Solution Processing of Small Molecule Organic Semiconductors: From 

*In situ* Investigation to the Scalable Manufacturing of Field Effect Transistors

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ABSTRACT

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Solution-processed organic field effect transistors (OFETs) are strong contenders to become a part of electronic circuitry because of being compatible with cost-effective high throughput roll-to-roll technology. Single crystal based OFETs can fulfill the stringent performance demands in terms of carrier mobility, switching speed, etc. and uniformity over large areas, but these suffer from major scale-up challenges. To achieve device performance approaching that of single crystals with scalable and industry-compatible manufacturing of small molecule organic semiconductors (OSCs) based FETs, requires understanding and ultimately controlling the solution-to-solid phase transformation phenomenon to produce high-quality thin films.

In this thesis, we develop an understanding of the process-structure-property-performance relationship in OSCs that bring fresh insights into the nature of solution crystallization and lead to novel ways to control OSC crystallization, and finally help achieve fabrication of high-performance OFETs by scalable, high throughput and industry-compatible blade coating method. We probe the solution crystallization of OSCs by employing a suite of ex & in situ characterization techniques. This leads us to an important finding that OSC molecules aggregate to form a dense amorphous intermediate state and nucleation happens from this intermediate state during blade coating under a wide window of coating
conditions. This phenomenon resembles the so-called two-step nucleation model. Two-step nucleation mediates the crystallization of a wide range of natural and synthetic products ranging from soft materials, such as proteins, biominerals, colloids and pharmaceutical molecules, to inorganic compounds. We go on to show that this nucleation mechanism is generally applicable to achieve formation of high-quality polycrystalline films in a variety of small molecule OSCs and their polymer blends. This phenomenon results in highly textured and well-connected domains, which exhibit reduced interfacial and bulk trap-state densities, helping raise the carrier mobility by one to two orders of magnitude in OFETs in comparison to direct nucleation. We extend the understanding developed for solution crystallization of various acenes and thiophene-based small molecule OSCs to the high-performance benzothieno-benzothiophene (BTBT) based small molecule OSCs. On this end, we develop protocols to fabricate high-quality thin films of BTBT based OSCs by blade coating at industrially compatible coating speeds (>100 mms⁻¹). These films show massive single-domains with very few apparent defects when crystallized via multiple liquid-crystalline phases in two-step nucleation conditions, resulting in an average carrier mobility of ~10 cm²V⁻¹s⁻¹.

To sum up, this thesis develops an understanding of OSC solution crystallization and efficient protocols to control polycrystalline thin film quality for high-performance OFETs. These protocols involve a combination of two-step nucleation pathway, solvent mixtures, polymer blends and device-manufacturing conditions. Our efforts enable to realize high-performance OFETs based on high-quality polycrystalline OSC thin films at industry-compatible conditions.
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Chapter 1

Introduction

Electronic devices have surrounded our lives and it is hard to live without the modern electronic technology ranging from computers, mobile phones, television/display screens, tracking devices, light-emitting devices, sensors, smart tags and etc. The basic component of electronic devices is a transistor working as a switch or amplifier utilizing the semiconductors to control the flow of current. The inorganic semiconductors such as silicon and III-V compounds are playing the major role in the evolution of electronic technology. The manufacturing of electronic devices based on these materials involve complex process, high temperatures (> 1000°C), high manufacturing costs and rigid substrates. The massive involvement of electronic devices in our daily lives is leading to non-eco-friendly production of waste electronic equipment and also loss of scarce III-V (gallium and indium) materials. United Nations commission has also defined to meet the current technological requirements without endangering the ability of our next generations to fulfill their necessities to achieve the goal of sustainable future. A paradigm shift is required to meet the sustainable future challenges and fortunately carbon based materials offer energy and cost-effective pathway to meet the challenges. These soft materials offer several advantages over their inorganic counterparts such as flexibility, lightweight and cost effective room-temperature processability. These materials offer development of countless classes of electronic devices with unimaginable functionalities compared to inorganic materials. These also meets the modern consumer demands of foldable, wearable and disposable electronic devices.
Carbon based electronics (organic electronics) came into the limelight in the 80s when a semiconducting-polymer was used as active material in a transistor and KODAK also announced first successful demonstration of organic light emitting diode (OLED).

The hardcore electronic circuitry (processors) still involves the high performance inorganic materials. In very near future, it is not possible to replace inorganic semiconductors with organic-semiconductors in integrated circuits or computer processors. But the unique applications offered by the organic based electronics ranging from E-papers, flexible displays, chemical and biosensors, flexible smart cards etc. have brought the thousands of chemists, physicists and engineers to work together in past three decades. These combined efforts have resulted in tremendous improvement in performance, stability and mass production of organic-electronics. Samsung is using OLEDs in mobile phones and now other companies also adopting. The E-paper and flexible OLED displays have been successfully demonstrated by companies like Plastic-logic and LG. In June 2017, LG displayed a 77-inch foldable OLED TV. The market of flexible displays and wearable electronics is predicted to have 25 billion USD market share by 2021. Currently, OLED display technology involves only vacuum deposition of organic materials through shadow masks. It results up to 90% wastage of OLED active materials and limited to certain size of displays, thus making this vacuum process highly cost inefficient. Typically, the backplane of these displays is based on polycrystalline silicon or metal-oxides transistors meet the criteria for OLED display performance pre-requisites as shown in Figure 1.1. But the polycrystalline silicon and metal-oxides require high processing temperatures in the range of 300-600°C. This makes it impossible to make back-panel flexible even if the front OLED panel is flexible. These technologies definitely meet the performance criteria but
are non-compatible with cost effective low temperature manufacturing on flexible and foldable plastic-panels. Organic field effect transistors (OFETs) technology offer the best choice (as a backplane) for flexible display technology due to material compatibility, room temperature processability and better mechanical properties for flexible and foldable OLED displays. The OLED displays are current driven and require continuous supply thus requiring stable and uniform OFET performance. In 2017, Flexenable co. have announced their cost-effective OFET technology for flexible OLED displays and sensors. It is a great motivation to contribute in these efforts for commercialization of fully flexible OFET driven OLED displays.

The soft organic semiconducting materials used as active layers in OFET devices have been classified into small-molecules and polymeric semiconductors. Amongst these organic semiconductors (OSCs), the small-molecules which crystallize have gained excellent attention in OFET community. Small molecules are leading the performance front but challenges associated with their processing create reproducibility and uniformity issues. On the other hand polymeric semiconductors offer uniformity and reproducibility but lag in performance front. Though recent advances in the molecular design and understanding of charge transport in polymeric semiconductors have resulted in several conjugated polymers with field effect mobility in excess of 1 cm²/Vs. But still the small molecule OSC are top technological contenders. The first decade of 21st century has brought some small molecule organic semiconductors which are soluble in common organic solvents. It allows depositing the solid-state thin films of these materials from inks, making deposition process potentially cost-effective in comparison to vacuum-based methods involving significant costly equipment. The solution based manufacturing is a
complex phenomenon and requires understanding and control to achieve desired functional properties in solid-state films. It involves spreading of ink on the substrate and drying by evaporation of solvent. The ink drying leads to solid state film formation. The solid-state thin film’s microstructure in most of the crystallizable small molecules develop during solution-to-solid phase transformation. The film formation often happens very quickly, phase transformation is strongly dependent upon drying kinetics, which can hinder the preferable microstructure required for better functional properties in thin films. This phase transformation process is significantly different from the solvent-free vacuum deposition of OSCs which involves the sublimation of OSCs under high vacuum conditions on a limited sized substrates. Multiple solution processing methods have been employed to manufacture OSC thin films involving laboratory scale drop-casting, spin-coating and large area compatible meniscus guided techniques. The meniscus guided techniques are technologically relevant and the thin-film formation or crystallization via meniscus guided techniques is very different from other coating processes such as the drop or spin coating. Solvent evaporation leads to the convective assembly of the OSC molecules. The evaporation leads to the supersaturated solution (meniscus), leading to crystallization near the contact line of the moving meniscus. As the drying mechanism (drying kinetics) are different than the spin-coating and drop-casting, thus all the optimization approaches used by our peers involving lab-based methods, cannot be directly employed to these meniscus guided techniques. The crystallization/film formation is strongly dependent upon drying kinetics, thus the functional properties of organic semiconductors vary under different processing methods. To control the OSC thin film quality, it requires an understanding of crystallization mechanism during solution printing of OSCs during lab-based and
commercial-scale techniques. Recent reports have showed that crystallization begins from liquid-air interface during solution shearing of OSCs. The control over OSC’s crystallization process plays the crucial role in realizing high quality thin films with two-dimensional in-plane \( \pi \)-stacking which will eventually help to realize OFETs in next-generation devices. But unfortunately, none of the efforts provide understanding about the liquid-to-solid phase transformation process in the large area compatible methods such as blade coating. Majority of these efforts involve limited range of coating speeds i.e., 1-10 mms\(^{-1}\). Industrial roll-to-roll manufacturing requires high coating speeds in excess of 100 mms\(^{-1}\). Very recently, couple of reports have been published reporting coating speeds of 25 mms\(^{-1}\). We also lack the knowledge to understand the nucleation and growth on pre-patterned substrates with electrodes (which are technologically very important) raising important questions about the OSC crystallization and film formation in potential real-life manufacturing conditions.

The solid-state thin films of the solution processed small molecule OSC materials are polycrystalline. The polycrystalline thin films of these small-molecules have multiple randomly oriented crystallites. The grain boundaries and defects originating due to multiple crystallites serve as the bottleneck to the key figure of merit “field effect mobility” of these materials. This figure of merit is a complex function of intrinsic properties of OSCs, device architectures, solid-state morphology, microstructure, pin-holes, grain and domain boundaries etc. As the charge transport (lateral) occurs at OSC: dielectric interface, thus the crystal structure (polymorphs), in-plane and out-of-plane orientations in few monolayers at this interface is crucial. The integration of OSC based transistors into applications have a range of other performance prerequisites, including high current on-off
ratio, low turn-on, and threshold voltages as well as low sub-threshold swing. These figures of merit are strongly coupled to the crystalline quality, energetic disorder, texture purity of lamellar stacks exhibiting two-dimensional in-plane $\pi$-stacking, and requires excellent continuity of the OSC thin film with closed domain and grain boundaries. The integration into applications also requires excellent performance yield, reproducibility, and uniformity over large areas, which puts significant stress on the solution-manufacturing process of OSCs.

Solution grown single crystals (SCs) of OSCs have resulted in the superior field effect mobilities but these SCs cannot be integrated into real life applications due to high throughput SC manufacturing challenges. Instead of growing single-crystals, various approaches have been used to modify the morphology of organic semiconductors to achieve functional properties of thin films on par with single crystals. These efforts often involve using processing aids (such as nucleating agents and polymer binders to control the crystallite size and crystallite quality) substrate-patterning, solvent additives and often combination of multiple approaches. Rapid crystallization of OSCs in solution processing, can lead to extreme sensitivity to drying kinetics and to a lack of control over nucleation and growth of crystals and substrate surface coverage. Blending small-molecule OSCs with amorphous semiconducting or insulating polymers has recently been demonstrated as a successful route for manufacturing high-performance OFETs with high reproducibility and low-performance spread. The polymer acts as a binder and helps to overcome the common dewetting challenges associated with small molecule OSC processing and achieve excellent uniformity of device performance over large areas. Efforts have therefore been made to optimize morphology, lamellar quality and thin film crystallinity from OSC:
polymer blends using amorphous insulating and semiconducting polymers under a wide range of processing conditions, including different blend ratios, concentrations, solvents and solvent mixtures, post thermal treatments, as well as different molecular weights of the polymer binder. Similarly, pre-patterned electrodes (before OSC deposition) have been functionalized with self-assembled monolayer to dictate the growth of preferred texture of organic semiconductor thin films, leading to improved carrier mobilities. These attempts have focused exclusively on spin-coating and drop-casting while both methods can be scaled to reasonably large substrate sizes, they are incompatible with continuous roll-to-roll processing. Thus, the fabrication of organic field effect transistors on large area substrates is very likely to require switching from spin coating/drop casting, to a more easily scalable, less wasteful and potentially more uniform large-area coating methods which do not require extensive post-treatment steps such as thermal or solvent vapor annealing, to recrystallize the kinetically trapped films often formed during lab-based methods.

This thesis is aimed to develop high performance OFETs through roll-to-roll compatible solution coating method and establishing a process-structure-property-performance relationship in conditions relevant to organic semiconductor deposition. We investigate the formation of solution-processed small molecule thin films using a combination of in situ diagnostics tools in combination of laboratory-scale solution processing methods such as drop-casting, spin-coating and the scalable blade-coating technique.

We start this by presenting a detailed literature review in chapter 2, discussing the organic semiconductors, the effect of molecular structure and packing motifs on their functional
performance, current understanding of nucleation and growth of OSCs and the strategies to control the OSC crystallization aimed at improving charge transport properties.

In chapter 3, we describe the details of OSC materials, surface modification monolayers, general methodology used for device fabrication, materials characterization and development of advanced in-situ diagnostics tools to conduct this dissertation research.

In this chapter, we investigate the formation of solution-processed small molecule thin films using a combination of in situ diagnostics tools in combination of laboratory-scale solution processing methods such as drop-casting, spin-coating and the scalable blade-coating technique.

In chapter 5, we describe the development of high performance OFETs based on small molecule: polymer blends by blade coating. We use in-situ tools to provide understanding about crystallization. Then, we investigate the impact of processing parameters such as coating speed, choice of the binder polymer, choice of solvent, on microstructure and morphology of OSC blend thin films on device figure of merits.

In chapter 6, we describe the impact of bottom metal contacts on crystallization and device performance of blade coated neat OSCs and their polymer blends. We provide the fundamental insights about the effect of non-chemical surface treatment on gold contacts using photoelectron spectroscopy.

In chapter 7, we describe the development of high performance OFETs based on technologically important small molecule BTBT derivatives at industrially compatible
coating conditions. We also investigate the role of solution-to-solid phase transformation on the functional properties of thin films.

We provide conclusions of this thesis in chapter 8, followed by the future perspectives.
Chapter 2

Strategies to control the crystallization of small molecule organic semiconductors: A Literature Review

In this chapter, we discuss the intrinsic and extrinsic factors which influence the functional properties of small-molecule organic semiconductor films in the context of organic field-effect transistors (OFETs). After introducing organic semiconductors, OFETs and the key figures of merit of these devices, we review the literature on the link between the properties of organic semiconductors and the molecular structure and packing motif, as well as thin film microstructure and morphology. Finally, we discuss the latest strategies to control the organic semiconductor film formation from solution, including crystallization and phase separation, with the aim of improving charge transport properties and OFET performance.

2.1 Beyond Moore’s law

During the 1930s, Lilienfeld suggested that conduction in a channel can be modified. Later on, Shockley et al. used this concept to invent an electronic device called the “transistor” (1947), altering the course of humanity. This led to the development of integrated circuits. State-of-the-art integrated circuits today integrate billions of transistors, utilizing silicon as the semiconductor. Transistors are the core components of electronic circuits. These are three terminal devices work as switches to modulate the electrical conduction in semiconductor layer using a variable electric field. Thus are often called as field effect transistors (FETs).\textsuperscript{1,2}
Gordon Moore was the founder of Intel Corporation. He published a paper in 1965, reporting his observation that number of transistor per chip (integrated circuit) were doubling every year but went on to self-correct this observation in 1975 to 18 months. This article was his most influential piece of writing. This law was not only about the density of components but it also suggested the efficient and economical devices. This law revolutionized the computer technology by becoming a mission of industry and created massive competition and also strong collaboration to achieve Moore’s predictions. The Figure 2.1 highlights the evolution of Moor’s law in past four decades. Due to massive advancements in semiconductor technology, now it just takes 3 months to double the density instead of 12 or 18 months.

In the past, the goal was achieved by reducing the transistor design dimensions, leading to the improved performance capability of circuits. Currently, leading computer technology giants such as Intel and IBM are using silicon based transistors having 14nm and 10nm node size. But there is a size reduction limitation after 5nm node mark after which severe current leakage issues will hamper further size reduction, thus staggering the Moor’s law. Very recently, IBM has announced its 5nm technology for the silicon processor. It is 40% more efficient than the 10nm technology without requiring any additional power. It may take 10 years to integrate this new 5nm technology into consumer devices but it has given a life to Moore’s law for next decade or so.

Presently, all technology giants are working on new roads beyond silicon technology. For instance, IBM is working on carbon based processors project. The research team is working to use carbon nanotubes to realize 10nm transistor size in a decade time from now on. If it
succeeded, the transparent and flexible computers will revolutionize the electronic applications. There is another technology called quantum computing, which has attracted massive financial investment. It has the potential to exponentially outclass classical computer technology (silicon technology). It is predicted that just 50 qubits (qubits is quantum analogue of classical unit bit) capability of a quantum computer will outperform the leading supercomputer of the world.

There are consumer applications where current silicon technology cannot fit in. For instance, flexible and foldable displays, E-papers/readers, wearable electronics, stretchable sensors, etc. There are other classes of semiconductor technology such as metal oxides, perovskites, quantum dots and organic semiconductors which have attracted a lot of interest by research community and industry for non-Moore’s applications. It is not the goal to replace current microprocessor silicon technology with any of the above materials in near future. But these materials meet the performance criteria for many modern consumer applications. The table 2.1 shows the current performance status of these materials. Each of these materials have its own advantages and potential applications.

**Table 2.1** The record FET mobility values reported to date for various semiconductors

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Mobility (cm²/Vs)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electron</td>
<td>Hole</td>
</tr>
<tr>
<td>Metal-oxides</td>
<td>&gt; 250</td>
<td>&gt; 1.0</td>
</tr>
<tr>
<td>Quantum-dots</td>
<td>&gt; 20</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Perovskites</td>
<td>&gt; 1</td>
<td>&gt; 15</td>
</tr>
</tbody>
</table>
The development of “organic semiconductors” (OSCs) in the last century brought the signs for a green revolution in electronic appliances. These materials got real attention when Heeger and his coworkers discovered the semiconducting nature of plastics in 1977. The demonstration of polymer thin film transistors in 1986 has attracted thousands of researchers both in academia and industrial labs to join hands for the successful implementation of organic field effect transistors (OFETs) in various electronic and optoelectronic applications. In past three decades, a variety of high performance OSCs with field effect mobilities in excess of 10 cm²/Vs have been developed. These OSCs are readily soluble in common solvents, offering solution processability. Solution based technology allows to manufacture electronic devices on large area flexible substrates in a roll-to-roll manner. This substantially reduces the cost of consumer applications. For instance, currently metal-oxide based TFTs (> 10 cm²/Vs) are being used as backplane in OLED displays. Unfortunately, the cost of these displays is 3-4 times higher than the best liquid crystal displays (LCD). This high price is due to costly vacuum deposition of OLED active materials. The vacuum sublimation involves costly equipment, high vacuums and high temperatures (> 1000°C). This price gap can be minimized by adopting cost-effective manufacturing technologies.

High performance metal-oxides FETs used in current OLED technology require high temperature (> 250°C) post-processing to achieve high carrier mobility in the devices. This limits their use in foldable and flexible OLED displays on low-temperature compatible thin plastic sheets, thus eventually rendering the cost effective OLED display manufacturing.
There are efforts underway to commercialize low cost solution-processed OLED displays. In this regard, the OFETs are perfect candidates to be used in backplane as current drivers for OLED frontplane due to material compatibility, superior mechanical properties and low temperature processing for a fully foldable and flexible OLED display.

Figure 2. 1 Processing temperature for semiconductors with respect to products

2.2 Organic field effect transistors

OSC find applications as active layers in many electronic devices such as organic photovoltaic (OPVs), organic light emitting diodes (OLEDs), OFETs, etc.\textsuperscript{12–15} All these devices have different requirements from active OSC layers. OPV device has a bulkheterojunction (BHJ) layer consisting of blend of donor and acceptor OSCs. This light absorber layer is sandwiched between cathode and anode. The higher charge carrier mobility in vertical direction plays an important role to minimize charge recombination and in improving the fill factor, eventually leading to efficient OPV devices.\textsuperscript{16} OLEDs have an emissive layer
instead of absorber. Transparent amorphous organic layers are used in OLEDs. The charge carrier mobility plays a crucial role in light emission. Generally, low mobility is preferred as it enhances the radiative recombination rate. But there is always a trade off in the mobility of emissive layer as very low mobilities can result in undesired recombination processes.\textsuperscript{17}

On the other hand, the OFETs have totally different functional requirements from OSCs. The charge transport occurs laterally at OSC: dielectric interface. The in-plane drift velocity of charge carriers is required to be high. In past few years, a new type of vertical OFETs (VOFETs) have been reported. In this type of device, all the device components, three electrodes, dielectric and active OSC layer are stacked vertically. The key requirement is to have patterned source. The device figure of merits are limited by the bulk carrier mobility rather than in-plane transport properties.\textsuperscript{18} OFETs find applications in chemical/bio sensors, active matrix displays, RFID tags, E-readers, E-papers/books, smart cards, mobile phone screens, flexible integrated circuits, inventory tags and etc.\textsuperscript{19}

2.2.1 OFET Architectures

OFETs comprise multiple components, including the semiconductor, two metallic electrodes in direct contact with the OSC, known as source and drain (emitter & collector), a gate electrode (base) and an insulating layer (dielectric), as shown in Figure 2.2. There are four types of OTFT device architectures as shown in Figures 2.2a-d.\textsuperscript{20} These four types fall into two main categories named as coplanar and staggered. In coplanar, source and drain contacts (electrodes) are deposited before the OSC deposition, commonly known as bottom contact configuration (Figures 2.2a-b). While in the case of staggered, the contacts
are deposited after the OSC deposition, generally called the top contact configuration. These two configurations are further subdivided into the bottom gate and top gate categories as depicted in Figures 2.2a-d. All of the above have in common two types of functional interfaces of crucial importance to device operation, namely the dielectric/OSC interface and the electrode/OSC contact.

**Figure 2.2** (a) Top gate bottom contact (b) Bottom gate bottom contact (c) Top gate top contact (d) bottom gate top contact (e) FET schematic highlighting the channel length (L) and width (W)

### 2.2.2 The Operation Principal of OFETs and their Figures of Merit

In any FET, the charges accumulate at the interface between the OSC and the dielectric, with the charge polarity opposite to that of the applied electric field between gate and source (V_{GS}). The accumulated charges can be moved through the OSC/dielectric interface by the application of a constant electric potential between drain and source (V_{DS}). This flow of charges (electric current, I) is denoted as (I_{DS}). V_{DS} serves as a driving force for the
movement of charges while $V_{GS}$ dictates the size of the active channel (charge carrier density in the accumulated layer). Thus, the magnitude of $I_{DS}$ depends on both the $V_{DS}$ and the $V_{GS}$. The electrical performance of OFETs can be determined from two types of current-voltage characteristics, known as the transfer and output characteristics, as shown in Figures 2.3a-b. In transfer characteristics, $I_{DS}$ is measured as $V_{GS}$ is swept under a constant $V_{DS}$ (Figure 2.3a). This type of curve is crucial to determining the key figures of merit, such as the drift velocity of charge carriers (field effect mobility, $\mu$), the on state $I_{DS}$, the off state $I_{DS}$, their ratio ($I_{ON}/I_{OFF}$), the threshold voltage ($V_{th}$) and the subthreshold swing (SS). Output characteristics, consist in measuring $I_{DS}$ while sweeping the $V_{DS}$ at constant $V_{GS}$ (Figure 2.3b). These characteristics exhibit two regimes: 1) a linear and 2) a saturation regime. $I_{DS}$ increases linearly with $V_{DS}$ ($V_{DS} < V_{GS}-V_{th}$) in the linear regime while the magnitude of $I_{DS}$ is independent of $V_{DS}$ in the saturation regime ($V_{DS} >> V_{GS}-V_{th}$). When $V_{DS} >> V_{GS}-V_{th}$, charges accumulated in the channel are depleted at the drain electrode, resulting in the loss of the two-dimensional charge carrier confinement effect. This generates a channel pinch-off and $I_{DS}$ becomes constant. This curve is critical to determining the charge injection behavior or contact resistance effects.
The operation of a p-channel OFET can be understood by using the metal-insulator-OSC and source-OSC-drain schematics presented in Figures 2.4a-g.\textsuperscript{21,22} In the absence of any external field at the metal (gate electrode), there is no band bending as shown in Figures 2.4a,e.\textsuperscript{23} Upon application of an external field ($V_{GS} < 0$), upward band bending takes place, and the HOMO level is pushed to Fermi level ($E_F$) of the metal. This leads to the formation of an accumulation layer at the OSC: dielectric interface, as shown in Figure 2.4b (accumulation regime). In the absence of an electric field between source and drain ($V_{DS} = 0$), no charge transport occurs as shown in Figure 2.4f. By applying $V_{DS} < 0$, charge carriers (holes) drift to the drain electrodes as depicted in Figure 2.4g. Similarly, when a small positive $V_{GS} > 0$ is applied to the metal, a downward band bending takes place and the channel area at the OSC/dielectric interface is depleted of charge carriers as shown in Figure 2.4c (depletion regime). In this situation, application of $V_{DS} < 0$ will not help drift.

**Figure 2.3** (a) Transfer characteristics (b) Output characteristics
any holes to the drain electrode. Furthermore, higher $V_{GS}$ will cause more downward band bending. In fact, the intrinsic level crosses the Fermi level, and the density of electrons overcomes that of holes, as depicted in Figure 2.4d (inversion regime). This regime is observed in metal-semiconductor field effect transistors (MESFETs).

Figure 2.4 Metal-Insulator-OSC energy level diagrams (a) in the absence of external field (b) external field applied, accumulation mode ($V_{GS} < 0$) (c) external field applied, depletion mode ($V_{GS} > 0$) (d) external field applied, inversion mode ($V_{GS} >> 0$) Source-OSC-Drain energy level diagrams (e) No fields (f) $V_{GS} < 0$, $V_{DS} = 0$ (g) $V_{GS} < 0$, $V_{DS} < 0$.

The $I_{DS}$ flowing through the device in the linear and saturation regimes can be calculated using classical MOSFET equations derived using the gradual channel approximation. This model assumes that $V_{GS} >> V_{DS}$, and mobility is not dependent on charge carrier density in the channel. The Equation 2.1 describes the $I_{DS}$ in the accumulation mode.
\[ I_{DS} = \frac{W C_i}{L} \mu [(V_{GS} - V_{th})] V_{DS} - \frac{1}{2} V_{DS}^2 \]  

(2.1)

Here, W is the width of the channel, L is the length of the channel, C_i is the gate dielectric capacitance per unit area, and \( \mu \) is the field effect mobility/carrier mobility (hole or electron). When \( V_{DS} = 0 \), the carrier concentration is uniform throughout the device channel. In the linear regime \( (V_{DS} \ll V_{GS} - V_{th}) \), Equation 2.1 becomes Equation 2.2.

\[ I_{DS}^{lin} = \frac{W C_i}{L} \mu_{lin} (V_{GS} - V_{th}) V_{DS} \]  

(2.2)

The linear mobility \( (\mu_{lin}) \) can thus be calculated from Equation 2.3, which is obtained by differentiating \( I_{DS} \) with respect to \( V_{GS} \) and reorganizing Equation 2.2.

\[ \mu_{lin} = \frac{L}{W C_i V_{DS}} \frac{\partial I_{DS}^{lin}}{\partial V_{GS}} \]  

(2.3)

The \( \frac{\partial I_{DS}^{lin}}{\partial V_{GS}} \) can easily be determined from the slope of the transfer characteristics (\( I_{DS} \) vs \( V_{GS} \)) measured in the linear regime \( (V_{DS} < V_{GS} - V_{th}) \), as shown in Figure 2.3a.

In the saturation regime \( (V_{DS} \gg V_{GS} - V_{th}) \), Equation 2.1 can be written as the follows:

\[ I_{DS}^{sat} = \frac{W C_i}{2L} \mu_{sat} (V_{GS} - V_{th})^2 \]  

(2.4)

The saturation mobility \( (\mu_{sat}) \) can then be calculated from Equation 2.5 which is obtained by reorganizing Equation 2.4.

\[ \mu_{sat} = \frac{2L \frac{\partial^2 I_{DS}^{sat}}{\partial V_{GS}^2}}{W C_i} \]  

(2.5)
The $\frac{\partial^2 I_{DS}^{sat}}{\partial V_{GS}^2}$ can be easily determined from the slope of the transfer characteristics ($\sqrt{I_{DS}}$ vs $V_{GS}$) measured in the saturation regime ($V_{DS} >> V_{GS}-V_{th}$), as depicted in Figure 2.5a.

Plotting the transfer characteristics on a logarithmic scale ($\log I_{DS}$ vs $V_{GS}$) and as $\sqrt{I_{DS}}$ vs $V_{GS}$, allows extraction of the other key figures of merit, such as $V_{th}$, $I_{ON}/I_{OFF}$, and SS. The linear curve fit to $\sqrt{I_{DS}}$ vs $V_{GS}$ results in a straight line whose x-intercept is $V_{th}$, as shown in Figure 2.5b. At this point, $I_{DS}$ starts to increase exponentially. $V_{th}$ close to zero is ideal for minimum power consumption by the device in the off state, a target that remains, to date, a gold standard for OFET research.

The switching quality ($I_{ON}/I_{OFF}$) of OFETs is evaluated by the ratio of maximum and minimum values of $I_{DS}$ from the transfer curve $\log I_{DS}$ vs $V_{GS}$ (Figure 2.5b). The SS is defined as the $V_{GS}$ required to vary $I_{DS}$ in decades (V/dec) in the subthreshold region of the transfer curve ($\log I_{DS}$ vs $V_{GS}$), as shown in Figure 2.5c and is represented by the following equation.

$$SS = \frac{d|V_{GS}|}{d\log|I_{DS}|}$$ (2.6)

As such, the SS determines the speed with which the device reaches the on state ($I_{ON}$). The SS is also linked to the interfacial trap state density ($N_{it}$), as given by Equation 2.7.

$$N_{it} = \frac{c_i}{q^2} \left( \frac{S}{k_B T \ln(10)} - 1 \right)$$ (2.7)

Where $c_i$ is the capacitance per unit area of the dielectric, $q$ is the elementary charge, $S$ is subthreshold slope, $k_B$ the Boltzmann constant, and $T$ the temperature.
Figure 2. 5  Transfer characteristics (a) Blue curve (saturation regime) $\sqrt{(I_{DS})}$ vs $V_{GS}$ to determine saturation mobility and Purple curve (linear regime) $I_{DS}$ vs $V_{GS}$ to determine linear mobility (b) $I_{ON}$, $I_{OFF}$ and $V_{th}$ are highlighted (c) Subthreshold swing determination method

2.2.3 Contact Resistance and Injection

The parasitic contact resistance at the electrode/OSC interface serves as a major bottleneck to the reliable operation and overall performance of OFETs. The contact resistance in OFETs is typically 100-1000 times greater than in silicon MOSFETs due to the heterogeneous nature of the metal contact and OSC, responsible for overall poor device figures of merit. The two key factors that cause nonlinear behavior in the output curves in the linear regime ($V_{DS} << V_{GS} - V_{th}$) are (1) the energy level mismatch between $E_F$ of the electrode and the OSC, leading to the formation of a Schottky barrier; (2) disorder or reorganization in the OSC layer in proximity to the electrode/OSC interface. The device geometry is also of vital importance to the charge injection behavior. For instance, a larger contact resistance is often observed in coplanar TFT architectures due to the lower charge injection area as compared to staggered designs. The contact resistance can also increase
due to the diffusion of metal atoms from the electrode into the OSC layer, leading to the generation of trap states at the interface and responsible for the nonlinear character of I-V curves in the linear regime.

Charge injection properties of OFET devices are determined from output curves. The contact resistance is extracted using the transmission line method (TLM).\(^{25}\) In this approach, output curves (\(I_{DS} \) vs \(V_{DS} \)) are determined for OFETs with various channel lengths. The following relationship calculates the total resistance \(R_{ON} \) (sum of the channel resistance (\(R_{ch} \)) and contact resistance (\(R_{C} \))):

\[
R_{ON} = \frac{\partial V_{DS}}{\partial I_{DS}} = R_{ch} + 2R_{C} \tag{2.9}
\]

The \(\frac{\partial V_{DS}}{\partial I_{DS}} \) can be calculated from the slope of output characteristics in the linear regime as shown in Figure 2.7a. The \(R_{ON} \) is then plotted as a function of channel lengths for various \(V_{GS} \) and extrapolation of this curve to Channel length (L) = 0 allows to extract \(2R_{C} \) as shown in Figure 2.7b. The first term in Equation 2.9 is the function of channel length, its contribution will decrease as the channel length of OFETs decrease, suggesting the total resistance is dominated by contact resistance.

