on to the targeted substrate upon conformal contact and removal. However, in some cases, it is susceptible to undesirable deformations such as roof collapse, buckling, lateral collapse and delamination during repeated stamping procedures:

(a) Roof collapse occurs when the aspect ratio of the height and width \((h/w)\) of the stamp relief features is too low that it causes the stamp to fall under its own weight or upon the application of an applied vertical load, and make contact with the substrate [27].

(b) Buckling occurs when the aspect ratio is too high that the stamp features collapse upon application of an applied vertical load [28].
(c) Lateral collapse, similar to buckling, occurs when the aspect ratio is also too high causing the neighbouring relief features of the stamp to collapse onto each other upon conformal contact. Lateral collapse can also occur when the stamp is compressed onto a solution where the attractive capillary forces of the surrounding solution are sufficiently large enough to neighbouring relief features to deform and come into contact with each other [27].

(d) Delamination occurs during the stamp lift off procedure when there is strong adhesion between the stamp and substrate, thereby leading to physical removal and damage to the patterned structures [29].

These phenomenon are illustrated in Figure 6.9.

![Figure 6.9: Illustration of stamp collapse during the application of an applied vertical force $F$ leading to (a) roof collapse, (b) buckling, (c) lateral collapse, and (d) delamination and/or removal of patterned features upon stamp lift off.](image)

These deformations pose a serious problem which often leads to inaccurate and defective patterning transfer in large area applications. A more extensive review into stamp deformation and collapse is given by several papers [28][30][31][32][33].

Optimal aspect ratios such as $0.5 < h/w < 5$ [23] and $0.2 < h/w < 2$ [1] have been recommended to minimise the effect of stamp deformation and collapse. However, the aspect ratio for reliable pattern transfer largely depends on the elastomeric material’s Young’s modulus, work of adhesion between the stamp and substrate, and the dimensions of the stamp relief features, which all tend to differ depending on the application [32].

High modulus elastomers such as PFPE have been found to increase feature resolution and create better replicated patterns [34]. However, it has also been observed that high modulus elastomers tend to separate from the master upon curing due to chemical and thermal shrinkage, leading to distorted or ruptured structures.
Release of stamps from masters at elevated temperatures has been recommended to reduce the chance of this kind of deformation [35]. High modulus elastomers also face difficulties in conformal contact with substrates with high surface roughness or non-planarity. And lastly, the higher the modulus, the lower the fracture toughness, which tends to increase the chances of plastic deformation and cracking of the stamp during lift off from the master or substrate [28].

Due to the small area of the substrates used for MIMIC and SAMIM deposition (20 × 20 mm²), PFPE and PDMS stamps were cured to a diameter <20 mm to allow sufficient space for placement with tweezers and stamp removal using scalpels. 2D line profiles were taken of the PFPE and PDMS relief structures. As can be seen in Figure 6.10, stamps surfaces were curved and not perfectly flat. Hence they had to be compressed during conformal contact to allow adhesion via van der waal forces due to the surface energy mismatch between the stamp and the substrate.

![PFPE and PDMS stamps relief structures](image)

**Figure 6.10:** 2D profilometry scans of (a) PFPE and (b) PDMS stamp relief structures.

PFPE and PDMS stamps patterned with rectangular capillary arrays of relief structures 100 µm and 2000 µm in width were brought into conformal contact with plain silicon substrates. Optical microscopy was used to detect regions of roof collapse, buckling or lateral collapse upon conformal contact. Figures 6.11 and 6.12 show conformal contact of PFPE and PDMS stamps patterned with ~2 µm and ~8 µm thick relief features. From the optical micrographs, regions that were light green in colour indicated no conformal contact while dark green areas indicated conformal contact with the substrate.

Height and width aspect ratios of 2 µm tall, 100 µm wide relief features were 0.02 for PFPE stamps in Figure 6.11(a). This was much lower than the recommended optimal ratios earlier however interestingly we did not observe roof collapse or buckling in the central regions. Height and width aspect ratios of 2 µm tall, 2000 µm wide relief features were 0.001 in Figure 6.11(b), which was much lower than 100 µm capillaries. Visible signs of roof collapse were observed around the central regions of the stamp, although the regions following the walls of the capillary were
not blocked.

Similarly for PDMS stamps with the same aspect ratios, no roof collapse was observed at the central region of the stamps in Figure 6.11(c). However, complete collapse of the channel was observed in the 2000 µm wide capillary in Figure 6.11(d), which could have been due to excess compression applied on the stamp to bring it into conformal contact for this particular case.

The same optical analysis was performed for the 8 µm tall relief structures in PFPE and PDMS stamps. Aspect ratios of 0.08 and 0.004 were calculated for 100 µm and 2000 µm wide capillary channels. In Figures 6.12(a) and (b) for 100 µm and 2000 µm capillaries in PFPE stamps, no roof collapse was observed. The same was observed for PDMS stamps in Figures 6.12(c) and (d).
Figure 6.11: Optical micrographs of stamp adhesion during conformal contact with a smooth silicon surface for 2 µm thick relief structures with 100 µm (a), (c) and 2000 µm (b), (d) wide PFPE and PDMS capillary channels. Dark green regions show regions where stamp is in good contact with the substrate, while light green regions show regions not in contact.

Figure 6.12: Optical micrographs of stamp adhesion during conformal contact with a smooth silicon surface for 8 µm thick relief structures with 100 µm (a), (c) and 2000 µm (b), (d) wide PFPE and PDMS capillary channels. Dark green regions show regions where stamp is in good contact with the substrate, while light green regions show regions not in contact.
6.4 Optimisation of confined crystallisation using soft lithography

Crystallisation involves a phase transformation from a liquid to a solid in two major steps: nucleation and crystal growth. Nucleation involves overcoming a free energy barrier and occurs when solute molecules in a supersaturated solution cluster together in a spontaneous or induced manner until a critical nuclei size is reached that is able to form stable periodic lattices that define the crystal structure [36]. Upon the formation of the first crystal seed, it acts as a convergence point for the crystal to increase and grow in size in successive layers. When exactly the solution reaches supersaturation largely depends on the solvent’s boiling point, concentration and solute used [3].

Crystallisation in the recesses of the stamp’s channels largely depend on the surface tension of the solution and the surface energy with respect to the stamp’s channels and substrate and temperature [37]. The ideal scenario for complete filling of the channels with crystal growth (called filling fraction) is when the solution reaches supersaturation while there is still solution filling the entire channel. However, if the solution reaches supersaturation when most of the solvent has evaporated, incomplete crystallisation and filling of the channel can occur [38][39].

In order to achieve good, reproducible patterning using MIMIC and SAMIM patterning, we first optimised the concentration and solvent for the organic semiconductors investigated. PDMS stamps were used for these trials due to the convenience of producing a large number of stamps that could be easily cured on a hotplates, producing at least 20 stamps or more within 30 mins. Due to the limited space inside the ELC-500 UV exposure system, in contrast to PDMS stamp fabrication, only 9 PFPE stamps could be cured at a time, and fresh N$_2$ had to be pumped inside for 10 mins before each curing cycle.

6.4.1 Optimal solutions for MIMIC

As described in Chapter 2.6.2.4, the technique of MIMIC relies on the transfer (via capillary forces) and crystallisation of organic semiconductor solutions inside capillary channels of an elastomeric stamp. Due to the large surface energy difference between the stamp and the substrate, good conformal contact was achieved with capillary channels intact. We noticed that how far the solutions travelled in the capillary channels was independent of concentration and solvent type used. Crystallisation was generally suppressed after travelling 2 – 3 mm through the capillaries. Assuming the average diameter of the PDMS stamps was roughly 15 mm, this travel length was estimated to be only about 20%.
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Figure 6.13 displays 100 µm wide rectangular arrays of MIMIC patterned F8T2 using PDMS stamps. Concentrations investigated were 0.25, 0.5 and 1.0 wt% in toluene (TOL), chlorobenzene (CB) and 1,2-dichlorobenzene (DCB) solvents. We observed with increasing concentration, F8T2 arrays were generally well defined. The dark green areas in the optical micrographs represented complete crystallisation of the F8T2 solution in the MIMIC channels, whereas the lighter green areas were regions of incomplete crystallisation. As explored in the previous chapter, TOL and CB solutions were found to swell PDMS the most, hence we can see in Figures 6.13(a)–(c) for TOL and Figures 6.13(d)–(f) for CB, the F8T2 arrays were rough and of poor quality. For DCB in Figures 6.13(g)–(i), good patterning was observed at 1 wt% concentration due to its low tendency to swell PDMS.

We next look at the MIMIC patterning of TIPS-Pentacene using concentrations of 1, 2 and 4 wt % in TOL, CB and DCB. Since TIPS-Pentacene is a small molecule, higher concentrations had to be used in order to increase long range crystallisation inside the capillaries. Similar to what was observed with F8T2, increasing concentration resulted in improved patterning of the TIPS-Pentacene arrays. TOL was the worst solvent, as little to no long range crystallisation was observed in Figures 6.14(a)–(c). For CB solvent, poor crystallisation and growth was observed at 1 and 2 wt% concentrations, although at 4 wt% long range crystallisation was observed in Figures 6.14(d)–(f). DCB solvent on the other hand gave improved long range crystallisation with increasing concentration. A concentration of 4 wt% gave the best patterning quality with TIPS-Pentacene crystallising in most of the
observed channels in Figure 6.14(i).

Figure 6.14: Optical micrographs of MIMIC patterned TIPS-Pentacene in PDMS stamps in different concentrated solvents of TOL (a–c), CB (d–f) and DCB (g–i). Images from left to right show increasing concentration from 1, 2 and 4 wt%.

6.4.2 Optimal solutions for SAMIM

The modified SAMIM technique that we used as described earlier in Chapter 2.6.2.5, relied on compressing a PDMS stamp with patterned relief structures to mold and absorb excess organic semiconductor solution deposited on a substrate. Over a short period of time, crystallisation should ideally occur within the recesses of the patterned structures. However we noticed that crystallisation generally was restricted to a few small areas randomly located around the substrates. This possibly occurred due to delamination of the PDMS stamp during swelling in the organic solvents used, hence resulting in poor conformal contact in certain areas.

F8T2 was patterned using SAMIM with PDMS stamps with relief structures that were 1000 µm wide and 100 µm long. Concentrations of 0.25, 0.5 and 1.0 wt% in TOL, CB and DCB solvents were tested. Patterning quality was seen to improve with increasing concentration. Good patterning was observed with CB and DCB solvents at 1 wt% in Figures 6.15(f) and (i). However this came with the drawback of a thin layer of F8T2 forming between the crystallised structures implying some of the solution did not get absorbed by the PDMS stamp.
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Figure 6.15: Optical micrographs of SAMIM patterned F8T2 in PDMS stamps in different concentrated solvents of TOL (a–c), CB (d–f) and DCB (g–i). Images from left to right show increasing concentration from 0.25, 0.5 and 1.0 wt%.

TIPS-Pentacene on the other hand gave very poor patterning for TOL and CB solvents at all concentrations in Figures 6.16(a)–(f). Crystallisation often occurred outside the boundary defined by the patterned stamp recesses and were very disordered. As can be seen in Figures 6.16(g)–(i), using DCB solvent at increasing concentrations seemed to improve patterning quality and enclose crystallisation within the defined recesses of the stamp. However, this was observed to occur at only a few positions around the substrate indicating poor conformal contact in some regions due to stamp swelling. Unlike F8T2, we did not observe a thin layer of TIPS-Pentacene form outside the boundaries of the stamp recesses, indicating the solution of TIPS-Pentacene was completely absorbed by the PDMS stamp.
Figure 6.16: Optical micrographs of SAMIM patterned TIPS-Pentacene in PDMS stamps in different concentrated solvents of TOL (a–c), CB (d–f) and DCB (g–i). Images from left to right show increasing concentration from 1, 2 and 4 wt%.

6.5 Characterisation of crystal growth using MIMIC

Based on our optimisation runs for MIMIC in Section 6.4.1, we chose DCB solvent to dissolve F8T2, TIPS-Pentacene and additionally, P3HT, in concentrations of 1, 4 and 1 wt% respectively. PFPE and PDMS stamps were molded on SU-8 2002 and 2005 master templates on silicon to achieve capillary heights of ∼2 µm and ∼8 µm respectively. Capillary channels were either 100 µm or 2000 µm wide in order to examine the shape and filling fraction of the crystallisation. The thickness and root mean squared roughness of crystallised structures was measured at 6 randomly chosen locations for each sample. Despite many features not exhibiting smooth and flat morphologies, the RMS was used as a simple classification tool to separate smooth and rough morphologies.