Self-assembled monolayers (SAMs) are most commonly used to modify the work function of the electrode. SAMs can form a dipole moment which can increase or decrease the work function of the electrode, depending on the sign of the dipole.\(^{29}\) SAM-based dipoles have two components: (1) a dipole at the electrode/SAM interface due to the interaction between the metal and SAM (bond dipole, BD), (2) and a dipole moment due to aligned SAM molecules which leads to a vacuum level shift (\(\Delta U_{vac} \)).\(^{30}\)
\[ \Delta \phi = BD + \Delta U_{\text{vac}} = -N \left( \frac{\mu_{M-S}}{\epsilon_0 k_{M-S}} + \frac{\mu_{\text{SAM}}}{\epsilon_0 k_{\text{SAM}}} \right) \] (2.8)

Here, \( N \) is the grafting density of SAM molecules, \( \frac{\mu_{M-S}}{\epsilon_0 k_{M-S}} \) is the dipole strength arising due to the metal/SAM interactions, \( \frac{\mu_{\text{SAM}}}{\epsilon_0 k_{\text{SAM}}} \) is the dipole moment due to the SAM molecules, \( \epsilon_0 \) is the permittivity of free space and \( k_{M-S} \) and \( k_{\text{SAM}} \) are, respectively, the interfacial and SAM dielectric constants.

SAMs based on alkane groups have been commonly used to reduce the barrier for injection into n-type OSCs, because the direction of the two dipoles oppose each other (Figure 2.6b).\(^{31}\) Similarly, SAMs utilizing halogen atoms are typically used for energy level alignment between the p-type OSC and WF of electrodes, by increasing WF, as shown in Figure 2.6c.\(^{30}\)

Figure 2.6 Energy level diagrams (a) in the absence of any SAM (b) metal modified with SAM containing alkane groups (c) metal modified with halogenated SAM
Figure 2. 7 Output characteristics of an OTFT, highlighting the determination of $R_{ON}$ in the linear regime (b) $R_{ON}$ plotted as a function of channel length for various $V_{GS}$, depicting the calculation of $R_C$.

2.2.4 Charge carrier mobility Extraction

The integration of OFETs in flexible OLED displays pretty much depend upon the true capability of the OFET devices. Sirringhaus et al. has highlighted the correct mobility extraction procedure. It is quite often that OFETs show non-linearity in transfer and output characteristics. Ideally, the $I_{DS}$ should follow Equation 2.2 & 2.4. There are two common issues encountered by OFET community during mobility extraction. Firstly, the mobility increases with increasing $V_{GS}$ and this has been noted for many conjugated polymers. It happens due to presence of low mobility localized states which are filled with increasing $VGS$ before delocalized states are accessed. In this case, mobility should be extracted at high gate voltage in a limited range and it
may represent true figure of merit. Secondly, if the transfer characteristics show a sharp kink as shown in Figure, it provides two slopes for mobility extraction. This has been observed for many donor-acceptor polymers and also for rubrene single crystals. It may be due to faster scaling of contact resistance with $V_{GS}$ as compared to channel resistance. Gundlach et al. found strong dependence of contact resistance on $V_{GS}$ (lower range) leads to non-linear transfer characteristics for Rubrene single crystal FETs. Very small range of VGS should be avoided to extract the mobility as this range may not be fulfill the criteria set by Equations 2.2 & 2.4.

Figure 2. 8 (a) & (b) Transfer characteristics highlighting non-linearity issues (a) Dual-slope\textsuperscript{32} (b) Trap-limited\textsuperscript{33}

2.3 Organic Semiconductors

OSC\textsubscript{s} are conjugated carbon-based materials combining alternating single and double bonds and capable of charge transport. This capability stems from the bonding nature (sp\textsuperscript{2}-
hybridization) of backbone carbon atoms in these materials. The electronic configuration (Figure 2.9a) shows that carbon has four valence electrons.

![Diagram showing sp² hybridization in C, excited state, and ground state](image)

![Diagram showing overlap of sp² orbitals](image)

Figure 2.9 (a) Electronic configuration of Carbon (b) schematic showing formation of sigma bonds (c) schematic showing formation of pi bond

When carbon atoms in the excited state undergo sp²-hybridization, they only use the 2s electrons and the 2px and 2py electrons, leaving behind the 2pz electron. The sp²-hybridized
orbitals of carbon atoms arrange themselves at 120° to each other in the same plane, leaving the 2p\textsubscript{z} orbital perpendicular to the plane of hybridization (Figure 2.9b). The hybridized atomic orbitals pointing towards each other thus overlap to form molecular orbitals (σ-bond), each having a pair of electrons (Figure 2.9c). The 2p\textsubscript{z} orbitals of two carbon atoms merge sideways, resulting in a molecular orbital (π-bond). The combination of these σ and π bonds forms a double bond. The electronic cloud in the π molecular orbital is delocalized, meaning that electrons can move from atom to atom. The electronic device dimensions (several µm) are several orders larger than the size of the molecular orbital overlap (nm). Thus, delocalized charges between molecules and the better overlap of the π-molecular orbitals are crucial for better charge transport properties in OSCs. The dominant mechanism of charge transport in weakly bonded (van der Waals interactions between molecules) OSCs is ‘carrier hopping’ due to the overlap of π-molecular orbitals between adjacent molecules. In contrast, inorganic semiconductors have strong covalent bonds resulting in highly ordered structures facilitating faster charge transport. The weak intermolecular interactions result in the lower structural order of OSCs, which is partly responsible for orders of magnitude slower charge transport in comparison to inorganic semiconductors.

2.3.1 Structure and Packing of Conjugated Small Molecules

Packing in OSCs is dominated by weak van der Waals forces in the presence of geometric considerations, such as molecular shape anisotropy, backbone planarity, π face and the location, size and steric of side- and end-groups. The molecular packing motif therefore dictates intermolecular wave function overlap. The intermolecular transfer integral depends on the nature of molecular packing (motif), molecular interactions and π-πstacking
distance, etc. \(^{34}\) The reorganization energy, which is strongly influenced by the rigidity of molecules and conjugation length in OSCs, also influences transport properties. \(^{35,36}\)

Equation 2.10 describes the relationship between transfer integral (t) and reorganization energy (\(\lambda\)) to the charge transfer rate (\(k_{et}\)). This model suggests, large transfer integral and lower reorganization energy will lead to the better hoping charge transport properties in OSCs. \(^{37,38}\)

\[
k_{et} = \left(\frac{4\pi^2}{h}\right) t^2 (4\pi\lambda RT)^{-0.5} \exp\left(-\frac{\lambda^2}{4RT}\right)
\]

(2.10)

Given the weak nature of van der Walls interactions, thermal variations in three dimensional space can occur with large displacement amplitude, thus affecting the wave function overlap and the overall charge transport in OSC films. \(^{39-41}\) Consequently, several charge transport models have been proposed which incorporate thermal vibration effects. The charge hopping model has been used primarily to describe transport at room temperature and above, whereas the band-like transport model has been used to describe charge transport at lower temperatures.

In the case of hoping model, the carrier mobility is described by the following Equation 2.11. \(^{37,42}\)

\[
u = \frac{eD}{k_BT}
\]

(2.11)

where D is the diffusion coefficient given by Equation 2.12

\[D = a^2 k_{et}\]

(2.12)
Where \( a \) is intermolecular spacing and \( k_{et} \) is hoping rate/charge transfer rate. The charge transfer rate is related to polaron binding energy and transfer integral (t) by the Equation 2.13. Where \( E_{pol} \) is related to reorganization energy by Equation 2.14.

\[
k_{et} = \frac{t^2}{\hbar} \left[ \frac{\pi}{2E_{pol}k_B T} \right]^{\frac{1}{2}} \exp \left( -\frac{E_{pol}}{2k_B T} \right) \tag{2.13}
\]

\[
E_{pol} = \frac{\lambda_{reorg}}{2} \tag{2.14}
\]

Now rearranging these Equations 2.10-2.14, we get Equation 2.15 that gives us hopping mobility.

\[
\mu_{hop} = \frac{ea^2 t^2}{k_BT \hbar} \left[ \frac{\pi}{\lambda_{reorg} k_B T} \right]^\frac{1}{2} \exp \left( -\frac{\lambda_{reorg}}{4k_B T} \right) \tag{2.15}
\]

The Equation 2.15 relates hopping mobility to transfer integral and reorganization energy. Higher transfer integral and lower reorganization is favorable for better hopping mobility.

The simplest way to evaluate the charge transport mechanism is to measure temperature dependence of carrier mobility. If the carrier mobility increases with decreasing temperature and mobility versus temperature plot show a power-law dependence as given by Equation 2.16; this OSC has a band-like charge transport. Where \( n \) should be \( 0.5 \leq n \leq 3 \).

\[
\mu \propto T^n \tag{2.16}
\]

On the other hand if mobility increases with increasing temperature, it is called thermally activated charge transport and it is follows Equation.

\[
\mu \approx \exp \left[ -\frac{E_A}{k_B T} \right] \tag{2.17}
\]
Where $E_A$ is activation energy. This type of charge transport behavior is often observed in disordered polycrystalline systems where higher temperatures provide energy to the carriers for hoping.

In the solid state, OSCs crystallize into one of the four molecular packing configurations (motifs) commonly seen in organic electronics: (1) herringbone, (2) co-facial herringbone (3) 1-D slipped stack and (4) 2-D bricklayer, as depicted in Figure 2.10a-d. These packing motifs also give rise to non-preferred in-plane charge anisotropy due to different magnitude of transfer integral in different crystallographic directions. Herringbone molecular packing motif results in balanced transfer integral thus suggesting isotropic in-plane charge transport. The detailed description of each can be found in the literature. Based on theoretical predictions considering each packing motif’s nature, OSCs with 2-D bricklayer lamellar motif should result in the superior charge transfer rates (hopping mobility) due to its larger transfer integrals and 2-D charge transport network. However, experimental OTFT device results reveal that OSCs adopting the herringbone packing motif typically exhibit the highest field-effect mobilities reported to date. This contrast between molecular-scale theory and device-level experimental results suggest that external factors such as device dimensions, thin film quality, solution processing approaches, molecular orientations in thin films, etc. must be taken into account to predict charge transport properties of an OSC under investigation accurately. Recently, Henning and coworkers have shown that dynamic disorder due to thermal vibrations also plays an important role in charge transport properties of OSCs. OSCs whose transfer integral is less sensitive to thermal vibrations, have been reported to be highest performing in OFETs. The OSCs
with solubilizing functional groups attached along the long-axis have reduced dynamic disorder, thus leading to high carrier mobilities.\(^\text{39}\)

**Figure 2.** Molecular packing motifs (a) Layered Herringbone (b) Co-facial Herringbone (c) 1D-slip stacked (d) 2D-bricklayer

Charge transport in OSCs is dependent on the molecular packing motif. However, charge transport in OFETs is confined to the OSC/insulator planar interface, making the molecular orientation and polycrystalline texture in the solid state film particularly crucial. In this respect, packing motifs favoring formation of large scale 2D lamellar sheets with 2D \(\pi\)-stacking are preferred. In such films, the carrier mobility becomes limited primarily by in-plane crystallite and domain size, as well as the nature of grain and domain boundaries.\(^{47-50}\)

There are in excess of 400 different small molecule OSCs reported to date in the literature. One of the oldest types involves benzene rings fused together to form a class of OSCs called “acenes.”\(^{51,52}\) The most diminutive acene synthesized to date is anthracene with
three benzene rings. Single crystals of anthracene showed only $10^{-2}$ cm$^2$/Vs due to shorter conjugation length. Fusing four or five benzene rings together resulted in tetracene and pentacene molecules respectively (Figure 2.11a-c). The OFETs based on single crystals of tetracene and pentacene resulted in 2.4 cm$^2$/Vs and 15-40 cm$^2$/Vs due to better conjugation. Hexacenes have larger transfer integral (60 meV) and lower reorganization energy (79 meV) as compared to anthracene’s smaller transfer integral (19 meV) and higher reorganization energy (138 meV). It is noteworthy that stability issues and complex synthesis of higher acenes (with six or more fused benzene rings) serve as a bottleneck to realizing these acenes as active layers in OFETs.

![Figure 2.11: Molecular structure of acenes (a) anthracene (b) tetracene (c) pentacene](image)

These acenes backbones can be modified by attaching substituents at both ends or the peri-positions of conjugated fused rings. For example, rubrene can be obtained by modifying tetracene with four phenyl rings, resulting in a co-facial herringbone molecular motif. Single crystal rubrene OFETs showed field-effect mobility in the range of 20-40 cm$^2$/Vs. Moving further to improve the molecular packing of acenes and pi-pi stacking, Anthony et al. came up with more useful guidelines to modify the slightly larger pentacene molecule. Though pentacene has shown very promising room temperature hole mobility (determined
from space-charge limited current measurement) as high as 35 cm$^2$/Vs, it is deposited by thermal sublimation,\textsuperscript{55,56} and the herringbone motif has relatively poor in-plane pi-pi stacking, suggesting further improvements in charge transport may be possible through crystal engineering. Pentacene has very poor solubility in common hydrocarbon solvents, prohibiting its use in ink-based low-cost large area organic electronics.\textsuperscript{58} Anthony et al. thus introduced bulky functional groups at the peri positions which resulted in modified pentacene molecules readily soluble in common solvents and with even better molecular packing, i.e., 2-D bricklayer motif. The key trick to achieve 2-D lamellar motif was to use a bulky side solubilizing group having half the length of the pentacene backbone. The triisopropyl-silylethynyl (TIPS) groups were attached at peri positions which resulted in the now famous OSC, 6,12-Bis(triisopropyl-silylethynyl)pentacene, commonly known as TIPS-pentacene (Figure 2.12).\textsuperscript{61} The advent of TIPS-pentacene for the first time produced solution-processed OSC films which could yield OFETs with carrier mobility on par or superior to most vacuum-deposited OSC films, marking an important milestone and a turning point in the field.

![Figure 2.12 Molecular structure of TIPS-pentacene](image-url)

**Figure 2.12** Molecular structure of TIPS-pentacene
The TIPS functionalization transforms the preferred molecular packing from that of pentacene (herringbone) to the 2-D bricklayer motif. Solution processed thin films of this OSC have shown field effect mobilities in the range of 1-11 cm²/Vs.⁶²-⁶⁴ Since the synthesis of TIPS-pentacene, Anthony et al. have successfully demonstrated other substituents and achieved field-effect mobility in the range of 1-5 cm²/Vs.⁶¹,⁶⁵,⁶⁶ Just as many small molecules, pentacene derivatives exhibit a rich polymorphic tendency in the solid state. Different polymorphs exhibit anywhere from slight differences to significant structural changes with respect to the equilibrium phase, resulting in non-negligible changes in intermolecular coupling, which influence transport properties. This makes device performance rather sensitive to processing conditions and to film thickness.⁶⁷,⁶⁸ This can challenge the ability of solution processing techniques to produce devices with consistent and reproducible carrier mobility and other figures of merit.⁶⁹

After the discovery of OSCs based on fused ring acenes, chemists in many research labs went beyond, functionalizing the rings themselves.⁵⁷ Katz et al. reported the first OSC in the series of anthradithiophene (ADT) at Bell Labs in 1998.⁷⁰ In 2004, Anthony et al. combined the concept of ADT and backbone functionalization by synthesizing an OSC known as 5,11bis(triethyl silyl)ethynyl)anthradithiophene (TES ADT), shown in Figure 2.13a.⁶¹ This molecule also resulted in a 2-D bricklayer structure and good field-effect mobility of 1 cm²/Vs on par with amorphous silicon.⁶⁶ As small molecule OSCs rely on crystalline packing and order in the solid state to promote transport, it was envisioned that the use of halogen interactions can improve charge transport properties by promoting crystallization. Thus, Anthony et al. modified the ADT backbone by introducing fluorine (F) atoms in the end substituted thiophene groups (Figure 2.13b).⁷¹ These molecules adopt
the same packing motif as TIPS-pentacene, but with stronger intermolecular interactions thanks to stronger molecular orbital overlap. Several OSCs based on this idea were designed and synthesized, and the resulting thin films have typically shown mobility > 1 cm²/Vs.\textsuperscript{72}

![Molecular Structure of (a) TES ADT (b) diF-TES-ADT](image)

**Figure 2.13** Molecular Structure of (a) TES ADT (b) diF-TES-ADT

One of the most successful modifications of OSC backbones was the alkyl side-chain substitution in chalcogen-phenes developed by Takimiya et al. in 2004.\textsuperscript{73} Initial OSCs had selenium atoms which presented a serious safety hazard, thus blocking their use in OFETs. This led the group to synthesize a series of sulfur-containing benzothiophene derivatives in 2006-2007.\textsuperscript{74,75} These air stable OSCs had alkyl groups at the ends of the benzothiophene core. Figure 2.14 shows the structure of C\textsubscript{n}-BTBT. These molecules adopt the layered herringbone molecular packing motif similar to pentacene, but with alkyl substituents exclusively outside the plane of π-π\textsuperscript{*} interactions. This class of OSC compounds has
demonstrated tremendous performance, with many groups reporting carrier mobility surpassing 10 cm²/Vs.

2.4 Strategies to control the crystallization in OSCs

Crystallization is a phase transformation process and has paramount importance in a variety of natural and industrial processes particularly medicine manufacturing. Crystallization starts with nucleation and the control over nucleation equips us to control the size, purity, morphology and crystal structure of the crystalline product.

Nucleation begins with the formation of a large cluster of crystalline particles (atoms or molecules). The formation of new crystal volume within solution results in free energy gain which overcomes the free energy cost to create this new volume of the crystalline phase. This phenomenon is the core process of nucleation, and it has been studied widely by experimental techniques as well as by simulations. The development of cryo-transmission electron microscopy has enabled us to monitor the early stages of nucleation. But yet, we don’t have a complete picture of nucleation from the solution because nuclei formation occurs at nanometer length and nano-second scales. The nanoscales make the in situ observations extremely difficult. The modern molecular dynamics simulations have been used to reproduce the nucleation from solution but the time scale involved and multiple assumptions involved in the theoretical frameworks have
been criticized, the effort is underway to address the criticism. The results obtained from simulations are dependent upon a century old Classical Nucleation theory (CNT) developed by Volmer and Weber based on Gibbs ideas. It was developed to explain the phase transformation process involved during condensation of supersaturated vapors into liquid. The concepts have also been applied to describe the phase transformation involved in super-cooled liquids and supersaturated solutions.

**Classical Nucleation theory**

Nucleation is considered to be occurring at constant temperature and pressure and phase transformation from solution to crystal is driven by free energy change. The formation of crystals is a first order phase transition process. The formation of new phase involves overcoming free energy barrier which is called Nucleation.

The phase transformation process is described by the following Equation 2.18.\(^7\)

\[
\Delta G_{cry} = \Delta H_{cry} - T\Delta S_{cry}
\] (2.18)

Where,

\(\Delta G_{cry}\) = Gibbs free energy change of crystallization at constant temperature

\(\Delta H_{cry}\) = Enthalpy change of crystallization at constant temperature

\(\Delta S_{cry}\) = Entropy change of crystallization at constant temperature

The crystallization constant at equilibrium \((K_{cry})\) is given by the Equation 2.19.\(^8\)
\[ K_{cry} = \exp\left(-\frac{\Delta G_{cry}}{RT}\right) = \frac{1}{c_e} \]  

(2.19)

Where,

\( C_e \) is the solubility of the material.

Nucleation events begin when concentration \( (C) \) is higher than \( C_e \). In other words, the chemical potential of solute (\( \mu \)) in crystallizing solution is higher than its equilibrium value (\( \mu_e \)). These potentials are given by the following relationships.

\[ \mu = \mu_o + RT \ln Y C \]  

(2.20)

and

\[ \mu_e = \mu_o + RT \ln Y_e C_e \]  

(2.21)

Where,

\( Y \) = the activity coefficients of solute in crystallizing solution

\( Y_e \) = the activity coefficients of solute at equilibrium conditions

\( \mu_o \) = Chemical potential of solution at standard conditions

The nucleation driving force is often expressed as Equation 2.22.

\[ \Delta \mu = \mu - \mu_e = RT \ln \left( \frac{Y C}{Y_e C_e} \right) \]  

(2.22)

Recently, Peter G. Vekilov modified the nucleation theory expressions by using the following consideration.\(^79\)

1. Cluster of \( n \) molecules of size \( a \) instead of cluster of radius \( r \).
In supersaturated solution, the formation of a new phase (cluster) results in the loss of free energy ($-n\Delta\mu$) and the formation of a phase boundary (area $S$ and surface free energy $\alpha$) between the new phase and the solution results in the gain in free energy ($Sa$). If the cluster is considered to be a cube of side $b$ then, $S = 6b^2n^{2/3}$.

This leads to the following expression for Gibbs free energy.

$$\Delta G(n) = -n\Delta\mu + 6b^2n^{2/3}\alpha \quad (2.23)$$

This is also plotted in Figure 2.15.

![Figure 2.15 Thermodynamic effects of formation of crystals](image)

Differentiating the Equation gives us the critical size of the cluster ($n^*$) required for nucleation.
\[ n^* = \frac{64b^6a^3}{4\mu^3} \]  \hspace{1cm} (2.24)

and,

\[ \Delta G^* = \frac{32b^6a^3}{4\mu^{12}} = \frac{1}{2} n^* \Delta \mu \]  \hspace{1cm} (2.25)

There are two important assumptions taken to get into Equation 2.24.

1. The size of the nucleus is not constant
2. Surface energy is independent of nucleus size

The first assumption limits the CNT relationship applicable only to large nuclei where the addition or removals of particles do not induce large error.

Volmer modeled the nucleation rate by considering Arrhenius relationship given in Equation 2.26.

\[ J = J_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right) \]  \hspace{1cm} (2.26)

The final expression for rate law is given by the Equation 2.27.

\[ J = v^* Z n \exp\left(-\frac{\Delta G^*}{k_B T}\right) \]  \hspace{1cm} (2.27)

Where,

\[ v^* = \text{rate at which particles attach to the nucleus} \]

\[ Z = \text{Zeldovich factor which accounts for width of energy profile} \]

\[ n = \text{number density of molecules in solution} \]
Two-step nucleation theory

The main assumption in deriving rate law of CNT is that the solution particles directly exchange with an ordered cluster of particles. This may not apply to crystallization from solution. This can be understood if we consider a phase diagram of a two-component system (concentration vs. temperature). This phase diagram has three phase regions which are typically named as a dilute solution, dense solution, and final crystal. The two ordered parameters (concentration and structure) are used to distinguish between different phases. Simply, the formation of crystals in solution is described by transition along concentration and structure simultaneously as depicted in Figure 2.16a. But theoretical and experimental results of protein crystallization suggested that it is more logical to consider the transition along concentration and structure in sequence. It was found that the nucleation of lysozyme involves two steps.\textsuperscript{77–79} It begins with the development of a dense liquid state which is followed by crystal nucleation as depicted in Figure 2.16b.

The modified rate law for two-step protein nucleation was developed, and it is given in Equation 2.28.

\[ J = \frac{k_2 C_1 \exp(-\Delta G_2^*/k_BT)}{\eta (C_1,T)[1 + U_1 \exp(-\Delta G_0^*/k_BT)]} \]  \hspace{1cm} (2.28)

Where,

- \(k_2\) = the nucleation rate of the crystal inside the clusters,
- \(C_1\) = the protein concentration inside the clusters, that is,
- \(\Delta G_2^*\) = the barrier for nucleation of crystals inside the clusters
\( \eta \) = the viscosity inside the clusters

\( U_1 \) = the effective rates of, respectively decay

\( U_0 \) = the effective rates of formation of clusters

\( \Delta G_c^0 \) = the standard free energy inside the clusters in excess of that in the solution

**Figure 2.16** Crystallization from solution along two ordered parameters (b) Schematic of nucleation steps as depicted by red guide line in (a) (c) The energy barrier along two pathways of the two-step nucleation phenomenon

The main assumption to derive the two-step nucleation rate law is that the first step (formation of dense state) is fast while second step (nuclei formation) is rate determining step. This has been verified experimentally. Apart from proteins, the two-step nucleation mechanism has been observed by other material systems such as colloids, bio-minerals,
pharmaceuticals, nanoparticles and also some polymers.\textsuperscript{76,77,80–83} The Figure 2.17 depicts the possible pathways for multistep crystallization in comparison to classical pathway.\textsuperscript{84}

\textbf{Figure 2. 17} Multiple pathways for crystallization Note: Classical pathway is depicted by gray line (monomer by monomer attachment), and final crystal can have complex morphology

The complete understanding of multistep crystallization will help to control the complex processes in various applications. Multistep crystallization has enabled the production of hierarchical structures while retaining the size-dependent characteristics of their building blocks. This solution-based growth of technologically important materials (semiconductors etc.) such as TiO\textsubscript{2}, ZnO, SnO\textsubscript{2},\textsuperscript{85–87} Two-step nucleation pathway has also enabled the production of branched nanomaterials having short electron free paths, large photon absorption cross section and desired optical scattering pattern.\textsuperscript{88} Metal-organic frameworks (for CO\textsubscript{2} capture, Hydrogen storage, biofuel purification, etc.) have been found to involve multistep crystallization pathway.\textsuperscript{89,90}
As we stated above, the research community in diverse fields has found technologically important implications of multistep crystallization pathway. But yet there are multiple unknowns as listed below.\textsuperscript{84}

1. Structure of solvent and solute at solid-solution interfaces
2. How the structure evolves at solid-solution interfaces
3. The fields, forces and their scale as the formation of assembly proceeds
4. Nanoscale physics and chemistry at interfacial regions that determine particle alignment
5. Size dependence of surface energy

There are models developed for particle interaction in colloids but unable to describe multistep crystallization process due to complex energy landscape and anisotropies in shape, atomic structure, dynamic nature of dense liquid or amorphous particles.

**Growth**

The second stage of crystallization after nucleation is growth. Crystallization of OSCs from solution can produce single crystals, needle-like crystals, spherulites, etc. Spherulites are polycrystalline aggregates. The spherulites are one of the most common morphology observed for small molecule organic compounds, proteins, polymers, minerals, elements (graphite, selenium, and sulfur), inorganic salts and some metals and their alloys. The spherulites can grow from melt, solids (such as amorphous films) and also solution and gels. The most common forms of spherulites grown from Melt are shown in Figure 2.18.\textsuperscript{91}
Figure 2. Polarized optical images for spherulites grown from melt (a) Coarse spherulites (b-e) Fine and compact spherulites (f) Open spherulites

Following are the general features of spherulite formation from melts, solutions or solid state.\textsuperscript{91}

1. The growth of spherulites can be diffusion or interface controlled. The spherulites formation during recrystallization of rubrene from melt has been found to be dictated by both diffusion and interfacial kinetics at growth front. In the case of spherulite growth from solutions also depends upon the interplay between diffusion and interface
kinetics. The Equation describes the relationship between diffusion and kinetic coefficients.

\[
V = B (\Delta c_s)^m = D (\Delta c - \Delta c_s)/\sigma_D \tag{2.29}
\]

Where,

V  = growth rate

B  = kinetic coefficient

D  = diffusion coefficient

\(\Delta c_s\)  = supersaturation at the growth front

\(\Delta c\)  = supersaturation in the growth medium

\(\sigma_D\)  = thickness of diffusion boundary layer

m  = order of reaction at the interface

2. The material systems which have small kinetic coefficients show spherulites growth from solutions suggesting that growth is mainly controlled by the interface dynamics.

3. The high supersaturation or high degree of super-cooling are required to observe the spherulite growth.

4. The higher degree of super-cooling results in thinner fibers of spherulites. Till date, no quantitative data is available for spherulites obtained from solutions. But qualitatively, it has been observed that high degree of supersaturation leads to similar fiber features as of melt-grown.

5. It does not require a viscous medium. The melt-grown spherulites result in more compact spherulites. The presence of foreign particles promotes the spherulite formation.
Confinement Effects

The charge transport in OSCs is strongly dependent upon the morphology. The molecular assembly processes during crystallization of OSC (via various solution processing methods) control the morphology. These assembly processes are not well understood in important OSC solution processing methods. The assembly processes are strongly linked to mass and momentum transport, and also to the energy fluxes in an evaporating system. All these parameters strongly impact the OSC deposition under a variety of conditions.

Molecular assembly under confinement has been found to be one of the influential pathways that affect the morphology of thin films, polymorph selection and thus influencing the functional properties. Both the nano and microscale dimensional constraints have been used to modify the crystallization behavior of materials (polymers, small molecules, inorganic materials, pharmaceuticals, etc.).

Multiple polymorphs of a material system have distinct molecular packing. This will result in different volumetric and interfacial contributions of CNT model, leading to differences in free energy as depicted in Figure 2.19a. This theoretical model has been successfully used to grow specific polymorphs of an aromatic acid. The metastable polymorph was grown by using glass pores of size 7.5 nm, while the stable polymorph was obtained using 55nm glass pores (due to larger critical nuclei requirement).
The confinement has also been successfully used to control the crystallization, and resulting morphology of PS/PEO blend films as shown in Figure 2.19b.94 The confinement of film thickness from micron scale to nanoscale resulted in a dramatic transformation in the final film morphology. Authors argued that it possibly happened due to a reduction in nuclei formation. Our group in collaboration with Professor Bao and co-workers has used the confinement effect to understand the growth of TIPS-pentacene polymorphs during blade coating.95 It was postulated with the help of in situ experiments that equilibrium polymorph crystallizes at the air-liquid interface. This results in confinement of remaining solution media between the bottom substrate and top thin crust of crystallized equilibrium polymorph. It allowed the growth of metastable polymorph of TIPS-pentacene. The metastable polymorph fraction increased by using such conditions which resulted in thinner films. The metastable
polymorph showed increased kinetic stability in thinner films as compared to thicker ones.\textsuperscript{42}

Recently, our group has used thickness confinement effect to program the crystallization in a variety of organic and inorganic material systems.\textsuperscript{96} It was observed that crystallization start earlier in thicker regions of thin films (Figure 2.18a-c). A relationship was proposed to explain this phenomenon, and it is given in Equation 2.30.

\[
R_A = \frac{N}{\Delta t \Delta A} = Rd \tag{2.30}
\]

Where,

\( R_A \) = areal nucleation rate

\( N \) = no of nucleation events

\( d \) = film thickness

\( R \) = Volumetric homogenous nucleation rate

The nucleation time for the first nucleation event \((N = 1)\) can be correlated to film thickness by Equation 2.31.

\[
t_1 = \frac{1}{Rd \Delta A} \tag{2.31}
\]

This relationship was experimentally observed (Figure 2.18d) for many thin films such as vacuum processed rubrene and molybdenum oxide, and also solution processed TES-ADT films. This thickness dependent crystallization control served a new pathway to control the morphology, polymorph selection and resulting functional properties.
Figure 2.20 (A) Optical microscopy images of TES-ADT films (B & C) POMs showing that crystallization begins earlier in thicker part of rubrene film (C) tFull phase transformation in thicker parts of the film while thin parts remain unchanged (D) Nucleation time vs processing temperature (top) for MoOx and Effect of thickness on the onset of nucleation time

2.4.1 Solution processing methods

We show major deposition techniques used for OSC solution processing in Figure 2.21. Among these, drop-casting and spin coating are not compatible with high throughput industrial manufacturing requirements. The meniscus guided and printing techniques have gained a lot of attention in past few years for solution based deposition. All of these methods involve solvent drying during material deposition. It has been reported that drying kinetics strongly influences the functional properties of OSCs.
2.4.1.1 Drop casting

The simplest method of OSC thin film fabrication is drop casting. A fixed volume of ink is simply cast on a substrate and left to spread and dry on its own. The solvent vapor pressure determines the drying rate and the ink’s wetting behavior combine with Marangoni flow to create a coffee ring. Heat, air flow and confinement can be used to control the drying kinetics. Drop casting is versatile and can be used to fabricate polycrystalline films as well as isolated single crystals, by engineering driving forces for dewetting/wetting and the kinetics of crystallization.\textsuperscript{98–101} Recently, Diemer et al. have introduced acoustic vibrations at 100 Hz to influence the crystallization behavior of OSCs and reduced the interfacial trap density, resulting in faster carrier transport in OFETs.\textsuperscript{102} Thin films of diF-TES-ADT grown by this method yielded a carrier mobility of 3 cm\textsuperscript{2}/Vs, nearly 6 times greater than conventional drop casting.
Li. R et al. used *in situ* GIWAXS and quartz crystal microbalance (QCM-D) experiments to investigate the crystallization kinetics of TIPS-pentacene thin films during drop-casting under variety of drying conditions. It was found that film growth starts with heterogeneous nucleation near solid-liquid interface under ambient conditions. QCM-D experiments helped to determine the critical concentration of OSC in solution required for heterogeneous nucleation (Figure 2.22a). The slow drying kinetics (deposition rate reduced to 0.26 nms\(^{-1}\) from 1.23 nms\(^{-1}\)) to heterogeneous nucleation and favored predominately surface growth rather than mixed growth (surface and bulk) as shown in Figure 2.22b, while the fast drying kinetics resulted in homogenous nucleation and mixed growth. Surface growth dominated OSC transformation into solid film increased to 90% from 25% by using slow drying conditions. This helped to achieve superior lamellar crystallinity and continuous thin films, leading to improved charge carrier mobility of drop-casted TIPS-pentacene films.

Spin cast TIPS-pentacene films generally have lower carrier mobility in comparison to drop-casted films. This can be understood by comparing the drying kinetics of two processes. Spin-coating involves fast drying conditions (few seconds) in comparison to very slow drying conditions involved in general drop casting experiments (tens to hundreds of seconds). The fast drying rates can lead to OSC transformation via mixture of surface and bulk growth similar to what Li. et al. observed. The fast drying will quench the crystallization and won’t allow the OSC lamellar structure to its potential which otherwise can be achieved under tuned drying conditions.
Figure 2.22 The critical concentration for heterogeneous nucleation, $C^*$, determined from QCM-D experiments. The plot shows rate-invariant behavior in conditions of slow evaporation and a rate-dependent behavior in ambient and accelerated drying conditions (b) The fraction of solute deposited while $C < C_B$. Schematic representations of TIPS-pentacene film growth during drop casting (c) ambient (d) slow (e) fast drying

2.4.1.2 Spin-coating

It is one of the best solution processing methods developed to date to manufacture uniform thin films based on inks (both OSCs and IOSCs) for multiple applications such as OFETs, OPVs, OLEDs and other energy harvesting applications, i.e., thermoelectrics and batteries. The substrate is rotated at a desired speed to spread the ink which results in a continuous thin film of desired thickness (a function of speed and concentration). OSC thin film fabrication by spin coating on patterned substrates containing wetting and non-wetting trenches for selective OSC deposition from high boiling point solvents has been demonstrated to control thin film morphology. Chou W. et al. found that spinning speed can be used to alter the morphology and crystallization of OSC. Slower spinning speeds
leave behind residual solvent molecules in the thin films hindering the crystallization quenching. This residual solvent allows the OSC molecules to achieve global potential energy minima resulting in improved crystalline quality. It is the simplest processing trick in the spin coating (reducing the spinning speed) to improve thin film quality for the enhancement of carrier mobility of TIPS-pentacene from $10^{-4}$ cm$^2$/Vs to 0.5 cm$^2$/Vs.

Conventional ‘on-center’ spin coating process involves placing the substrate in the center of rotating holder. This crystallization kinetics can be altered by making small adjustments such as speed of spinning process it can also be modified by placing the substrate 2-4 cm away from rotating center.\textsuperscript{105} So called “off center’ spin coating approach enabled quenching of crystallization process due to faster solvent evaporation rates, resulting in improved thin film quality having record carrier mobilities of $> 40$ cm$^2$/Vs.\textsuperscript{67} This method also offers unidirectional centrifugal force which has been used to achieve grains of TIPS-pentacene aligned in one direction with superior crystallinity to regular spin coated films by optimizing the spinning speed/acceleration and distance from off center.

### 2.4.2 Single crystal and single domain OSCs from solution crystallization

Single crystals (SCs) are the purest embodiment of any form of material. Single crystal OSCs therefore offer the potential for achieving the maximum performance for any given OSC by removal of common defects formed in polycrystalline films. SCs can be free of many types of structural defects, such as grain boundaries, and typically possess highest chemical purity through a self-purification process. The combination of these two benefits has been shown to yield trap free charge transport.\textsuperscript{106,107} In the last twenty years or so, extensive effort has been committed to develop fabrication methods of small molecule SC
films and arrays of OSCs.\textsuperscript{108,109} Unfortunately, scalable printing of OSC SCs and arrays thereof is difficult and tedious. The growth, nucleation, and orientation of discrete OSC single crystals depend upon the wettable area dimensions.\textsuperscript{110} These aspects require tedious optimization for each OSC. Moreover, the highest mobility SC-OFETs are manufactured using the physical vapor transport approach.\textsuperscript{111} In the case of rubrene, this method involves closed chamber, inert environment and high temperatures (280°C), long growth times and almost impossible to grow uniform sized crystals, making this approach currently incompatible with scalable solution processing and effectively limiting SCs for fundamental materials and device physics studies.

Ink-based methods of SC manufacturing have been developed successfully and can be separated in two categories: (1) solvent evaporation-based methods and (2) anti-solvent crystallization methods. Controlled solvent evaporation is the most common and facile method of producing single crystals or single domain films. This involves drop-casting an OSC ink on a flat or slightly tilted substrate. Crystallization The solvent evaporates with time leading to supersaturation of the OSC ink. Single crystals of tetrathiafulvalene-based molecules have achieved a carrier mobility of 1 cm\textsuperscript{2}/Vs.\textsuperscript{112} Takeya et al. used an inclined substrate modified with a SAM to grow single crystal and single domain films of C\textsubscript{8}-BTBT via drop-casting. This was done by sandwiching the ink droplet between two substrates, with one modified with a hydrophobic SAM and the other modified with polymer pillars to act as nucleation cites for C\textsubscript{8}-BTBT crystals. SC films yielded a carrier mobility of 5 cm\textsuperscript{2}/Vs.\textsuperscript{113} Similarly, Bao et al. adopted this pinned ink droplet method to grow single crystals of fullerene C\textsubscript{60}, a n-type OSC.\textsuperscript{114} An electron mobility >10 cm\textsuperscript{2}/Vs was achieved in some of the SC devices.
Figure 2.23 (a) Schematic representations of the single crystal growth method used for C60 (b) Single crystal growth of C8-BTBT on tilted substrate (c) Inkjet-printed single crystals of C8-BTBT on pre-patterned substrates

The solubility of OSCs and its temperature-dependence are key handles on crystallization, with lower solubility at room temperature than at elevated temperature. By dissolving near the saturation point at higher temperature and cooling the ink below the super-saturation limit results in the nucleation and growth of OSC crystals. Similarly, temperature variations on a substrate can be used to preferentially seed nucleation at a particular location. SCs of
rubrene have been manufactured by this approach using different solvents to achieve the common triclinic and orthorhombic polymorphs.\textsuperscript{115,116}

The anti-solvent method of manufacturing SCs typically involves the use of two more solvents, either separately or in a mixture. TIPS-pentacene SCs can be grown by a solvent exchange method, which involves the transfer of OSC molecules into an orthogonal (non) solvent from a good solvent.\textsuperscript{117} The strong interactions between OSC molecules in an orthogonal solvent can lead to the precipitation of the OSC forming high-quality single crystals.\textsuperscript{118}

Solvent vapor annealing has also been used to grow SCs.\textsuperscript{119} This involves the use of saturated solvent vapors, either a good or a bad solvent. This is allowed to partially dissolve the OSC molecules to allow their reorganization and crystallization into superior ordered crystals. Tsukagoshi et al. utilized this scheme to grow single crystals on an insulating polymer, which is an important feat given the tendency of polymers to dissolve or swell in the presence of a solvent vapor.\textsuperscript{120,121}

Substrate pre-patterning to create alternating wetting and non-wetting areas on the substrate is another common method for single crystal fabrication.\textsuperscript{122} The non-wetting regions/trenches are formed using a hydrophobic SAM or polymer, such as OTS and CYTOP, respectively. In 2006, Bao et al. successfully demonstrated the fabrication of single crystals of pentacene, rubrene, and C\textsubscript{60} via vapor deposition.\textsuperscript{123} The substrate patterning idea was later on used by several groups to grow OSC single crystals from solution. For instance, Tsukagoshi et al. used patterned substrates to spin coat C8-BTBT using the high boiling point solvent anisole. Tiny droplets of ink were confined to wettable
regions which solidified upon drying. The patterned substrates were subsequently exposed to a solvent vapor to locally recrystallize the material into needle-shaped single crystals.

Minemawari et al. used a dual approach combining anti-solvent crystallization and substrate patterning methods to grow C8-BTBT SCs. The hydrophilic trenches were filled with anti-solvent followed by the OSC ink by inkjet printing. Small crystal seeds formed at the liquid-liquid solvent/anti-solvent interface, growing laterally into the asymmetric well with a pre-determined orientation. The random nucleation was avoided by designing patterns that have hydrophilic trenches with the higher surface to volume ratios of OSC ink droplets. This design resulted in higher solvent evaporation rates on one side of an ink droplet in the wettable region, leading to seeds of OSC which causes the further growth to the other end of the ink droplet. SCs obtained by this method have shown field-effect mobilities in the range of 5-31 cm²/Vs. Though this approach has produced the highest reported mobility in C8-BTBT, it is hard to control the quality of SCs, resulting in a large spread in device performance.

While single crystals are the best performing semiconductors, none of the schemes mentioned above have yielded high throughput manufacturing, easy device fabrication and integration, let alone high yield and reproducible device performance. Efforts have been made to address these challenges, for instance, by combining substrate patterning, with a roll-to-roll compatible solution printing technique by Bao et al. A silicon wafer was patterned with micrometer-sized pillars and used as a blade to spread the ink. The pillars enhanced the flow rate of the OSC ink in a way to improve the mass transport of OSC
molecules laterally. A triangular wetting pattern was also designed to emulate the coffee ring effect locally by pinning the contact line of the moving meniscus and thus guiding the growth of the OSC crystalline domains. TIPS-pentacene single crystalline domains were thus fabricated using this approach, yielding a field-effect mobility of 11 cm²/Vs. This demonstration is a positive step towards the fabrication of high-performance OSC single crystals by roll-to-roll compatible methods.

### 2.4.3 Controlling the crystallization by Nucleating agents

OSC crystallization can also be controlled using processing aids such as nucleating agents which can modulate the crystallization kinetics to offer desired control over nucleation density, grain size, and even polymorphs selection thus excellent control over OSC thin film morphology for better charge transport properties. Historically, these agents have been used to modify the crystallite size and shapes in crystalline polymers. Treat N. et al. used two commercially available electrically insulating nucleating agents; DMDBS and BTA to serve as nucleating sites promoting heterogeneous nucleation of OSC. It's hard to get uniform coverage of OSC thin films by ink jet printing due to poor control over a solution to the liquid phase transformation process. The crystallization kinetics were modulated during inkjet printing of TIPS-pentacene ink blended with nucleating agents to achieve continuous and uniform thin films without disturbing the solid-state crystal packing of TIPS-pentacene. This strategy resulted in 100% yield of working OFETs as compared to 0-40% yield (dependent on channel lengths) of devices without nucleating agents. This approach offered better control over thin film morphology, crystallite size distribution thus making the crystallization of OSC less dependent on other factors such as substrate treatment with SAMs and solvent evaporation rates, etc. But the TFT field effect mobility
was found to be $10^{-2}$ cm$^2$/Vs, much lower than the previously reported mobilities for TIPS-pentacene thin films. The lower mobility in these high yield devices can be attributed to the anisotropic nature of charge transport associated to this OSC in randomly distributed small crystallites with massive grain boundaries density. Similarly, Lee S. et al. used OSC as nucleating agents in controlled amounts to modulate the crystallization rate, nucleation density and crystallite size to achieve uniformly distributed crystallites on large areas.$^{129}$ They employed up to 2% diF-TES-ADT as nucleating agents in the TES-ADT matrix. Crystallization time was found to be 25 times faster than the reference samples (without nucleating additives). Higher nucleation density and smaller crystallites had a higher density of grain boundaries which serve as trapping sites for moving hoping charge carriers, leading to an order of magnitude lower charge carrier mobility. The solubility in a primary solvent, crystalize-ability (driving force to solidify) and chemical structure of OSC serving as nucleating agent affected the crystallization kinetics. For instance, nucleating agents with dissimilar chemical structures and having poor solubility resulted in small crystallites (higher nucleation density).$^{130}$ Highly conductive dopants have also been used to promote heterogeneous nucleation resulting in improved structural order, crystallinity, grain boundary connectivity and coverage on the substrate. These factors facilitated 30 times enhancement in carrier mobility of an n-type OSC.

2.4.4 Controlling the crystallization by Solvent additives

The high boiling solvents are often added to the low boiling point solvent matrix as additives. This is a well-known approach in the organic photovoltaic community to enhance the solar cell performance based on small molecules or polymers additives.$^{131,132}$ The strategy has been used to show that tiny amounts of solvent additives facilitate the
growth of well-ordered domains eliminating the need for post-processing steps such as thermal or solvent annealing. These high boiling solvent additives get trapped in the solid-state film for a longer time to provide sufficient energy to the molecules to adjust the structural order. The most significant processing factor related to the usage of a particular additive is the concentration and aging time to achieve improved crystalline order in OSC thin films. Chae G. et al. used CN and DPE to slow down the solvent evaporation rate, facilitating self-assembly of OSC molecules into well-ordered needle-like crystallites with enhanced crystallinity as confirmed by XRD and UV-Vis spectroscopy. Similar methodologies have been adopted by other groups to improve the thin film quality of polymer thin films for better charge transport properties. The coffee ring effect is a well-known problem occurring during drop casting or similar solution crystallization techniques such as inkjet printing. Coffee ring effect happens due to convective flow of OSC molecules towards the periphery of the droplet (contact line), and this flow can be changed by inducing Marangoni flow. This kind of fluid flow happens due to surface tension profile in the solution droplet and flow proceeds towards high surface areas within the droplet. Cho. et al. used this concept to improve crystalline quality and film uniformity of TIPS-pentacene inkjet-printed thin film. High boiling point solvent additive (Dodecane) in parent matrix solvent (Chlorobenzene) reduced the coffee ring effect due to enhanced OSC molecule flow away from contact line (inward Marongoni flow). The resulting thin films showed two orders of magnitude enhancement in carrier mobility.
2.4.5 Controlling the crystallization by post processing

The solution printing processes involving high deposition rates (several hundred nm\(^{-1}\)) often produce kinetically trapped OSC films which may limit the charge transport properties in OFETs.\(^\text{139}\) The vapors of annealing solvent interact with the surface of the thin film and may diffuse depending upon surface topography and solubility. The solvent molecules weaken the intermolecular interactions, facilitating the movement of OSC molecules to achieve thermodynamic equilibrium. If the annealing solvent has a strong affinity towards OSC molecules, de-wetting takes place resulting from condensation of solvent vapors on the film’s surface and subsequent dissolution of the film.\(^\text{140}\) Similarly, SVA time duration severely affects the morphology of thin films.\(^\text{141}\) Khan H. et al. demonstrated the use of QCM-D to identify the processing conditions necessary for achieving optimized thin film quality in terms of surface coverage, grain boundary quality, connectivity and charge carrier mobility of these films in TFTs.\(^\text{142}\) A molecular vapor annealing regime was suggested to exist during the first half minute of the exposure. During this regime, solvent molecules are only present at the surface and in bulk but do not soften the OSC film. After the 30s, the film starts to take up more solvent molecules (detected by QCMD), leading to softening of the thin film. AFM imaging showed that the 30s exposure of solvent vapors transformed the as cast dendrite-like crystals to uniformly distributed crystals of TIPS-pentacene forming a continuous thin film. The longer solvent exposures lead to reduced thin film coverage due to dewetting of thin films with the formation of laterally larger but isolated crystals of OSC on the substrate surface. In situ X-Ray scattering revealed a plateau in the (001) Bragg diffraction, suggesting that softening detected by QCMD is linked to a liquid state on the thin film surface. The carrier mobility
of vapor annealed TIPS-pentacene thin film in molecular regime improved by order of magnitude as compared to as cast films.

Uyeda N. et al. discovered that solvent vapors of alcohol could transform zinc phthalocyanine (ZnPc) to thermodynamically stable β-form from an amorphous form. In 2005, Dickey et al. used this concept to grow large spherulites of TES-ADT from its optically amorphous disordered form. It was found that dichloroethane is the best solvent to facilitate spherulites growth from the disordered state after testing various polar and non-polar solvents. SVA of TES-ADT improved the crystalline order (XRD crystallinity) in thin films leading to enhanced charge carrier mobility from $10^{-3}$ to $10^{-1}$ cm$^2$/Vs. Later on Lee. S demonstrated that SVA could also be used to grow TES-ADT spherulites on patterned substrates in desired shapes along predesigned pathways. They modified the surface energy of substrate to modulate the crystallization kinetics by three times during SVA to control the crystallite sizes. TES-ADT crystallizes into spherulites which have molecules distributed in all direction along the radius in a symmetric fashion, resulting in massive orientation distribution. It would lead to grain boundaries with low ($<20^\circ$) and high angles ($>20^\circ$). Lee SS. et al. found that solvent vapor crystallizes TES-ADT into multiple spherulites on substrates which do not have large crevices in between two spherulites impingement point (grain boundaries). This finding is in contrast to what has been observed for thermally deposited thin films of OSC, possessing massive crevices at grain boundaries. The overall charge transport properties of these films can be improved by avoiding the high angle grain boundaries, guiding the growth of crystals along such pathways that will have low angles of molecular orientation mismatch. Recently, Yu. L et al. also used solvent vapor annealing to directionally crystallize TES-ADT thin films into
high mobility $\alpha$-phase from $\gamma$-phase. After deposition of the TES-ADT thin film, it was locked in $\gamma$-phase by thermal annealing at 100°C. The sharp height contrast was created at desired locations (near the device channels) to allow vapors to mobilize the OSC molecules from thicker parts of scratched films. These areas served as seeds for the further growth of crystallites along the same direction. This approach resulted in low device to device performance spread and overall improved average charge carrier mobility of 1 cm$^2$/Vs. Similarly, Kim K. et al. laterally confined TES-ADT thin films on substrates. The as cast films were placed in contact with PDMS patterned stamp (soaked in DCE vapors). In 10 minutes, the growth of TES-ADT domains ($\alpha$-phase) took place, with the help of vapors present in the confined space between PDMS grooves. These films of TES-ADT showed record carrier mobility in the range of 2.5-3.0 cm$^2$/Vs reported for this OSC. GIWAXS patterns revealed the highly aligned molecular texture of TES-ADT both in and out of the plane.

Figure 2.24 Schematic representing PDMS assisted solvent vapor annealing of TES-ADT
2.4.6 Controlling the crystallization by fluid flow

Solution printing of OSCs by cost effective and roll-to-roll compatible methods is a key industrial requirement. There are two basic types of large area roll-to-roll compatible meniscus guided techniques, known as self-metered and pre-metered. Blade, knife, wire bar and drag and dip coating all fall into the self-metered category.\textsuperscript{118,149–151} On the other hand, slot-die, zone casting, hollow pen writing, curtain and slide coating, are pre-metered coating techniques. In pre-metered coating techniques, the amount of coating ink is pre-decided depending upon desired film thickness.\textsuperscript{150} While in self-metered techniques film thickness is controlled by the coating speed. The thin-film formation or ink solidification via meniscus guided techniques is very different from other coating processes such as the drop or spin coating. Solvent evaporation leads to the convective assembly of the OSC molecules.\textsuperscript{152} There are two regimes (Evaporation (low speed) and Landau-Levich regime (high-speed)) that arise due to differences in viscous forces at different speeds.\textsuperscript{153–155} In the evaporation regime, the convective assembly of molecules is influenced by capillary flow due to solvent evaporation, similar to the coffee ring effect often observed during solution crystallization in drop casting. The evaporation leads to the supersaturated solution (meniscus), leading to crystallization near the contact line of the moving meniscus.\textsuperscript{156} Giri et al. used this concept to grow highly aligned needle like crystals of TIPS-pentacene by solution printing via blade coating. The solution crystallization in Landau-Levich regime produced spherulites like isotropic crystallites.\textsuperscript{63} The highly aligned crystals showed mobility of 1.5–4.6 cm\textsuperscript{2}/Vs outperforming randomly oriented spherulites having field effect mobility of 0.5-1.5 cm\textsuperscript{2}/Vs. Later on, Diao Y. et al. used a modified blade with micro-pillars to further improve the alignment of TIPS-pentacene crystals in evaporation
regime, resulting in record carrier mobility of 8-11 cm²/Vs. Becerril H. et al. sandwiched the OSC ink between two preheated silicon wafers moving relative to each other at a certain velocity. The bottom wafer was used to coat continuous OSC film while the top wafer was modified with hydrophobic SAM for forced OSC de-wetting from the top wafer. Careful optimization of crystallization process involving ink concentration, type of solvent, coating speed and temperature of wafers led to continuous OSC thin films with desired thicknesses in the range of 20-50 nm on large substrates. This study paved the way to use this simple and large area compatible process for the crystallization of a variety of OSCs for improved charge transport in OSC thin films.

In dip coating, the substrate is immersed in OSC ink bath and then slowly withdrawn. Wu. Kuniie et al. investigated the relationship between thin film quality of various OSCs (TIPS-pentacene, C8-BTBT, C60) and processing parameters such as speed, solvent, and concentration. The balance amongst nucleation rate, molecular assembly to the seeds and withdrawal rate was found to be crucial in achieving continuous thin films of OSCs. The nucleation rate, substrate drawing rate (recession) and molecular assembly (growth of crystallites) are controlled by the boiling point of the solvent, coating speed, and OSC ink concentration. Small OSC concentrations near solubility saturation points or addition of an orthogonal solvent in the primary OSC solution matrix can improve the balance between nucleation and recession rates eventually improving the thin film quality. The C8-BTBT and TIPS-pentacene needle like crystallites showed field effect mobility of 1.7 cm²/Vs and 0.1 cm²/Vs respectively. Similarly, this method has been used by other groups to fabricate highly aligned ribbon like crystals of various OSCs by OSC crystallization on patterned substrates. At slow pulling speeds (2-5 µm/s) after optimization of solvent and ink
concentration, directional crystallization of U-BBTT-8 (a thiophene U shaped derivative)\textsuperscript{160} and a new n-type derivative of pentacene family (TIPS-TAP)\textsuperscript{161} resulted in highly aligned ribbon like crystals with carrier mobilities of 3.8 cm\textsuperscript{2}/Vs, and > 10 cm\textsuperscript{2}/Vs. AFM imaging revealed the step and terrace like topography. Unfortunately, the charge transport in these films is highly anisotropic (100 times in perpendicular direction to the growth direction) due to the molecular packing of OSC. To the best of my knowledge, dip coating at higher pulling speeds has not yielded any continuous thin film based on small molecular OSCs, limiting its applicability for industrial coating of organic electronics. It also involves massive usage of expensive OSC inks which also hinder its integration.

The pre-metered meniscus guided techniques such as zone casting, hollow pen-writing or slot die coating require the flow of OSC ink through a supply area (slot/nozzle or a capillary) onto the moving substrate.\textsuperscript{162,163} The OSC crystallization and eventually thin film quality are affected by processing parameters such as the temperature of the supply zone, OSC ink concentration (viscosity), substrate speed and temperature along with wettability of OSC ink on to the substrate.\textsuperscript{164} The industry has adopted this method for solution printing of solar cells and OLEDs.\textsuperscript{165–167} Recently, efforts have been made to demonstrate successful control of OSC crystallization in pre-metered coating techniques. For example, Chang J. et al. showed that optimized solvent mixture ratios (toluene and anisole (orthogonal solvent)) and coating speed (low speed, 0.4 mm/s) is critical to growing millimeter-length ribbon-like well-connected uniform crystals of TIPS-pentacene with carrier mobility of 1.7 cm\textsuperscript{2}/Vs.\textsuperscript{151} Recently, Wan J. et al. also used slot die coating technique with optimized processing parameters (concentration and temperature) to
solution print C8-BTBT thin films with carrier mobility of 3 cm²/Vs at high speeds (25 mm/s) in Landau-Levich regime.  

2.4.7 Tuning the Polymorphism by solution crystallization

As discussed in section 2.1, charge transport in OSCs is strongly dependent on π-π stacking. Thus any change in molecular orbital overlap’s nature can influence charge transport properties of OSCs in solid-state films. OSCs have very weak van der Waals molecular interactions, allowing these material systems to undergo polymorphism (molecular packing habits) at ambient conditions. McCrone\textsuperscript{168} said, “Every compound has different polymorphic forms and that, in general, the number of forms known for each compound is proportional to the time and money spent in research on that compound.” It is evident from the number of publications increased by three-fold as compared to mid-90s, suggesting the importance of polymorphic materials.\textsuperscript{169}

Polymorphism excludes the need of crystal engineering (which requires chemical modifications to the OSC molecular structure) to understand the fundamental relationship between molecular packing and charge transport characteristics. Crystal packing directly influences the mobility of OSCs in thin films.\textsuperscript{63,69} Charge transport in OFETs happens within few monolayers at OSC: insulator interface. At this interface, it is widely reported that molecular assembly, orientation, packing can be different from the bulk of the OSC thin film.\textsuperscript{170,171} It is of prime importance to determine the crystal structure of thin films at OSC: dielectric interface for understanding the charge transport properties of thin films. Raman spectroscopy, X-Ray scattering, and theoretical modeling are often used to determine this information. To date, it is complicated to control the formation of individual polymorph in pure form at desired interface.
The choice of solvent to influence the solution crystallization process can be used to obtain selective polymorphs. For instance, Matsukawa T. et al. reported the growth of Rubrene single crystals in its two different crystal structures namely monoclinic and orthorhombic. They used polar solvent aniline (1.5 D) to grow orthorhombic form having better pi-pi orbital overlap. On the other hand, the single crystal growth from p-xylene (0.0 D) resulted in a triclinic form which lacks pi-pi stacking due to slippage of tetracene backbone. The orthorhombic Rubrene crystals showed charge carrier mobility of 1.6 cm²/Vs as compared to 0.1 cm²/Vs (triclinic crystal phase). TES-ADT exhibited two different polymorphs depending upon the polarity of the solvent. It was found that strongly polar solvent (THF, 1.75 D) promotes the growth of triclinic bulk phase while weakly polar solvent (Toluene, 0.3 D) induces the growth of α-polymorph). This α-polymorph is necessary for high-performance OFETs based on TES-ADT. Apart from dipole moment, Li R. et al. found that solvent molar volume can also be as an effective handle to tune the polymorphism in TIPS-pentacene thin films during solution crystallization in blade coating. The molecular simulation showed that OSC unit cell loses its configurational stability in the case of a large molar volume of the solvent. Solvents with higher molar volumes such as Decalin (molar volume, 256 Å³) resulted in the greater displacement of crystal packing from the equilibrium packing.

The crystal packing can be tuned by using appropriate solution printing process. Giri et al. used a solution shearing method to crystallize TIPS-pentacene with strained crystal packing than its equilibrium. This nonequilibrium crystal packing in thin films resulted in OFETs with carrier mobility of 11 cm²/Vs compared to 2 cm²/Vs in regular thin films by the same coating method. This strategy offers a very efficient approach to enhance the
carrier mobility of OSC thin films. Similarly, Yuan Y. et al. used off center spin coating to obtain meta-stable polymorphs of C8-BTBT.\textsuperscript{67} GIWAXS revealed the closed in-plane molecular packing for the metastable C8-BTBT polymorph, resulting in record carrier mobility of 43 cm\textsuperscript{2}/Vs as compared to equilibrium polymorph (5 cm\textsuperscript{2}/Vs).

\textbf{2.4.8 Controlling the crystallization by Substrate functionalization}

Self-assembled monolayers (SAMs) are also used to modulate the crystallization of OSCs. SAMs possess two-dimensional order after spontaneous formation. SAMs of thiols (sulfur-containing molecules) and silanes are extensively used to modify the physical or chemical nature of bottom electrodes (gold, silver, etc.) and gate dielectrics (SiO\textsubscript{2}) in OFETs respectively.\textsuperscript{174,175} The quality of SAMs effects the OSC crystallization on the electrode or dielectric surfaces. OTS, PTS, and HMDS are few of the typical SAMs used to modify the SiO\textsubscript{2} surface for OFETs.\textsuperscript{176} These SAMs not only passivate the gate dielectrics but also affects the solid-state morphology of OSCs both in vacuum deposited and solution printed thin films. Vacuum deposited films of pentacene and C60 on OTS modified SiO\textsubscript{2} show 2D layer by layer growth as compared to 3D growth on unmodified dielectric surfaces.\textsuperscript{177} The 2D growth behavior hinders the formation of grain boundaries usually observed in 3D growth, thus leading to improved charge carrier mobility. The role of these SAMs has been studied extensively for solution crystallization of OSCs. OTS is often used to create non-wetting regions (lower surface energy) to promote dimensional domain growth of OSCs during blading or to confine OSC ink in trenches for single crystal growth of OSCs. The modification of SiO\textsubscript{2} with HMDS or OTS was found necessary to grow micrometer-sized single crystals of DB-TTF having the mobility of 3.6 cm\textsuperscript{2}/Vs as compared to regular thin film mobility of 0.6 cm\textsuperscript{2}/Vs.\textsuperscript{178} There are also other SAMs such as Z-cat-Ben-F which are
used to increase the surface energy (reduced water contact angle, <10°) of SiO₂ for better
growth of polymer films resulting 1-2 order of magnitude increase in carrier mobility.\textsuperscript{179}
The modification of electrodes with SAMs is very often used to tune the energetics of OSC:
electrode interface for better charge carrier injection. Now, it is a well-established fact that
electrode modification can also influence the crystallization process of OSC.\textsuperscript{72,180,181} It was
found that Au-electrodes treated with PFBT induce the growth of small crystallites towards
the center of OTFT channel.\textsuperscript{180,182} The carrier mobility decreases by an order of magnitude
as soon as channel length becomes higher than > 50µm. This contact driven growth was
found to be necessary for spin coated OSC thin films of diF-TES-ADT and TIPS-
pentacene.\textsuperscript{183} Li R. et al. used µGIWAXS to map the thin film texture inside the channel
of OFETs with different channel lengths.\textsuperscript{184} It was found that PFBT treatment promotes
the <001> edge-on (stronger pi-pi overlap, high mobility) textured crystallites of diF-TES-
ADT and these crystallites can only bridge the device channels up to 50µm. For long
channels, central areas consisted of small randomly oriented <111> face-on (stronger pi-pi
overlap, high mobility) textured crystallites, resulting in decreased OTFT mobility.

\subsection{2.4.9 Controlling the crystallization of Small molecule OSCs by polymer blends}

Small molecular OSCs have weak van der Waals molecular interactions which cannot
induce long-range order, and solid-state thin films are often polycrystalline. Polycrystallinity brings density of multiple grains which induce grain
boundaries, limiting the charge transport properties of OSCs. An easy way to improve thin
film quality is to use processing aids with the ability to form uniform thin films having
better mechanical properties than small molecular OSCs such as polymers. This blending
approach has been extensively used by OPV and OLED community to improve charge
separation, charge collection or light emission, etc.\textsuperscript{185,186} De-wetting of small molecule is often observed during fast solution processing which can be mitigated by introducing polymer as processing aid to achieve uniform thin films over large areas. OTFT community has also made efforts to improve device figure of merits. As conduction occurs at the OSC: dielectric interface, phase separation between OSC and polymers plays a decisive role in the resulting device performance. Phase separation in blended systems can be controlled by nucleation and growth (crystallization) or spinodal decomposition.\textsuperscript{187} Phase separation depends upon ink concentration, OSC: polymer blend ratios, miscibility of OSC and polymer, solution viscosity, the molecular weight of the polymer, choice of solvent (boiling points), processing temperature, and nature of substrate (wetting properties) and solubility of both components in solvent and thin film coating method. Poor control over phase separation can result in undesired microstructure and composition at OSC: dielectric interface, leading to poor device performance, eventually undermining the processing advantageous achieved from processing aids. Depending upon the architecture of OFETs (bottom gate or top gate), segregation of small molecular OSC at top air interface or bottom substrate interface is crucial.