6.5.1 F8T2

Figure 6.17 displays polarised optical micrographs of F8T2 crystallised inside PFPE capillary channels of different heights and widths. The presence of optical birefringence indicated regions of orientational crystallinity inside the capillary channels. Crystallisation inside the 100 µm channels was generally well defined compared to the 2000 µm channels. However for the 8 µm tall channels in Figure 6.17(b) we noticed some amount of crystallisation outside the boundary of the
channels indicating perhaps there was inadequate conformal contact of the stamp with respect to the substrate. Referring to the box and whisker plots in Figure 6.19(a), median thickness of the crystallised F8T2 structures inside 2 µm tall PFPE capillary channels were 1015 nm and 267 nm for 100 and 2000 µm wide channels respectively. Inside 8 µm tall channels, median thicknesses rose to 957 nm and 928 nm for 100 and 2000 µm channels. 2D line shapes of the best and worst crystallised structures inside PFPE channels are shown in Figure 6.20. It was noticed that most of these crystals were very rough, uneven and jagged. The best uniform crystal shape with the lowest RMS (43.7 nm) was with 2 µm tall 100 µm wide channels. The average filling fraction of F8T2 in PFPE channels was 24%.

Figure 6.17: Optical polarised micrographs of MIMIC patterned F8T2-DCB-1WT% in PFPE stamps with channel widths 100 µm (a–b) and 2000 µm (c–d). Images from left to right show different channel heights of 2 µm and 8 µm.

Figure 6.18 displays polarised optical micrographs of F8T2 inside PDMS capillary channels. Some amount of residue outside the boundary of the 2 µm tall capillaries was noticed in Figure 6.18(a) which was possibly due to inadequate conformal contact. No residue outside the boundary was noticed for 8 µm tall capillaries in Figure 6.18(b). Crystallisation inside the 2000 µm was slightly disordered and formed thick layers in Figures 6.18(c)–(d). There were also large disrupted areas of no crystallisation, possibly due to roof collapse of the stamp. Referring to Figure 6.19(b), median thickness inside 2 µm tall PDMS capillary channels were much shorter than 2 µm tall PFPE channels: 144 nm and 123 nm for 100 and 2000 µm wide channels respectively. Inside 8 µm tall channels however, median thicknesses rose to 2954 nm and 408 nm for the 100 and 2000 µm channels. Figure 6.21 displays the best and worst crystal shapes inside PDMS channels. The
best crystal shape with the lowest RMS (65.2 nm) was with 2 μm tall 100 μm wide channels. However the crystal had a distinctive $U$ shape around the edges, with a fairly uniform and flat center. The average filling fraction of F8T2 in PDMS channels was 18%, slightly lower than in PFPE channels.

![Figure 6.18](image)

**Figure 6.18:** Optical polarised micrographs of MIMIC patterned F8T2-DCB-1WT% in PDMS stamps with channel widths 100 μm (a–b) and 2000 μm (c–d). Images from left to right show different channel heights of 2 μm and 8 μm.

![Figure 6.19](image)

**Figure 6.19:** Box and whisker plots showing thickness variation in MIMIC patterned F8T2-DCB-1WT% features with different channel widths (100 μm and 2000 μm) and heights defined by SU-8 2002 (2 μm) and SU-8 2005 (8 μm) with PFPE (a) and PDMS (b) stamps.
Figure 6.20: Selected feature height profiles of MIMIC patterned F8T2-DCB-1WT% using PFPE stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PFPE stamps were molded on SU-8 2002 masters (2 µm) for (a) – (d) and SU-8 2005 masters (8 µm) for (e) – (h). PFPE channel widths were 100 µm for (a) – (b) and (e) – (f), and 2000 µm for (c) – (d) and (g) – (h).
Figure 6.21: Selected feature height profiles of MIMIC patterned F8T2-DCB-1WT% using PDMS stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PDMS stamps were molded on SU-8 2002 masters (2 µm) for (a) – (d) and SU-8 2005 masters (8 µm) for (e) – (h). PDMS channel widths were 100 µm for (a) – (b) and (e) – (f), and 2000 µm for (c) – (d) and (g) – (h).
6.5.2 TIPS-Pentacene

Figure 6.22 displays optical polarised micrographs of TIPS-Pentacene in PFPE capillaries with different heights and widths. Crystal growth inside 2 µm tall 100 µm wide channels was aligned in the direction of travel inside the capillaries and showed a mixture of different morphologies from uniform to disordered growth in Figure 6.22(a). Inside 8 µm tall channels however, crystal growth was threaded and branched along the entire length of the capillaries in Figure 6.22(b). For the 2 µm tall 2000 µm wide channels, crystal growth was spread out from the center and disordered in Figure 6.22(c). Whereas for the 8 µm tall channels in Figure 6.22(d), crystal growth was poor, isolated and randomly oriented. Median thicknesses for 2 µm tall PFPE capillaries were 555 nm and 247 nm, for 100 µm and 2000 µm wide channels in Figure 6.24(a). Inside 8 µm tall capillaries, thicknesses were reduced to 94 nm and 79 nm for 100 µm and 2000 µm wide channels. Best and worst crystal shapes for TIPS-Pentacene in PFPE capillaries are shown in Figure 6.25. The best crystal shape was uniform and smooth with a low RMS of 21.4 nm inside 2 µm tall 100 µm wide PFPE capillaries. The average filling fraction of TIPS-Pentacene in PFPE channels was 14%.

Figure 6.22: Optical polarised micrographs of MIMIC patterned TIPS-DCB-4WT% in PFPE stamps with channel widths 100 µm (a–b) and 2000 µm (c–d). Images from left to right show different channel heights of 2 µm and 8 µm.

Figure 6.23 displays optical polarised micrographs of the crystallisation process in the PDMS capillaries. Crystal growth inside 2 µm tall 100 µm wide channels was very disordered despite following the direction of travel inside the capillaries in Figure 6.23(a). Inside 8 µm tall channels, crystal growth was largely suppressed and showed no long range ordering along the entire length of the capillaries in Figure.
6.23(b). For the 2 \( \mu \)m tall 2000 \( \mu \)m wide channels, crystal growth did not cover the entire width of the channel and showed stacked crystalline layering along the walls of the capillary in Figure 6.23(c). The same phenomenon was observed for the 8 \( \mu \)m tall channels in Figure 6.23(d). Median thicknesses for 2 \( \mu \)m tall PDMS capillaries were 549 nm and 1006 nm, for 100 \( \mu \)m and 2000 \( \mu \)m wide channels in Figure 6.24(b). For 8 \( \mu \)m tall capillaries, thicknesses were 6596 nm and 515 nm for 100 \( \mu \)m and 2000 \( \mu \)m wide channels. Best and worst crystal shapes for TIPS-Pentacene in PDMS capillaries are shown in Figure 6.25. The best crystal shape was jagged around the edges but fairly uniform at the center, and had a RMS of 164.8 nm inside 2 \( \mu \)m tall 100 \( \mu \)m wide PDMS capillaries. The average filling fraction of TIPS-Pentacene in PDMS channels was 47%, much higher than in PFPE channels.

![Figure 6.23: Optical polarised micrographs of MIMIC patterned TIPS-DCB-4WT% in PDMS stamps with channel widths 100 \( \mu \)m (a–b) and 2000 \( \mu \)m (c–d). Images from left to right show different channel heights of 2 \( \mu \)m and 8 \( \mu \)m.](image-url)
Figure 6.24: Box and whisker plots showing thickness variation in MIMIC patterned TIPS-DCB-4WT% features with different channel widths (100 µm and 2000 µm) and heights defined by SU-8 2002 (2 µm) and SU-8 2005 (8 µm) with PFPE (a) and PDMS (b) stamps.
Figure 6.25: Selected feature height profiles of MIMIC patterned TIPS-DCB-4WT% using PFPE stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PFPE stamps were molded on SU-8 2002 masters (2 \( \mu \text{m} \)) for (a) – (d) and SU-8 2005 masters (8 \( \mu \text{m} \)) for (e) – (h). PFPE channel widths were 100\( \mu \text{m} \) for (a) – (b) and (e) – (f), and 2000 \( \mu \text{m} \) for (c) – (d) and (g) – (h).
Figure 6.26: Selected feature height profiles of MIMIC patterned TIPS-DCB-4WT% using PDMS stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PDMS stamps were molded on SU-8 2002 masters (2 µm) for (a) – (d) and SU-8 2005 masters (8 µm) for (e) – (h). PDMS channel widths were 100 µm for (a) – (b) and (e) – (f), and 2000 µm for (c) – (d) and (g) – (h).
6.5.3 P3HT

We also patterned P3HT using MIMIC in PFPE and PDMS stamps with varying height and width. Crystallisation was observed along the full length of the capillaries with some isolated areas of disruption for both 2 and 8 \( \mu m \) tall 100 \( \mu m \) wide PFPE capillaries in Figures 6.27(a)-(b). Crystal growth was poor in the 2 \( \mu m \) tall 2000 \( \mu m \) wide channel occurring mainly along the walls of the capillary in Figures 6.27(c) as opposed to what was observed for the 8 \( \mu m \) tall capillaries in Figure 6.27(d).

Median thicknesses for 2 \( \mu m \) tall PFPE capillaries were 101 nm and 77 nm, for 100 \( \mu m \) and 2000 \( \mu m \) wide channels in Figure 6.29(a). For 8 \( \mu m \) tall capillaries, thicknesses were 341 nm and 143 nm for 100 \( \mu m \) and 2000 \( \mu m \) wide channels. Best and worst crystal shapes for P3HT in PFPE capillaries are shown in Figure 6.30. The best crystal shape was fairly uniform with a smooth RMS of 7.6 nm inside 2 \( \mu m \) tall 100 \( \mu m \) wide PFPE capillaries. The average filling fraction of P3HT in PFPE channels was 6%.

![Figure 6.27: Optical polarised micrographs of MIMIC patterned P3HT-DCB-1WT% in PFPE stamps with channel widths 100 \( \mu m \) (a–b) and 2000 \( \mu m \) (c–d). Images from left to right show different channel heights of 2 \( \mu m \) and 8 \( \mu m \).](image)

P3HT crystallisation inside PDMS stamps was generally poor, with partial filling of the 100 \( \mu m \) capillaries in Figures 6.28(a) and (b). The 2000 \( \mu m \) capillaries in Figures 6.28(c) and (d) showed little or no birefringence under cross polarisers indicating the features were largely amorphous and disordered. Median thicknesses for 2 \( \mu m \) tall PDMS capillaries were 181 nm and 131 nm, for 100 \( \mu m \) and 2000 \( \mu m \) wide channels in Figure 6.29(b). For 8 \( \mu m \) tall capillaries, thicknesses were 2137 nm and 256 nm for 100 \( \mu m \) and 2000 \( \mu m \) wide channels. Best and worst crystal shapes for P3HT in PFPE capillaries are shown in Figure 6.30. P3HT feature growth was
generally very poor and rough for all channel heights and widths. Although the feature with the lowest RMS (57.9 nm) was with 8 μm tall 2000 8 μm wide PDMS capillaries. The average filling fraction of P3HT in PDMS channels was 19%, much higher than in PFPE channels.

![Image](image_url)

**Figure 6.28:** Optical polarised micrographs of MIMIC patterned P3HT-DCB-1WT% in PDMS stamps with channel widths 100 μm (a–b) and 2000 μm (c–d). Images from left to right show different channel heights of 2 μm and 8 μm.

![Box and whisker plots](box_plot_url)

**Figure 6.29:** Box and whisker plots showing thickness variation in MIMIC patterned P3HT-DCB-1WT% features with different channel widths (100 μm and 2000 μm) and heights defined by SU-8 2002 (2 μm) and SU-8 2005 (8 μm) with PFPE (a) and PDMS (b) stamps.
Figure 6.30: Selected feature height profiles of MIMIC patterned P3HT-DCB-1WT% using PFPE stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PFPE stamps were molded on SU-8 2002 masters (2 \( \mu \text{m} \)) for (a) – (d) and SU-8 2005 masters (8 \( \mu \text{m} \)) for (e) – (h). PFPE channel widths were 100\( \mu \text{m} \) for (a) – (b) and (e) – (f), and 2000 \( \mu \text{m} \) for (c) – (d) and (g) – (h).
Figure 6.31: Selected feature height profiles of MIMIC patterned P3HT-DCB-1WT% using PDMS stamps with varying capillary height and width. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness. PDMS stamps were molded on SU-8 2002 masters for (a) – (d) and SU-8 2005 masters for (e) – (h). PDMS channel widths were 100 µm for (a) – (b) and (e) – (f), and 2000 µm for (c) – (d) and (g) – (h).
6.5.4 MIMIC filling fractions

In general, it was observed that MIMIC crystallisation did not completely fill the entire height of the stamp channels, defined by the filling fraction. Filling fractions were generally reduced with wider stamp channel widths, with the exception of TIPS-Pentacene. However, the improvements were only minimal. The filling fractions and median root mean squared (RMS) roughness for F8T2, TIPS-Pentacene and P3HT crystallisation in PFPE and PDMS stamps are summarised in Table 6.1.

**Table 6.1:** MIMIC filling fractions and median root mean squared (RMS) roughness for F8T2, TIPS-Pentacene and P3HT crystallisation inside stamp channels. FD1 = F8T2-DCB-1WT%, TD4 = TIPS-DCB-4WT% and PD1 = P3HT-DCB-1WT%. Filling fraction considers the fraction of the MIMIC patterned feature height relative to the maximum height of the stamp channels.

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<th>RMS (nm)</th>
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<td>3</td>
<td>140</td>
</tr>
</tbody>
</table>

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Chapter 6. Soft lithographic patterning and transistor devices

6.6 Characterisation of crystal growth using SAMIM

Organic semiconductor crystal growth using SAMIM was characterised with optical polarised microscopy. We used primarily PDMS stamps with rectangular 100 µm wide relief structures that were either 2 µm or 8 µm tall. Based on solution optimisation trials carried out in Section 6.4.2, DCB solvent was used at a concentration of 1 wt% for F8T2, 4 wt% for TIPS-Pentacene and 1 wt% for P3HT.

6.6.1 F8T2

Figures 6.32(a) and (b) display SAMIM patterned F8T2 with channel heights 2 µm and 8 µm. Similar to what was observed in Section 6.4.2, a thin layer of F8T2 was patterned outside the boundary regions of the stamp recesses for both 2 µm and 8 µm heights. These layers were roughly 200 nm and 500 nm thick as shown in Figures 6.34(a) and (c). Optical birefringence of the features outside the channel boundaries showed a more prominent contrast, implying perhaps the orientation order inside the defined channels was slightly weaker. Median thicknesses were 138 nm and 1120 nm for 2 µm and 8 µm channel heights, with a larger spread of thicknesses observed for the latter in Figure 6.33. Features showed a distinctive U shape indicating the solution reached supersaturation when most of the solvent had evaporated, hence F8T2 layers formed primarily around the walls of the channel. The average filling fraction of F8T2 in PDMS stamp channels was 13%.

Figure 6.32: Optical polarised micrographs of SAMIM patterned F8T2-DCB-1WT% in PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a) and 8 µm (b).
Figure 6.33: Box and whisker plots showing thickness variation in SAMIM patterned F8T2-DCB-1WT% features with PDMS channel widths 100 µm, and channel heights 2 µm (SU-8 2002) (a) and 8 µm (SU-8 2005)(b).

Figure 6.34: Selected feature height profiles of SAMIM patterned F8T2-DCB-1WT% using PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a–b) and 8 µm (c–d). Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness.

6.6.2 TIPS-Pentacene

Figures 6.35(a) and (b) display SAMIM patterned TIPS-Pentacene with channel heights 2 µm and 8 µm. Good crystal growth occurred in some regions inside the 2 µm tall channels. However for the most part, crystal growth failed to occur in the central recesses of the stamp channels, with tiny disordered crystals forming mainly around the edges of the walls. Due to poor conformal contact in some regions, TIPS-Pentacene growth occurred in boundaries outside of the channel. Median
thicknesses were 684 nm and 4047 nm for 2 µm and 8 µm channel heights, with a larger spread of thicknesses observed for 8 µm heights in Figure 6.36. Filled channels generally had showed a profile similar to Figures 6.37(a) and (c), while incomplete crystallisation showed profiles similar to Figures 6.37(b) and (d), with the central region largely devoid of crystal growth. The average filling fraction of TIPS-Pentacene in PDMS stamp channels was 44%.

**Figure 6.35:** Optical polarised micrographs of SAMIM patterned TIPS-DCB-4WT% in PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a) and 8 µm (b).

**Figure 6.36:** Box and whisker plots showing thickness variation in SAMIM patterned TIPS-DCB-4WT% features with PDMS channel widths 100 µm, and channel heights 2 µm (SU-8 2002) (a) and 8 µm (SU-8 2005)(b).
Figure 6.37: Selected feature height profiles of SAMIM patterned TIPS-DCB-4WT\% using PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a–b) and 8 µm (c–d). Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness.

6.6.3 P3HT

Figures 6.32(a) and (b) display SAMIM patterned P3HT in PDMS stamps with channel heights 2 µm and 8 µm. No optical birefringence was observed in 2 µm tall channels and appeared dark indicating features were amorphous with no orientational order in Figure 6.32(a). However, optical birefringence was observed in 8 µm tall channels in Figure 6.32(b). Similar to what was observed with SAMIM patterned F8T2, a thin layer of P3HT roughly 200 nm thick developed around the boundaries of the channels indicating P3HT solution did not completely absorb into the PDMS stamp. As can be seen in Figure 6.40, patterned features predominantly had a U shape, with P3HT layers growing around the walls of the channel. Median thicknesses were 86 nm and 1342 nm for 2 µm and 8 µm channel heights, with a larger spread of thicknesses observed for 8 µm heights in Figure 6.39. The average filling fraction of P3HT in PDMS stamp channels was 13%.
Figure 6.38: Optical polarised micrographs of SAMIM patterned P3HT-DCB-1WT% in PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a) and 8 µm (b).

Figure 6.39: Box and whisker plots showing thickness variation in SAMIM patterned P3HT-DCB-1WT% features with PDMS channel widths 100 µm, and channel heights 2 µm (SU-8 2002) (a) and 8 µm (SU-8 2005)(b).
Figure 6.40: Selected feature height profiles of SAMIM patterned P3HT-DCB-1WT% using PDMS stamps with channel widths 100 µm, and channel heights 2 µm (a–b) and 8 µm (c–d). Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness.

### 6.6.4 SAMIM filling fractions

Filling fractions and median root mean squared (RMS) roughnesses are summarised in Table 6.2. Similar to MIMIC, filling fractions were still very low for SAMIM patterned features. A slight increase in filling fraction was observed using 8 µm tall channels, however these generally resulted in a larger spread of thicknesses with the SAMIM process.

**Table 6.2:** SAMIM filling fractions and median root mean squared (RMS) roughness for F8T2, TIPS-Pentacene and P3HT crystallisation inside 100 µm wide PDMS stamp channels. FD1 = F8T2-DCB-1WT%, TD4 = TIPS-DCB-4WT% and PD1 = P3HT-DCB-1WT%. Filling fraction considers the fraction of the SAMIM patterned feature height relative to the maximum height of the stamp channels.

<table>
<thead>
<tr>
<th>OSC</th>
<th>Channel height (µm)</th>
<th>Filling Fraction (%)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD1</td>
<td>2</td>
<td>11</td>
<td>101</td>
</tr>
<tr>
<td>FD1</td>
<td>8</td>
<td>15</td>
<td>786</td>
</tr>
<tr>
<td>TD4</td>
<td>2</td>
<td>39</td>
<td>321</td>
</tr>
<tr>
<td>TD4</td>
<td>8</td>
<td>48</td>
<td>1050</td>
</tr>
<tr>
<td>PD1</td>
<td>2</td>
<td>10</td>
<td>73</td>
</tr>
<tr>
<td>PD1</td>
<td>8</td>
<td>15</td>
<td>627</td>
</tr>
</tbody>
</table>
6.7 Issues with patterned layer morphology

Since the organic solutions often reached supersaturation after when most of the solvent had evaporated, we noticed a tendency of incomplete crystallisation and filling of the channels for both MIMIC and SAMIM processes. This posed a problem when fabricating OFETs in BGTC and TGBC staggered architectures. Figures 6.41(a)–(c) display the possible illustrations of organic semiconductor and Au morphologies in the BGTC architecture observed. MIMIC or SAMIM patterned organic semiconductors would often form non-ideal, rough and uneven morphologies such as the diagram illustrated in Figure 6.41(b). This particular morphology would still allow the OFET to function upon the application of a voltage. However, despite the staggered architecture, there would be an increase in contact resistance and threshold voltage due to the uneven current pathway across the conducting channel from the source to the drain electrode [40]. On the other hand, Figure 6.41(c) would not function as an OFET, and would instead short upon the application of a voltage, due to the rough, jagged and discontinuous morphology. Optical micrographs of this shorting phenomenon are shown in Figure 6.41. We assume that this shorting phenomenon is caused by joule heating where the high local current densities in the electrode edge causes disorderly defect states in the semiconductor to rapidly heat up and expand, thereby causing a rupture through the Au contacts [41].

![Illustrations of ideal and non-ideal morphologies of organic semiconductor, dielectric and Au source/drain contact layers in staggered BGTC (a–c) and TGBC (d–f) geometries. (a) and (d) show idealised BGTC and TGBC geometries with flat planar layers, while illustrations to the right show increasing non-ideal and worsening morphology. (Note: For BGTC Si/SiO\textsubscript{2} OFETs, the doped Si substrate acts as the gate and SiO\textsubscript{2} as the dielectric.)](image)

Figures 6.41(d)–(f) displays possible illustrations of organic semiconductor,
dielectric and Au morphologies in the TGBC architecture. Spin coated dielectrics and evaporated Au gate electrodes would form uneven morphologies on the rough MIMIC or SAMIM patterned organic semiconductors as illustrated in Figure 6.41(e). Although contact resistance should be lower in staggered architectures due to continuous charge injection pathways [42][43], there would still be an increase in contact resistance and threshold voltage due to the roughness of the interacting layers. Unlike the bottom gate architecture before, the top gate architecture posed some risks in operation as the measuring probe tip could potentially pierce through the thin 50 nm Au gate and into the uneven dielectric layer and/or underlying semiconductor, causing the device to short during voltage application. Figure 6.41(f) on the other hand, would simply not function due to the gaps and discontinuities in the rough and jagged organic semiconductor, spin coated dielectric and Au layers.

![Image](a) ![Image](b)

**Figure 6.42:** Examples of shorting phenomenon due to joule heating caused by rough jagged morphology of a MIMIC patterned TIPS-Pentacene crystal in the BGTC architecture (a), and poor spin coated dielectric morphology in the TGBC architecture (b).

There is still some debate as to whether there is any dependance of the mobility on organic semiconductor thickness since charge transport in the accumulation layer is limited to a few monolayers [44][45]. However, since MIMIC and SAMIM patterned semiconductors generally resulted in thicknesses of up to 1 µm, it should be noted that the majority of these papers mainly investigated the effect of film thickness on mobility well below 200 nm [45][46][47][48].
6.8 MIMIC patterned OFETs with varying dielectric

MIMIC patterned organic semiconductors were incorporated into OFETs with predominantly staggered geometries in the BGTC and TGBC architectures. Dielectrics such as SiO$_2$ (230 nm) were used in the BGTC architecture, and PVP (700 nm) and CYTOP (700 nm) in the TGBC architecture. For both geometries, Au source and drain contacts had a fixed channel length $L = 50\mu m$ and width $W = 2000\mu m$ ($W/L = 40$). PFPE stamps with 2 $\mu m$ tall and 100 $\mu m$ wide channels were chosen as median crystallised thicknesses for F8T2 (1015 nm), TIPS-Pentacene (555 nm) and P3HT (101 nm) were generally below 1 $\mu m$ as determined in Section 6.5. This was done in order to reduce the impact of step coverage and non-uniformity when spin coating 700 nm dielectrics or evaporating 50 nm Au contacts. Figure 6.43 displays optical polarised micrographs of MIMIC patterned F8T2, TIPS-Pentacene and P3HT with evaporated Au source and drain contacts. Polarised micrographs for TGBC devices could not be taken due to the opacity of the 50 nm Au contact evaporated on top of the dielectric and underlying semiconductor layers.