Two types of amorphous polymers have been blended with small molecular OSCs; 1) semiconducting polymers and 2) insulating polymers. In past decade or so, this strategy has been successfully employed to tune the OSC’s thin film quality (morphology, lamellar crystallinity, preferable polymorph, etc.) using optimized conditions. These conditions include different blend ratios, concentrations, coating temperatures, solvents and solvent mixtures, post treatments (both thermal and solvent vapor annealing), hydrophobicity of polymers, as well as different molecular weights of the polymer binder.\textsuperscript{188–197} In the first
case, the small molecular OSC ensures high mobility, while the polymer binder facilitates solution printing and microstructure control. Hamilton et al. spin coated OSC: semiconducting polymer blends (diF-TES-ADT with PTAA or PFTAA) with TGB devices resulting in maximum mobility up to 5.6 cm²V⁻¹s⁻¹. This strategy bridged the gap between single crystal (6 cm²V⁻¹s⁻¹) and diF-TES-ADT thin film based FETs. TEM revealed vertically phase separated layers with OSC segregated at the air interface. Superior in-plane lamellar quality and smoother topographic features, and excellent carrier mobility of PFTAA binder were critical to achieving high performance than diF-TES-ADT: PTAA systems. The optimized blend ratio (> 50% OSC) and use of a high boiling solvent (Tetralin) allowed sufficient time for phase separation were vital to achieving desired vertical phase separation, thin film quality, and high carrier mobility. These blends films are polycrystalline and can have varying sized grains. Charge carrier mobility in these systems was found to be independent of morphological feature size/grain size. Hunter et al. used conducting AFM to investigate the effect of grain size on device performance in these blends (semiconducting polymer binder). Conducting AFM revealed that grain boundaries in blended thin films were highly conductive as compared to those present in neat diF-TES-ADT thin films. The high conductivity of these grain boundaries was associated with the presence of binder semiconducting polymer at grain boundaries, making charge transport independent of thin-film morphology in these systems. These blend systems historically involved top gate bottom contact architectures, limiting their utility with other device designs and processing methods. Recently, Zhao K. et al. reported that only processing conditions such as spin speed could be used to change the vertical stratification in blends. High mismatch in physicochemical parameters (OSC
polymer interaction parameter and different Hansen solubility parameters) lead to immiscibility and serve as driving force behind vertical phase separation. The lower spin speed reduces the preferential loss of OSC diF-TES-ADT to maintain the overall small molecule polymer blend ratio in solution, promoting the tri-layer vertical phase separation (small molecule solidified at the bottom substrate and air interfaces, sandwiched between PTAA middle layer). The bottom buried diF-TES-ADT layer was used to fabricate top contact bottom gate devices with carrier mobility as high as 2.1 cm²/Vs.

The insulating polymers are also used as binder polymers with small molecular OSC in OFETs. The insulating polymers have their own advantages and disadvantages except being processing aid similar to semiconducting polymers. It is a well-known fact that OSCs performance is strongly influenced by the environment such as moisture and O₂, requiring a passivation layer. This passivation layer is of prime importance in bottom gate devices in contrast to the top gate where the top dielectrics such PMMA, PS or CYTOP automatically serve as protection to active layers of OSCs. It’s also essential to control the composition of phase separated layers as the formation of mixed OSC: polymer interface can lead to charge trapping, hindering the charge carrier mobility. Any non-phase separated insulating polymer from OSC, mixed within domains or grains of small molecular OSC can also limit the carrier mobility.

Many research groups have used inert polymer binders such as PMMA, PS, PaMS to blend with small molecular OSCs such as Rubrene, TIPS-pentacene, DBTTF, diF-TES-ADT, TES-ADT, and C8-BTBT, etc. These efforts involved a variety of solution printing methods such as drop casting, spin coating, off-center spin coating, wire bar coating. Often post processing methods such as solvent vapor annealing and thermal annealing have also
been used to improve thin film quality by enhancing the degree of phase separation due to crystallization of small molecular OSC from the kinetically trapped amorphous state. For instance, solvent vapor annealing improved the vertical phase separation profile (seen by SIMS) in TES-ADT: PMMA spin coated blend layer.\textsuperscript{206} The OSC crystallization drives phase separation leading to the formation of the high-quality TES-ADT layer at air interface having improved charge carrier mobility compared to as cast blend thin films.

The following crucial rules can control crystallization of small molecular OSCs from blend solutions deduced from the majority of the work published on small molecular OSC: polymer blends for OFETs. The most important thing is to choose the right type of polymer based on its dielectric constant, molecular weight and its degree of crystallinity. All the polymers used as binders to date are low dielectric polymers. Phase separated insulating binder polymer acts as a dielectric and conduction occurs at this phase separated OSC: polymer interface. Veres J. et al. compared low and high \textit{k} dielectric polymers as gate insulators.\textsuperscript{207} They found that high-\textit{k} binder polymer made active interface strongly polar, broadening the density of states with more trap states. Charge carriers faced a higher potential barrier to hope, thus reducing the carrier mobility by order of magnitude.

Secondly, the high molecular weight of binder polymers along with larger Flor-Huggins interaction parameter will result in positive Gibbs free energy (\(\Delta G_m\)). Higher molecular weight of polymer reduces the entropy (\(\Delta S_m\)) while the interaction parameter (\(\chi\)) effects change in enthalpy (\(\Delta H_m\)). Kang J et al. demonstrated that higher molecular weight of PaMS resulted in stronger vertical phase separation with better quality crystals as compared to low molecular weight PaMS blend with TIPS-pentacene.\textsuperscript{208} The resulting drop cast thin films based on high molecular weight binder showed carrier mobility as high as
0.54 cm$^2$/Vs. Similarly, the smaller solubility parameter of PiBuMA than PaMS resulted in lower values of $\Delta H_m$, leading to homogeneously mixed blend film of PiBuMA: TIPS-pentacene blend as compared to PaMS: TIPS-pentacene blend films with bilayer phase separation.$^{209}$ Furthermore, Cho Y. et al. inkjet-printed TIPS-pentacene blended with APC and PS. OFETs based on APC blends showed higher mobility of 0.53 cm$^2$/Vs as compared to 0.1 cm$^2$/Vs of PS based blends.$^{190}$ Significantly larger interaction parameter of APC (1.5) as compared to 0.8 of PS resulted in better vertical phase separation (SIMS profile) along with better crystal quality.

Thirdly, the degree of crystallinity can also modulate the crystallization and vertical phase separation in small molecular OSC polymer blends. Madec et al. found that using a semi-crystalline binder polymer such as isotactic polystyrene (iPS) leads to trilayer phase separated film with TIPS-pentacene segregated to bottom and top interfaces.$^{210}$ This kind of phase separation is driven by the faster crystallization of TIPS-pentacene as compared to iPS and the enthalpic interactions due to polymer’s crystallization serve as the driving force behind trilayer phase separation.$^{211,212}$ But the use of semicrystalline polymers is more complicated as compared to amorphous binders, requiring more careful selection of binder ratio, solvent, and processing conditions. For instance, Shin N. et al. found that diF-TES-ADT: PaMS films (amorphous binder) showed carrier mobility of $10^{-1}$ cm$^2$/Vs as compared to $10^{-4}$ cm$^2$/Vs blend films with syndiotactic polystyrene (s-PS, crystalline binder).$^{213}$ It was found that s-PS blends did not have any continuous phase separated layer of diF-TES-ADT. The fast solidification kinetic conditions during spin coating of these blends render the crystallization of small molecular OSC due to competing crystallization of binder polymers. The OSC molecules cannot diffuse through the bulk to segregate at an
interface, becoming kinetically trapped due to gelation of the crystalline polymer during solidification. Recently, Galindo et al. used low molecular weight polystyrene to blend with DBTTF.\textsuperscript{214} Optimized blend films showed vertically bilayer phase separated thin films with DBTTF crystallized on air interface without post processing (which is often required for low molecular weight binder to induce phase separation).\textsuperscript{215} These blend films are wire bar coated on a heated substrate (105\textdegree C) from a heated chlorobenzene blend solution. This exception points out that processing method also plays a crucial role in the thin film quality and phase separation profiles due to different kinetic nature. Further investigations are underway by the same group using a range of molecular weights to understand the above results.

The ability of binder polymer (due to its chemical structure) to interact with substrate surface can also influence crystallization of small molecular OSCs. Multiple reports show that OSCs blended with PMMA outperform other amorphous polymers. PMMA has a carbonyl functional group which has strong tendency to interact with silanol groups of Si/SiO\textsubscript{2} substrates. Lee et al. found that using high boiling point solvent (Trichlorobenzene, 214\textdegree C) along with high molecular weight PMMA can improve the carrier mobility of diF-TES-ADT: PMMA blends to 0.1 cm\textsuperscript{2}/Vs as compared to 10\textsuperscript{-3} cm\textsuperscript{2}/Vs from neat diF-TES-ADT spin-coated films from low boiling solvent (Toluene, 110\textdegree C).\textsuperscript{216} The OSC formed continuous well-connected plate-like crystallites due to strong film forming properties of PMMA. The high-performance blend films had higher crystalline order, better vertical phase separation along with the only edge on <001> crystallites. Slow evaporation of TCB avoided the kinetic trapping of diF-TES-ADT into the undesired face-on <111> textured crystallites during spin coating. There is also a solvent mixture approach used to control
the crystallization, phase separation in small molecular OSCs: polymer blends.\textsuperscript{217} The high boiling point solvents are selected with differential solubilities for both components. For instance, Lada M. et al. investigated a series of solvent mixtures and found that a combination of mesitylene and anisole based ink resulted in well-connected plate-like crystallites of TIPS-pentacene blended with polystyrene. Hansen solubility parameters of mesitylene suggest better dissolution of TIPS-pentacene while anisole is a good solvent for polystyrene as compared to mesitylene. TIPS-pentacene: PS films showed carrier mobility of $1.5 \text{ cm}^2/\text{Vs}$ compared $0.5 \text{ cm}^2/\text{Vs}$ from other solvent mixtures with a non-optimized combination of solubility parameters or solvent ratios.

### 2.5 In situ investigations to understand crystallization

The discussion in above sections suggests that the functional properties of the small molecular OSCs in the solid-state thin film, strongly depend upon the thin film quality (grain boundaries, etc.) and microstructure (short and long-range order). The effective control over the microstructure development during solution printing is linked to the understanding of its real-time evolution.\textsuperscript{218} There are only a handful of reports focused at investigating the crystallization behavior of small molecular OSCs in real time in the context of OFETs. In 2014, for the first time, Chou W. et al. used \textit{in situ} optical reflectometry and grazing incidence wide angle X-Ray scattering to investigate the crystallization of TIPS-pentacene during spin coating.\textsuperscript{219} The former technique revealed that OSC solidification involves a fast quenching step (deposition rate of 100 nm/s), three times faster than drop casing followed by a gradual solidification. GIWAXS showed that the second step is strongly dependent upon spinning speed and controls the resulting carrier mobility. The lower spin rate results in more solvent trapping in the film which allows slow
crystallization of TIPS-pentacene (few seconds) after first quenching step (milliseconds). The slow crystallization during the second step resulted in enhanced carrier mobility of 0.5 cm²/Vs as compared to 10⁻⁴ cm²/Vs via fast crystallization during the second stage. The insights gained from time-resolved measurements provide understanding about the relationship between process and functional performance of the film. Zhao K. et al. followed this work to use in situ UV-Vis absorption measurements to investigate the solidification of diF-TES-ADT: PTAA blends in spin coating. Vibronic progressions of diF-TES-ADT and PTAA were monitored to understand how crystallization and solidification occur in this blended system.²⁰⁵ It revealed that intensity of associated absorption for both components decreases during spin coating due to loss of the ink/material. The peak positions did not change indicating that both components remain in solvated form (no solidification) during spin coating. The ratio of absorption intensities for both components revealed that diF-TES-ADT is preferentially lost during spin coating as compared to PTAA and it increases with increasing spin speed. This increased outflow of diF-TES-ADT resulted in bilayer phase separated blend films. These experiments also revealed that trilayer phase separation observed at low spin speeds was due to minimized outflow during ejection stage of spin coating and maintaining the overall composition of the ink. In situ thickness monitoring revealed that rotating speed affects the evaporation rate, film thickness and ink volume left on the substrate. These factors play a crucial role in morphology development during these liquid-liquid phase separated blend films.

Industrial scale manufacturing of OFETs requires solution printing via roll-to-roll coating processes. In 2012, Giri G. et al. showed that TIPS-pentacene unit cell in the solid-state thin film is strained when solution printed via blade coating. Tips-pentacene has different
polymorph than its equilibrium form, and this polymorph results in carrier mobility of 8-11 cm$^2$/Vs as compared to regular carrier mobility of 1-2 cm$^2$/Vs from equilibrium polymorph. Based on this, Li R. et al. investigated the formation of this meta-stable polymorph using in situ GIWAXS and in situ HSPOM during blade coating. The intensity and position of (011) peak was monitored and it was found that equilibrium polymorph forms first during 0-120 ms followed by the evolution of meta-stable polymorph with shifted in-plane (011) Bragg diffraction. In situ HSPOM revealed that the appearance of the film does not change after the formation of ribbon-like crystallites in 0-120 ms. It suggested that these two different crystal structures are not lying next to each other and could be vertically stacked. Static GIWAXS showed that peak intensity associated to the metastable polymorph increases with increasing grazing incidence angle of X-rays. It suggested that metastable form is buried at the bottom interface. The combination of in-situ and ex-situ measurements reveal that crystallization occurs at liquid air interface during blade coating of OSCs. In this particular case of TIPS-pentacene, the formation of metastable polymorphs occurs due to confinement of OSC solution in one dimension between top thin crust (equilibrium polymorph) and the solid substrate. Recently, Li Y. et al. used a combination of in-situ reflectometry, in-situ HSPOM, and in-situ GIWAXS to investigate the crystallization of TIPS-pentacene during hollow pen writing (a variant of slot die coating). They found that film consists of three distinct regions; meniscus, supersaturated featureless region and crystalline solid film region. Supersaturated region showed large red shift as compared to meniscus suggesting the formation of TIPS-pentacene aggregates. Then these aggregates lead to the crystallization of TIPS-pentacene indicated by the further red shift in absorption spectra. Wan J. et al.
used in situ GIWAXS to investigate the solution printing of C8-BTBT thin films by hollow pen writing.\textsuperscript{68} It was found that coating temperature and thin film thickness plays a significant role in the functional properties of the film. Solution printing at < 60°C did not show the formation of any intermediate metastable crystalline state after solidification of C8-BTBT. In situ GIWAXS demonstrated that coating temperatures > 60°C induce a metastable crystalline state before final stable crystalline state which causes the cracking in thin films of C8-BTBT (observed by HSPOM). It was observed that by optimizing the processing conditions to achieve film thickness < 20nm, resulted in crackles films even at 80°C with the stable crystalline state. In-situ investigation helped to determine the processing window (speed, temperature, concentration, etc.) to achieving carrier mobility of 5 cm\textsuperscript{2}/Vs from C8-BTBT thin films.
Chapter 3

Methodology and general description of the work

In this chapter, firstly, we describe the materials, characterization tools and \textit{in-situ} process diagnostics methodology used to conduct the research in this PhD thesis. The latter tools are crucial to establishing an understanding of how solution-to-solid phase transformation (crystallization) occurs during solution processing of organic semiconductors and how the coating methods, processing conditions, ink formulation, etc. can control the crystallization process, particularly in conditions that yield high-performance OFETs.

3.1 Materials

Several OSCs and polymer binders were used to conduct the research presented throughout this dissertation. All variants of the polystyrene binder were purchased from Alfa-Aesar (Thermo Fisher Scientific) corporation, USA. PaMS and C8-BTBT were acquired from Sigma Aldrich. Prof. Yves Geerts (UCBA, Brussels) shared ditBu-BTBT for this research. Prof. John Anthony (University of Kentucky, USA) provided all the acene derivatives. SAMs for contact modifications were bought from Sigma Aldrich. The structure and names of all materials are shown in Figure 3.1a-d. Silicon substrates (thermal oxide - 300nm) for device fabrication (bottom gate configuration) were purchased from Silicon Quest International (SQI), USA.
Figure 3.1 (a) Acenes from Prof. John Anthony (b) Chemical structures of BTBT derivatives (c) Chemical Structure of insulating binder polymers (d) chemical structure of charge injection self-assembled monolayers
3.2 Ink preparation

All small molecules and binder polymers were dissolved in organic solvents and the recipes corresponding to different coating experiments is given in Table 3.1. Polymer solutions were stirred overnight at 50°C for dissolution. Blend solutions were stirred for 10-15 minutes before use.

Table 3.1 Ink recipes used throughout this thesis

<table>
<thead>
<tr>
<th>System</th>
<th>Materials</th>
<th>Concentration</th>
<th>Blending ratios (OSC: Polymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Solvent</td>
<td>All acenes and their blends</td>
<td>10 mg/ml</td>
<td>(0.95-0.05 to 0.2:0.8)</td>
</tr>
<tr>
<td>(Toluene, Mesitylene, Anisole)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single Solvent</td>
<td>BTBT derivatives</td>
<td>3, 5, 8, 10, 20, 30 mg/ml</td>
<td>Not Applicable</td>
</tr>
<tr>
<td>(Toluene)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dual Solvent</td>
<td>diF-TES-ADT: Polystyrene</td>
<td>10 mg/ml</td>
<td>(0.95-0.05 to 0.2:0.8)</td>
</tr>
<tr>
<td>(Mesitylene: Anisole)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

3.3 Solution processing

We used drop casting, spin coating and blade coating as thin film coating methods. Drop casting involved dropping 30-40 µl of OSC solution on substrate in air at room temperature or elevated temperature. In the case of spin coating experiments, the spinning speed was in the range of 1000-5000 rpm and all films were coated in air. The in-house built blade coating setup is shown in Figure 3.2. Silicon wafer modified with a hydrophobic SAM was used as a blade. The attack angle was set in the range of 15°-20°. The distance between blade edge and substrate was fixed at 100µm throughout this research. The hot plate was used to coat the thin films on substrates at desired temperatures. We used blade coating speed in the range of 0.1-300 mms⁻¹. In the blade coating process, the moving blade spreads the ink on the substrate while bulk-ink is held between the moving blade and the
substrate (meniscus) by capillary forces. Thin film forms with the evaporation of solvent as the blade is translated linearly.

Figure 3. 2 (a) Schematic of blade coating (b) Home built blade coating setup.
3.4 OFETs fabrication and characterization

3.4.1 Substrate cleaning procedure

BGBC and BGTC OFETs were fabricated using Si/SiO₂ substrates while TGB OFETs were made on glass substrates. The cleaning procedure is shown below in Figure 3.3.

Substrates sonicated for 15 minutes using the solvents in the sequence 1-3

1. Acetone
2. 2-Propanol
3. Ethanol

Cleaning in RCA-1 solution
Substrates immersed in this mixture for 30 minutes at 90°C
\[ \text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{DI Water} \]
1 : 1 : 5

Figure 3.3 Substrate cleaning procedure is detailed out

3.4.2 Electrode deposition

Metal electrodes (source, drain, and gate (top gate) were deposited by thermal evaporation (Angstrom thermal evaporator) using shadow masks. Shadow masks were purchased from Ossilla Co. Limited, Sheffield, UK. The device dimensions were as follows:

- Channel width: 500-1000 µm
- Channel length: 30-100 µm

Gold or silver was used as metals. We used Ag as top contact material for BGTC devices.
3.4.3 Contact Modification

Bottom contacts were cleaned with O$_2$-Plasma or charge injection self-assembled monolayers. We used Plasma cleaner PDC 32G with O$_2$ pressure of 600 mHg for 10-12 minutes. SAM solution were prepared in ethanol (20 milimolar solution). Substrates were kept in SAM solution for 10-15 minutes and then washed with ethanol and dried at 150°C for 20 minutes.

3.4.4 Device Characterizations

The device characterization was carried out using Keithley 4200 SCS inside Nitrogen filled Glove box. The transfer and output IV curves were recorded, and figures of merits were determined using the details provided in chapter 2.

3.5 In situ and ex situ characterizations

3.5.1 Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

Time-resolved GIWAXS experiments were carried out in situ to investigate the thin film formation mechanism and crystallization during solution processing and ex situ to determine the structure and texture of OSC thin films in the final state. GIWAXS is a structural characterization method used to interrogate the crystalline structure, polymorphism and texture of polycrystalline films. Synchrotron X-ray sources have high photon flux which enables fast data acquisition with minimal exposure times particularly useful for time-resolved measurements on soft matter samples which do not scatter particularly well. The 2D detectors allow the collection of a 2D diffraction pattern containing both in-plane and out-of-plane structure, as well as crystalline texture (see Figure 3.4). As the refractive index of most materials is below 1 in the hard x-ray range, x-
rays can undergo total external reflection below the critical angle of the material. The refractive index of X-rays is given by the Equation 3.2.

\[ n = 1 - \sigma - i\beta \]  

(3.1)

Where \( \sigma \) and \( \beta \) are X-ray dispersion and absorption contribution. The critical angle can be calculated by following procedure.

We begin with Snell’s law as given in Equation 3.2

\[ \frac{\sin \theta_i}{\sin \theta_o} = \frac{n_1}{n_2} \]  

(3.2)

Where \( n_1 \) and \( n_2 \) correspond to refractive indices in matter and in the medium, respectively. \( \theta_i \) and \( \theta_o \) correspond to incidence and outgoing X-ray angle, respectively.

Total external reflection will take place when \( \theta_o \) becomes 90°, so the Equation 3.2 can be written as Equation 3.3.

\[ \cos \theta_c = n_2 \]  

(3.3)

Where \( n_2 = 1 - \sigma \) and using Taylor expansion of cosine function, the critical angle of total external reflection is given by Equation 3.4.

\[ \theta_c = \sqrt{2\sigma} \]  

(3.4)

For \( \theta_i < \theta_c \), the x-ray beam creates an evanescent wave which can probe the near-surface \( ca. 10 \) nm of the sample, making this technique very strongly surface sensitive. Measurements above the critical angle probe the entire depth of the film.

We performed GIWAXS experiments carried out as part of this thesis at the D1 beam station at the Cornell High Energy Synchrotron Source (CHESS) at Cornell University (Ithaca, NY, USA). The monochromatic X-ray beam used had a wavelength in the range of 0.111-0.115 nm (>10 keV) and had a photon flux of \( 10^{12} \) photons/s mm\(^2\) and a 2D detector from Dectris (Pilatus 100k) was used to collect GIWAXS images. For static
characterization, the grazing incidence angle with respect to the thin film plane was in the range of 0.05 to 0.5°. The X-ray grazing incidence angle was fixed at 0.15° during in situ experiments. It lies between the critical angle for the SiO₂ substrate (0.24°) on which experiments were performed and the typical critical angle for organic thin films (0.13°). The sample to detector distance was in the range of 166 to 190 mm. The measurement integration time was set to 40 ms and 1 s per GIWAXS image for all in situ and ex situ experiments, respectively.

Figure 3. 4 Schematics (a) GIWAXS experimental setup in projection with Ewald sphere (b) Three dimensional view showing the X-ray beam striking the sample at an incidence angle (αi), scattered X-rays at exit angle (αo) detected by 2D areal detector (oriented vertically at a certain distance from sample stage) Note: χ is an angle between q_x and q, 2θ is in-plane scattering angle, Φ is polar angle on the detector plane w.r.t X-ray beam

For in situ measurements, we used capillary optics to focus the x-ray beam to a microspot (15x15 μm²). This is necessary to enable in situ time-resolved measurements for experiments involving a lateral moving meniscus and crystallization front, such as during in situ blade coating experiments, since the true time resolution of the measurement is a
convolution of the integration time and beam size. We also used this µGIWAXS to map the texture of solution-printed thin films inside OTFT channels. The shape and position of 2D diffraction peaks are used to describe the orientation of crystallites in thin films, polymorphs, and texture. The crystallites can have any of the four possible textures as shown in Figure 3.5.

Figure 3.5 (a) Perfect horizontal orientation, Out of plane Bragg diffraction (b) planes oriented both parallel and perpendicular to the substrate (in-plane and out-plane Diffractions) (c) Horizontally distributed crystallographic planes at an angle (d) Randomly oriented crystallites (2D powder)

3.5.2 High Speed polarized optical microscopy (POM)

Spin coating often involves high rotation speeds in the range of 1000-5000 rpm, while blade coating often involves a fast-moving blade and fast solvent evaporation, especially
at elevated temperature. POM images were recorded using a high-speed camera (Photron FASTCAM SA3, Model 120K), capable of 1024 x 1024 pixel resolution at frames rate up to 2000 frames per second (fps) and at reduced resolution up to 120000 fps, to record the OSC film formation under all conditions of blade and spin coating. The camera was coupled to a Nikon LV 100 polarized optical microscope in the configuration shown in Figure 3.6. The built-in microscope stage was removed and replaced with the miniature blade coater placed beneath the objective lens. Objectives with magnifications 5x, 10x and 20x were used.

Figure 3.6 High speed Polarized optical microscopy setup.

3.5.3 In situ spectroscopic ellipsometry

Time-resolved spectroscopic ellipsometry (SE) measurements were carried out during coating processes using an M-2000XI (J. A. Woollam Co., Inc.) operating over the spectral range from 245 – 1700 nm, and angular range of 45°-90°. We performed in situ experiments
at an incidence angle of 70° with respect to the substrate normal (Figure 3.7), using an integration time of 100 ms. A monocrystalline Si substrate with a 300 nm thermal oxide was used for these in situ experiments. The spectra were fitted over the wavelength range of 700-1500 nm using the EASE™ software to extract the thickness of the solution during the coating processing.

The light reflected from sample undergoes amplitude and phase changes. Thus, ellipsometric measurements are normally described by two parameters $\psi$ and $\Delta$ in the following form:

$$p = \frac{R_p}{R_s} = \tan\psi e^{i\Delta}$$  \hspace{1cm} (3.5)

Where,

$R_p =$ the reflection coefficients of the sample for p-polarized light

$R_s =$ the reflection coefficients of the sample for s-polarized light

$\tan(\Psi) =$ amplitude ratio upon reflection

$\Delta =$ the phase shift

The $\tan(\Psi)$ and $\Delta$ are related to optical constants. We used multiplayer optical Cauchy model to determine thickness. The Cauchy relationship is given in Equation 3.6.

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$  \hspace{1cm} (3.6)

Where A, B and C are fitting parameters.
In situ spectra were collected at 70° and its transparent region (800-1700 nm) was used as a fitting region in Cauchy model.

**Figure 3.7** Schematic of an ellipsometry experiment.

### 3.5.4 In situ optical reflectometry

Time resolved optical reflectivity measurements were performed using a Filmetrics F20-UVX instrument. Tungsten and deuterium lamps were used as the white light source. Spectra were collected using a diffraction grating and two different spectrometers, covering the spectral range 350-1800 nm. An integration time of 50-100 ms was used for most experiments. In some instances, optical reflectometry measurements were performed by coupling the spectrometer to an optical microscope, thus allowing to focusing the light spot to a 50 µm diameter. This enabled *in situ* measurements of the local thickness of the solution and thin film during blade coating with improved spatial resolution (Figure 3.8). The reflection spectra were analyzed using FILMeasure software.
3.6 Ex situ Characterization

3.6.1 Atomic force microscopy

We used two different atomic force microscopy machines located in KAUST core labs and KAUST Solar center. Agilent 5400 SPM is in KAUST core labs, and Veeco Dimension icon AFM machine is located in KAUST solar center. The measurement stages for both machines are placed in isolated chambers to reduce the vibrations during measurements. The silicon probe was used to scan the thin film surface. Freeware Gwyddion software processed the AFM images for topography, height distribution profiles, and surface roughness analysis. All the AGM images used throughout this thesis are taken in tapping mode.
3.6.2 X-Ray Diffraction

X-ray diffraction (XRD) is a standard technique to evaluate the crystallinity of powder samples, single crystals, thin films, etc. The constructive interference of X-rays with sample produces a diffraction pattern which satisfies Bragg’s law given in equation 3.3. The schematic of XRD experiment is shown in Figure 3.9.

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (3.5)

Where,

\( d \) = interplanar spacing  
\( \lambda \) = X-ray wavelength  
\( \theta \) = Bragg angle between crystal plane and incident/diffracted x-rays  
\( n \) = order of diffraction

We used Bragg-Brentano geometry to record 2\( \theta \) versus intensity plots for organic thin films. We integrated area under the (001) Bragg peak to determine lamellar crystallinity.

Figure 3.9 Schematic of XRD principle
3.6.3 Photo-thermal deflection spectroscopy

The charge transport in TFTs based on OSCs is strongly linked to the energetic disorder of thin films. Photothermal deflection spectroscopy (PDS) can evaluate the energetic disorder. PDS was used to assess Urbach energy. The absorption coefficient is expected to follow the Urbach relation in the tail states given in Equation 3.5.

\[
\alpha(E) = \alpha_o \exp\left(\frac{E}{E_u}\right)
\]  

(3.6)

Where,
\(\alpha\) = Absorption coefficient
\(E_u\) = Urbach energy

The Urbach energy determines the width of tail states. This width measures the energetic disorder in the materials. Generally, OSC thin films with higher crystallinity show smaller Urbach energies.

**Principle**

It involves two laser beams; 1) probe beam 2) pump beam. Pump laser beam passes through the sample and creates a thermal wave inside the sample due to the conversion of optical energy into thermal energy. This thermal wave diffuses and enters the surrounding medium. The probe beam, moving near the surface (also parallel to surface) gets deflected. A position sensitive detector records the changes in the probe beam. The schematic about working principle of PDS is shown in Figure 3.10.
3.6.4 X-ray and Ultraviolet photoelectron spectroscopy (UPS and XPS)

**XPS measurements**

XPS characterization was carried out in an Omicron ultrahigh vacuum system. This system is mounted with a SPHERA U7 hemispherical energy analyzer. The other important experimental details are as follows:

- X-ray source: Al Kα
- Incident photon kinetic energy: 1486.6 eV
- Total energy resolution: 0.1 eV
- Chamber pressure: < 5 × 10⁻⁹ mbar.

For the fitting of the Au 4f core level peaks, we employed the LF lineshape, a generalized Voigt lineshape, to account for the asymmetric observed for Au core levels on the higher BE side. For the oxide components, however, a Gaussian-Lorentzian shape was used.
**UPS measurements**

These experiments were done in the same system as of XPS characterization. The important details are given below:

- Base pressure: $8 \times 10^{-9}$ mbar
- Photons source: He I photons (21.2 eV)
- Photon line-width: 250eV
- Beam spot size: 1 mm
- Detector: Seven channel MCD detector

Sample was biased at -10 V to acquire correct data of the secondary cutoffs. The Ar$^+$ sputtering was carried out by directing a beam of 1.0 keV Ar$^+$ ions onto the sample for 5 mins. The chamber pressure was maintained $< 2.0 \times 10^{-6}$ mbar and the current *ca* 5 µA.

### 3.6.5 Cross sectional Transmission Electron microscopy (TEM)

We used TEM from Titan Cryo Twin, FEI Company, Hillsboro, OR to acquire cross-sectional images. We recorded carbon jump ratio in the thin film specimen in EFTEM mode using CCD Camera (US4000). The Specimen was prepared by using Focused ion beam (FIB: Helios 400s, FEI). A 22nm gold layer was used to avoid charging effects and Pt layer was used to protect thin film specimen from ion damage during milling process. Firstly, thin film specimen was obtained from bulk thin film which was attached to a copper grid. Here, it was sliced down to get uniform high quality specimen for cross section TEM experiments.
Chapter 4

Understanding the Crystallization of Organic Semiconductors during Solution Processing

4.1 Introduction

As was detailed in chapter 2, tremendous effort has been put into tuning the microstructure, crystalline texture and morphology of polycrystalline small molecule organic semiconductors. While most of the work has focused on trial-and-error as well as ex situ correlation studies linking processing conditions to the functional properties of small molecular organic semiconductors, there has been little work on understanding the solution-to-solid phase transformation process of these materials, including in realistic solution-processing conditions. In the recent past, our group at KAUST has developed powerful in situ diagnostics tools by which to probe the ink solidification process resulting in thin film formation. This work has shown that unlike vacuum deposition, in which material deposition is non-additive, the thin film formation and crystallization in solution processes can occur in less than a second, and is additive, but only upon removal of the solvent from the ink. In addition, solution processes typically spread and dry the ink differently, for instance compare spin-coating to blade-coating, making the comparison of film formation mechanism and kinetics both scientifically important and technologically relevant.

In this chapter, we investigate the formation of solution-processed small molecule thin films using a combination of in situ diagnostics tools in combination of laboratory-scale solution processing methods such as drop-casting, spin-coating and the scalable blade-
coating technique. *In situ* high speed polarized optical microscopy (HSPOM), *in situ* grazing incidence wide angle X-ray scattering (GIWAXS), *in situ* spectroscopic ellipsometry and *in situ* micro-spot optical reflectometry are used in combination or separately to provide a holistic understanding of ink solidification. For this purpose, we investigate the solution-to-solid phase transformation in several different small molecule OSCs using a wide range of processes and processing conditions. The structure, morphology and properties of thin films are investigated *ex situ* by X-ray diffraction, GIWAXS, photo-thermal deflection spectroscopy (PDS), POM and atomic force microscopy (AFM). Finally, we fabricate and test OTFT devices based on all materials and conditions investigated.