![Figure 6.43: Optical polarised micrographs of evaporated Au source (S) and drain (D) contacts on MIMIC patterned F8T2 (a), TIPS-Pentacene (b), and P3HT (c).](image)

One thing that can be noticed from Figure 6.43 is that the rectangular semiconductor features were separated by 100 $\mu m$ gaps. It would have been more accurate to say that they had a $W = 100\mu m$. However, there was an error margin of the equivalent amount when aligning and evaporating Au contacts on often very small areas of viable patterned semiconductor regions. Evaporated contacts with an area of $1000 \times 1000 \mu m^2$ would sometimes completely miss these patterned regions, hence preventing the completion of the OFET device. Furthermore, based on our current setup, it was impractical and unproductive to measure the total number of crystallised regions between the contacts for several dozen devices. Hence we normalised calculations of the saturation mobility by assuming $W = 2000\mu m$ across the whole channel in order to compare performance between devices, even though this would have slightly overestimated the overall saturation mobility.
In total, 24 BGTC SiO$_2$, 22 TGBC PVP and 16 TGBC CYTOP OFETs were fabricated with different semiconductors. Table 6.3 displays the device success rates and average performance for operational OFETs that did not short and had leakage currents less than than the drain current at $V_D = -60$ V. Device success rates for F8T2, TIPS-Pentacene and P3HT OFETs with SiO$_2$ dielectric were 44%, 56% and 83% respectively. With the exception of F8T2, poor yields were achieved with TGBC architectures with PVP as all of the TIPS-Pentacene ($RMS_{\text{median}} = 103$ nm) and P3HT ($RMS_{\text{median}} = 37$ nm) devices shorted upon the application of a minor voltage. This was possibly due to the reasons discussed in Section 6.7 where rough and jagged morphologies might have pierced through the dielectric layer and/or Au contacts causing the devices to short. The same problem was observed with TIPS-Pentacene in TGBC architectures with CYTOP, however device success rates for F8T2 and P3HT were 50% and 44% respectively.

Table 6.3: Device success rates and average performance for MIMIC patterned F8T2, TIPS-Pentacene and P3HT organic semiconductors (OSC) in OFETs with SiO$_2$ (230 nm), PVP (700 nm) and CYTOP (700 nm) dielectrics. PFPE stamps with 2 µm tall 100 µm wide capillary channels were used. FD1 = F8T2-DCB-1WT%, TD4 = TIPS-DCB-4WT% and PD1 = P3HT-DCB-1WT%. OFET architectures were bottom gate, top contact (BGTC) and top gate, bottom contact (TGBC) with $L = 50$µm, $W = 2000$µm. Device success rate considers OFETs that did not short upon operation and have $|I_D/I_G| > 1$.

<table>
<thead>
<tr>
<th>OSC</th>
<th>Dielectric Architecture</th>
<th>Total devices measured</th>
<th>Device success rate (%)</th>
<th>$I_D/I_G$</th>
<th>$\mu_{\text{sat}}$ (cm$^2$/Vs)</th>
<th>$V_{th}$ (V)</th>
<th>On/Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD1</td>
<td>SiO$_2$</td>
<td>BGTC</td>
<td>9</td>
<td>44</td>
<td>1.8</td>
<td>2.3x10$^{-5}$</td>
<td>-19.6</td>
</tr>
<tr>
<td>TD4</td>
<td>SiO$_2$</td>
<td>BGTC</td>
<td>9</td>
<td>56</td>
<td>2.7</td>
<td>6.0x10$^{-4}$</td>
<td>-12.5</td>
</tr>
<tr>
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<td>BGTC</td>
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<td>83</td>
<td>4</td>
<td>5.8x10$^{-4}$</td>
<td>25.3</td>
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<td>FD1</td>
<td>PVP</td>
<td>TGBC</td>
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<td>50</td>
<td>4</td>
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<td>-18</td>
</tr>
<tr>
<td>TD4</td>
<td>PVP</td>
<td>TGBC</td>
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<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>-</td>
</tr>
<tr>
<td>FD1</td>
<td>CYTOP</td>
<td>TGBC</td>
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<td>50</td>
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<tr>
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<td>CYTOP</td>
<td>TGBC</td>
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<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>CYTOP</td>
<td>TGBC</td>
<td>9</td>
<td>44</td>
<td>24</td>
<td>4.1x10$^{-4}$</td>
<td>75</td>
</tr>
</tbody>
</table>

It was observed that average leakage current magnitudes were generally very high for SiO$_2$ and PVP dielectrics, with gate currents at $V_D = -60$ V for F8T2, TIPS-Pentacene and P3HT being only less than 4 times the drain current.

The leakage current in OFETs is thought to have two origins: a lateral current along the source, conducting channel and drain electrode ($L_L$), and a vertical current from the gate, dielectric to the drain electrode [49]. The latter is broken down into two components: the current through the gate, dielectric, semiconductor and source electrode ($L_{VS}$), and the current through the gate, dielectric and drain electrode ($L_{VD}$) (see Figure 6.44). Although our parameter analyser is capable of measuring the total gate leakage due to $L_L$, $L_{VS}$ and $L_{VD}$, the current due to $L_{VD}$ is thought to
be the major contributing factor to leakage current and depends on the permittivity and morphology of the dielectric [50]. Since the morphology of MIMIC patterned semiconductors and subsequent layers of spin coated dielectrics and evaporated Au contacts were generally very rough, and in some case unaligned, we assume that this could be a potential cause of the high gate leakage in SiO$_2$ and PVP devices.

Leakage currents could have been reduced by simple adjustment of the geometry by minimising the contact source/drain and dielectric layer area in the BGTC architecture, and reducing the gate contact to within the conduct channel area in the TGBC architecture. Although this was harder to achieve in practice due to alignment issues faced with soft lithography and evaporation of Au contacts using shadow masks.

![Figure 6.44](image)

**Figure 6.44**: Illustration of leakage current paths in BGTC (a) and TGBC (b) geometries. $L_L$ is the lateral leakage current, $L_{VS}$ is the vertical leakage current through the semiconductor, and $L_{VD}$ is the vertical leakage current through the dielectric. Note: Although not shown, the source electrode is grounded, while a voltage bias is applied through the gate and drain electrodes.

F8T2 was the only organic semiconductor out of three that were incorporated into functional BGTC and TGBC OFETs. The average saturation mobility and on/off ratio was the lowest with PVP, and the highest with CYTOP. Despite the roughness in the semiconductor morphology, leakage currents were over 3 orders of magnitude lower with CYTOP than with SiO$_2$ and PVP. This leads us to assume that surface roughness of the dielectric was not the underlying cause of high gate leakage because the measured root mean squared (RMS) roughness for CYTOP (7.0 nm) was much higher compared to SiO$_2$ (0.7 nm), glass (0.7 nm) and PVP (1.8 nm). Hence we assume that the cross-linked CYTOP dielectric was of higher quality and had lower density of pinholes that reduced overall vertical gate leakage. Furthermore, CYTOP’s hydrophobicity and low surface energy prevents O$_2$ and H$_2$ diffusion into the conducting channel that would otherwise disrupt the charge transport [51].

Figure 6.45 displays the best performing output and transfer characteristics of an
F8T2 OFET with CYTOP dielectric out of the batch. This had a $\mu_{\text{sat}}$ of $1.3 \times 10^{-3}$ cm$^2$/Vs, $V_{\text{th}}$ of -16.7 V, low hysteresis of -4.8 V, $|I_{D}/I_{G}|$ of $1.1 \times 10^{3}$ and a high on/off ratio of $1.2 \times 10^{4}$. Our result is comparable, if not, better than (unaligned) spin coated F8T2 OFETs in the staggered geometry that have mobilities in the range of $10^{-4} - 10^{-3}$ cm$^2$/Vs with various self assembled monolayer (SAM) treatments [52]. Considering that the median thickness of MIMIC patterned F8T2 was about 1015 nm, F8T2 thickness does not appear to influence the mobility in the TGBC staggered geometry.

![Figure 6.45: Selected output (a) and transfer (b) characteristics of MIMIC patterned F8T2-DCB-1WT% in a TGBC OFET with CYTOP (700 nm). $L = 50 \mu m, W = 2000 \mu m$ ($W/L = 40$).](image)

Top gate OFETs with TIPS-Pentacene on the other hand, failed to perform due to its rough and jagged morphology. Selected characteristics for TIPS-Pentacene are shown Figure 6.46. We observed a $V_D$ offset of about -10 V of the $I_D$ during operation, which increased to -15 V at $V_G = -60$ V. This seems to imply the presence of charge carrier trap states and defects in the rough TIPS-Pentacene morphology that resulted in the large $V_D$ offset. The device had a $\mu_{\text{sat}}$ of $5.8 \times 10^{-4}$ cm$^2$/Vs, $V_{\text{th}}$ of -16.6 V, high hysteresis of -14.1 V, low $|I_{D}/I_{G}|$ of 7.8 and a low on/off ratio of $8.0 \times 10^{3}$. The mobility measured here was more than 3 orders of magnitude lower than similar MIMIC patterned TIPS-Pentacene OFETs (0.29 cm$^2$/Vs) in the literature [17]. Since we did not use any SAM treatments or annealing, P3HT OFETs in general performed poorly, yielding very high threshold voltages and low on/off ratios, even though electrical measurements were taken in N$_2$. 
6.9 SAMIM patterned OFETs with varying dielectric

F8T2, TIPS-Pentacene and P3HT were also patterned using SAMIM in OFETs with the same geometries and dielectrics as before. Median crystallised thicknesses for F8T2, TIPS-Pentacene and P3HT in 2 µm tall channels were 138 nm, 684 nm and 86 nm respectively. Figure 6.47 displays optical polarised micrographs of SAMIM patterned F8T2, TIPS-Pentacene and P3HT with evaporated Au source and drain contacts. The same issues with aligning and evaporating Au contacts on the SAMIM patterned features were faced, hence we normalised the channel width to \( W = 2000 \mu m \) to allow comparison between different devices.

**Figure 6.47:** Optical polarised micrographs of evaporated Au source/drain contacts on SAMIM patterned F8T2 (a), TIPS-Pentacene (b), and P3HT (c).

We fabricated 22 BGTC SiO\(_2\), 21 TGBK PVP and 19 TGBK CYTOP OFETs with different semiconductors. Table 6.4 shows the average device success rate and performance for operational OFETs that did not short and had low leakage currents with respect to the max drain current at \( V_D = -60 \text{ V} \). Device success rates...
for SAMIM patterned F8T2 and TIPS-Pentacene OFETs with SiO₂ dielectric were 33% and 31%. The RMS for P3HT increased from 37 nm (MIMIC) to 73 nm with SAMIM. All devices with PVP dielectric failed to function. F8T2 ($RMS_{median} = 101$ nm) and TIPS-Pentacene ($RMS_{median} = 321$ nm) saw respective increases in the RMS compared to MIMIC. Finally, with CYTOP dielectrics, only F8T2 devices functioned giving success rates of 57%. Similar to what was observed with MIMIC, top gate devices with TIPS-Pentacene failed to function with SAMIM patterning as well, presumably due to the rough and jagged morphology piercing through the spin coated dielectric. Unfortunately, all P3HT devices failed to function for the dielectrics tested.

### Table 6.4: Device success rates and average performance for SAMIM patterned F8T2, TIPS-Pentacene and P3HT organic semiconductors (OSC) in OFETs with SiO₂ (230 nm), PVP (700 nm) and CYTOP (700 nm) dielectrics. PDMS stamps with 2 μm tall, 1000 μm long and 100 μm wide rectangular channels were used. FD1 = F8T2-DCB-1WT%, TD4 = TIPS-DCB-4WT% and PD1 = P3HT-DCB-1WT%. OFET architectures were bottom gate, top contact (BGTC) and top gate, bottom contact (TGBK) with $L = 50μm, W = 2000μm$.

| OSC | Dielectric | Architecture | Total devices measured | Device success rate (%) | $|I_D/I_G|$ | $\mu_{sat}$ (cm²/Vs) | $V_{th}$ (V) | On/Off |
|-----|------------|--------------|------------------------|------------------------|----------|----------------------|----------|--------|
| FD1 | SiO₂       | BGTC         | 6                      | 33                     | 3.2      | $1.9\times10^{-4}$   | -6.1     | 3.4$\times10^4$ |
| TD4 | SiO₂       | BGTC         | 13                     | 31                     | 2.8      | $2.4\times10^{-3}$   | -10.7    | 2.2$\times10^4$ |
| PD1 | SiO₂       | BGTC         | 3                      | 0                      | -        | -                    | -        | -      |
| FD1 | PVP        | TGBK         | 6                      | 0                      | -        | -                    | -        | -      |
| TD4 | PVP        | TGBK         | 9                      | 0                      | -        | -                    | -        | -      |
| PD1 | PVP        | TGBK         | 6                      | 0                      | -        | -                    | -        | -      |
| FD1 | CYTOP      | TGBK         | 7                      | 57                     | 118      | $9.2\times10^{-4}$   | -18.6    | 8.0$\times10^4$ |
| TD4 | CYTOP      | TGBK         | 3                      | 0                      | -        | -                    | -        | -      |
| PD1 | CYTOP      | TGBK         | 9                      | 0                      | -        | -                    | -        | -      |

Average gate leakage currents at $V_D = -60$ V were less than 4 times greater than the drain current for SiO₂ OFETs, which was similar or lower than what was observed for MIMIC OFETs. We saw average leakage currents reduce by 2 orders of magnitude for F8T2 with CYTOP than compared to SiO₂. However the leakage current magnitude increased by roughly 50% for P3HT with CYTOP compared to PVP. Despite the lower yield of devices with the SAMIM process, average mobilities and on/off ratios were much higher, and threshold voltages were lower, for F8T2 and TIPS-Pentacene than compared to the MIMIC process. The best F8T2 OFET with the lowest leakage current was with CYTOP dielectric in the top gate geometry, and this had a $\mu_{sat}$ of $1.2\times10^{-3}$ cm²/Vs, $V_{th}$ of -20.1 V, very low hysteresis of -2.2 V, $|I_D/I_G|$ of $2.0\times10^2$ and an on/off ratio of $4.2\times10^4$. The corresponding output and transfer characteristics are shown in Figure 6.48. From the output characteristics, we observed a $V_D$ offset of $I_D$ which increased with $V_G$, indicating more charge carrier...
trap states induced with the SAMIM process. Despite the slight increase in mobility and on/off ratio, leakage currents and threshold voltage were increased. Hence these performances were slightly lower than F8T2 MIMIC OFETs with CYTOP in Table 6.3.

Figure 6.48: Selected output (a) and transfer (b) characteristics of SAMIM patterned F8T2-DCB-1WT% in a TGBC OFET with CYTOP (700 nm). $L = 50\mu m, W = 2000\mu m$ ($W/L = 40$).

As top gate OFETs of TIPS-Pentacene failed for SAMIM as well, the output and transfer characteristics for the BGTC SiO$_2$ result is shown instead in Figure 6.49. An offset of $V_D$ for the $I_D$ was again observed in the output characteristics with a value of -8 V. This was lower than the offset measured for TIPS-Pentacene MIMIC OFETs before (-15 V). This implies that the trap states and defects in the TIPS-Pentacene morphology appear to be slightly reduced despite the higher median RMS roughness. The performance of the TIPS-Pentacene SAMIM OFET were an improvement compared to the MIMIC patterning, with a $\mu_{sat}$ of $1.3 \times 10^{-3}$ cm$^2$/Vs, $V_{th}$ of $–14.4$ V, hysteresis of $-4.9$ V, $|I_D/I_G|$ of 3.0 and an on/off ratio of $5.5 \times 10^4$. However, as leakage currents were still high, being only 3 times lower than maximum drain current with SiO$_2$ dielectric, the 2 orders of magnitude higher mobility recorded for TIPS-Pentacene SAMIM OFETs compared to MIMIC OFETs could perhaps be overestimated [53].
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Figure 6.49: Selected output (a) and transfer (b) characteristics of SAMIM patterned TIPS-DCB-4WT% in a BGTC OFET with SiO$_2$ (230 nm). $L = 50 \mu m, W = 2000 \mu m$ ($W/L = 40$).

6.10 Confined crystallisation of F8T2 azeotropic binary solutions

The MIMIC and SAMIM process flows were also applied to azeotropic binary solutions of F8T2. Similar to Chapter 5, we dissolved F8T2 in a 1 wt% binary mixture of hexane and 1,2-dichlorobenzene solvents (HEX-DCB) in a 1:1 ratio. PFPE stamps with fixed channel heights and widths of 2 $\mu m$ and 100 $\mu m$ were used for MIMIC while PDMS stamps stamps with 2 $\mu m$ tall, 1000 $\mu m$ long and 100 $\mu m$ wide channels were used for SAMIM. Using a sample size of 6 thicknesses randomly measured at different points of the patterned features, median thicknesses of 341 nm and 717 nm were measured for MIMIC and SAMIM patterns respectively in Figure 6.52. From the figure, it was also observed that features patterned with SAMIM had a much larger spread of thicknesses compared to MIMIC.

The filling fractions and median RMS roughness for these features were 20% and 87 nm for MIMIC, and 30% and 118 nm for SAMIM. Figures 6.51(a)–(d) display the best and worst HEX-DCB shapes patterned using MIMIC and SAMIM. The best HEX-DCB MIMIC feature had a max thickness of 500 nm and RMS of 47 nm. For SAMIM features, a thin layer of F8T2 was measured outside the channel boundaries and these were between 50 nm – 600 nm in thickness for best and worst features. Compared to mono solvent F8T2-DCB in Sections 6.5 and 6.6, HEX-DCB features generally had smaller thicknesses and increased RMS roughness with the MIMIC and SAMIM patterning process.
Figure 6.50: Box and whisker plots showing thickness variation of F8T2 HEX-DCB features with MIMIC and SAMIM patterning. Stamp channel widths and heights were 100 µm and 2 µm respectively.

Figure 6.51: Selected feature height profiles of MIMIC (a–b) and SAMIM (c–d) patterned F8T2 HEX-DCB with stamp channel widths 100 µm and heights 2 µm. Images displayed from left to right represent BEST and WORST features defined by the measured RMS roughness.
In order to examine the electrical characteristics, F8T2 HEX-DCB OFETs were fabricated in staggered geometries with the BGTC and TGBC architectures using SiO$_2$ (230 nm), PVP (700 nm) and CYTOP (700 nm) dielectrics. The OFET channel width was normalised to $W = 2000 \mu m$ in order to compare between devices. Figure 6.52 displays optical polarised micrographs of HEX-DCB MIMIC and SAMIM OFETs with Au top contacts. The observation of birefringence under cross polarisers indicated that these features had developed orientational crystallinity.

Table 6.5: Device success rates and average performance for MIMIC and SAMIM patterned F8T2 HEX-DCB binary solvent OFETs with SiO$_2$ (230 nm), PVP (700 nm) and CYTOP (700 nm) dielectrics. For MIMIC, PFPE stamps with 2 $\mu$m tall, 100 $\mu$m wide channels were used. For SAMIM, PDMS stamps with 2 $\mu$m tall, 1000 $\mu$m long and 100 $\mu$m wide rectangular channels were used. OFET architectures were bottom gate, top contact (BGTC) and top gate, bottom contact (TGBC) with $L = 50 \mu m$, $W = 2000 \mu m$.

| Dielectric | Architecture | Method | Total devices measured | Device success rate (%) | $|I_D/I_G|$ | $\mu_{sat}$ (cm$^2$/Vs) | $V_{th}$ (V) | On/Off |
|------------|--------------|--------|------------------------|------------------------|----------------|----------------|-------------|---------|
| SiO$_2$    | BGTC         | MIMIC  | 6                      | 17                     | 1.1            | 2.9x10$^{-6}$ | -10.1       | 8.2x10$^4$ |
| PVP        | TGBC         | MIMIC  | 9                      | 11                     | 1.1            | 4.3x10$^{-6}$ | -13.8       | 4.8x10$^2$ |
| CYTOP      | TGBC         | MIMIC  | 4                      | 100                    | 362.7          | 1.3x10$^{-3}$ | -22.8       | 7.0x10$^4$ |
| SiO$_2$    | BGTC         | SAMIM  | 13                     | 15                     | 1.7            | 5.8x10$^{-6}$ | -13.1       | 3.9x10$^2$ |
| PVP        | TGBC         | SAMIM  | 4                      | 100                    | 101.8          | 7.1x10$^{-4}$ | -18.5       | 1.8x10$^4$ |
| CYTOP      | TGBC         | SAMIM  | 7                      | 57                     | 8.7            | 9.5x10$^{-4}$ | -18.9       | 1.0x10$^5$ |

Table 6.5 shows the device success rates and average performance of the HEX-DCB MIMIC and SAMIM OFETs. A total of 19 MIMIC OFETs and 24 SAMIM OFETs were measured with different dielectrics. Device success rates and average drain to leakage current magnitudes $|I_D/I_G|$ were quiet low for MIMIC OFETs, being 17% and 1.1 with SiO$_2$ and 11% and 1.1 for PVP. For CYTOP however, all devices functioned with an average $|I_D/I_G|$ of 362.7. Hence the best HEX-DCB MIMIC OFET was with CYTOP, with its output and transfer characteristics shown in Figure 6.53. The output graphs showed good current operation starting at $V_D = 0 V$, although there was some minor hysteresis observed at
higher $V_G$. Regarding its performance, it had a $\mu_{sat}$ of $1.8 \times 10^{-3}$ cm$^2$/Vs, $V_{th}$ of -23.7 V, hysteresis of -4.3 V, $|I_D/I_G|$ of $2.3 \times 10^2$ and a high on/off ratio of $9.6 \times 10^4$. This was a slight improvement to the mono solvent F8T2-DCB MIMIC OFET measured earlier, which had a $\mu_{sat}$ of $1.3 \times 10^{-3}$ and on/off ratio of $1.2 \times 10^4$ (see Section 6.8).

![Figure 6.53: Selected output (a) and transfer (b) characteristics of MIMIC patterned F8T2 HEX-DCB in a TGBC OFET with CYTOP (700 nm). $L = 50\mu m, W = 2000\mu m$ ($W/L = 40$).](image)

For HEX-DCB SAMIM OFETs, device success rates $|I_D/I_G|$ magnitudes and were 15% and 1.7 for SiO$_2$, 100% and 101.8 for PVP, and 57% and 8.7 for CYTOP. The high leakage current observed for CYTOP compared to PVP was surprising. Mono solvent F8T2-DCB SAMIM OFETs with CYTOP in Table 6.4 had a $RMS_{median} = 101$ nm and generally obtained functional devices with relatively low average leakage currents of $I_D/I_G = 49.3$ compared to MIMIC OFETs. As HEX-DCB features had a slightly higher $RMS_{median} = 118$ nm and a much larger spread of thicknesses was observed in Figure 6.52 earlier, this seems to indicate that patterned morphology with SAMIM was generally unfavourable with the CYTOP dielectric for this particular batch. Hence the best HEX-DCB SAMIM OFET was with a PVP dielectric and its output and transfer characteristics are shown in Figure 6.54. Regarding the performance, it had a $\mu_{sat}$ of $6.9 \times 10^{-4}$ cm$^2$/Vs, $V_{th}$ of -18.0 V, hysteresis of -4.0 V, $|I_D/I_G|$ of $1.4 \times 10^2$ and on/off ratio of $2.6 \times 10^4$. This OFET underperformed compared to mono solvent F8T2-DCB SAMIM OFETs which had a $\mu_{sat}$ of $1.2 \times 10^{-3}$ and on/off ratio of $4.2 \times 10^4$. A slight offset in the $V_D$ for $I_D$ was observed at -2.5 V in the output characteristics which indicated presence of charge carrier trap states that were responsible for the lower performance.
Chapter 6. Soft lithographic patterning and transistor devices

6.11 Modelling and analysis of selected MIMIC patterned OFETs

Figure 6.54: Selected output (a) and transfer (b) characteristics of SAMIM patterned F8T2 HEX-DCB in a TGBC OFET with PVP (700 nm). \( L = 50\,\mu m, W = 2000\,\mu m \) \((W/L = 40)\).