4.2 *In situ* investigation of the crystallization of OSCs

4.2.1 Drop-casting and spin-coating

We begin our comparative investigations of film formation by establishing a baseline with drop-casting and spin-coating. We do so by performing high speed polarized optical microscopy (HSPOM) to collect snapshots of the crystallization process. Figure 4.1 shows the HSPOM snapshots taken for two drop-casting experiment using a TIPS-pentacene ink (1 wt.% in toluene) on Si/SiO₂ substrate at room temperature (25°C) and at elevated temperature (70°C). The snapshots are taken at 2.8, 6.8 and 24.4 s for room temperature drop-casting and at 1.0, 2.8 and 5.4 s for drop casting at elevated temperature, highlighting the much faster process of drying and film formation in the latter case. In both cases, the crystallization front propagates laterally with the drying and receding solution.
As thin film formation at 70°C is done in almost 5 s, as compared to 25 s at room temperature, the overall rate of crystalline growth is nearly five times faster at 70°C than at room temperature, primarily due to faster removal of the solvent, which effectively dictates the solidification rate. The imaging experiments highlight the crystallization process is non-uniform as it follows a receding contact line of the ink, resulting in very non-uniform microstructure and morphology across the sample.

We also imaged the crystallization of the same OSC during spin-coating by mounting a home-built miniature spin-coater under the microscope objective. As this process involves a rotating substrate and typically much faster drying rates, it was necessary to perform high speed imaging at a frame rate on the order of 3000 fps (see section 3.2.2 for more details). Performing HSPOM imaging on a rotating sample makes it difficult to track the crystallization behavior of the same location. Consequently, the experiment was designed
after a few trials so that the spinning would be arrested exactly after 3 s of spin coating, just before crystallization can be observed. HSPOM snapshots taken immediately after stopping the spin coating process of TIPS-pentacene ink (1 wt.% in toluene) and during the subsequent second, are shown in Figure 4.2.

![Spin Cast TIPS-pentacene](image)

**Figure 4.2** HSPOM snapshots taken of the crystallization of TIPS-pentacene after spin coating for a duration of 3 s. Note: Rotatable polarizer was set to 70°.

The first image from left (3.0 s) shows interference fringes (alternating blue and green bands) which is a clear sign of a non-uniform liquid solution on the substrate. At 3.4 sec, the top left of the sample shows formation of crystals while the bottom right is still covered in wet ink. The center of the sample appears to be coated in a thin layer of ink. As time goes by, crystallites are formed within the thin blue wet layer in the center and propagate toward where the bulk ink was prior to drying. The visual observation clearly shows crystallites forming in the midst of a drying, but still wet ink.

*In situ* GIWAXS measurements were performed both during drop-casting and spin-casting of diF-TES-ADT and TIPS-pentacene in toluene, to measure the overall progression of crystallization during ink drying. Performing the measurements over a wide enough q-range allows observation of the solvent liquid scattering halo simultaneously with the diffraction features of the OSC’s crystalline phase itself. We plot the integrated intensity
versus time for the solution scattering ring, $q = 11 \text{ nm}^{-1}$ (red) and OSC’s Bragg sheet (001), $q = 3.8 \text{ nm}^{-1}$ (green) in Figures 4.3 a & b, for drop-casting and spin-casting experiments, respectively.

![Figure 4.3 In-situ GIWAXS during (a) drop-casting and (b) spin-coating.](image)

In the case of drop casting, the onset of crystallization of diF-TES-ADT ($\sim 25 \text{ s}$) occurred while there was still a very significant solution scattering signature (Figure 4.3a). The crystallization lasts approximately 15 s and during this time the solution scattering signature subsides only a little, indicating that crystallization occurs directly from solution and the solidification process overlaps entirely with ink drying, with some solvent still remaining even after crystallization is complete.\(^{139}\) In the case of spin coating, we performed the same type of investigation for both diF-TES-ADT and TIPS-pentacene in toluene. In both cases, the onset of crystallization occurs at $\sim 2 \text{ s}$ and lasts less than 0.5 s. Importantly, the crystallization begins and ends while there is still a significant solvent scattering signature. Unlike the case of drop-casting, crystallization halts almost
completely upon disappearance of the solvent scattering, indicating that crystallization is quenched with solvent drying.\^{219}

4.2.2 Blade-coating

Blade-coating is a meniscus guided solution coating method involving two main coating regimes: (1) the evaporation regime and (2) the Landau-Levich (L-L) regime, which depend primarily on the coating speed. Prior to starting in situ investigations, we mapped out the coating-speed-dependent regimes. For this purpose, we used a 1 wt.% diF-TES-ADT in toluene solution and performed the coating experiments at 70°C. Figure 4.4 summarizes the thickness versus coating speed and reveals that evaporation regime occurs for coating speeds in the range of <3-4 mms\(^{-1}\) and Landau-Levich regimes for speeds >4-5 mms\(^{-1}\).

![Figure 4.4](image)

**Figure 4.4** Thickness versus blade-coating speeds plot. Note: We used 1 wt.% diF-TES-ADT toluene solution to blade coat thin films at 70°C.
We have performed *in situ* time-resolved HSPOM and GIWAXS measurements during blade-coating in these different regimes in order to shed light on the crystallization mechanisms. HSPOM was used to image the crystallization of diF-TES-ADT at different speeds, both in the evaporative and L-L regimes at 70°C (Figure 4.5). Snapshots taken at 0.5, 2 mms$^{-1}$ (evaporative) and 100 mms$^{-1}$ (L-L) reveal very different crystallization mechanisms. At the lowest speed (0.5 mms$^{-1}$), we observe the formation of ribbon-like, highly textured and oriented crystals propagating at the trailing edge of the meniscus guide. This observation is remarkably similar to that seen during drop-casting at 70°C. The key difference is that in blade coating the meniscus is guided, whereas it is not controlled in drop-casting experiments. Increasing the speed four-fold to 2 mms$^{-1}$ reveals a transformation of the microstructure from ribbons to spherulites. The latter form significantly downstream from the blade and meniscus. This suggests that the speed of the blade surpasses the natural rate of lateral crystallization, resulting instead in crystallization through a stochastic nucleation process far downstream of the blade. We note that both of these microstructures resulting from different growth behaviors coexist in the evaporation regime.
Increasing the coating speed another 50-fold (100 mms$^{-1}$) places the process squarely in the L-L regime. As expected, we detect an interference pattern providing a clear visual signature of bulk liquid ink (Figure 4.5b). Rapid drying of the solvent leads to disappearance of the liquid after only 150 ms, leading to formation of what appears to be a continuous amorphous film in the absence of bulk liquid. The image taken at 300 ms shows the stochastic formation of diF-TES-ADT spherulites. As such, the microstructures of the
films formed at 2 and 100 mms\(^{-1}\) are rather similar despite being in different coating regimes.

*In situ* GIWAXS measurements were performed using a focused x-ray microbeam (15×15 \(\mu\)m\(^2\)) incident parallel to the edge of the blade. The small lateral size of the beam is crucial to deconvoluting the ink drying and crystallization processes with sufficiently good spatial and temporal resolutions. We plot in Figures 4.6a-c, the integrated intensities versus time for the solution scattering ring \((q = 11 \text{ nm}^{-1}; \text{red})\) and the OSC’s (001) Bragg sheet \((q = 3.8 \text{ nm}^{-1}; \text{green})\), similar to drop-casting and spin-coating experiments.

![Evaporation regime and Landau-Levich regime](image)

**Figure 4.6** In-situ GIWAXS during blade coating of diF-TES-ADT in (a) Evaporation regime and (b) Landau-Levich regime.

At the lowest coating speed (0.5 mms\(^{-1}\), 70°C), crystallization occurred directly from solution, as indicated by the simultaneous presence of solvent liquid and crystal for a period of at least 100 ms (Figure 4.6a), providing strong evidence that crystallization occurs directly from solution.
The crystallization behavior at 2 mms\(^{-1}\) is different in that the solution scattering signature fades quickly, giving way to a thin film regime characterized by no liquid scattering nor diffraction for 0.4-0.5 s. This confirms that the trailing meniscus observed in POM images is most likely to be an amorphous phase of the OSC. A similar observation can be made in the L-L regime (25 mms\(^{-1}\), 70\(^\circ\)C), although the onset of crystallization appears to be much closer to the loss of bulk liquid. We investigate whether the intermediate phase is indeed amorphous and not a liquid crystalline phase, by performing HSPOM experiments under fully cross-polarized conditions, at 1.5 mms\(^{-1}\) (Figure 4.7). The intermediate phase appears completely dark, indicating that it is not birefringent, and therefore amorphous.

![diF-TES-ADT, 1.5 mms\(^{-1}\), 70\(^\circ\)C](image)

**Figure 4.7** HSPOM (cross-polarized) snapshot taken during blade coating of diF-TES-ADT at 1.5 mms\(^{-1}\), 70\(^\circ\)C.

Further insight into the intermediate state and its solvation can be gained through *in situ* optical thickness monitoring using the microspot optical reflectometry method described in section 3.2.3. In Figure 4.8, we plot the time-resolved thinning behavior of the ink during spin-coating and blade-coating experiments. The final film thickness reached after completion of crystallization is found to be ~52 nm (~47 nm) after spin-coating (blade-
coating). However, the onset of crystallization is detected when the film thickness is ~1400 nm, corresponding to a solution concentration (v./v.%) of ~4.3%. This observation is consistent with the solubility limit of the OSC at room temperature (~5 wt.%) and indicates that crystallization of the OSC proceeds directly from solution. By contrast, the intermediate amorphous film formed immediately downstream of the blade has a thickness of ~63 nm, consistent with the observation of a solid-state amorphous film. Interestingly, the thickness of this intermediate phase decreases albeit slowly to ~56 nm over the next ca. ~0.4 s, prior to the onset of crystallization. Assuming the amorphous film retains a bit of residual solvent, we estimate its concentration by volume to be ~70% at the edge of the blade and ~90% just before crystallization. An alternative explanation is that the amorphous film slowly undergoes densification through reorganization of molecules prior to crystallization. Either way, crystallization of the OSC occurs primarily from a solid-state amorphous OSC film, in contrast to drop-casting, spin-coating, and blade-coating performed at low speed.
Using a combination of in situ HSPOM, µGIWAXS and micro-spot optical reflectometry measurements we have proven that blade-coated OSCs tend to crystallize indirectly from an amorphous intermediate phase which forms from solution. These measurements provide conclusive evidence that crystallization of OSCs can proceed via two-step nucleation, a
mechanism increasingly identified as the pathway to crystallization of soft materials, as discussed in Chapter 2. In Figure 4.9, we schematically illustrate the energetics of the classical and two-step nucleation processes. In the case of two-step nucleation (Figure 4.9a), OSC molecules overcome a first energy barrier to nucleate a kinetically trapped amorphous state. Nucleation of the crystalline phase within the amorphous phase occurs once the critical nucleus is achieved, overcoming the second energy barrier. The crystalline OSC can also nucleate directly from the bulk solution by overcoming one energy barrier, as depicted in Figure 4.9b.

Figure 4.9 Energy diagrams of (a) Two-step nucleation model (b) Classical nucleation model

In Figure 4.10a, we propose growth mechanisms in the solution processes we have investigated thus far, including spin-coating, drop-casting and low-speed blade coating. Crystallization appears to follow a direct route based on the observations made thus far, whereby growth of crystallites occurs via molecular diffusion and incorporation of OSC
molecules at the ink-crystal interface at the growing front. In Figure 4.10b, we illustrate the growth mechanism of OSCs via the two-step nucleation mechanism during high speed blade coating experiments. Evaporation of the solvent from the trailing meniscus leads to formation of a highly dense, high concentration region of the ink which has the properties of amorphous OSC. The amorphous OSC has 90% of the density of the crystalline phase prior to crystallization, hence there is very small volume contraction upon crystallization. This has very significant implications for the film formation mechanism. The OSC molecules are sufficiently close to each other and abundant so as not to require any long range diffusion. Instead, local conformational changes and rotation of the molecules suffice to incorporate the molecules into the growing front of crystallites, allowing the latter to propagate rapidly and over long distances. The rate-limiting factor for crystal growth in classical nucleation from solution is likely to be the diffusivity of OSC molecules toward crystal facets and stops when nearby molecules are depleted. The formation of a dense disordered film of OSC molecules with minimal density difference with respect to the final crystalline OSC film lifts the limitations associated with the classical nucleation and growth processes. As soon as the crystalline phase is nucleated, it proliferates over long distances by incorporating OSC molecules via a short range conformational change and incorporation into the rapidly propagating crystal facet. The abundance of molecules in the amorphous phase also changes the nature of grain boundaries, since these are not characterized by material deficiency, but rather as the lines where two propagating crystal fronts meet within the amorphous phase. These differences are expected to have important implications on the structure, morphology and properties of OSC films, as will be discussed below.
Figure 4.10 Schematics showing the OSC crystallization via (a) Classical nucleation model (b) Two-step nucleation model.
4.2.4 Generalization of two-step nucleation

We have sought to generalize the blade-coating observations made thus far to other OSCs, namely TIPS-pentacene, Allyl-DIPS-pentacene, and CP-DIPS-pentacene. All of these OSCs assume the brickwork packing motif in solid thin film. In Figure 4.11a we show the HSPOM snapshots taken during blade coating of all OSCs from a 1 wt.% toluene solution at low coating speeds in the evaporation regime. All the images indicate the directional ribbon-like growth near the edge of the slow-moving meniscus. Moving to higher coating speed, but still in the evaporation regime, results in the formation of an extended amorphous intermediate film followed by deformed and extended spherulitic domains (Figure 4.11b). Moving to the L-L regime (Figure 4.12) shows the same pattern of behavior as previously seen. The fast moving blade leaves behind bulk ink (first column), which subsequently dries to form an amorphous film (second column). The spherulites nucleate stochastically (third column), resulting in dry films made of entirely spherulitic domains (last column). The similarity between the growth modes of the pentacene and anthradithiophene derivatives indicates two-step nucleation is operant and can be induced in different OSC materials.
Figure 4.11 HSPOM snapshots taken during blade coating of TIP-pentacene, Allyl-DIPS-pentacene, and CP-DIPS-pentacene showing the crystallization via (a) Classical Nucleation pathway (b) Two-step nucleation pathway.
Figure 4. 12 HSPOM snapshots taken during blade coating of TIP-pentacene, Allyl-DIPS-pentacene and CP-DIPS-pentacene showing the crystallization via Two-step nucleation pathway in Landau-Levich Regime at 100 mms⁻¹, 70°C

4.3 Impact of crystallization pathway on device performance

We evaluate the impact of the solidification pathway on the performance of OTFT devices, and in particular on the field-effect mobility ($\mu_{FE}$) of the OSC. We fabricated bottom gate bottom contact (BGBC) and top gate bottom contact (TGBC) devices (see chapter 3) using all four OSCs investigated in the previous section. The OSC films were prepared via spin-
coating and by blade-coating in the two-step regime. In Figure 4.13 we summarize the resulting field effect mobilities from all the BGBC and TGBC devices, along with representative transfer and output characteristics for Allyl-DIPS-pentacene and transfer characteristics for all OSCs.

Figure 4.13 Field effect mobility (saturation) extracted from OFETs based on all four OSCs as active layers in two device configurations (a) BGBC & TGBC (b) Transfer and output characteristics of BGBC and TGBC OFETs.

The field effect mobility of OSC films in BGBC devices increases by an order of magnitude or more, from \(~3 \times 10^{-3} - 2 \times 10^{-2}\) cm\(^2\) V\(^{-1}\)s\(^{-1}\) for spin-cast films to \(~10^{-1}\) cm\(^2\) V\(^{-1}\)s\(^{-1}\) for OSC films prepared by blade-coating in the two-step nucleation regime. In TGBG devices, the carrier mobility is generally found to be higher and its increase is more material-dependent. In case of diF-TES-ADT, the average mobility increases from 0.7 to 1.1 cm\(^2\) V\(^{-1}\)s\(^{-1}\), whereas it increases by an order of magnitude to 0.2 cm\(^2\) V\(^{-1}\)s\(^{-1}\) in case of TIPS-pentacene. The BGBC devices used thermal SiO\(_2\) as the dielectric while TGBG used solution
processed CYTOP as the dielectric, partly explaining differences in performance. We have calculated the interfacial trap densities ($N_{it}$) for all OSCs based on BGBC device configuration (Figure 4.14a). In most of the cases, we notice a significant reduction of the $N_{it}$ from $\sim 10^{13}$ eV$^{-1}$ cm$^{-2}$ to $\sim 10^{12}$ eV$^{-1}$cm$^{-2}$. The comparisons of mobility and $N_{it}$ data confirm that the crystallization pathway has a very significant impact on the functional properties of OSCs in OFETs. We look beyond the device and the semiconductor-dielectric interface by evaluating trap states within the semiconductor film coated directly on glass. The density of states (DOS) within the band gap was evaluated using Grunewald’s method (Figure 4.14b). We observe a decrease of in-gap DOS for the OSC crystallized via two-step nucleation as compared to the spin-cast film. PDS measurements of the sub-gap absorption of the OSC (Figure 4.14c) allows extraction of the Urbach energy, which relates to the presence of trap states. The Urbach energy is found to be significantly lower (27.5 meV) for two-step nucleated films as compared with directly crystallized films (39.2 meV), confirming that two-step nucleation produces higher quality and less defective OSC films.
Figure 4.14 Interfacial trap density obtained from OFETs based on all four OSCs as active layers in two device configurations (a) BGBC (b) Density of states determined from linear OTFT I-V curves of diF-TES-ADT (c) PDS measurements for diF-TES-ADT.
4.4 Crystallization pathway and its impact on microstructure and morphology

In Figures 4.15a & b we show POM and AFM micrographs for all four OSCs in order to help summarize the microstructure and morphology of OSC films prepared in conditions that yield direct (spin-coating) and two-step nucleation (blade-coating), respectively.

![Figure 4.15](image)

**Figure 4.15** Polarized optical microscopy and Atomic force microscopy micrographs for all four OSCs crystallized via (a) The direct classical nucleation route (b) Two-step Nucleation pathway.
In comparing POM images, it is useful to note that the micrographs of spin-cast films are presented with significantly higher magnification (Figure 4.15a) in order to compare its spherulitic features to those formed by blade coating (Figure 4.15b). This is because of a higher density and smaller size of spherulitic domains in spin-cast films as opposed to blade-cast ones. The morphology and topography of the polycrystalline films was compared by AFM imaging of the surface of the films. The topographic images reveal interesting differences. The spin-cast film shows evidence of ribbons exhibiting liquid-like morphology (diF-TES-ADT) or made of an assembly of tiny crystallites (TIPS-pentacene), consistent with crystallization at the receding liquid meniscus. By contrast, blade-cast films show longer ribbons which appear to have propagated with ease and without disruption over long distances. The same observation can be made for all four OSCs, which crystallize through propagation of needle-like oriented crystalline domains.

This observation is in line with coherent growth of crystalline domains by propagation through a dense and amorphous film without leaving behind topographically deep domain boundaries. This behavior also resembles to the TES-ADT case, where high quality topographically defectless crystallites grow from amorphous film. Quantitative insight into the topography of the spherulitic films can be obtained by computing the statistical distributions of surface height and their root mean square (RMS) roughness (Figure 4.16a&b). For convenience, we have centered the height distributions at a height of zero, because the AFM tip does not detect the substrate in most instances. The height distributions are dramatically narrower for blade-coated films (green) as compared with spin-coated films (red), a fact which is reflected in the RMS roughness comparisons plotted in Figure 4.16b, highlighting the smoothness of blade-cast films as compared with spin-
cast ones. RMS roughness values were found to be 3-7 times lower for two-step nucleation (blade-cast, green bars) printed films in comparison to direct nucleation case (spin-cast, red bars). In one case, (TIPS-pentacene), the height distribution shows a significant hump on the deeper side of the distribution, corresponding to the substrate, which appears to be partially exposed revealing pin holes, cracks or deep valleys at some of the grain and domain boundaries. By contrast, the height distribution of diF-TES-ADT reveals molecular terraces on the surface of the film, whose height corresponds to the lamellar stacking of molecular sheets.

**Figure 4.16** (a) The statistical height distribution plots (b) RMS roughness extracted from AFM micrographs in Figure 4.15.
The differences in surface topography and the formation of long range ribbons with molecular terrace features on the surface in blade-coated films indicates that the crystallinity and texture of films produced via two-step nucleation are superior to the conventional alternative. We have performed XRD measurements in θ-2θ mode and plotted the (001) Bragg peak for all OSCs (Figure 4.17a), as well as its integrated intensity (Figure 4.17b). The (00n) diffractions relate to the lamellar stacking of molecular sheets with 2D in-plane transport. Hence, improving the vertical lamellar crystallinity in thin films is qualitatively linked to improved stacking of the molecular sheets responsible for in-plane charge transport. The (001) intensity was integrated and normalized to the actual thickness in order to make a direct comparison of the lamellar crystallinity. As can be seen, the normalized intensity of the lamellar diffraction peak is nearly an order of magnitude greater for all OSCs when crystallization proceeds via two-step nucleation (Figure 4.17b).
The out-of-plane XRD analysis presented above is incomplete without looking at the in-plane structure, mosaicity and texture, which can be obtained via GIWAXS measurements (Figure 4.18). Both sets of GIWAXS data reveal in-plane features (21L), (11L) and (10L), as well as out-of-plane lamellar Bragg sheets (00L). Upon closer examination, we find the GIWAXS data reveals OSC films grown via direct crystallization by spin-coating result in a mixture of edge-on (<001>) and face-on (<111>) textures.
The latter texture leads to the loss of in-plane π-stacking necessary for transport in the context of OFETs. The in-plane diffraction peaks are smeared in case of spin-coating, revealing a degree of mosaicity that is absent from blade-coated films, where the in-plane peaks are sharp and show no evidence of smearing. For instance, we compared the in-plane Bragg peak (212) (belonging to <001> edge-on texture) of diF-TES-ADT films processed by both crystallization methods. In Figure 4.19a, we show the corresponding 2D-GIWAXS
maps for both films, while in Figure 4.19b, we show the integrated (212) plots and their corresponding film thickness-normalized integrated intensities in the inset. Azimuthal plots of the same peak and its corresponding FWHM are shown in Figure 4.19c. These results show significantly improved in-plane ordering and reduced azimuthal smearing of the two-step crystallized diF-TES-ADT thin films as compared to directly crystallized ones.

The comparative morphological and microstructural analyses performed thus far on OSC films prepared via direct crystallization and two-step crystallization routes highlight important differences, including smoother and more compact films exhibiting reduced grain and domain boundary defects, improved texture purity, reduced lamellar and in-plane mosaicity, as well as significantly greater lamellar crystallinity and coherence. These improvements in turn explain the reasons for reduced sub-gap DOS and Urbach energy, reduced interfacial trap state density, and significantly improved in-plane carrier mobility both in BCBG and BCTG device geometries.
Figure 4.19 (a) 2D-GIWAXS micrographs highlighting the (212) in-plane Bragg peak (b) The integrated plots of (212) Bragg peak, inset showing the normalized corresponding integrated intensities (c) The Azimuthal integrated plots of (212) Bragg peak, inset showing the normalized corresponding integrated intensities

4.5 Processing window for two-step nucleation

The results presented in section 4.2 demonstrated that two-step nucleation can be achieved with relative ease using blade coating for several small-molecule OSCs. As these observations depended upon coating speed and were usually performed at elevated temperature, we sought to identify more rigorously the blade-coating processing window within which OSCs can be crystallized via two-step nucleation mechanism. For this purpose, we have first mapped out the influence of coating speed at constant substrate temperature, i.e., 70°C, on the formation of the extended amorphous film prior to diF-TES-
ADT crystallization (Figure 4.20a), using a combination of in situ HSPOM and in situ μGIWAXS.

**Figure 4.20** (a) Transition conditions required to crystallize diF-TES-ADT thin films via two-step nucleation pathway, data is extracted from HSPOM and in-situ GIWAXS experiments performed at 70°C (b) Impact of substrate temperature on the scaling of liquid meniscus and amorphous intermediate state at a constant coating speed, i.e., 2 mms⁻¹.

It can be seen that for coating speeds <1 mms⁻¹ the OSC crystallizes in ribbon-like microstructure at the trailing edge of the liquid meniscus, as was shown above. At 70°C, the solvent evaporates rapidly and the meniscus is very short and almost undetectable visually by HSPOM, but detected via solvent-scattering in μGIWAXS measurements. With increasing coating speeds, the crystallization front falls behind the trailing meniscus and we detect a separation which was previously identified as the amorphous intermediate film.
Initially the length of the amorphous region is short, typically in the tens 100 µm, but its length is sufficient to break the directional growth of ribbons from the edge of the meniscus and give way to stochastic nucleation of spherulites. The length of the amorphous region at constant substrate temperature is directly related to the speed of the moving blade, hence it increases with speed and is measured to be as long as ~4 mm at 100 mms⁻¹.

Next, we have sought to evaluate the effect of coating temperature at a constant blade speed of 2 mms⁻¹, noting the boiling point of toluene is 110°C. In Figure 4.20b, we show HSPOM snapshots of the blade coating process proving that the temperature influences the extent of the trailing meniscus downstream from the blade. At room temperature, the liquid meniscus is extended significantly, as indicated by the formation of interference fringes, with a shorter amorphous region that nevertheless remains intact, followed by nucleation of fine crystalline domains with a high nucleation density. As the temperature is increased, the meniscus becomes quite a bit shorter and nearly disappears from view for $T > 60°C$. Interestingly, the amorphous region becomes further extended for $T > 40°C$, and it is also noteworthy that the size of crystalline domains increases significantly at elevated temperature.

The observation of a long trailing meniscus at room temperature was made in the evaporative regime (2 mms⁻¹) of blade coating. We therefore increase the coating speed well into the L-L regime whereby the wet thickness increases, all the while maintaining the low coating temperature to limit evaporation. Figure 4.21 shows the HSPOM snapshots taken during blade coating at 100 mms⁻¹ (30°C). It is evident that crystallization is happening from the bulk OSC solution near the moving contact line. This thin film was
highly non-uniform and inhomogeneous, and it showed different morphologies at different locations of the substrate. We find that the crystallization behavior becomes more chaotic in this regime behaving like a mixture of meniscus-guided direct crystallization and two-step nucleation. However, the blade is no longer the guide to the moving meniscus as the former moves far too quickly and the meniscus recedes without a guide. We refer to this as the “mixed” growth regime.

![TIPS-pentacene, 100 mms⁻¹, 30°C](image)

**Figure 4.** 21 HSPOM snapshots taken during blade coating of 1 wt% TIPS-pentacene toluene solution at 100 mms⁻¹, 30°C.

We performed AFM experiments to evaluate the morphological quality of this film and its uniformity compared to thin films coated in “only” two-step nucleation conditions (Figure 4.22). The micrographs confirm that OSC thin films crystallized in the mixed regime exhibit some of the behaviors seen in spin-cast films, whereby very fine crystallites have formed next to each other, forming ribbon-like features with deep groves nearby. By contrast, the ribbons formed in two-step nucleation appear to be much better connected and exhibit long range lateral coherence of growth. The RMS roughness comparing the two types of samples confirmed the mixed growth films to be far rougher, with ~20 nm as compared to ~2 nm for two-step nucleated films.
We mapped out the transition conditions required for two-step nucleation in the speed range from 0.25 to 100 mms\(^{-1}\) and substrate temperatures from 25 to 90\(^{\circ}\)C (Figure 4.23) using HSPOM. We found that OSCs can be crystallized via two-step nucleation at all coating temperatures above the critical velocity where ribbons no longer form. The critical velocity changes with coating temperature, for instance, the transition from the ribbon-like regime to spherulitic regime occurs at 0.3 mms\(^{-1}\) at room temperature and increases monotonically to 1 mms\(^{-1}\) at 70\(^{\circ}\)C. This shows that two-step nucleation can occur at low coating speeds as long as the substrate temperature is low. More importantly, we find that upon entering the two-step nucleation regime, it is operant at all coating speeds (evaporative and L-L) for \(T > 50^{\circ}\)C. By contrast, there is a breakdown of two-step nucleation in the L-L regime for \(T < 50^{\circ}\)C. This has serious implications on OTFT device performance and reproducibility, as shown in Figure 4.23b. OSC films crystallized in the mixed regime result in a large device performance spread (\(\mu_{FE} = 10^3-10^1\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)), also found in spin-coating (\(\mu_{FE} = 10^3-10^1\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and drop-casting (\(\mu_{FE} = 10^3-10^1\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)), as compared to the OSC films coated in two-step window (\(\mu_{FE} = 10^1\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)). This is a very encouraging result for blade-coating in the two-step regime.
Figure 4.22 (a) AFM micrographs for blade coated TIPS-pentacene films in mixed regime (100 mm/s, 30°C) and two-step nucleation window (100 mm/s, 70°C) (b) Corresponding RMS roughness values extracted from images presented in (a).

Figure 4.23 (a) Transition conditions required to crystallize OSC thin films via two-step nucleation pathway, data is developed using in-situ HSPOM (b) Field effect mobility of diF-TES-ADT thin films from BGBC OTFT 2 mm/s and 100 mm/s at different substrate temperatures.
4.6 Structural mapping of thin films in OFETs

We have used the µGIWAXS technique in static mode in order to map the structure and texture of solution-processed TIPS-pentacene and diF-TES-ADT. We scanned a 2×2 cm² area of the sample collecting a total of 600 µGIWAXS measurements. In Figures 4.24a & b, we have plotted integrated intensity maps for three different TIPS-pentacene films prepared in conditions yielding direct (spin coating and blade-coating in mixed regime) and two-step (blade-coating) crystallization. The spin cast film has the undesired <111> texture in most parts of the scanned area of the sample, showing only a small region with pure <001> texture. Interestingly, the blade-coated film prepared in the mixed growth regime (L-L; 100 mm s⁻¹, 25°C) also shows the undesired <111> texture in some parts of the film. By contrast, the TIPS-pentacene films crystallized via two-step nucleation pathway does not show the undesired <111> texture in any part of the film. This might be due to the fact that direct crystallization is initiated in a micrometer thick bulk ink, and therefore mixed crystal textures can form. Two-step crystallization is confined to a thin amorphous film, thus forcing nuclei exhibiting the lamellar texture to propagate laterally.⁹⁶
In Figure 4.25a, we show the integrated intensity maps of three different diF-TES-ADT films prepared via direct (spin-cast and blade-coated in mixed regime) and two-step crystallization routes. Figure 4.25b shows the full GIWAXS measurements of the same films. The white box highlights the area used for integration. The behaviors of diF-TES-ADT and TIPS-pentacene films are similar across processes and explain the overall poor performance and large spread in device performance obtained from films grown in this way, as was highlighted in Figure 4.23b.

**Figure 4.24** (a) Schematic of structural mapping experiment using μGIWAXS and (b) & (c) Integrated scattering maps showing the different textures present in thin films of TIPS-pentacene
Figure 4. 25 (a) Integrated intensity scattering maps showing the different textures present in thin films of diF-TES-ADT (b) GIWAXS maps highlighting <001> and <111> textured Bragg peak positions, White box points to the integration area used to construct intensity

Similarity between mixed growth regimes in blade coating and other coating methods

We find that blade-coating of small molecular OSCs in Landau-Levich regime at lower substrate temperature produces similar thin films as with spin coating which we named as “mixed” growth regime. Spin-coating of OSCs results in mixed morphology (spherulites and small crystals) similar to what we observed for blade coating in mixed regime. It suggests that nucleation and growth behavior are also similar in these two processes. In situ HSPOM showed that OSC crystallizes from bulk solution or intermediate amorphous state near the receding contact line in blade coating. This situation resembles drop-casting where crystallization of OSCs follows the receding contact line of the OSC ink, resulting
in very non-uniform microstructure and morphology across the sample. The OFETs performance in all three cases i.e. drop-casting, spin-coating, blade coating (mixed regime) is also comparable as we showed earlier in section 4.2.5 & 4.3.

4.7 Conclusions

*In-situ* investigations reveal the solution-to-solid phase transformation mechanism during drop-casting, spin coating and roll-to-roll compatible blade coating method. It is found that crystallization of small molecular OSCs happens from the bulk of OSC liquid during drop-casting, spin-coating and very low-speed blade-coating (Ribbon-like crystallites). It is confirmed by in-situ GIWAXS and HSPOM experiments. This type of crystallization behavior follows the direct nucleation model (classical nucleation theory). *In-situ* HSPOM, GIWAXS, and optical reflectometry reveal that OSC molecules aggregate to form a dense amorphous intermediate state during blade coating after a critical transition speed depending upon the coating temperatures. The nucleation and growth of OSC crystallites proceed from this intermediate state. We observe this type of crystallization behavior, both in Evaporation and Landau-Levich coating regimes. This kind of solution-to-solid phase transformation mechanism has been predicted by the so-called two-step nucleation theory. This theory was initially developed for proteins and then verified for other soft materials such as bio-minerals, organic molecules, and colloids. The OSCs crystallized via this two-step nucleation pathway show superior figure of merits in comparison to direct-crystallization, when used as active layers in BGBC and TGBC field effect transistors. We find that interfacial trap density in these films decreases by order of magnitude and it is complemented by lower in-gap density of states (calculations using Grunewald’s method) and lower Urbach energy values (PDS measurements). The POMs and AFM micrographs
reveal the superior morphology of two-step crystallized OSC thin films, having better grain and domain boundary quality. XRD show that out of plane lamellar quality is also superior in these films. Furthermore, GIWAXS shows that two-step nucleation always leads to pure <001> textured growth of OSC crystallites. Direct nucleation during spin coating produces a mixture of <001> and the undesired <111> textured crystallites. The face on <111> texture leads to loss of π-π stacking in OSC films. We also find that blade-coating of OSC thin films at lower substrate temperatures in Landau-Levich regime produces a mixed-growth of spherulites and small crystallites. These films perform on-par with spin-coated thin films. The AFM show that both films have similar kind of defective topographic features. GIWAXS maps reveal that these films also have a mixed ( <001> + <111>) texture of crystallites. This suggests that “just” blade coating is not enough to achieve texture purity in these OSC films, but optimized coating window is a necessary tool. We show a map of these conditions on a coating speed versus substrate temperature plot. The OSC films prepared in two-step nucleation window show uniform texture and morphology as found by AFM micrographs and μGIWAXS structural mapping.
Chapter 5

Small-molecule: polymer blends for high performance organic field effect transistors

5.1 Introduction

Small molecule: polymer blends are an important class of composite materials in organic electronics. In organic photovoltaics, this blend is designed, in terms of material choice, ink formulation and processing conditions, to yield a nanocomposite, known as the bulk heterojunction (BHJ). The BHJ is thus the photoactive layer responsible for light absorption, exciton generation, splitting, and collection of charge carriers at the anode and cathode vertically sandwiching the thin film solar cell. In OFETs, the blend is designed instead to form stratified layers which help move charges laterally from source to drain or vice versa, at the semiconductor-dielectric interface. The polymer can thus act as a binder and, in some conditions, as dielectric.

Since the first reports showing the success of blending in OFETs, tremendous effort has been made to investigate their use in OFETs and improve the performance of devices. To date, very little has involved roll-to-roll compatible solution coating methods. In this chapter, we describe the blade-coating of small molecule: polymer blends in the context of OFETs. We begin our investigation by comparing the crystallization behavior of the OSC in the blend using in situ HSPOM and μGIWAXS and demonstrate that two-step nucleation is operant in the crystallization behavior of the OSC in blends. We go on to investigate the roles of processing parameters such as coating speed, molecular weight of the polymer binder and ink formulation on phase separation, microstructure and morphology of OSC
blend thin films. We fabricated and tested BGBC OFETs to correlate device performance to microstructure and morphology of the blend films. We demonstrate high performance OFETs with performance approaching single-crystal devices of the same OSC and small performance variability over a wide range of processing conditions, making this strategy potentially suitable for large area manufacturing of electronic circuits.

5.2 In situ investigation of small-molecule: polymer blend film formation

We show in Figure 5.1a the HSPOM snapshots taken during blade-coating of diF-TES-ADT: polystyrene (PS) blend films coated at 0.5 and 1.5 mm/s using a substrate temperature of 70°C. We observe qualitatively similar behavior in these blend films as we did in neat diF-TES-ADT films prepared by blade-coating (Chapter 4), namely films coated at the lower speed form directional ribbons which crystallize at the trailing edge of the liquid meniscus, while films coated at higher speed lead to formation of an amorphous intermediate region with spherulites forming downstream. The observation of extended lateral crystallization of ribbons and spherulites indicates that the OSC is able to freely crystallize in the plane of the substrate without any obstruction from the amorphous PS, thus indicating the polymer and OSC are vertically phase separated prior to crystallization of the OSC. In situ μGIWAXS measurements were used in a similar manner as in the previous chapter. We plot the time-evolution of integrated intensity of the solution scattering ring \( q = 11 \text{ nm}^{-1}; \) red) and the \( (001) \) Bragg sheet of the OSC \( q = 3.8 \text{ nm}^{-1}; \) green) in Figures 5.1a-c. The data reveal coexistence of the OSC crystallization and liquid scattering from the ink, indicating crystallization happens directly from solution at low speed. The increasing speed creates a significant gap between the end of solvent evaporation and the onset of OSC crystallization, pointing to two-step nucleation. Moving
squarely in the L-L regime (25 mms\(^{-1}\)) shows a similar behavior with a small-time lag between the end of solvent evaporation and the onset of OSC crystallization.

Figure 5. 1 (a) HSPOM snapshots taken from movies recorded during blade coating of diF-TES-ADT: PS at 0.5 and 1.5 mms\(^{-1}\), 70\(^\circ\)C and In-situ GIWAXS during blade coating of diF-TES-ADT in (b) Evaporation regime and (c) Landau-Levich regime

5.3 Influence of coating speed on Microstructure, Texture, and OTFT’s Figure of merits

The blade speed has been established to be a critical parameter for controlling film formation in case of blends just as in neat materials, with low speeds yielding ribbon formation while high blading speed leading to spherulite formation. We have therefore fabricated BCBG devices based on neat diF-TES-ADT and 1:1 blends of diF-TES-ADT with PS (123kDa) and P\(\alpha\)MS (100kDa) for blade speeds ranging between 0.5 and 2 mms\(^{-1}\).
Polarized optical micrographs (POM) of the films in conditions of low (0.5 mm s\(^{-1}\)) and high (1.5 mm s\(^{-1}\)) blade speeds are shown in Figure 5.1, confirming the ribbon formation at low speed and more of a spherulitic microstructure in conditions of high blading speed.

In Figure 5.2, we have plotted the carrier mobility as a function of blading speed for neat diF-TES-ADT, as well as its blends with PaMS (100 kDa) and PS (123 kDa).

![Figure 5.2](image)

**Figure 5.2** (a) Field effect mobility (b) Threshold voltage (c) \(I_{on}/I_{off}\) (d) Subthreshold swing for the cases of neat diF-TES-ADT, diF-TES-ADT: PS [123k g/mol] and diF-TES-ADT: PaMS [100k g/mol] at different blade coating speeds at 70°C substrate temperature

In the low speed regime (0.5mm s\(^{-1}\)) blends achieve ~3-4 times higher mobility than neat samples. In the high speed regime (1.5mm s\(^{-1}\)) the difference is even greater, surpassing an order of magnitude, while the device performance spread is substantially reduced by use of the blending approach, as indicated by smaller error bars. The threshold voltage (\(V_{th}\))
for neat devices is positive for all speeds, ranging from 10 V at low speed to 70 V at higher speeds as shown in Figure 5.2b. Similarly, the sub-threshold swing (SS) increases from 7 V dec⁻¹ at low speed to 50V dec⁻¹ at high speed (Figure 5.2d). Blending with the insulating polymer substantially reduces both $V_{th}$ and SS to the range of 0.1-4 V and 0.35-1 V dec⁻¹, respectively, over the entire blading speed range. The corresponding transfer and output curves representing all three cases are shown in Figure 5.3. This highlights the remarkable benefits of blending the OSC with an insulating polymer and its apparent ability to reduce the interfacial trap state density apparently responsible for elevated SS and $V_{th}$ values in neat devices.

**Figure 5.3** Transfer Characteristics of neat diF-TES-ADT, diF-TES-ADT: PaMS and diF-TES-ADT: PS  (d) Output Characteristics of diF-TES-ADT: PS BCBG Note: All the representative devices have W/L = 1000µm/80µm

As shown in Table 1, the interfacial trap state density ($N_{it}$), decreases by one to two orders of magnitude from $\sim 10^{13} \text{ eV}^{-1} \text{ cm}^2$ to $\sim 5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^2$ by virtue of blending an insulating polymer with the OSC. In the high speed regime we also systematically observe PS-based blends outperforming PaMS-based blends in terms of all figures of merit. We used same recipe (toluene, concentration, and blending ratios etc.). Both polymers are equally soluble
in toluene and exhibit very similar Flory-Huggins parameters (~0.4), we therefore expect the thermodynamic driving forces for phase separation to be nearly identical.

Table 5. 1 Interfacial trap density for neat diF-TES-ADT and its blends with PaMS and PS

<table>
<thead>
<tr>
<th>Trap Density</th>
<th>Neat diF-TES-ADT</th>
<th>diF-TES-ADT: PaMS</th>
<th>diF-TES-ADT:PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{it}}$ (eV$^{-1}$cm$^2$)</td>
<td>8.2x10^{12} - 4.6x10^{13}</td>
<td>4.5x10^{11} - 1x10^{12}</td>
<td>3.2x10^{11} - 6.5x10^{11}</td>
</tr>
</tbody>
</table>

However, the performance of PaMS-based devices produced at a blade speed > 1 mms$^{-1}$ suffers with respect to PS-based devices. Looking more closely at the AFM of blends produced at 2 mms$^{-1}$ (Figure 5.4), we find the topography of diF-TES-ADT: PaMS blends to be less continuous and more defective as compared to the PS-based blend. This is probably the key reason for the lower performance from PaMS devices. We take the view that as the temperature dependence of viscosity of the polymer solution follows the Williams-Landel-Ferry model, the viscosity of polymer solutions is dependent upon the glass transition temperature. Polystyrene has lower glass transition temperature of (ca. 100$^\circ$C) than PaMS (ca. 170$^\circ$C) which is likely to yield higher viscosity of PS blend solutions at a coating stage temperature of 70$^\circ$C. This may factor into the well connected, smooth and defect free morphology of diF-TES-ADT films produced by blending with PS.
Figure 5.4 Interfacial trap density for neat diF-TES-ADT and its blends with PaMS and PS at 2.0 mms\(^{-1}\), 70°C

AFM taken of the surface of neat diF-TES-ADT and polymer blends are shown in Figure 5.5. For the lower blade speed (0.5 mms\(^{-1}\)), the micrographs reveal significant crevices between adjacent ribbon-like crystals, whereas at higher speed (1.5 mm s\(^{-1}\)) all films show spherulite-like crystals connected by tall domain boundaries and exhibit significant topographic defects, such as gaps and cracks within the spherulites. Blending with PaMS or PS in the low-speed regime results in well-connected ribbons with topographically smoother boundaries. Blending with PaMS in the high speed regime results in topographically smooth boundaries between spherulites as well, suggesting they are well connected, but still reveals significant topographic features and defects within the spherulites themselves. Blending with PS on the other hand leads to well-connected smooth spherulites with apparently smooth and continuous boundaries with fewer tomographic defects, hinting at the presence of morphological reasons for the better performance observed in PS-based blends over PaMS-based blends at higher blading speeds.
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We performed static GIWAXS measurements to investigate the texture of these thin films as shown in Figure 5.6. We can see from this data taken in different processing conditions that only the <001> texture is formed by blade coating, irrespective of blending or not. The reason behind this remarkable result is still unknown, but we postulate as we did in the previous chapter, that this may be related to the blade coating method’s demonstrated confinement effect during crystallization of the OSC.

We blade coated thin films of neat diF-TES-ADT and its blend with PS on pre-patterned substrates with bottom contacts as shown in schematic (Figure 5.7a). At lower speeds, in the ribbon like regime, we found massive anisotropic charge transport behavior in both

**Figure 5. 5** Atomic force microscopy images for neat diF-TES-ADT and its polymer blends with PaMS and PS (a) 0.5 mms$^{-1}$, 70°C and (b) 1.5 mms$^{-1}$, 70°C
neat and blend cases as presented in Figure 5.7b&c. In the spherulites regime (higher speeds), thin films charge transport becomes isotropic.

**Figure 5.6** Static GIWAXS images (a) & (b) neat diF-TES-ADT (c) & (d) diF-TES-ADT: PaMS showing the existence of only pure <001> texture (a) & (c) samples were prepared at blading speed of 0.5, 1.0 and 2.0 mms$^{-1}$ and substrate temperature of 70°C (b) & (d) samples were prepared at blading speed of 0.2 and 0.8 mms$^{-1}$ and substrate temperature of 25°C.
We performed GIWAXS experiments to understand the structural origins behind the anisotropic and isotropic charge transport behavior at low and high speeds respectively. We show in Figure 5.8, the GIWAXS data of neat diF-TES-ADT at 0.5 and 1.5 mms\(^{-1}\) and diF-TES-ADT: PaMS [100kDa] blend at 0.5 mms\(^{-1}\). We used two different x-ray beam incidence orientations of 0\(^{\circ}\) to 90\(^{\circ}\) (0\(^{\circ}\) being defined as parallel to blade’s moving direction). We can see that for the neat sample at 0.5 mms\(^{-1}\), the (21L) peaks are present at 90\(^{\circ}\) while they disappear at 0\(^{\circ}\). The peaks are present in both orientations at 1.5mms\(^{-1}\).

Firstly, it specified that (21L) is the growth direction of diF-TES-ADT crystallites. Secondly, it indicated that crystal growth is highly anisotropic at low speed while at higher speed it is more isotropic. A similar observation is made for diF-TES-ADT: PS system. This highlights the remarkable microstructure achievable using the blade coating method and is likely to be at least partly responsible for achieving the typically higher carrier mobility even in neat films.
5.4 Influence of Molecular weight of Insulating polymer binder on Microstructure, Texture, and OTFT’s Figure of merits

The molecular weight (Mw) of the polymer binder is known to influence the viscosity of the solution, as well as its solubility and miscibility. It is consequently an important parameter to investigate and understand. In Figure 5.9, we have plotted the mobility as a function of the Mw of PS for dif-TES-ADT:PS (1:1) blends. In the low-speed regime, blending the OSC with low-Mw PS dramatically reduces the mobility, whereas increasing the Mw beyond 100kDa yields mobility as high as ~4.5 cm²/Vs, far superior to the neat dif-TES-ADT blade coated best sample (0.6 cm²/Vs). POM and AFM images of the blend samples (low Mw) as shown in Figure 5.9b, indicate that the ribbon formation is disrupted by blending with low-Mw PS, whereas it is not disrupted by high Mw (Figure 5.5). AFM image also reveal that this blend film is also highly defective and contains pinholes.
Figure 5.9 (a) shows field effect mobility of BCBG devices based on neat diF-TES-ADT and blends of diF-TES-ADT with different molecular weights of Polystyrene at low speed of 0.5 mms\(^{-1}\) and high speed of 1.7 mms\(^{-1}\) (b) Images taken from in-situ HSPOM videos and corresponding AFM image showing the disruption of regular crystal growth process in case of low Mw PS: diF-TES-ADT blend at 0.5 mms\(^{-1}\)

We achieve a remarkable boost in performance when casting the blend in conditions of higher blading speed (1.7 mms\(^{-1}\)) as it can be seen in Figure 5.9. The carrier mobility increases steadily with increasing Mw, rising to as high as 4.5 cm\(^2\) V\(^{-1}\)s\(^{-1}\). The device figures of merit include ON/OFF > 10\(^6\) and threshold voltage of -0.1 V. The remarkable mobility can be understood by examining and comparing POM and AFM images of the neat film (Figure 5.10a) to the low Mw (Figure 5.10b) and high Mw (Figure 5.10c) blends. The micrographs reveal the formation of substantially larger domains in the high Mw case than in neat OSC or low Mw blends. The best films appear to be topographically smoother, are crack-free and appear to have sharp domains and grain boundaries, as indicated by AFM.
Figure 5.10 Top images show Polarized optical microscopy images while lower images show AFM images of thin film based on (a) Neat diF-TES-ADT (b) diF-TES-ADT: PS (Mw = 2.2k [50%]) (c) diF-TES-ADT: PS (Mw = 900k [50%]) (d) Height distribution profiles for all three cases extracted from AFM images.

Statistical distributions of the surface height were calculated from the entire AFM scan area (10μm x 10μm) and summarized in Figure 5.10d. The distributions have been centered at an arbitrary height of zero since the AFM tip does not sense the substrate in either case. From the shape and width of the distribution it is quite clear that the neat film is the roughest sample ($\sigma_{\text{RMS}} \sim 5$ nm) with features both tall and deep. The low Mw blend ($\sigma_{\text{RMS}} \sim 1.8$ nm) has a significant hump on the deep side, indicating the film contains pin holes, cracks or deep valleys at grain boundaries. By contrast, the high Mw blend appears to show a very narrow and symmetric distribution ($\sigma_{\text{RMS}} \sim 1.1$ nm), consistent with a very smooth OSC surface free of pin holes, cracks and exhibiting closed grain/domain boundaries. Polymer solution viscosity is strongly dependent on molecular weight of polymers and increases
with increasing molecular weight of polymer. The significant differences observed from the morphological investigations suggest that higher solution viscosities of high Mw PS blend solutions are possibly factoring into the formation of crack-free and topographically smooth domains of tightly connected OSC domains. In Figure 5.11a we have plotted the lamellar (001) x-ray diffraction (XRD) peak for diF-TES-ADT for the low and high Mw blends, normalized to film thickness estimated by ellipsometry. It is clear that lamellar crystallinity is substantially improved by OSC blending with the high Mw polymer. We have also plotted in Figure 5.11b the atomic ratio of carbon and fluorine extracted from x-ray photoelectron spectroscopy (XPS) analysis of the top surface of blends prepared using low and high Mw PS at low blading speed. The ratio is expected to be 19.6 for the pure OSC. However, the analysis reveals lower fluorine / higher carbon content in the low-Mw case, indicating the presence of some PS near the exposed surface of the blend.

Figure 5.11 (a) XRD spectra for diF-TES-ADT: PS blends with low (M_w = 2.2k g/mol) and high Molecular weight PS (M_w = 900k g/mol) at 1.7 mms^{-1} (b) shows C/F atomic ratio extracted using XPS analysis of diF-TES-ADT blend film with low (M_w = 2.2k g/mol) and high Molecular weight PS (M_w = 900k g/mol) at 1.7 mms^{-1}
By contrast, the high Mw blend seems to have an OSC-rich surface, consistent with the formation of a bilayer with the OSC near the top. These results clearly indicate the Mw of PS strongly influences the vertical stratification of the blend components which is believed to promote or disrupt long range lateral crystallization of the OSC. This may be related at its origin to differences in phase separation behavior in the presence of low and high Mw blends, which can exhibit Mw-dependent solubility and miscibility. We have imaged the vertical phase separation of the optimal high Mw blend film prepared at 1.5 mms\(^{-1}\) using cross-sectional EFTEM as shown in Figure 5.12a.

**Figure 5.12** Cross section Energy filtered transmission electron microscopy images of diF-TES-ADT: PS [400 kDa] thin films (a) 1.5 mms\(^{-1}\) (b) 0.5 mms\(^{-1}\) & 1.0 mms\(^{-1}\)

The micrograph clearly shows a bilayer phase separation with the OSC on top and the PS layer sandwiched between the OSC and the SiO\(_2\) dielectric. The total thickness of the bilayer is found to be ~21 nm with sub-layer thicknesses of ~11 nm and ~10 nm for the OSC and PS, respectively. We also performed similar analysis for samples prepared at 0.5 and 1.0 mms\(^{-1}\) (Figure 5.12b&c) to confirm that vertical phase stratification is similar at
different speeds. These observations are in agreement with the recent report of BCBG OFETs of diF-TES-ADT: PS in which the blend film has been shown to undergo bilayer vertical phase stratification as characterized by TEM. In the case of low Mw PS, we observe a mixed phase of OSC and polymer on top as seen from XPS results in Figure 5.11b. By contrast, the high Mw PS case yields a PS-free surface as confirmed by cross sectional EFTEM analysis as well (Figure 5.12). The above results clearly highlight the critical role the molecular weight of the insulating polymer plays in promoting long range lamellar order via effective phase separation and vertical stratification. They also marginalize the low Mw polymer as a poor candidate for high performance blend OFETs.

Our investigations of influences of blade speed and polymer Mw have been restricted thus far to a 1:1 w/w blend ratio of the OSC and polymer. In Figure 5.13a, we plot the mobility with respect to the blend ratio of OSC:PS for a fixed Mw of 900k to assess the compositional window over which the blending scheme is effective at promoting vertical stratification for a fixed overall solute concentration.
Figure 5.13 Represents field effect mobility of BCBG devices based on diF-TES-ADT: PS ($M_w = 900$ k g/mol) blend with different weight fraction of Polystyrene (PS) at 1.7 mms$^{-1}$.

The plot reveals three distinct regions: a PS-deficient device regime for $[\text{PS}] < 20\%$, a stable high performance regime for a composition $20\% < [\text{PS}] < 60\%$, and an OSC-deficient regime for $[\text{PS}] > 60\%$. Approaching either extreme appears to disrupt the uniform surface morphology or crystalline domains as revealed by POM and AFM (Figure 5.13b). Both extremes lead to smaller and distinctive crystallites of the OSC with high density of grain boundaries and cracks, whereas the stable performance regime, including 50% PS, is characterized by very large and well-connected domains with few gaps, cracks and surface morphological features visible to either AFM or POM. It seems that even a small amount of PS can have significant benefits with respect to device operation. If we look at the transfer curves and figures of merits such as $V_{th}$ and SS (Figure 14a-d) for devices with very low PS content (10% PS), we find that $V_{th}$ decreases substantially from 40 V (neat) to 15 V. Continuing to add PS, $V_{th}$ decreases to 2.5 V for $[\text{PS}] = 20\%$ and 0.4 V when $[\text{PS}] = 50\%$. Meanwhile, SS improves from 7 V dec$^{-1}$ (neat) to 2.5 V dec$^{-1}$ (10% PS), 0.55 V dec$^{-1}$ (20% PS) and 0.3 V dec$^{-1}$ (50% PS). We have calculated $N_{it}$ for these cases and summarized it in Table 2. $N_{it}$ decreases gradually from $\sim 10^{13}$ eV$^{-1}$ cm$^2$ in the neat OSC case to $2.7 \times 10^{12}$ eV$^{-1}$ cm$^2$ with 10% PS and $2.65 \times 10^{11}$ eV$^{-1}$ cm$^2$ with 50% PS. These remarkable improvements suggest that addition of PS to the diF-TES-ADT solution leads to significant improvements to the OSC-dielectric interface.
Figure 5.14 Transfer characteristics of BCBG OFETs corresponding to different blend ratios of PS (900 kDa) with diF-TES-ADT, highlighting the decrease in threshold voltage and subthreshold swing.

Table 5.2 Interfacial trap density corresponding to different blend ratios of PS (900 kDa) with diF-TES-ADT

<table>
<thead>
<tr>
<th>Trap Density</th>
<th>0% PS</th>
<th>10% PS</th>
<th>20% PS</th>
<th>50% PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_i$ (eV$^{-1}$cm$^2$)</td>
<td>3x10$^{13}$</td>
<td>2.69 x10$^{12}$</td>
<td>5.4x10$^{11}$</td>
<td>2.65x10$^{11}$</td>
</tr>
</tbody>
</table>

5.5 Influence of solvent selection on microstructure, texture and OTFT figures of merit

Blending diF-TES-ADT with the high Mw PS has led to a remarkable ~50× improvement in carrier mobility and dramatic improvements of other OTFT figures of merit. However, the carrier mobility of the films is still inferior to what has been achieved by spin-coating.
of semiconducting polymer: OSC blends ($5.4 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) or by single crystals of the OSC ($6 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$). Close inspection of POM images of the PS: OSC blends in actual devices reveals that the domain size is smaller than the area of a single device (Figure 5.10c), hinting that better results might be achieved if more could be done to extend the domain and grain sizes. We recall a previous study in which a dual solvent approach was used consisting of a mixture of polar and non-polar solvents to increase the size of OSC domains in neat films. We take the view that the appropriate solvent mixture can enhance polymer solubilization, e.g., in the main solvent, and lead to enhanced phase separation which might further promote the in-plane growth of lamellar OSC sheets. We have selected anisole and mesitylene as the polar and nonpolar (main) solvents, respectively, and varied their mixing ratio. To explain the rationale for this choice, we consider the Hansen solubility parameters for anisole, mesitylene, toluene, and PS (Table 3; $\delta_d$, $\delta_p$ and $\delta_h$ represent the energy associated to dispersion, dipolar and hydrogen bonding forces, respectively).

Table 5. 3 Hansen solubility parameters for the various solvents and polystyrene

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\delta_d$ (MPa)$^{1/2}$</th>
<th>$\delta_p$ (MPa)$^{1/2}$</th>
<th>$\delta_h$ (MPa)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>18.5</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>18</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Anisole</td>
<td>17.8</td>
<td>4.4</td>
<td>6.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.1</td>
<td>1.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Based on these parameters, anisole is a better solvent for PS, while mesitylene is a poor solvent. Furthermore, we confirm the differences in solubility of diF-TES-ADT in both solvents and in mixtures thereof by performing UV-Vis absorption measurements of dilute
diF-TES-ADT:PS blend solutions (ca. 0.5 mg/ml) as shown in Figure 5.15. The addition of anisole in the blend solution causes a red shift which indicates an increase in the aggregation of diF-TES-ADT. This shift also suggests that anisole is a poorer solvent for diF-TES-ADT than mesitylene. Possibly, these two solvents can also form an azeotropic binary solvent mixture (different solubility of the solute in binary solvent mixture) which has been proven to be beneficial to grow single crystals of TIPS:pentacene.

**Figure 5.15** UV-Vis absorption spectrum for diF-TES-ADT: PS [400 kDa] in neat and mixed solvents

In the solid state we observed a clear transition from ribbon-like crystallites (mesitylene) to sheet-like crystallites (mesitylene: anisole). This transition is consistent with what has been reported for TIPS-pentacene by using the binary azeotropic mixture of toluene/isopropanol. In Figure 5.16 we plot the field effect mobility of OSC: PS blends prepared in different solvent mixtures using both low and high Mw PS as binder. All films were blade coated at a lower speed of 0.5 mm s\(^{-1}\) using a base temperature of 100°C. Similar trends can be seen with respect to molecular weight as with single solvent devices. High Mw blends consistently outperform low Mw ones by nearly an order of magnitude. This trend appears to hold across solvent mixtures. Importantly, we find that devices behave rather poorly in the case of pure solvents whereas solvent mixtures, especially those rich
in mesitylene (poor in anisole), behave particularly well. Pure anisole and mesitylene yield mobilities on the order of $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ and $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, respectively. We achieve the highest field effect mobility of $6.7 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ when the solvent mixture is 20% anisole/80% mesitylene.

![Graph](a) ![Graph](b)

**Figure 5.16** Device performances representing field effect mobilities for the cases of (a) blends of dif-TES-ADT with low (2.2k g/mol) and high (400k g/mol) molecular weights of PS for varying amounts of solvent mixtures containing Mesitylene and Anisole (b) XRD spectra showing (001) Bragg peak for single solvent and dual solvent blend

The solvent mixture appears to form higher quality films than the single solvent (anisole or mesitylene) cases. The solvent mixture leads to significantly higher lamellar crystallinity as indicated by XRD measurement shown in the inset of Figure 5.16b. However, the higher order Bragg peaks of these very thin films are extremely weak and do not show up in the
XRD analysis. We also observe by POM remarkably large domains spanning the millimeter scale (Figure 5.17b). Closer examination by AFM reveals few if any topographic defects and boundaries (Figure 5.17b). In the pure mesitylene case (0% anisole) ribbon-like crystalline features with significant cracking are observed by POM and AFM in Figure 5.17a, whereas films cast from pure anisole result in the formation of very small grains (Figure 5.17c). The statistical distribution of surface height extracted from the full AFM scan (50μm x 50 μm) reported in Figure 5.17d which is quite revealing in that it shows once more the remarkable flatness of the blend prepared by using a solvent mixture ($\sigma_{RMS} \sim 4.57$ nm) as opposed to the single solvent cases. We observe significant height variations ($\sigma_{RMS} \sim 15.71$ nm) associated to grain and domain boundary features between ribbons in the case of pure mesitylene and smaller but still significant height variations ($\sigma_{RMS} \sim 6.24$ nm) due to formation of fine crystallites in the pure anisole case. The record-breaking dual solvent blend was cast at a lower blading speed (0.5 mm/s) than the optimal speed for the single solvent (toluene) case, suggesting that changes in formulation can help to maintain high performance across a broad window of coating conditions.
We have summarized in Figure 5.18a, the blade coating speed dependence of device performance for neat OSC as well as blends based on the single solvent (toluene) and dual solvent (anisole/mesitylene) approaches. This comparison shows that a broad processing window exists within which consistently high carrier mobility (>3 cm$^2$ V$^{-1}$s$^{-1}$) can be achieved simply by adjusting the formulation. By contrast, neat films prepared using toluene typically yield mobility < 0.1 cm$^2$ V$^{-1}$s$^{-1}$. Comparison between the (001) lamellar Bragg peak intensities of the best dual solvent blend and the best single solvent blend based on toluene (Figure 5.18b) suggests a further improvement in the lamellar stacking quality obtained by the use of the solvent mixture. We therefore find mounting evidence suggesting that an improvement in lamellar crystalline quality and texture coupled with a
flat, pinhole- and crack-free OSC film with few topographically visible domain boundaries have the potential to yield carrier mobilities approaching and even on par with those of single crystal devices of the same OSC.

Figure 5. 18 (a) Device performances representing field effect mobilities at different blade coating speeds for the cases of neat dif-TES-ADT and blends of dif-TES-ADT: PS [400k g/mol] with single solvent (Toluene) and dual solvent (Mesitylene: Anisole) (b) XRD (001) Bragg peak showing the difference between the best single solvent blend film and the best dual solvent blend film (c) POM and AFM images for best diF-TES-ADT: PS single solvent and dual solvent blends.

We compare in Figure 5.18c the morphological features of the neat OSC and blends prepared using toluene and dual solvent approach obtained in conditions yielding the best OTFT devices for each approach. The single solvent blend approach yields polycrystalline OSC films with several large domains visible under POM and well-connected as evidenced by AFM. The dual solvent blend approach shows no distinctive domains under POM and yields films with little if any boundaries on the scale of the OTFT device. This absence of any microstructurally distinct domains in the dual solvent case yields ultrathin films which appear single-crystal-like in many ways and certainly yield performance on par or even
surpassing state-of-the-art single crystal FET devices made from the same OSC. The field effect mobility of dual solvent blend decreases after 1 mm/sec at 100°C as it can be seen in Figure 5.18a (blue data). AFM images shown in Figure 5.19 reveal that the dual solvent blend films at 1.5 mms⁻¹ and 2 mms⁻¹ is defective and contains high density of grain boundaries. It suggests that further optimization of substrate temperature, blend ratios and solvent mixture ratio is necessary to achieve high quality thin films at higher speeds.

![Dual solvent diF-TES-ADT: PS blend](image)

**Figure 5.19** Atomic force microscopy images of diF-TES-ADT: PS [400 kDa] blend films coated at 1.5 mm/sec and 2.0 mm/sec, 100°C

### 5.6 In situ Investigations by HSPOM and in situ GIWAXS

We used *in situ* μGIWAXS and HSPOM to investigate the nucleation and growth behavior of high performing blend films based on dual solvents under different processing conditions. POM images from HSPOM movies for neat diF-TES-ADT and its blend using mesitylene as a solvent at 0.5 mms⁻¹, 100°C are shown in Figure 5.20. It reveals that ribbon like crystals grow in both cases. The polymer binder improves the growth and crystallites
are more oriented. The close examination of HSPOM videos suggest that nucleation is happening from bulk liquid meniscus near the edge of the blade in both cases as shown in Figure 5.20c. There is clear evidence of extended amorphous intermediate state as highlighted in the images but nucleation and growth is not disturbed by this extended region. The crystallites are growing from liquid and are visible underneath the amorphous region.
Figure 5.20 POM images taken from HSPOM videos recorded during blade coating at 0.5 mm/sec, 100°C using mesitylene as a solvent for (a) Neat diF-TES-ADT (b) diF-TES-ADT: PS [400 kDa] (c) Zoomed in images highlighting the liquid meniscus and extended amorphous region.

We also investigated the crystallization behavior for solvent mixture cases as shown in Figure 5.21. These POMs suggest that crystallization proceeds from an extended...
amorphous state. Crystallites grow in the form of sheets instead of ribbon like crystals as we have seen from pure mesitylene. The growth rate of these single domain-like sheets of diF-TES-ADT from dual solvent blend system is approximately 0.4 mm/sec and it is similar to the blade coating speed. This growth rate is twice as slow compared to growth rate of diF-TES-ADT crystallites (0.8 mm/sec) from blend films coated at 1.6 mm/sec and 70°C. This suggests that slow growth rate is favorable to grow high quality thin films of OSC.