Based on our results, MIMIC patterned top gate F8T2-DCB and F8T2-HEX-DCB OFETs gave the best performance, and these were fitted to the Tanase, Vissenberg and Matters model for charge transport in amorphous, glassy disordered organic semiconductors. Fitting parameters to the linear and saturation drain currents are displayed in Table 6.6. As shown in Figure 6.55, excellent fits were obtained within the 95% confidence interval bands for both devices. \( T_0 \) disorder values of 617 K for MIMIC patterned F8T2-DCB and 906 K for F8T2-HEX-DCB were quite high compared to results of the same material with spin coating in Chapters 4 and 5. This seems to indicate that the deposited F8T2 exhibited considerable disorder, and possibly amorphous in nature rather than crystalline. Despite exhibiting
birefringence under optical polarisers in Figures 6.43 and 6.52 earlier, this seems to indicate that several aggregates of F8T2 were sedimented on top of each and solidified during the MIMIC deposition process, rather than possessing any long range crystalline order. Ideally we would have liked to verify this with GIWAXS data, but this was not possible at the time. Nevertheless, the mobilities obtained for F8T2 patterned using the MIMIC process were one order of magnitude higher than spin coated and drop cast techniques that used similar top gate staggered geometries and much lower dielectric thicknesses in the literature [52].

Table 6.6: V&M modelling fit parameters for MIMIC patterned top gate F8T2-DCB and F8T2-HEX-DCB with 700 nm CYTOP dielectric. The modelled $\mu_{sat}$ is compared to the $\mu_{sat}$ obtained experimentally to give a fit variation.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$V_{lo}$</th>
<th>$\rho$</th>
<th>$m$</th>
<th>$\mu_{sat}$</th>
<th>$T_0$</th>
<th>$\mu_{sat}$ fit variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>-8.7</td>
<td>$1.4 \times 10^{19}$</td>
<td>1.06</td>
<td>$1.5 \times 10^{-3}$</td>
<td>617</td>
<td>49</td>
</tr>
<tr>
<td>DCB-HEX</td>
<td>-12.3</td>
<td>$1.3 \times 10^{19}$</td>
<td>2.02</td>
<td>$2.2 \times 10^{-3}$</td>
<td>906</td>
<td>72</td>
</tr>
</tbody>
</table>

6.12 Conclusions

This chapter investigated the patterning and transistor application in staggered geometries of F8T2, TIPS-Pentacene and P3HT semiconductors using two soft lithography techniques: micro molding in capillaries (MIMIC) and solvent assistant micro molding in capillaries (SAMIM). Two different stamp materials, PDMS and PFPE were applied using varying channel geometries.

Despite using very tall channel heights, patterned semiconductor features were generally in the nanometre regime due to low filling fractions inside the channel. An optimal stamp channel height of 2 $\mu$m was chosen as it gave consistent patterned features with the MIMIC process. However, the SAMIM process in general had very large variations in patterned thicknesses that were in continuous contact with each other due to unintentional patterning of a thin semiconductor layer outside the channel boundaries. This resulted in poorer quality devices with high leakage currents than compared to the MIMIC process. High leakage currents observed in MIMIC and SAMIM patterned TIPS-Pentacene OFETs generally gave lower saturation mobilities than compared to the literature.
Table 6.7: Selected performances of MIMIC and SAMIM 1 wt% mono and binary solution F8T2 OFETs with staggered TGBC architectures. $L = 50\mu m$, $W = 2000\mu m$ ($W/L = 40$).

| Solvent  | Dielectric | Method  | $|I_D/I_G|_{\text{sat}}$ | $\mu_{\text{sat}}$ (cm$^2$/Vs) | $V_{\text{th}}$ (V) | On/Off  |
|----------|------------|---------|---------------------|-------------------------------|------------------|---------|
| DCB      | CYTOP      | MIMIC   | 1.1$\times$10$^4$   | 1.3$\times$10$^{-3}$          | -16.7            | 1.2$\times$10$^4$ |
| HEX-DCB  | CYTOP      | MIMIC   | 2.3$\times$10$^2$   | 1.8$\times$10$^{-3}$          | -23.7            | 9.6$\times$10$^4$ |
| DCB      | CYTOP      | SAMIM   | 2.0$\times$10$^2$   | 1.2$\times$10$^{-3}$          | -20.1            | 4.2$\times$10$^4$ |
| HEX-DCB  | PVP        | SAMIM   | 1.4$\times$10$^2$   | 6.9$\times$10$^{-4}$          | -18.0            | 2.6$\times$10$^4$ |

OFETs with P3HT generally failed to function as they generally had very high threshold voltages and low on/off ratios since fabrication in an inert environment, annealing or SAM treatment was not attempted. Despite these negative results, the performance of MIMIC and SAMIM patterned F8T2 OFETs were far better, and in some cases comparable, if not, higher than reported values for spin coated F8T2 in staggered geometries. The highest mobility for F8T2 OFETs was with the MIMIC process, and this had a $\mu_{\text{sat}}$ of 1.3$\times$10$^{-3}$ cm$^2$/Vs, $V_{\text{th}}$ of -16.7 V, hysteresis of -4.8 V, $|I_D/I_G|$ of 1.1$\times$10$^3$ and a high on/off ratio of 1.2$\times$10$^4$.

Finally, azeotropic binary solutions of F8T2 in HEX-DCB binary solvent in staggered OFET geometries were also fabricated via MIMIC and SAMIM. It was observed that their performances were somewhat lower compared to mono solvent F8T2-DCB due to higher leakage currents in terms of $|I_D/I_G|$, although $\mu_{\text{sat}}$ and on/off was slightly higher on average when patterned using the MIMIC process. Table 6.7 summarises selected MIMIC and SAMIM OFET performances for F8T2-DCB and F8T2 HEX-DCB binary solvent for comparison purposes. Based on modelling analysis using the Tanese and Vissenberg-Matters models, we found that MIMIC patterned devices of F8T2 were highly disordered and possibly amorphous. Despite this drawback, mobilities obtained with the MIMIC patterning technique were a magnitude higher than spin coated or drop casted techniques reported in the literature.

References


Chapter 7

Conclusions and future work

This thesis has provided experimental groundwork where future researchers would be able to refer back to and ascertain which techniques work, and which could be further improved on, when fabricating organic transistors. We thereby conclude this thesis by providing an overview of the main conclusions arrived in this final chapter.

In essence, our research can be broken down into two core topics:

1. The effect of ageing induced solution aggregation on the optoelectronic properties of mono and binary solvent F8T2 thin films and transistors

2. Performance of fabricated OFET devices using confined crystallisation of F8T2, TIPS-Pentacene and P3HT via soft lithography techniques

Chapter 2 first introduced the key physics behind organic semiconductors and field effect transistors. Using the gradual channel approximation, we derived current-voltage characteristics that were applied on experimental OFET data to extract key parameters such as the mobility, threshold voltage, on/off ratio, subthreshold slope, hysteresis and leakage current. We also introduced the Campbell model for fitting the current-voltage characteristics of disordered amorphous semiconductors [1]. The model applied the Vissenberg and Matters framework using the unified theory developed by Tanase and coworkers for low and high carrier charge density regimes [2]. Key background into the H-J aggregation model by Spano and coworkers was also provided and an equation for the exciton bandwidth from the $I_{0-0}/I_{0-1}$ peak ratios from the PL spectra was derived [3][4].

Chapter 3 outlined the various methods and experimental processes used in this thesis such as transistor characterisation, photolithography, soft lithography and surface energy, to name a few. In particular, the relative permittivities of PVP
Chapter 7. Conclusions and future work

(\varepsilon_r = 6.3) and CYTOP\textsuperscript{TM} (\varepsilon_r = 3.7) dielectrics were deduced experimentally and incorporated in to staggered OFET devices throughout the thesis. However, values for \varepsilon_r were relatively overestimated as we did not implement longer cross-linking times compared to other researchers [5][6]. Nonetheless, in order to ensure reliability and reproducibility of analysing OFET devices, we used our values of \varepsilon_r throughout calculations in this thesis.

Chapter 4 identified a gap in the literature involving beta-phase formation in F8T2 using solution ageing techniques. Using the H-J aggregation model, we found that F8T2 thin films in toluene (TOL) and chlorobenzene (CB) predominantly adopted H-aggregate (interchain) ordering from UV-vis and PL analysis, and after ageing in solution for 7 days, there was a general increase in J-aggregate (intrachain) ordering (the characteristic beta-phase). Thin films from 1,2-dichlorobenzene (DCB) on the other hand, showed predominant J-aggregate ordering due to the higher boiling point. We also found that between the solution concentration range (0.125 – 2 wt\%) and solvent type (TOL, CB and DCB), the PLQE was proportional to the exciton bandwidth for fresh solutions. This trend was broken for aged TOL and CB, but remained for DCB, owing to its lower tendency to aggregate upon ageing.

In the high thickness regime involving spin coated F8T2-CB at 1500 rpm, we observed ageing yielded improved OFET performance in the BGBC architecture. The situation was reversed for the low thickness regime at 4000 rpm, although interestingly, the overall performance was much higher than in the high thickness regime. Using the Campbell model, the Vissenberg and Matters DOS distribution characteristic temperature \(T_0\) decreased after ageing 1500 rpm films of CB and DCB, but increased for 4000 rpm films, indicating increased disorder. Interestingly, the mobility of DCB OFETs improved after ageing, although an increase of \(T_0\) and threshold voltage was also observed. The trends observed with ageing and film thickness remained consisted in top gate geometries, but with improved performance due to reduced contact resistance. Aged F8T2-DCB in the TGBC architecture had a \(\mu_{sat}\) of \(2.2\times10^{-3}\) cm\(^2\)/Vs, which was the highest obtained in this work, and only a magnitude lower than the highest mobility recorded for F8T2 with polyimide alignment [7].

The effects of annealing were also investigated on F8T2-CB devices. Similar to what was initially observed by Wang and coworkers [8], the threshold voltage increased considerably with annealing, and also in some cases, with solution aggregation induced ageing. GIWAXS analysis indicated that annealed F8T2-CB thin films exhibited part-crystalline order. This indicating that certain regimes of the beta-phase, mainly the J-aggregate part, was perhaps detrimental to device performance. However more research needs to be conducted in this area since the
Chapter 7. Conclusions and future work

films still exhibited amorphous regions from the GIWAXS data. We found that for both low and high film thickness regimes, OFET mobilities were reduced by an order of magnitude in both BGBC and TGBC architectures, corresponding to an increase in the exciton bandwidth and $T_0$ disorder. A slight improvement in the mobility was observed with annealing aged films, although this corresponded with an increased threshold voltage, $T_0$ disorder, and reduced on/off ratio.

Due to time and resource limits there were a number of experiments that could have been performed in order to obtain a better picture of the ageing induced aggregation effect in F8T2 solutions. Although it was already indirectly implied that those devices which improved OFET performance upon ageing had to have had a reduced contact resistance upon examining the output characteristics, future work could perhaps experimentally deduce the exact values of contact resistance with ageing. Since we mainly worked with two extremes of film thicknesses spin coated at 1500 and 4000 rpm, we would also explore the effect of solution ageing at an expanded number of film thicknesses at different spin speeds in obtain a clearer picture of ageing films in the high and low thickness regimes.

Chapter 5 investigated the beta-phase in thin films of F8T2 prepared from azeotropic binary solutions. Binary solutions in hexane (HEX) and tetralin (TET) in chlorobenzene (CB) were chosen as they were identified as regions of extreme H and J aggregation from the UV-vis and PL spectra. Despite lower exciton bandwidths compared to mono solvent F8T2-CB, the PLQE obtained was much higher, with a maximum of 24% for aged HEX-CB films. GIWAXS data did not show any long range crystalline order, indicating films of both HEX-CB and TET-CB were mostly amorphous. This was surprising because TET-CB films in particular showed predominant J-aggregate ordering from the UV-vis and PL spectra, and optical birefringence when viewed under polarised microscopy. Hence we assumed that this attributed to orientational ordering resulting from deposited aggregates, rather than long range structural ordering extending throughout the TET-CB lattice.