![POM images](image)

**Figure 5.21** POM images taken from HSPOM videos for diF-TES-ADT: PS [400 kDa] blend coated at 0.4 mm/sec, 100°C with varying volume fraction of Mesitylene and Anisole

We used *in situ* µGIWAXS to validate our HSPOM observations about nucleation and growth mechanism in these high performance blend systems. We plot the integrated intensity of (001) Bragg sheet and solution scattering ring vs. time in Figure 5.22. Crystallization signal appears at 0.6 sec after detection of bulk solution by GIWAXS and it overlaps with the solution scattering signal which fades away at 0.8 sec for pure mesitylene case (Figure 5.22a). We can see that solution scattering signal fades away at 0.6
sec, and crystallization signature coming from (001) appears at 0.9sec. There is delay of 0.3sec. This corresponds to the formation of intermediate amorphous state, leading to Two-step nucleation phenomenon. It is noteworthy that two-step nucleation can be triggered at such low speeds by using appropriate processing conditions. This crystallization behavior in these solvent mixture blend systems is playing a key role to achieving high quality single crystal like sheets of diF-TES-ADT.

![Graph showing crystallization behavior](image)

**Figure 5. 22** Integrated intensity (solution scattering and (001) Bragg sheet of OSC) vs. time plots for diF-TES-ADT: PS [400 kDa] blade coated at 0.4 mm/sec, 100°C

### 5.7 Conclusions

In this study, we showed that optimized coating conditions (speed and temperature) in the context of polymer:OSC blends can lead to the formation of very high quality OSC thin
films. These thin films are polycrystalline but with well-connected grains and domain boundaries. High molecular weight amorphous polymer such as polystyrene is a very good binder. It helps small molecules to crystallize uniformly on large areas with good grain boundary quality as compared to neat which end up having defects in grains and crevices at grain boundaries. EFTEM revealed a bilayer vertical phase separation with small molecule crystallized on air interface. We find that thin layer of PS stratified on bottom surface modifies the SiO₂ dielectric surface. This thin phase separated PS layer also becomes part of dielectric. We believe that the phase separated interface between small molecule OSC and PS serve as conduction interface. This high quality interface leads to massive reduction in interfacial trap states density from 10^{13} \text{cm}^{-2}\text{eV}^{-1} (neat) to 10^{11} \text{cm}^{-2}\text{eV}^{-1} (blend). The blend films also have lower threshold voltages (close to 0) and high on/off ratios of 10^5-10^6 as compared to neat films lower on/off ratios of 10^3 and massive positive threshold voltage. The charge carrier mobility is also improved to the average values of 2 \text{cm}^2/\text{Vs} and maximum reaching to 4 \text{cm}^2/\text{Vs}. On the other hand neat films showed carrier mobility < 0.5 \text{cm}^2/\text{Vs} under all processing conditions. Furthermore, using appropriate solvent mixtures such as mesitylene and anisole under optimized coating conditions improved the quality of OSC crystallites and it yielded sheet like polycrystalline thin films of diF-TES-ADT: PS. These thin films had coherent domains with few boundaries and with very smooth, pinhole- and crack-free topography of the OSC surface both within the domains and at their boundaries. These blend films showed average carrier mobilities of 3 \text{cm}^2/\text{Vs} and maximum reaching to 6.7 \text{cm}^2/\text{Vs} along with lower threshold voltage of 0.1 V and high on/off ratios of 10^5-10^6. \textit{In situ} investigations by HSPOM and GIWAXS reveal that all the high performance blend films crystallize via two-step
nucleation pathway. The intermediate amorphous state is key to achieve uniform high quality thin films. HSPOM showed that crystallites growth rate for best optimized dual solvent (Mesitylene: Anisole) blend case is 0.4 mm/sec which is two times slower than the growth rate for best single solvent case (0.8 mm/sec) at 1.4 mm/sec, 70°C in toluene. The lower growth rate is also facilitating the high quality sheet like large domains of OSC in dual solvent case. We conclude that optimized coating speed in two-step nucleation window, Mw of binder polymer, blending ratio, choice of solvents and crystal growth rate are key factors influencing thin film quality and eventually charge carrier mobility.
Chapter 6

Contact-induced nucleation in small-molecule OSC films prepared via blade-coating

6.1 Introduction

Solution-coating of organic semiconductors on pre-patterned electrodes and circuit arrays is increasingly common and is expected to be the route toward manufacturing of organic electronic circuits. In this regard, bottom contact device architectures are good model systems by which to investigate the influence of metal contacts terminated with different surface chemistries and surface energy on the nucleation and growth of OSCs coated from neat solutions and polymer:OSC blended inks. Self-assembled monolayers (SAMs) have been used extensively to modify metal electrodes. In this respect, surface treatment of metal contacts by halogenated SAMs, such as pentafluorobenzenethiol (PFBT) has been successfully implemented to modify the WF of metal contacts in aim to reduce the injection barrier and also to control the crystallization behavior and texture of spin-cast OSCs on BCBG or bottom contact top gate (BCTG) device architectures with great benefit. PFBT treatment of contacts has been shown to induce preferential lamellar texture in spin-cast diF-TES-ADT films, both on contacts and within the channel of OFETs, eventually boosting the OTFT performance by several orders of magnitude. However, we have shown that the crystallization behavior of OSCs is dramatically different when switching to scalable processes, such as blade coating, in particular when two-step nucleation is the dominant crystallization and film formation pathway, both for neat OSCs and blends. It is therefore expected that the conventional wisdom with regards to contact-induced
nucleation effects must be reviewed in the context of scalable coating processes. Apart from SAM treatments, it is also reported that chemical treatments such as O\textsubscript{2}-Plasma can also be used to tune the WF of metal contacts. But its impact on crystallization behavior of OSCs during blade-coating is yet to be elucidated.

In this chapter, we investigate the influences of halogenated SAM treatments and cleaning procedures (O\textsubscript{2}-plasma) of gold contacts on the crystallization behavior of the halogenated diF-TES-ADT and non-halogenated TIPS-pentacene, Allyl DIPS-pentacene, and CP-DIPS-pentacene, as well as blends thereof, when prepared by blade-coating as compared with spin-coating. We begin by presenting the influence of SAMs and O\textsubscript{2}-plasma treated Au-contacts on the morphology and OFETs performance of spin coated OSCs. We investigate the impact of O\textsubscript{2}-plasma treatment on the Au contacts by photoelectron spectroscopy to understand the changes in WF of as-deposited Au and their impact on OTFT performance. Then, we investigate the influence of SAMs and O\textsubscript{2}-plasma treated Au-contacts on the morphology and OFETs performance of blade-coated OSCs. We use \textit{in situ} HSPOM and \textmu GIWAXS to understand the crystallization mechanism of OSCs during blade coating on O\textsubscript{2}-plasma and PFBT treated Au-contacts. Then, we investigate the microstructure of spin-cast and blade-cast OSC films across the device channel of O\textsubscript{2}-plasma and PFBT-treated Au contacts by \textmu GIWAXS. We also fabricated and tested BGBC OFETs (with as-deposited Au, O\textsubscript{2}-plasma treated Au and SAM treated Au contacts) to correlate device performance to microstructure, morphology and phase separation of the blade coated blend films of various OSCs.
6.2 Contact-induced nucleation in neat OSCs

6.2.1 The case of spin-coating

It is useful to recall the effects of contact-induced nucleation in spin-coating, the reference process. For this purpose, we have used two OSCs, diF-TES-ADT and TIPS-pentacene, in combination with four different halogenated SAMs, to illustrate the conventional effects of contact-induced nucleation. This selection was made on the basis that diF-TES-ADT has halogen atoms in its structure which have been postulated to interact strongly with halogenated SAMs through F-F interactions. On the other hand TIPS-pentacene does not have any halogen atoms in its structure. The selected SAMs have fluorine (F) atoms at different positions, depending on their chemical structure. We have selected PFBT and 3,5-MFBT to allow multiple interaction opportunities while 2-MFBT and 4-MFBT allow only a single interaction with the halogen in the OSC. We spin-cast OSCs at 1000 rpm for 60 s from a 1 wt.% toluene solution on substrates pre-patterned with Au contacts. It is worth noting that when a SAM was not used, the electrodes were exposed to an O$_2$-plasma for cleaning purposes (more on the effects of this cleaning procedure below), prior to spin-coating the OSC. POMs of both OSCs on plasma-treated Au are shown in Figure 6.1.
Figure 6.1 Polarized optical microscopy images of spin coated OSCs on O2-plasma treated pre-patterned substrates (a) TIPS-pentacene (b) diF-TES-ADT.

Fine and isotropic-looking crystals are observed everywhere on the surface without any apparent difference between the microstructure or morphology of the OSC on the contact or the dielectric (SiO2). When the same experiment was carried out on substrates treated with the SAMs mentioned above, then both diF-TES-ADT and TIPS-pentacene films showed evidence of contact-induced nucleation as indicated by the growth of oriented crystallites from the edges of the metal contacts, as shown in Figure 6.2. It can be seen that both OSCs interact with halogenated SAM treated Au contacts, irrespective of whether or not they have halogen atoms in their structure. It is also evident that both OSCs interact very strongly with PFBT-treated Au as compared to other two treatments. The fluorinated SAMs are hydrophobic and naturally change the wetting properties of the contact, as can be seen in Figure 6.3. The contact angle measurements show that PFBT treatment results in the highest contact angle of 93° as compared to 71° for 4-MFBT and 24° for plasma-
treated Au contacts. This hydrophobic nature of PFBT/Au might be playing a key role in
inducing early onset of crystallization on contacts before this occurs on the surface of the
SiO$_2$ dielectric, where the contact angle is 17°. An interesting observation can also be
made with respect to the significant difference in the contact angles of as-deposited Au and
plasma-treated Au, with the latter being hydrophilic while the former is quite hydrophobic.
We will come back to this point later in this chapter.

Figure 6.2 Polarized optical microscopy images of spin coated OSCs on untreated pre-
patterned substrates (a) TIPS-pentacene (b) diF-TES-ADT.

Figure 6.3 Sessile drop water contact angle on (a) As deposited Au (b) O2-Plasma treated
Au (b) (c) Halogenated SAMs treated Au.
6.2.2 Work function measurements of Au contacts by UPS

We employed ultraviolet photoemission spectroscopy (UPS) to compare the work functions of the various modifications of the Au substrate. Figure 6.4a shows the secondary electron (SE) cutoffs for bare Au, O$_2$-Plasma treated Au, 3, 5-MFBT treated Au, 4-MFBT treated Au and PFBT treated Au surfaces. The work function (WF) values of all of these cases, as extracted from the SE cutoffs, are shown in Figure 6.4b. For the as-deposited Au case, WF value (-4.7 eV) matches quite well with the reported values. It is important to note that WF values for PFBT-treated Au and O$_2$-plasma treated Au are quite similar i.e., 5.5 and 5.6 eV respectively. We have summarized the WF values of Au under all the studied conditions (our results and reported in literature$^{182}$) and apparent injection barrier in Table 6.1. It is noteworthy to note that only as-deposited Au has an injection barrier for both OSCs while all the other cases do not have any injection barrier suggesting that charge transport is not limited by contacts.$^{24,182}$ For all the SAM-treated cases, we observe slight deviations from the values mentioned in reported data. This can be ascribed to the metal WF being extremely sensitive to surface coverage by SAM, orientation of SAM, environmental conditions, surface roughness and ordering in the end groups of a particular SAM due to lab to lab processing differences.
Figure 6. 4 (a) Secondary electron cutoffs (SE) obtained by ultraviolet photoemission spectroscopy (UPS) for the various cases are shown (b) shows the work function values obtained from (a) The HOMO for the OSCs is also shown.

Table 6. 1 Summary of work function measurements and injection barriers for all the studied cases
Note: All the values have units of eV.

<table>
<thead>
<tr>
<th></th>
<th>As-deposited Au</th>
<th>4-MFBT/Au</th>
<th>3.5-MFBT/Au</th>
<th>PFBT/Au</th>
<th>O₂-Plasma Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our WF data</td>
<td>4.7</td>
<td>5.2</td>
<td>5.3</td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Literature WF data</td>
<td>4.7-4.9</td>
<td>5.3</td>
<td>5.0</td>
<td>5.3</td>
<td>5.3-5.4</td>
</tr>
<tr>
<td>Injection barrier</td>
<td>0.3</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>(diF-TES-ADT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection barrier</td>
<td>0.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>(TIPS-Pentacene)</td>
<td></td>
<td></td>
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</tbody>
</table>
6.2.3 Investigation of O₂-plasma treated Au contacts

The plasma-cleaning of Au contacts has been shown to significantly change the wetting behavior, workfunction and crystallization of the OSC with respect to as-deposited Au contacts. To shed light onto the effects of O₂ plasma cleaning on the Au contacts we deployed X-ray photoemission spectroscopy (XPS), which can successfully yield crucial chemical and electronic information regarding the top nanometers of the Au contact. We maximize the surface sensitivity of XPS by collecting the photoelectrons at smaller take-off angles with respect to the sample plane. Figure 6.5 shows the angle-resolved XPS (ARXPS) spectra for the Au substrate treated with oxygen plasma for 10-15 minutes. Figure 6.5a shows the 4f doublet components, 4f\(_{7/2}\) and 4f\(_{5/2}\) for the bare, as-prepared Au film, observed at 84.0 eV and 87.6 eV, respectively, as expected. The panels (b)-(f) show the 4f region of the plasma-treated Au for take-off angles varied in steps from 90° (more bulk-sensitive) to 15° (more surface sensitive). Minor components at higher binding energies, BE, (85.8 eV and 89.4 eV) are observed having the same split-orbit splitting as the main 4f peaks. This is in agreement with the XPS spectra reported for gold (III) oxide, Au\(_2\)O\(_3\). As the photoelectron take-off angle is decreased making the measurements increasingly surface sensitive, the components associated with the oxide increase, confirming that the oxide layer is accumulated at the top surface. The O1s core level can lead to important insights into the nature of the oxide. O1s peak is found to consist of two components centered at 529.7 eV and 530.7 eV. Although the lower BE component has been suggested to be associated to the surface oxide, there is no general consensus in literature regarding the origin of the higher BE component, which has been suggested to be either from surface hydroxyls or the three-dimensional gold oxide beneath.
Interestingly, we find that the higher BE component decreases for more surface sensitive angles, suggesting that, in our case, it originates from the three-dimensional gold oxide rather than surface hydroxyls (Figure 6.5g &h).

**Figure 6.5** ARXPS showing the Au 4f core levels for (a) bare, as-prepared Au film and (b)-(f) the oxygen plasma-treated Au for increasingly surface-sensitive electron take-off angles. The oxide components (pink) increase in intensity relative to the metallic components (yellow) for highly surface sensitive angles suggesting that the Au2O3 phase is located at the top of the film. (g) & (h) O1s core level peak is deconvoluted into two components. The 529.7 eV component (pink) corresponds to the surface oxide whereas the 530.7 eV component (blue) is related to the oxide from the bulk. As expected, the surface oxide peak becomes stronger for the surface-sensitive take-off angle (15°) as compared to bulk sensitive angle 90°.

The relative atomic concentrations of Au and O found from XPS curve fitting of the ARXPS spectra are summarized in **Table 6.2**. Expectedly, the ratio of the oxide component in the 4f peaks, Au(III), and the metallic gold, Au(0), shows an increase for
higher surface sensitive angles. This is commensurate with a similar trend found for the 
O/Au ratio. However, we observe that the O/Au ratio is smaller than the 1.5 expected for 
the Au$_2$O$_3$ phase, even for the highly surface sensitive take-off angles. This suggests the 
possibility that the oxide layer is ultra-thin or partially oxidized, and will be discussed later.

Table 6. 2 Relative atomic concentrations for Au and O found from ARXPS on oxygen 
plasma-treated gold sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au</th>
<th>O</th>
<th>O/Au</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au(0)</td>
<td>Au(III)</td>
<td>Au(III)/Au(0)</td>
</tr>
<tr>
<td>Bare</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90°</td>
<td>66.5</td>
<td>6.9</td>
<td>0.10</td>
</tr>
<tr>
<td>75°</td>
<td>68.3</td>
<td>6.0</td>
<td>0.09</td>
</tr>
<tr>
<td>60°</td>
<td>65.7</td>
<td>6.4</td>
<td>0.10</td>
</tr>
<tr>
<td>45°</td>
<td>59.6</td>
<td>7.1</td>
<td>0.12</td>
</tr>
<tr>
<td>15°</td>
<td>41.5</td>
<td>9.3</td>
<td>0.22</td>
</tr>
</tbody>
</table>

We next studied the effect of plasma-treatment on the electronic properties of the gold 
interface. A dissociative chemisorption of oxygen on gold surface is known to increase the 
work function of the treated surface. Conversely, an increased work function of the oxygen-
treated gold surface implies charge transfer from Au to O and hence the formation of Au-
O chemical bonds.[8-9] Oxygen physisorption, on the other hand, has been suggested to 
reduce the gold work function.[10] It is also possible to gain information regarding such a 
charge transfer by studying the valence band structure of the treated gold samples. It has 
been suggested that the Au-O bond formation takes place via hybridisation of the Au 5d 
and O 2p orbitals, meaning that the Au d-band features will undergo changes upon plasma
With this important insight, we probed the valence band structure and the work function of our gold sample before and after plasma treatment, using UPS. The bare, as-prepared gold film is found to exhibit a work function of *ca.* 4.7 eV, in accordance with reported values. The valence band of gold shows a high density of states (DOS) at the Fermi edge and sharp features associated with the d-band, as expected. The UPS spectra are shown in Figure 6.6b, c and d. Importantly, we find that the plasma-treated gold shows significantly reduced d-band features and Fermi edge, suggestive of reduction of metallicity of the surface and the fact that the Au 5d electrons are involved in hybridization and hence bond formation. This is accompanied with a significantly increased work function. We suspect that a surface dipole arising out of the Au-O species might be responsible for the large work function increase.
Figure 6. (a) XPS spectra of the Au 4f core levels for the bare, oxygen plasma-treated and sputtered gold film. All the three spectra are shown for normal emission (90° take-off). (b) Valence bands for the three scenarios are shown, dashed-lines indicate the important d-band features and the Fermi edge. (c) Fermi edge for the three cases are compared after normalizing the spectra with the region at 10 eV (beyond the d-band). (d) Secondary electron cutoffs as obtained from UPS.

To elucidate this, we removed the oxide layer under ultra-high vacuum (UHV) conditions by sputtering the plasma-treated gold sample via Ar$^+$ irradiation for a few minutes. The chemical composition of the sputtered surface was studied by XPS and is shown in Figure 4(a)-(iii). The sputtered Au 4f core levels resemble those of the bare gold prior to plasma treatment, indicating a complete removal of the oxide. This is complemented with the reappearance of the Au d-band features and a strong Fermi edge. The work function,
however, is found to be *ca.* 5.2 eV, as is expected for clean gold surfaces, which is *ca.* 0.4 eV smaller than the value obtained for the plasma-treated surface. This allows us to directly determine the energy of the surface dipole (*ca.* 0.4 eV). As suggested by a previous report, such a value of the surface dipole might correspond to a sub-monolayer gold oxide, a scenario which seems to agree with the <1.5 O/Au ratio we obtain even for the highly surface-sensitive angles in ARXPS.

### 6.2.4 BCBG OFETs by Spin coating

We have summarized in Figure 6.5 the carrier mobility of BCBG devices prepared with both OSCs on all surface treatments by spin coating. Looking at these spin-cast devices (Figure 6.7a), we find the mobility is lowest on O₂-plasma treated Au and is typically \(~10^{-4}\) cm²/Vs (slightly lower in case of diF-TES-ADT as opposed to TIPS-pentacene) and increases to \(~10^{-2}\) cm²/Vs when halogenated SAM treatment is applied. This improvement in the device performance is drastic for both OSCs. We attribute it to the formation of better-aligned crystalline domains within the channel as a result of contact-induced nucleation, as shown by POM. This observation is in agreement with reports by several research groups which have highlighted the necessity of using SAMs for contact modification in order to achieve performance improvements in spin-cast OSCs.
Figure 6. 7 (a) Field effect mobility for spin coated OSCs BGC OFETs with different halogenated SAMs (b) & (c) Transfer characteristics of TIPS-pentacene based BCBG OFETs with O\textsubscript{2}-Plasma and PFBT-treated Au contacts respectively.

Spin-cast OSCs on as-deposited Au contacts which have not been subject to plasma cleaning result in similar morphology as observed for PFBT/Au case, as shown in Figure 6.8. However, the mobility of these devices was 2-3 orders of magnitudes lower than PFBT/Au. This lower performance can be attributed to the known charge injection problems due to Schottky barrier formation between as-deposited gold metal contact and the ionization potential of the OSCs. We noticed that in some areas of the substrate (O\textsubscript{2}-plasma treated Au), spherulitic domains were formed which is not commonly observed for spin-coating of these OSCs. The BCBG device performance in these areas was similar to the best PFBT/Au devices, suggesting that careful selection of processing conditions can result in film formation which does not necessarily require SAM modification for Au contacts.
6.2.5 The case of Blade Coating

We have repeated the same set of experiments as above, focusing on blade coating in conditions which yield directional crystallization of ribbons at low coating speed (0.5 mms\(^{-1}\)) as well as spherulite formation at higher speeds (1.5 & 2.5 mms\(^{-1}\)). In Figure 6.9 a-c, we show micrographs of blade-cast diF-TES-ADT and TIPS-pentacene thin films on O\(_2\)-plasma treated and SAM-treated Au contacts.
Figure 6.9 Polarized optical micrographs of blade coated neat diF-TES-ADT (0.5 mms⁻¹, 1.5 mms⁻¹, 70°C) and TIPS-pentacene (2.5 mms⁻¹, 70°C) (a) O₂-Plasma treated Au (b) PFBT/Au (c) 2-MFBT treated Au

In the ribbon-like regime, both OSCs exhibit identical crystallization behaviors irrespective of whether or not the contacts are plasma-treated or modified with a SAM, indicating that ribbon-like OSC growth is substrate and contact-independent. In the spherulitic regime, the contacts appear to matter much more. Formation of spherulites appears to be independent of the presence of contacts when these are only plasma-treated, resulting in the unobstructed formation of large spherulites to bridge channels and contacts. However, the presence of halogenated SAMs on Au contacts is seen to disrupt spherulite formation both for diF-TES-ADT and TIPS-pentacene, with stronger effects observed for the PFBT SAM than for the other SAMs. This indicates the SAM-OSC interactions drive heterogeneous
nucleation not only in halogenated OSCs, but also in non-halogenated OSCs. The contact-induced nucleation gives rise to smaller crystallite formation on the gold and at its edges, compared to what is typically achieved by blade coating in the absence of such interactions. This results in a larger grain boundary density in the channel of devices, whereas in the case of spin-coating, the contact-induced nucleation results in lower GB density in the channel, since spin-coating typically yields much finer crystals in the absence of the treatment.

In Figure 6.10 a&amp;b, we have summarized the carrier mobility of BCBG devices prepared with both OSCs on all surface treatments by blade coating in the ribbon like and spherulites regime. The corresponding transfer characteristics for blade coated thin films in ribbon like and spherulites regime are shown in Figure 6.10 c&amp;d. Looking at blade coated devices, we find the device performance in the ribbon-like regime (0.5 mms⁻¹) to be substantially better (~10⁻¹-10⁰ cm²/Vs) than spin-coating on untreated Au (~10⁻⁴ cm²/Vs) and on PFBT/Au (~10⁻² cm²/Vs). Device performance is substrate-independent at low speed, in agreement with POM observations made in the ribbon-like growth regime. By contrast, the spherulitic regime demonstrates high performance (similar to ribbon-like regime) on plasma-treated substrates, with the performance on SAM-treated Au substantially degraded. Mobility decreases to ~10⁻²-10⁻¹ cm²/Vs on PFBT/Au and to ~10⁻³-10⁻² cm²/Vs on the other two SAMs, nearly approaching the low performance of spin-cast devices on untreated Au. The performance trend in the spherulitic regime of blade coating is therefore the complete opposite of the behavior of devices prepared by spin-coating on identical substrates, and constitutes a major and surprising finding of this investigation.
Figure 6.10 Field effect mobility for blade coated OSCs BGBC OFETs with different halogenated SAMs (a) Ribbon like regime (b) Spherulites regime Transfer characteristics of blade coated TIPS-pentacene BCBG OFETs in (c) ribbon like and (d) spherulitic growth regimes.

6.3 In situ investigation of nucleation and growth on patterned substrates in Blade coating

The HSPOM investigation of the crystallization process of OSCs on pre-patterned substrates (Au contacts on Si/SiO$_2$ substrates) treated with O$_2$-plasma or halogenated SAMs such as PFBT is summarized in Figures 6.11 and 6.12. The HSPOMs in Figure 6.11 were taken in the ribbon-like crystallization regime (1 mms$^{-1}$, 70°C) on O$_2$-plasma and PFBT treated substrates pre-pattered with Au. It is quite evident that ribbon like crystallites propagate the same way and at the same speed on both types of substrates, both on the Au and SiO$_2$, irrespective of surface treatment carried out before thin film, confirming ex situ POM observations. These observations explain the findings that field-effect mobility is independent of surface treatment effects in the ribbon-like growth regime at low coating speeds.
Figure 6.11 POM snapshots taken from HSPOM videos recorded during blade coating of neat diF-TES-ADT (1 wt% toluene solution) at 1 mms$^{-1}$, 70°C on (a) O$_2$-Plasma treated BCBG substrates (b) PFBT treated BCBG substrates.
Two-step nucleation regime  
2 mms$^{-1}$, 70$^\circ$C

(a) O$_2$-Plasma/Au  
(b) PFBT/Au

Figure 6.12 POM snapshots taken from HSPOM videos recorded during blade coating of neat diF-TES-ADT (1 wt% toluene solution) at 2 mms$^{-1}$, 70$^\circ$C on (a) O$_2$-Plasma treated BCBG substrates (b) PFBT treated BCBG substrates.

In Figure 6.12 we show the HSPOM snapshots taken during blade-coating of neat diF-TES-ADT films in the spherulite growth regime (2 mms$^{-1}$, 70$^\circ$C), previously identified as the two-step nucleation regime. The comparison includes O$_2$-plasma-treated and PFBT-treated Au contacts on SiO$_2$. We find that the growth of the OSC is identical in SiO$_2$ and Au regions when O$_2$-plasma treatment is used, as shown in Figure 6.10a, resulting in large spherulite formation everywhere, significantly downstream from the edge of the blade. On the other hand, diF-TES-ADT interacts strongly with the halogenated SAM (PFBT)
treatment on Au and results in early onset of crystallization of the OSC as well as a significant increase of the nucleation density of OSC crystallites on Au contacts, with the implication that the OSC microstructure is strongly impacted in the device channel (Figure 6.10b). In both cases, the crystallization takes place from the amorphous intermediate phase, but the treatment of Au promotes early nucleation, suggesting it is heterogeneous in nature when PFBT treatment of Au is used.

We monitored the crystallization behavior of neat diF-TES-ADT on plasma-cleaned Si/SiO$_2$ substrates, and PFBT-treated Au coated substrates using time resolved $\mu$GIWAXS (Figure 6.13 a&b). We have plotted the integrated intensity of solution scattering ring and (001) Bragg sheet of diF-TES-ADT versus the position of the blade with respect to the x-ray beam position. We define zero position as the point when maximum intensity from solution scattering is recorded. We can see that diF-TES-ADT crystallizes from an intermediate amorphous phase (Figure 6.13a), in agreement with the two-step nucleation mechanism presented in chapter 4. The crystallization of diF-TES-ADT starts from the amorphous phase when the liquid meniscus is nearly 0.8 mm away from the position of the x-ray beam. Nucleation begins much closer to the blade on PFBT treated Au contacts, i.e., just 0.2 mm downstream from the blade.

The HSPOM and $\mu$GIWAXS measurements together prove the halogenated SAM interacts very strongly with the OSC in the amorphous phase and leads to heterogeneous nucleation of the OSC with a high nucleation density. These differences can be understood by the schematics presented in Figure 6.13a& b (bottom).
Figure 6.13 (Top) In-situ μGIWAXS data recorded during blade coating of diF-TES-ADT in the two step nucleation regime (2 mm/s, 70°C) showing the evolution of solution scattering and Bragg sheet (001) of diF-TES-ADT (Middle) POM image taken during HSPOM experiments (Bottom) Schematic showing the nucleation and growth mechanism of OSC during blade coating on: (a) O₂-plasma treated Si/SiO₂ substrates (b) PFBT treated Au coated Si/SiO₂ substrates

The schematic representation of growth shows the OSC solution is held between the blade and substrate due to capillary forces (light green). As the blade moves to the left, it leaves behind a liquid meniscus (dark green molecules) which dries quickly, especially under the action of a heated substrate, and transforms into an amorphous solid film (blue part). The
OSC crystallizes primarily through a substrate-independent nucleation process which is homogeneous-like, and growth of spherulites propagates quickly and unobstructed over long distances through short range molecular conformational changes within the dense, amorphous OSC film. When PFBT-treatment is used, the OSC crystallization is initiated earlier and very likely from the OSC-contact interface. This interface contains PFBT molecules, which appear to promote the early nucleation, similarly to the crystallization of the OSC during spin-coating. The OSC nucleation density is very high in the case of spin-coating, hence contact-induced nucleation offers real benefits. However, in case of blade coating, the nucleation density is orders of magnitude lower and domains are very large, hence contact-induced nucleation significantly reduces domain size both on top of contacts and in the channel of the transistor. This effect is catastrophic in the case of OSC: polymer blends, since the interactions with the contact alter the vertical stratification of the OSC and polymer, resulting in significant disruptions of the microstructure and dramatic reduction of carrier mobility.

6.4 Microstructural mapping in OFETs channels

The strong dependence of microstructure upon the underlying patterned electrodes requires microstructural mapping of the OSCs in the channel of actual OFETs. This is made possible by the μGIWAXS technique used throughout this thesis. We have mapped the microstructure of spin-cast and blade-cast diF-TES-ADT films across the device channel of untreated and PFBT-treated Au contacts, as shown in Figure 6.14.
Figure 6.14 μGIWAXS structural mapping of diF-TES-ADT thin films across the OTFT device channel on Si/SiO2 substrates with Au contacts for the cases of films prepared by (a) spin-coating on plasma-treated substrates, (b) spin-coating on PFBT-treated Au contacts, (c) blade-coating on plasma-treated substrates and (d) blade-coating on PFBT-treated Au contacts.

A cartoon of the device along with an actual micrograph are shown alongside the μGIWAXS maps of the integrated intensity of diffraction peaks associated to the <001> (green) and <111> (red) textures of diF-TES-ADT. For spin-cast films, we observe a mixture of <001> and <111> textures (Figure 6.14a) and pure <001> lamellar texture on PFBT-treated samples (Figure 6.14b). Interestingly, the blade-cast diF-TES-ADT film does not show anything other than the <001> lamellar texture whether the substrate is untreated or SAM-treated, as shown in Figures 6.14c & d, respectively. The POMs of blade-cast films in the spherulitic regime on PFBT/Au reveal smaller domains, as discussed
above, but there is no apparent effect on the lamellar texture. This important observation indicates that \(<001>\) lamellar texture purity may not require elaborate surface modification when blade coating is used. In Figures 6.15 we show the channel length dependence of mobility for spin and blade coated diF-TES-ADT OFETs. It is clear that in spin coating, the mobility of diF-TES-ADT films is strongly coupled with channel length while there is no such dependence in blade coated films. It is also noteworthy that devices made on plasma-treated contacts out-perform PFBT-treated contacts when comparing blade-coated OSCs, since large spherulitic domains produced on plasma-treated electrodes shrink in the presence of PFBT treatment.

![Graph](image)

**Figure 6.15** Channel length dependence of BCBG OTFT field effect mobility for (a) Spin cast diF-TES-ADT (b) Blade cast diF-TES-ADT films at 1.5 mm/s, 70°C.

The channel length dependence is due to the smaller domain sizes typically achieved by spin coating, whereas blade coating produces comparatively larger domains. PFBT treatment on Au has been shown to promote the \(<001>\) textured grains in channels as long
as 50 μm, beyond which the nucleation of <111> textured grains results in a mixture of
textures which lowers the overall mobility in spin coated diF-TES-ADT films coated in
long channel OFETs.