In OFET devices, improved performance was observed for HEX-CB compared to mono solvent F8T2-CB in the BGBC architecture. In the top gate architecture, performance of binary OFETs was somewhat lower than mono solvent F8T2-CB, although ageing improved the mobility of HEX-CB to the region of $\sim 10^{-3}$ cm$^2$/Vs. The $T_0$ disorder was generally observed to increase with ageing for both 1500 and 4000 rpm films, corresponding to a decrease in mobility and increase in threshold voltage. TET-CB devices on the other hand performed poorly with a low mobility and a high threshold voltage and hysteresis observed in all cases.

Since thin films were mostly randomly aligned and disordered with spin coating, for future work, we could investigate the characteristics of aged F8T2 binary solvent
films aligned with a polyimide layer (or similar) [7]. We would also investigate the effect of annealing in the nematic liquid crystalline phase, in order to examine the interesting optical and charge transport characteristics of the binary solvent systems.

**Chapter 6** moved on from the aggregation work and instead focused on the second topic of our research: soft lithography patterning of the organic semiconductor layer by confined crystallisation. We singled out the MIMIC and SAMIM process flows for further investigation into depositing the semiconducting layer on OFET devices. First, we focused on the master template development on silicon with SU-8 resist. Process flows for FLUOROLINK® MD 700 PFPE and PDMS stamp fabrication were established and the solvent 1,2-dichlorobenzene was chosen to dissolve organic semiconductors due to its high boiling and low swelling tendency. We then investigated the patterning and confined crystallisation of F8T2, TIPS-Pentacene and P3HT semiconductors using the MIMIC and SAMIM process flows with varying stamp types and geometries. MIMIC and SAMIM patterned features were generally observed to exhibit orientational crystallinity based on optical polarised microscopy observation.

We eventually settled on 2 µm tall, 100 µm wide PFPE stamps for MIMIC and similarly for SAMIM, PDMS stamps were used to utilise its tendency to swell and absorb organic solutions. Despite using 2 µm tall stamp channels, crystallised thicknesses were several hundred nanometres thick due to the low filling fractions inside the stamp channels. Hence, we were able to successfully incorporate these patterned semiconductors into OFET devices. SiO$_2$ (230 nm), PVP (700 nm) and CYTOP (700 nm) dielectrics were constructed in the staggered BGTC and TGBGC geometries for each semiconductor. Due to the rough and jagged morphology developed by crystallising TIPS-Pentacene, low device yields and performances were obtained. Although patterning of P3HT was generally acceptable using MIMIC and SAMIM, working devices were unfortunately poor and yielded high threshold voltages and extremely low (<10) on/off ratios due to its tendency to dope in ambient during the fabrication process. Hence in general, we observed that F8T2 devices with CYTOP (and/or PVP) dielectrics gave the lowest leakage currents and excellent OFET performance. Mobilities and on/off ratios reaching as high as $\sim 10^{-3}$ cm$^2$/Vs and $\sim 10^4$ were achieved with both MIMIC and SAMIM processes for F8T2 to date. Furthermore, despite using a very high dielectric thickness (700 nm), threshold voltage operation for mono solvent F8T2-DCB was on average $>-20$ V for both PVP and CYTOP.

Azeotropic binary solutions with F8T2 in HEX-DCB were also patterned with MIMIC and SAMIM to similar degrees of success with the CYTOP dielectric, for the first time based on our knowledge. We obtained similar mobilities and on/off
ratios to that of mono solvent F8T2-DCB with the MIMIC process, although leakage currents were about a magnitude higher. In contrast, for the SAMIM process, all the CYTOP devices failed to function reliably due to high leakage currents ($I_D/I_G < 10$). HEX-DCB OFETs with the PVP dielectric however, gave lower leakage, but also lower mobilities in the region of $\sim 10^{-4}$ cm$^2$/Vs. Furthermore, threshold voltage operation for binary solvent HEX-DCB was on average $>-23$ V for both MIMIC and SAMIM processes, although slightly higher than mono solvent F8T2-DCB.

As we observed the filling fractions obtained with MIMIC and SAMIM was generally quite low compared to the 2 $\mu$m tall stamp channel heights, future work could perhaps carry a more thorough study on improving it. It was also observed that the solution reached supersaturation when most of the solvent had evaporated leading to incomplete crystallisation, hence the first step would be to address this particular problem. Simply increasing the solution concentration would not suffice as this could increase the risk of delamination and damage of the patterned features during stamp removal. Hence, we could potentially investigate further on optimising the stamp channel height and width aspect ratio, and explore whether solutions with polymer or even binary blends has any effect on improving the filling fraction, crystal quality and growth. As a large dielectric thickness of 700 nm in top gate geometries was used as proof of concept in this work, threshold voltages were generally quite high compared to the literature. If high performance, low voltage transistors are to be fabricated with the MIMIC and SAMIM patterning techniques, it would hence be essential to use a dielectric which not only has a low thickness, but also does not rupture during the layer-by-layer deposition process [9][10][11].

References


[6] Walser, M. P., Kalb, W. L., Mathis, T., and Batlogg, B. Low-voltage organic transistors and


Appendix A

Supplementary material for ageing induced solution aggregation

A.1 Top gate OFETs with PVP dielectric for aged annealed F8T2-CB thin films

The effect of ageing and annealing in F8T2-CB-1WT% films was also investigated using a top gate, bottom contact (TGBC) architecture for 4000 rpm thin films. PVP dissolved in 8 wt% IPA and spin coated to a thickness of 700 nm was used as the dielectric. Table A.1 displays the yield of the devices measured. A total of 21 TGBC devices were fabricated. Unfortunately a poor yield was obtained for aged non-annealed devices due to high gate leakage currents and shorting. In comparison, annealed devices generally gave a high yield of working top gate devices.

Table A.1: Device success rate for aged annealed TGBC F8T2-CB-1WT% films spin coated at 4000 rpm with a 700 nm PVP dielectric. Device success rate considers OFETs that did not short upon operation and have $|I_D/I_G| > 1$. In the table, no annealing = NA and annealing = A.

<table>
<thead>
<tr>
<th>Ageing</th>
<th>Annealing</th>
<th>Total measured</th>
<th>Device success rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>NA</td>
<td>6</td>
<td>67</td>
</tr>
<tr>
<td>Aged</td>
<td>NA</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Fresh</td>
<td>A</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Aged</td>
<td>A</td>
<td>4</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure A.1 summarises the mean OFET performance metric of these TGBC devices. The TGBC devices generally had mobilities an order of a magnitude higher than BGBC devices despite the thicker dielectric thickness and lower drain current. Higher on/off and low hysteresis was also observed in fresh non-annealed films, and
aged annealed films. However, the mobilities of the aged annealed films were still a magnitude lower than the fresh non-annealed films as observed before for BGBC devices. The best performing device was with a fresh non-annealed OFET which had a $\mu_{sat}$ of $1.4 \times 10^{-3}$ cm²/Vs, $V_{th}$ of -7 V and an on/off ratio of $2 \times 10^5$.

![Image of graphs showing comparison of saturation mobility ($\mu_{sat}$), threshold voltage ($V_{th}$), on/off ratio, sub threshold slope (SS), hysteresis and max drain current ($I_D(max)$) from the transfer characteristics of non-annealed (NA) and annealed (A) fresh and 7 day aged TGBC F8T2-CB-1WT% OFETs with a 700 nm PVP-IPA-1WT% dielectric. F8T2 thin films were spin coated at 4000 rpm, 30s. Error bars were calculated at the 80% confidence interval from the standard error of 3–4 separate measurements. The channel lengths and widths used were 50 µm and 2000 µm ($W/L = 40$) respectively.

**Figure A.1:** Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage ($V_{th}$), on/off ratio, sub threshold slope (SS), hysteresis and max drain current ($I_D(max)$) from the transfer characteristics of non-annealed (NA) and annealed (A) fresh and 7 day aged TGBC F8T2-CB-1WT% OFETs with a 700 nm PVP-IPA-1WT% dielectric. F8T2 thin films were spin coated at 4000 rpm, 30s. Error bars were calculated at the 80% confidence interval from the standard error of 3–4 separate measurements. The channel lengths and widths used were 50 µm and 2000 µm ($W/L = 40$) respectively.
A.2 Analysis for aged binary F8T2-HEX-DCB devices

Binary OFETs with DCB solvent were also fabricated for comparison purposes with CB devices. DCB binary films showed a more enhanced beta-phase compared to CB binary films from the UV-vis and PL spectra. Ageing DCB binary films reduced PLQEs and exciton bandwidths by approximately half compared to CB binary films. In OFET devices, there was little variation in performance between fresh and aged HEX-DCB films, but it was observed that bottom gate mobilities were at least 2 – 3 times higher than CB binary OFETs. However, this came with the price of increased threshold voltages < -20 V.

Figure A.2: Normalised UV-vis (a) and PL spectra (b) of fresh and 7 day aged DCB and HEX-DCB (1:1) thin films spin coated at 4000 rpm.

Figure A.3: Normalised UV-vis (a) and PL spectra (b) of fresh and 7 day aged DCB and TET-DCB (1:1) thin films spin coated at 4000 rpm.

Mean results for the $\mu_{sat}$, $V_{th}$ and on/off for HEX-DCB and TET-DCB are
Appendix A. Supplementary material for ageing induced solution aggregation
displayed in Table A.2. Results for HEX-CB and TET-CB previously determined are repeated in the table for comparison purposes. A general increase in the $V_{th}$ was observed with ageing and solvent boiling point which corresponded to the beta-phase ordering for the DCB films. These follow similar trends to what was observed earlier in Table 4.3 in Chapter 4 for mono-solvent TOL, CB and DCB systems.

Table A.2: Comparison of mean saturation mobility $\mu_{sat}$, threshold voltage $V_{th}$ and on/off ratio fresh and 7 day aged BGBC OFETs with a 230 nm SiO$_2$ dielectric and 1 wt% F8T2 in CB, DCB, HEX and TET binary solvent thin films spin coated at 4000 rpm. The mean was taken over 3 – 4 OFET devices with constant $L = 10\mu m$ and $W = 10,000\mu m$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ageing</th>
<th>$\mu_{sat}$ (cm$^2$/Vs)</th>
<th>$V_{th}$ (V)</th>
<th>On/Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>I</td>
<td>$8.3 \times 10^{-5}$</td>
<td>-11.1</td>
<td>$6.0 \times 10^{4}$</td>
</tr>
<tr>
<td>CB</td>
<td>II</td>
<td>$2.1 \times 10^{-5}$</td>
<td>-12.3</td>
<td>$4.2 \times 10^{3}$</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>I</td>
<td>$2.5 \times 10^{-4}$</td>
<td>-8.7</td>
<td>$2.3 \times 10^{4}$</td>
</tr>
<tr>
<td>HEX-CB</td>
<td>II</td>
<td>$1.7 \times 10^{-4}$</td>
<td>-15.2</td>
<td>$1.1 \times 10^{5}$</td>
</tr>
<tr>
<td>TET-CB</td>
<td>I</td>
<td>$2.0 \times 10^{-4}$</td>
<td>-30.1</td>
<td>$1.1 \times 10^{5}$</td>
</tr>
<tr>
<td>TET-CB</td>
<td>II</td>
<td>$5.9 \times 10^{-5}$</td>
<td>-31.6</td>
<td>$4.1 \times 10^{4}$</td>
</tr>
<tr>
<td>DCB</td>
<td>I</td>
<td>$1.4 \times 10^{-4}$</td>
<td>-19.8</td>
<td>$6.9 \times 10^{4}$</td>
</tr>
<tr>
<td>DCB</td>
<td>II</td>
<td>$3.8 \times 10^{-4}$</td>
<td>-24.7</td>
<td>$3.6 \times 10^{5}$</td>
</tr>
<tr>
<td>HEX-DCB</td>
<td>I</td>
<td>$4.6 \times 10^{-4}$</td>
<td>-25.5</td>
<td>$2.2 \times 10^{5}$</td>
</tr>
<tr>
<td>HEX-DCB</td>
<td>II</td>
<td>$4.7 \times 10^{-4}$</td>
<td>-25.8</td>
<td>$8.9 \times 10^{5}$</td>
</tr>
<tr>
<td>TET-DCB</td>
<td>I</td>
<td>$2.6 \times 10^{-7}$</td>
<td>-29.4</td>
<td>$1.2 \times 10^{2}$</td>
</tr>
<tr>
<td>TET-DCB</td>
<td>II</td>
<td>$2.9 \times 10^{-6}$</td>
<td>-37.7</td>
<td>$6.0 \times 10^{3}$</td>
</tr>
</tbody>
</table>
Figure A.4: Comparison of the mean saturation mobility ($\mu_{sat}$), threshold voltage $V_{th}$, on/off ratio, sub threshold slope ($SS$), hysteresis and max drain current $I_D(max)$ from the transfer characteristics of fresh and 7 day aged BGBC OFETs with 1 wt% F8T2 in DCB, HEX-DCB (1:1) and TET-DCB (1:1) thin films spin coated at 4000 rpm. Error bars were calculated at the 80% confidence interval from the standard error of 3–4 separate measurements. The channel lengths ($L$) and widths ($W$) were 10 $\mu$m and 10,000 $\mu$m ($W/L = 1000$) respectively.
Appendix B

Supplementary material for confined crystallisation

B.1 Patterning the active layer in the nanometre regime with soft lithography

Attempts were made to fabricate master templates in the nanometre regime however they were largely unsuccessful. Since we did not possess an SU-8 resist capable of going below <1 $\mu$m at the time, we used S1813 G2 positive resist in order to photolithography pattern aluminium (Al) features on to silicon substrates. The method used to achieve $\sim$2 $\mu$m thick S1813 G2 positive resist features was as follows:

- Treatment of Si/SiO$_2$ substrates with HMDS
- Spin coating of S1813 G2 at 2000 rpm for 45 seconds (acceleration: 1000 rpm/s)
- Soft bake at 115$^\circ$C for 1 min
- 15 second exposure time at 10 mW UV radiation (150 mJ/cm$^2$ dosage)
- Post exposure annealing at 115$^\circ$C for 1 min
- Development in MF-26A developer for 20-30 seconds with no stirring
- Rinsing in DI water and drying with a stream of N$_2$
- Plasma ashing at 40 W for 1 min to descum residual resist
- Hard bake anneal at 150$^\circ$C for 5 min
We then thermally evaporated 100 nm thick Al features through a shadow mask using a thermal evaporator onto the S1813 G2 master where it neatly filled the regions that were devoid of any resist. The substrate was then developed in acetone solvent by ultrasonication for 5 – 10 mins. After this the substrate was dehydrated at 120°C for 5 mins on a hotplate. The quality of the Al features were very good in the final result as can be seen in Figure B.1(a). However, when attempts were made to cure and remove stamps, the Al features delaminated or were removed from the silicon base as can be seen in Figure B.1(b). Even though imprinting of the Al features onto the stamp was successful, we observed complete roof collapse of both 2 µm and 8 µm relief structures in the stamp when brought into conformal contact with a smooth silicon surface, as can be seen in Figures B.1(c) and (d).

Figure B.1: Optical micrographs of (a) 100 nm thick photolithography patterned aluminium (Al) features on a silicon substrate, (b) delamination of Al features during stamp removal, and complete roof collapse of PDMS stamp with (c) 2 µm and (d) 8 µm thick relief structures.
Appendix C

Sample code for Gauss-Newton minimisation

Using the equations defined in Chapter 2.2.6, we present the following sample code which demonstrates implementation of the Gauss-Newton algorithm in Python 3.7. This algorithm was used to perform non-linear least squares minimisation to find optimal parameters that fit the $I/V$ transfer characteristics of OFETs in certain chapters of this thesis. To provide a reproducible example, we show how the parameters in Table 4.7 in Chapter 4.5.5 for annealed CB-4000 films from fresh F8T2 solutions were determined here.

```python
# -*- coding: utf-8 -*-
# Author: Abhimanyu Mukherjee

import numpy as np
from scipy import stats

class ChargeCarrierDisorderModels:
    
    # Formulations of the Campbell et. al. models using the Tanase, Vissenberg and Matter's theoretical framework for the charge carrier density dependent mobility in amorphous disordered organic semiconductors.

    @staticmethod
    def linear_regime_model(beta):
        
        Estimates the drain current (ID) in the linear regime.

        Parameters
        ----------
        beta: array-like
            Array of integers or floats consisting of initial guesses for parameters in the models

        Returns
        -------
        i_lin: array-like
            Returns an array consisting of floats for the fitted drain current
```
Appendix C. Sample code for Gauss-Newton minimisation

```python
in the linear regime

```aa = ((w * mu_lin * cap) / l)
bb = ((cap / (chargeConst * delta_x * beta[0] * density_exponent)) ** beta[1])
cc = ((np.abs((VG - beta[2])) ** (beta[1] + 1)) * v_ds)
i_lin = (aa * bb * cc)
return i_lin

```@staticmethod
def saturation_regime_model(beta):
    
    Estimates the drain current (ID) in the saturation regime.

    Parameters
    ----------
    beta: array-like
        Initial guesses for parameters in the models

    Returns
    -------
    sqrt_i_sat: array-like
        Returns an array consisting of floats for the fitted drain current
        in the saturation regime

    ```aa = ((w * beta[0] * mobility_exponent * cap) / ((m + 2) * l))
bb = ((cap / (chargeConst * delta_x * rho * density_exponent)) ** m)
cc = (np.abs((VG - v)) ** (m + 2))
sqrt_i_sat = np.sqrt(np.abs(aa * bb * cc))
return sqrt_i_sat

```def gauss_newton(f, exp, beta, eps, res):
    
    The Gauss-Newton algorithm is a Non-linear least squares algorithm which
iteratively finds the value of the parameters of a function (beta) that
minimises the sum of squared residuals. This is done by first linearising
a non-linear function by applying the finite difference method to form a
Jacobian matrix consisting of partial derivatives. The pseudoinverse of the
Jacobian is then multiplied with the residuals using the dot product and added
to the value of beta, which is then updated iteratively until a local optimum
is reached. The number of iterations is user-defined, and convergence can occur
in a few iterations or more. In cases where the Jacobian does not have an
inverse (i.e. determinant is 0), convergence will fail, and the user is
advised to readjust the initial guesses for the parameters used in the function.

    Parameters
    ----------
    f: callable function
        Charge carrier disorder models without the input parameters
    exp: array-like
        Array of floats consisting of experimental drain current data
    beta: array-like
        Array of integers or floats consisting of initial guesses for
        parameters in the models
    eps: float
        Epsilon is a scalar parameter to adjust the precision of the finite
difference method when evaluating the Jacobian.
    res: array-like
        Returns an array of floats for the residuals

```
Returns

----------
beta, ss_arr: Tuple of array-like objects consisting of floats
Returns an array of floats consisting of the parameters, beta, and the sum of squared residuals, ss_arr.

ss = sum_of_squares_residuals(res(f, exp, beta))
ss_arr = [ss]
for i in range(iterations):
  J = np.zeros((len(f(beta)), len(beta)))
  for row in range(0, len(beta)):
    dd = np.zeros(beta.shape)
    dd[row] = eps
    J[:, row] = (f(beta + dd) - f(beta)) / eps
    dBeta = np.linalg.pinv(J).dot(res(f, exp, beta))
    beta = beta + dBeta
  ss = sum_of_squares_residuals(res(f, exp, beta))
  ss_arr.append(ss)
return beta, ss_arr

def residuals(model, exp, beta):
  """
  Returns residuals of experimental drain current data minus the model data.
  Parameters
  ----------
  model: function
    These are the linear or saturation models without the parameters
  exp: array-like
    Array of floats consisting of experimental drain current data
  beta: array-like
    Array of integers or floats consisting of initial guesses
  Returns
  -------
  res: array-like
    Returns an array of floats for the residuals
  """
  return exp - model(beta)

def sum_of_squares_mean(data):
  """
  Returns the sum of squares with respect to the mean.
  Parameters
  ----------
  data: array-like
    Requires an array consisting of relevant data
  Returns
  -------
  ss: float
    Returns a float (or numpy float)
  """
Appendix C. Sample code for Gauss-Newton minimisation

```python
mu = np.mean(data)
ss = np.sum((data-mu)**2)
return ss

def sum_of_squares_residuals(res):
    """
    Returns sum of squares error of the residuals wrt drain current data and model data.
    """
    Parameters
    ----------
    res : array-like
        Requires residuals calculated from residuals(...)
    Returns
    -------
    ssr : float
        Returns a float (or numpy float)
    """
    ssr = np.sum(res**2)
    return ssr

""" Testing with sample data"""
VG = np.array([-1.00E-07,  -3.3333,    -6.6667,  -10,    -13.3333,  -16.6667,    -20,   -23.3333,  
                -26.667,    -30,     -33.333,    -36.667,    -40,    -43.333,    -46.6671,    -50,    
                -53.333,    -56.667,    -60])
ID1 = np.array([-4.39E -10,  -2.86E-10,  -2.81E-10,  -2.48E-10,  -3.72E-10,  -3.81E-10, 
                -3.94E-09,  -1.02E-08,  -1.87E-08,  -2.93E-08,  -4.09E-08,  -5.27E-08, 
                -6.51E-08,  -7.75E-08,  -8.94E-08,  -1.01E-07,  -1.12E-07,  -1.21E-07, 
                -1.33E-07])
ID2 = np.array([-5.76E-10,  -3.67E-10,  -4.86E-10,  -3.02E-10,  -2.85E-10,  -6.91E-10, 
                -6.44E-09,  -1.82E-08,  -3.78E-08,  -6.70E-08,  -1.06E-07,  -1.58E-07, 
                -2.19E-07,  -2.89E-07,  -3.69E-07,  -4.51E-07,  -5.52E-07,  -6.54E-07, 
                -7.60E-07])

ID2 = np.sqrt(np.abs(ID2))
# Number of iterations allowed
iterations = 5
# Initial guesses for the charge carrier density (cm^-3), constant m to calculate # width of the exponential DOS (T0) and turn on voltage (V)
lin_guess = np.array([1, 0.5, 0])
# Initial guesses for the charge carrier mobility (mu_sat) in the saturation regime # at VD = -60 V
sat_guess = np.array([1])
# Linear regime mobility from experimental transfer curves at VD = -10 V (cm^2/Vs)
mu_lin = 2.0e-05
# Depth of the accumulation layer near the semiconductor/dielectric interface (cm)
delta_x = 1.0e-7
```
Appendix C. Sample code for Gauss-Newton minimisation

```python
# Charge constant (C)
chargeConst = 1.6E-19

# Channel length (cm)
l = 0.001

# Channel width (cm)
w = 1

# Capacitance (F/cm^2)
cap = 1.5e-08

# Linear drain voltage (V)
v_ds = -10

# Exponent parameter for density (must be separated otherwise gauss-newton does not converge). For F8T2, exponent of 1e19 seems to work well. May be different for other organic semiconductors
density_exponent = 1e19

# Exponent parameter for mobility (must be separated otherwise gauss-newton does not converge). If algorithm still does not converge, check the exponent of the experimental mu_sat to get a rough ball park
mobility_exponent = 1e-5

# Instantiate models class and apply gauss-newton minimisation
models = ChargeCarrierDisorderModels()

lin_model_output = gauss_newton(models.linear_regime_model, ID1, lin_guess, 0.01, residuals)
lin_params = lin_model_output[0]

sat_model_output = gauss_newton(models.saturation_regime_model, ID2, sat_guess, 0.01, residuals)
sat_params = sat_model_output[0]

mu_sat = sat_params[0]

print(r""
##### OUTPUT FITTED PARAMETERS #####
Total iterations: {}
RHO: {:.1e} cm^-3
M: {:.1f}
T0: {:.0f} K
V: {:.1f} V
MU_SAT: {:.1e} cm^-2/Vs
RESIDUAL SUM OF SQUARES (Linear) = {:.1e}"")
```

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RESIDUAL SUM OF SQUARES (Saturation) = (1.1e)

############################

## OUTPUT FITTED PARAMETERS ##

Total iterations: 5
RHO: 5.6e+19 cm^-3
M: 0.7
TO: 510 K
V: -8.5 V
MU_SAT: 5.9e-05 cm^2/Vs
RESIDUAL SUM OF SQUARES (Linear) = 3.7e-16
RESIDUAL SUM OF SQUARES (Saturation) = 1.0e-08

############################
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