6.5 Contact induced nucleation in OSC: polymer blends

In sections 6.16 & 6.17, we demonstrated the importance of substrate-OSC interactions on
the nucleation behavior of OSCs, including the fact that these effects may be undesirable
when switching from spin-coating to scalable coating methods. We now turn our attention
to the technologically important case of insulating polymer:OSC blends, where vertical
phase separation is an important factor in device operation and performance. As we
demonstrated in chapter 5, solution processed blends of diF-TES-ADT with PS or PαMS
led to bilayer stratification on O₂ plasma-treated contacts, with the insulating polymer
going toward the gate dielectric and contacts at the bottom, while the OSC formed a
continuous layer on top. A key question which we now seek to address is whether the
vertical stratification can be altered by using SAM modifications in the context of blade
casted blends and whether this has any impact on the behavior and performance of bottom-
contact devices. In Figure 6.16a, we show POM micrographs of TIPS-pentacene:PαMS
blends blade coated at 0.5 mm s⁻¹ and 1.25 mm s⁻¹ on untreated and PFBT-treated Au
contacts. Similar results for diF-TES-ADT:PαMS blends are shown in 6.11b. In the slow
blade coating regime characterized by ribbon-like growth, the POMs reveal no difference
in thin film morphology whether the films are cast on untreated or PFBT-treated contacts.
This is in line with the observations previously made for blade coating of neat OSCs. In
the case of both blend films coated at higher speeds 1.25 mm s⁻¹, PFBT-treated Au appears
to completely disrupt the millimeter-scale crystal propagation by promoting heterogeneous nucleation on the PFBT/Au contacts.

**Figure 6.16** Polarized optical micrographs showing (a) TIPS-pentacene:PaMS blend film morphology on Si/SiO$_2$ substrates with PFBT/Au and O$_2$-plasma treated Au contacts at 0.75 and 1.25 mms$^{-1}$ (b) diF-TES-ADT:PaMS blend film morphology on Si/SiO$_2$ substrates with PFBT/Au and O$_2$-plasma treated Au contacts at 0.5 and 1.5 mms$^{-1}$

POMs reveal that heterogeneous nucleation induces small crystallite formation in the channel, similar to what was observed in case of neat materials in the previous sections. In Figure 6.17a, we plot the saturation hole mobility of blend OFETs based on blends of TIPS-pentacene and diF-TES-ADT with PαMS. It can be seen that the OSC:polymer blend OTFT mobility trend is similar to what we observed for neat OSCs early on. The corresponding transfer characteristics for TIPS-pentacene:PαMS and diF-TES-ADT:PαMS blends are shown in Figure 6.17b &c. The carrier mobility on plasma-treated
Au electrodes reaches values as high as 3.6 cm²/Vs for diF-TES-ADT:PαMS blends and 4.6 cm²/Vs for TIPS-pentacene:PαMS blends. By contrast, for PFBT- treated devices we observe a dramatic reduction of carrier mobility to the level of 10⁻¹ cm²/Vs for both blends as the growth transitions to the spherulitic regime as highlighted in Figure 6.17b. Figure 6.17d shows the corresponding output curves of BCBG OFETs based on blade coated TIPS-pentacene:PαMS at 1.25 mms⁻¹, revealing the hysteresis free characteristics.

**Figure 6. 17** (a) Hole mobility of BCBG blade cast devices with two surface conditions of Au contacts at different blade-coating speeds for the cases of TIPS-Pentacene:PαMS blend (black solid and open symbols) and diF-TES-ADT:PαMS blend (black solid and open symbols) (b) Transfer characteristics of blade coated TIPS-pentacene: PαMS (c) diF-TES-ADT: PαMS BCBG OFETs based on O₂-Plasma and PFBT treated Au contacts (d) Output
characteristics of TIPS-pentacene: PαMS based on O2-Plasma and PFBT treated Au contacts.

The POMs and device measurements presented above in the case of blade-coated blends suggest the nucleation of the OSC occurs from the contact in the presence of strong OSC-contact interactions and risk disrupting the vertical stratification observed in high performance BCBG devices based on untreated contacts. To confirm this, we present in Figure 6.18 cross-sectional EFTEM micrographs showing the elemental mapping of TIPS-pentacene:PαMS blends on untreated and PFBT-treated Au contacts both in the channel and contact regions. The micrographs clearly show bilayer stratification with the OSC on top of PαMS on untreated contacts (Figure 6.18a), with identical bilayer stratification extending in the channel region (Figure 6.18b). By contrast, the vertical phase separation behavior is different on PFBT-treated contacts. The micrographs reveal a trilayer stratification with PαMS sandwiched between two OSC layers, both on top of the contacts and inside the channel, as shown in Figures 6.18c & d, respectively. The OSC layers are substantially thinner than in the bilayer films and yield laterally smaller crystalline domains (according to POM) which proves detrimental for device performance.
**Figure 6.18** Cross-sectional EFTEM showing the vertical phase separation of TIPS-pentacene: PaMS blend films blade-coated on substrates with a,b) O₂-Plasma Au contacts and c,d) Au contacts treated with PFBT.

### 6.6 Generalization for other OSCs and OSC: polymer blends

We summarize the BCBG device results obtained for all neat OSCs and their polymer blends in the two-step nucleation regime in Figure 6.19a &b. In Figure 6.19a &b, we plot the resulting field effect mobility (top) and threshold voltage (bottom) of BCBG OFETs from neat and blend films. It is evident that devices based on O₂-plasma treated Au contacts outperform as deposited Au and SAM modified Au contacts.
Figure 6.19 Field effect mobility and threshold voltage extracted from BCBG OFETs based on (a) neat OSCs; diF-TES-ADT, TIPS-pentacene, CP-DIPS-pentacene, and Allyl-DIPS-pentacene (b) polystyrene blends of all OSCs mentioned in (a)

Note: All of the above devices are fabricated at 1.5 mms⁻¹, 70°C by blade coating.

This trend is remarkable and highlights as to how blade coating is significantly different from the spin coating process. We looked at neat and blend film morphologies by POM and found that heterogeneous nucleation took place in all neat OSCs and their blends in the two-step nucleation regime. It resulted in increased nucleation density of grain boundaries along with disturbed vertical phase separation in blend cases, leading to poor...
device performance. We can see that modification of Au contacts with any treatment used in this study pushes the threshold-voltage from high positive voltages closer to 0V or to slightly negative volts (for p-type OSCs) which is an important requirement in applications. We can see that threshold voltage is shifted to negative values in the case of SAM treated devices for most of the neat and blend devices (blend devices having values closer to 0V). This trend is however not explainable only with electrode work function-OSC HOMO level separation shown in Figure 6.15. Because, the threshold voltage also depends upon morphology of active layers, nature of gate dielectric, device configuration and interface traps at OSC: dielectric interface. So, the threshold shift towards OV or to negative volts might be strongly affected by interfacial traps. As we discussed in chapter 5, blending reduces the interfacial trap density by 1-2 orders of magnitude. This lower trap density plays a major role in the decreased threshold voltage in all blend devices as compared to neat OSCs.

6.7 Conclusions
We have probed the interaction of bottom contacts under different surface treated conditions with OSCs in large area compatible blade coating process. We demonstrate that film formation in blade coating in two-strep nucleation regime is sensitive to bottom surface conditions. If bottom contacts are modified with SAMs, the modified surface can act as template for heterogeneous nucleation and alter the regular film growth mode. It introduces a competition for the OSCs to crystallize from air-liquid and solid liquid interfaces at the same time. We find that blade coating achieves texture purity (only edge on <001>) in case of halogenated OSCs, such as diF-TES-ADT, irrespective of whether the contact is chemically treated with a halogenated self-assembled monolayer (SAM) or
not. This behavior changes the regular bilayer vertical stratification of OSC: Polymer blend thin films to trilayer with polymer sandwiched between top and bottom OSC layers. The heterogeneous nucleation leads to the formation of small crystals with larger grain boundary density which eventually serve as bottleneck to charge transport. We believe that any modification which has the ability to interact with OSCs can possibly be detrimental to OFETs performance. We propose the use of non-chemical treatment methods to modify work function of electrodes in coating processes where crystallization initiates from air-liquid interface. Using UPS and XPS, we also find that O$_2$-plasma treatment leads to the formation of Au$_2$O$_3$ monolayer on Au electrodes. We believe that this gold oxide monolayer might be acting as charge injection monolayer similar to PFBT and other SAMs used for work function modifications of the electrodes.
Chapter 7

Role of Intermediate Phases on the Functional Properties of small molecule OSCs with BTBT conjugated core

7.1 Introduction

We have shown in the last few chapters that solution to solid phase transformation during blade coating can proceed via two-step nucleation, with great benefit to the microstructure and morphology of the polycrystalline OSC film. So far, we have demonstrated this behavior in acene molecules, which can be considered a narrow set for the purposes of generalizing these conclusions to other relevant small-molecule systems. Thermal fluctuations in the transfer integral create dynamic disorder which affects the transport properties of OSCs. In 2016, Henning and Coworkers used transmission electron microscopy to characterize the dynamic disorder in crystalline organic semiconductors. They found that thermal vibrations (resulting in dynamic disorder) have more pronounced effect in those OSC which have side groups attached to short-axis of core such as diF-TES-ADT and TIPS-pentacene. The dynamic disorder hurts the performance of these OSCs in transistors even after tedious optimization to get high quality thin film. The OSCs such as C8-BTBT have lower dynamic disorder in the pi-pi direction (as functional groups are attached to the long-axis of core) and this contributes to the high charge carrier mobility values observed by many groups for this material.

In past ten years, a new class of small-molecule OSCs has emerged and garnered great interest for OTFT applications. These materials have a benzo-thiophene (BTBT) core which is functionalized by attaching side groups with the aim of solubilizing it in common
solvents. BTBT derivatives have shown remarkable field effect mobilities in the range of 1-43 cm$^2$V$^{-1}$s$^{-1}$. Amongst these BTBT derivatives, C8-BTBT is one of the most famous and high performing materials. It has a rich thermal behavior and can form liquid crystalline phases. The detailed understanding of how these liquid crystalline phases impact the functional properties of thin films still needs exploration. During past 3 years, Yves Geerts and coworkers have synthesized multiple BTBT derivatives with different bulky functional end groups in aim to change the molecular packing for better charge transport properties.$^{226-228}$ Amongst these newly synthesized derivatives, 2,7-di-tert-butylBTBT (ditBu-BTBT) has large and balanced charge transfer integral values and it showed remarkable carrier mobility of 17 cm$^2$V$^{-1}$s$^{-1}$ (PVT grown single crystals). The detailed structure function property relationships for this high performing BTBT derivative are still unknown.

We have investigated the solution-to-solid phase transformation of BTBT derivatives in the context of spin-coating and blade-coating with the aim of understanding its behavior and relationship to its microstructure and functional properties. We use in situ and ex situ GIWAXS to understand the texture and crystallization mechanism of blade-coated and spin-coated films and look into the formation of the liquid crystal phase. We fabricate bottom gate top contact OFETs to investigate the structure-performance relationships in these films. We use high coating speeds (> 100 mms$^{-1}$), compatible with industrial requirements-to coat very thin films of C8-BTBT. We also show that recrystallizing C8-BTBT films from its isotropic form (melt), a common but inconvenient approach to produce high-performance devices, can be addressed directly by blade-coating without the need for melting and recrystallization. The in situ diagnostics shed light on the role of liquid
crystalline phases and on the formation of morphological defects in the C8-BTBT blade coated films under certain processing conditions. We use this insight to achieve high charge carrier mobility in C8-BTBT and another BTBT derivative, ditBu-BTBT, demonstrating successful new design rules for processing BTBT derivatives using scalable methods.

7.2 Spin Coating and Recrystallization from Melt

C8-BTBT is known to melt to an isotropic phase at 125°C. Melt recrystallization has been used by several groups to fabricate high-performance devices with carrier mobility > 10 cm²V⁻¹s⁻¹. These efforts involved a combination of polymer blending (both insulating and semiconducting polymers) and dopants. We decided to establish a baseline by making BGTC OFETs of spin-coated and recrystallized C8-BTBT films. To do so, we placed as-cast spin coated films on hot plat at 125°C for 30 seconds and then quickly transferred the sample to a nearby second hot plate at a lower, optimized temperature of 85°C. The recrystallization at lower temperatures did not change the morphological feature size (observed by POM). However, super-cooling too much would quench the crystallization process, increasing the nucleation density and resulting in very small crystallites, similar to as-cast spin-cast films. Figures 7.1a & b show the POMs and GIWAXS measurement for as-cast spin coated and recrystallized C8-BTBT films. The POM micrographs reveal that crystallite size (lateral) increases more than an order of magnitude from a few microns to hundreds of microns. This was achieved thanks to the low nucleation density achieved by the small super-cooling. The insets in Figure 7.1a & b shows the AFM micrograph of the as-cast and recrystallized film. The RMS roughness of as-cast films was found to be 3 nm which is significantly higher than 0.7 nm of recrystallized film. We performed GIWAXS measurements to find out if the films exhibit any differences in structure or
texture (Figure 7.1a & b). We focus on the (11L) in-plane Bragg peaks, which have been previously used to identify the polymorph of C8-BTBT. Yuan et al. reported growth of metastable C8-BTBT films with (11L) Bragg peaks located at $q_{xy} = 13.4$ nm$^{-1}$ as compared to 13.2 nm$^{-1}$ for the equilibrium polymorph. The zoomed in 2D-GIWAXS maps show that recrystallized film has primarily the metastable (11L) Bragg peaks ($q_{xy} = 13.4$ nm$^{-1}$) with closer in-plane packing. We compare the azimuthal integrated intensity versus $q_{xy}$ plots of in-plane (113) Bragg peak for both films in Figure 7.1c.

![2D-GIWAXS maps](image)

**Figure 7.1** (a & b) POMs, AFMs and 2D-GIWAXS micrographs for as cast spin-coated and recrystallized film from melt along with zoomed-in maps highlighting the equilibrium and metastable (11L) Bragg peak positions (c) Azimuthal integrated intensity versus $q_{xy}$ plot of (113) Bragg peak for both films and inset shows the FWHM of these peaks.

The field-effect mobility measured in BGTC OFETs is summarized in Figure 7.2a. The recrystallized films performed better than as-cast films. The recrystallized films showed an average mobility 7.5 cm$^2$V$^{-1}$s$^{-1}$ ($\pm 1.2$) from 68 tested devices with the highest mobility of
10.2 cm²V⁻¹s⁻¹ observed in several devices. The corresponding transfer and output characteristics are shown in Figures 7.2b & c.

Figure 7.2 (a) The average field-effect mobility along with standard deviation for C8-BTBT BGTC TFTs for as cast spin-coated and recrystallized films (b) The representative transfer characteristics (c) output characteristics of recrystallized film.

7.3 Blade-coating of C8-BTBT

Prior to starting a detailed investigation, we mapped out the coating-speed dependent regimes. For this purpose, we used 8 mg/ml C8-BTBT in toluene solution and performed the coating experiments at 90°C. Figure 7.3 summarizes the thickness versus coating speed and reveals that evaporation regime occurs for coating speeds in the range of <7-8 mms⁻¹ and Landau-Levich regimes for speeds >8-9 mms⁻¹.
Firstly, we attempted to coat C8-BTBT films at a slow speed with the aim of inducing ribbon-like growth (Figure 7.4a) as previously achieved in the case of acenes. This was achieved with a toluene solution (8 mg/ml) used with a substrate temperature of 90°C and a coating speed of 1.8 mms⁻¹. AFM micrographs reveal well-connected ribbon-like domains with a very smooth surface with sub-nanometer RMS roughness (Figure 7.4b). The same micrographs nevertheless reveal that adjacent ribbons are separated with a row of small pin-holes (Figure 7.4c). Topographic line scans reveal these defects to be shallow, just ~9 nm deep, corresponding to approximately three monolayers of C8-BTBT molecules in the lamellar stacking orientation, whereas the physical thickness of the film (determined by SE) is ~30 nm. The height distribution profile extracted from the AFM image in Figure 7.4c is very narrow and symmetric with very weak satellite peaks.
Figure 7.4 (a) POM snapshot of C8-BTBT thin film coated at 1.8 mm s⁻¹, 90°C from 8 mg/ml solution in toluene. (b & c) AFM micrographs and (d) height distribution extracted from (b).

Figure 7.5 (a) Schematic showing bottom gate top contact device architecture (b) POM along with top Ag electrodes, highlighting the parallel and perpendicular directions (c) Transfer characteristics from highest performing devices in both directions (d) The average field effect mobility along with standard deviation for C8-BTBT BGTC TFTs for both directions.

We have fabricated BGTC OFETs (Figure 7.5a) based on these films and measured an impressive field-effect mobility (saturation) as high as of 11 cm²V⁻¹s⁻¹, with the average of
85 devices yielding a respectable mobility of 7.5 cm²V⁻¹s⁻¹. Devices in which the growth direction of ribbons was perpendicular to the device channel out-performed devices in which ribbons grew parallel to the channel (See Figure 7.5b). The transfer characteristics from best-measured devices are shown in Figure 7.5c. The devices in parallel direction averaged a mobility of 6.5 cm²V⁻¹s⁻¹ (±1.3) as compared to 8.5 cm²V⁻¹s⁻¹ (±2.4) in perpendicular direction, as summarized in Figure 7.5d. The performance differences are not dramatic, but are nevertheless statistically meaningful, indicating anisotropic charge transport.

GIWAXS measurements (Figure 7.6a) were performed along the parallel and perpendicular directions (Figure 7.6b & c, respectively) to investigate the in-plane microstructure and texture with respect to the blade’s direction. Close-up view of GIWAXS measurements show the (02L) in-plane Bragg peaks appear only in the perpendicular direction, indicating that the b-axis of C8-BTBT crystallites is aligned with the coating and growth directions of ribbon-like domains, where we also observed higher carrier mobility. These observations are in line with transfer integral calculations for the C8-BTBT packing motif, which predicted larger transfer integral along a-axis as compared to b-axis.
Figure 7.6 (a) X-ray beam directions to perform GIWAXS experiments (b & c) 2D-GIWAXS maps recorded in parallel and perpendicular directions, with close-up views of the 02L peaks shown on the right.

7.4 Thickness-dependent morphology and device performance in C8-BTBT films

The performance of OFETs made from blade-coated C8-BTBT at low speed was impressive, but the in-plane anisotropy is not ideal for most applications and the coating speed (1.8 mms\(^{-1}\)) is short of expected industrial requirements (>100 mms\(^{-1}\)). Moving toward higher speed, however, means making thicker films, which brings new challenges in the case of BTBT films, not previously observed with acenes in the previous chapters. In Figure 7.7a we show an illustrative example. POM snapshots show C8-BTBT films of different thickness coated using different ink volumes (10 vs. 6 \(\mu\)l) at otherwise identical solution concentration (8 mg/ml), coating speed (100 mms\(^{-1}\)) and substrate temperature
(90°C). The larger volume yields a thicker film (~42 nm), while the smaller volume yielded a thinner film (~29 nm). The POM image of the thicker films reveals very large domains, while the smaller film features much smaller, spherulitic domains, highlighting significant effects of film thickness on microstructure and morphology.

Figure 7.7 POM snapshot of C8-BTBT thin film coated at 100 mm s⁻¹, 90°C from 8 mg/ml solution in toluene (b & c) AFM micrographs (d) Height distribution profile extracted from (b) Note: We used 10 µl and 6 µl OSC ink to coat film A and B on 2x1.5 cm² Si/SiO₂ substrate respectively.

The AFM micrograph in Figure 7.7b reveals significant cracking in the thicker film, resulting in a skewed height distribution and higher RMS roughness (5.6 nm). The thinner film is comparatively smoother with a narrower and more symmetric height distribution and a lower RMS roughness (2.4 nm). The thinner film appears to show small and fine features, but the film seems to be better percolated and connected than the thicker film, which shows locally flat and large domains, but larger pin holes and cracks (Figures 7.7b/c). The field-effect mobilities extracted from BGTC devices based on these films are
summarized in Figure 7.8a. The thinner film B showed a higher average mobility of 3.6 cm$^2$V$^{-1}$s$^{-1}$ (±1.5) as compared to the thicker film B: 1.6 cm$^2$V$^{-1}$s$^{-1}$ (±1.1). The transfer characteristics associated to the best-measured devices are shown in Figure 7.8b. These results highlight a typical challenge we have faced with C8-BTBT, that is the sensitivity of its microstructure, morphology and device performance to otherwise moderate differences in film thickness under identical coating conditions.

Figure 7.8 (a) The average field effect mobility along with standard deviation for C8-BTBT BGTC TFTs for both A and B films (b) The representative transfer characteristics for films A & B.

We performed GIWAXS measurements to find out if the films of different thickness exhibit any differences in structure or texture (Figure 7.9a&b). The zoomed in 2D GIWAXS maps show that in-plane (11L) Bragg peaks of the thicker film are shifted to
higher $q_{xy}$ values, resulting in a closer in-plane packing as compared to the thinner film. Yuan et al. reported growth of metastable C8-BTBT films with (11L) Bragg peaks located at $q_{xy} = 13.4$ nm\(^{-1}\) as compared to 13.2 nm\(^{-1}\) for the equilibrium polymorph. In our case, the (11L) peaks are located at $q_{xy} = 13.2$ nm\(^{-1}\) and 13.6 nm\(^{-1}\). The thicker film exhibits two polymorphs, while the thinner film appears to form primarily the equilibrium phase.

![Figure 7.9](image)

**Figure 7.9** (a & b) 2D-GIWAXS micrographs for films A and B and zoomed in maps highlighting the equilibrium and metastable (11L) Bragg peak positions

We further investigate the effect of thickness by turning to the spin-cast films C8-BTBT with different thicknesses, namely 19, 52, and 71 nm. We varied the OSC concentration from 30 mg/ml to 5mg/ml to obtain different thicknesses by keeping the spin speed constant at 2500rpm. The films exhibit similar morphological features as shown in Figure 7.10. GIWAXS measurements (Figure 7.11b) reveal spin-cast films with different
thickness have the same (11L) Bragg peak locations corresponding to the equilibrium and meta-stable $q_{xy}$ positions. All the three films showed the same peak positions and overall shapes, indicative of similar crystal texture. However, we noticed large differences in field-effect mobilities of BGTC devices made from these films, as summarized in Figure 7.12a,b. We obtained an average field-effect mobility of 4.4 cm$^2$V$^{-1}$s$^{-1}$ ($\pm 0.5$) from the 19 nm spin-coated film of C8-BTBT in comparison to 1.7 cm$^2$V$^{-1}$s$^{-1}$ ($\pm 0.6$) from a 42 nm thick film. The differences in device performance may be due to higher contact resistance in thicker films as reported by many groups for TC devices.

Figure 7.10 POM micrographs of spin coated C8-BTBT films
Figure 7. (a &b) 2D-GIWAXS micrographs for spin coated thin films of C8-BTBT with different thicknesses along with zoomed in maps highlighting the equilibrium and metastable (11L) Bragg peak positions.
The device performance from the spin-coated films was higher than the best blade-coated films produced at 100 mms$^{-1}$, but not compared to blade-coated films produced at low speed, where ribbons are formed. This observation is in contrast to the behavior seen thus far in acenes in previous chapters. This suggests that different mechanisms are at play with C8-BTBT and that further improvements in thin film formation should be possible in blade coating with further understanding and optimization. We opted to further reduce the thickness of the blade-coated film to make it comparable to spin-coated films. Two pathways immediately come to mind: decrease the coating speed or reduce the solution concentration. Both approaches produced similar thicknesses (15-20 nm) and, importantly, achieved a very similar morphology (Figure 7.13), again pointing to thickness-dependent morphology.

**Figure 7.12** (a) The average field effect mobility along with standard deviation for C8-BTBT BGTC TFTs for spin coated films with different thicknesses (b) The representative transfer characteristics (c) output characteristics of 19 nm spin-coated film.
We fabricated BGTC devices based on these thin films, and achieved an average mobility of $9.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ($\pm 1.2$) from 61 tested devices. The highest field-effect mobility reached as high as $13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. We did not observe any drop in the field-effect mobility during continuous testing of the same device for 90 minutes in a cyclic manner.

It is interesting to note from POM and AFM micrographs from the best blade-coated and spin-coated C8-BTBT films (Figure 7.14a & b) that blade-coated films are very smooth with no apparent grain or domain boundaries but with molecular terraces with ~2.7 nm step height (green curve, Figure 7.14d), whereas spin-cast films are characterized by large nucleation density and smaller crystallites. The RMS roughness of spin-coated films was found to be 3 nm which is significantly higher than 0.7 nm of blade-coated film.
Figure 7.14 (a & b) POM and AFM micrographs for blade and spin coated C8-BTBT films (c) Height distribution profiles for spin and blade coated films (d) Line scans extracted from AFM micrographs shown in (a) & (b).

Figures 7.15a & b show GIWAXS measurements for the spin and blade-coated films. The zoomed-in regions reveal the (11L) Bragg peaks are at the same position for both films, exhibiting the metastable polymorph in both cases, known to exhibit closer in-plane packing of molecules. We compare the azimuthal integrated intensity versus $q_{xy}$ plots of in-plane (113) Bragg peak for spin and blade-coated films in Figure 7.15c. It can be seen in the inset that the corresponding FWHM extracted from azimuthally integrated peaks for blade coated films decreases to 4.1° as compared to 6.9° for spin coating. This suggests improved in-plane order and reduced mosaicity in the blade-coated films, perhaps partly responsible, along with the larger domain size and tight grain boundaries, for the improved charge transport properties in these films.
Figure 7.15 (a & b) 2D-GIWAXS micrographs for spin and blade coated films and zoomed-in maps highlighting the equilibrium and metastable (11L) Bragg peak positions (c) Azimuthal integrated intensity versus $q_{xy}$ plot of (113) Bragg peak for both films and inset shows the FWHM of these peaks.

For comparison, we also recrystallized blade-coated films which had yielded thus far the best performance. We did not observe any improvement in the resulting field-effect mobility of BGTC devices based on these films. The Figure 7.16a & b show the POMs and 2D-GIWAXS maps of as-cast blade coated and its recrystallized film at 85°C. The POM micrographs reveal that crystallite size (lateral) is similar on the order of few hundred micrometers. Both films possess similar metastable texture as highlighted by the (11L) Bragg peak positions in the close-up GIWAXS data. The azimuthal integrated intensity plots of (113) Bragg peak reveal a very similar FWHM values, suggesting the similar in-plane ordering and mosaicity in these films.
We have found, thus far that high quality C8-BTBT films with mobility of $>10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are typically achieved when the film thickness is very low and the so-called metastable polymorph of C8-BTBT is formed. This can be done through melt recrystallization of very thin spin-cast films or directly through blade-coating at elevated temperature. The latter is far more advantageous as it is scalable and can be done at industrially compatible coating speeds in the range of 100-300 mms$^{-1}$. The as-spin-cast films performed reasonably well, but showed mobility $<6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ without recrystallization. Though POM, AFM and static GIWAXS analysis, we found substantial differences between the films produced using different processes, which can explain the functional performance differences. The crystallization method influenced the in-plane order and mosaicity. The as-cast blade-coated films (at 90°C) and melt-recrystallized films (from 125°C to 85°C) showed very similar lateral crystallite features by POM and AFM. The in-plane order was also similar.
and exhibited the pure metastable polymorph. A common feature of these high performing films is their thickness was in the 10-20 nm range.

7.5 The role of crystallization mechanism on functional properties of C8-BTBT films

Naturally, we asked ourselves how phase transformation proceeds in these systems and how it influences the microstructure, morphology and functional properties of the OSC films. Why is it that as-cast blade-coated films and recrystallized films under certain conditions performed on par, while spin-cast films did not? Why does the thickness of the film matter so much?

We performed in situ GIWAXS measurements during spin-coating and blade-coating. Figures 7.17a & b show the integrated intensities versus time for the solution scattering ring, \( q = 11 \text{ nm}^{-1} \) (red) and OSC’s Bragg sheet (001), \( q = 2.2 \text{ nm}^{-1} \) (green). In the case of spin-casting, the crystallization signature (001) appeared when a substantial solution scattering signal was also present (Figure 7.17a), indicating that crystallization occurs from the liquid solution, similar to our previous observations for spin-coating of diF-TES-ADT and TIPS-pentacene. On the other hand, blade-coating of C8-BTBT thin films at a speed of 25 mms\(^{-1}\) and 90\(^\circ\)C leads to extremely fast crystallization occurring soon after the liquid scattering has disappeared. This indicates that crystallization occurs via a two-step nucleation mechanism similar to the acenes studied in previous chapters. The observation of two-step nucleation in conditions of blade-coating that yield very high-quality films should not come as a surprise. Indeed, the fact that C8-BTBT films achieve the same microstructure and morphology whether formed via two-step nucleation or melt-recrystallized highlights the importance of forming an intermediate amorphous or melt-
phase from which to crystallize the OSC, rather than directly from solution. Crystallization from solution is likely to be limited by the availability and diffusion of molecules, and is strongly coupled to the drying of the solvent. As such, it is likely to result in a higher nucleation density, as consistently observed in POMs. By contrast, promoting the formation of a dense disordered film, whether an amorphous solid or a melted liquid of the OSC, can lead to rapid and extended lateral crystal growth via conformational changes of molecules and lattice incorporation, resulting in overall larger domains of very high crystalline quality.

![Figure 7.17 In-situ GIWAXS results showing the evolution of (001) and solution scattering during (a) Spin-coating (b) Blade-coating.](image)

We have shown the crystallization of C8-BTBT in different conditions to have important implications on polymorphism too. We have therefore investigated the time-evolution of out-of-plane as well as in-plane scattering peaks (Figure 7.18a) during blade coating of C8-BTBT at 90°C. The top plot summarizes the process over a duration of 10 s. The bottom plot offers a close-up view of the initial 200 ms and shows the solution scattering feature disappearing and the (001) Bragg sheet appearing after loss of the solution. The (001)
Bragg sheet appears after 70 ms and saturates by 160 ms. Higher order (00L) and in-plane Bragg peaks appear much later, after 1.5 s. The corresponding GIWAXS data of this in situ experiment are shown in Figure 7.18b. We have marked the final (11L) Bragg peak $q_{xy}$ position corresponding to the so-called metastable polymorph with a white line as a guide to the eye. We observe some in-plane diffraction features, highlighted by the green line, which appear during the coating and before formation of the metastable polymorph (white line). We ascribe these features to an intermediate liquid crystalline (LC) phase of C8-BTBT. In Figure 7.18b we show the (112) in-plane Bragg peak observed at 1.64 s. The (112) peak position is ascribed to the LC phase, which has a lower $q_{xy}$ (13.15 nm$^{-1}$) and higher $q_z$ (5.55 nm$^{-1}$) than the crystalline (112) Bragg peak ($q_{xy} = 13.4$ nm$^{-1}$, $q_z = 4.45$ nm$^{-1}$). A few more Bragg peaks belonging to the LC phases appear by the 2 s mark, along with a very weak signature from the crystalline phase (metastable polymorph), as indicated by Bragg peaks (111) and (113). At 2.6 s, the crystalline phase appears to form while the LC diffraction remains intact until 2.8 s, where it disappears entirely, leaving only the crystalline phase in the film. No further changes are seen beyond this point.
Figure 7.18 (a) The time-evolution of in-plane and out-of-plane Bragg peaks during blade coating of C8-BTBT at 25 mm s$^{-1}$, 90$^\circ$C, lower image is zoomed-in part highlighting the solution scattering (b) 2D-GIWAXS maps at recorded during in-situ blade coating experiment as described in (a).

We show the integrated intensity plot belonging to the out-of-plane Bragg sheet (001) in Figure 7.19a at three different stages during the blade-coating experiment. The peak is located at $q_z = 2.21$ nm$^{-1}$ initially and broadens after appearance of the LC phase after 1.5 s, shifting its center to 2.31 nm$^{-1}$. This suggests a decrease in the inter-planar spacing from 2.84 nm to 2.7 nm, assuming the peak is associated to a single phase. It is worth noting that there is no meaningful shift in the out-of-plane $q_z$ values of the in-plane Bragg peaks through the coating process (Figure 7.19b).
Figure 7.19 (a) Intensity versus qz plots of (001) Bragg sheet recorded in situ during blade coating of C8-BTBT at 25 mms\(^{-1}\), 90\(^\circ\)C (b) 2D-GIWAXS maps recorded in situ during blade-coating experiment as described in (a).

The in situ experiments performed during blade-coating of C8-BTBT indicate the phase transformation is complex and proceeds via three intermediate phases (an amorphous and two intermediate liquid crystalline phases) from which the final high-quality crystalline film forms. The schematic in Figure 7.20 depicts this solution-to-solid phase transformation process during spin coating and blade coating at different temperatures.

Figure 7.20 Schematic showing the sequence of solution-to-solid phase transformation process of solution processed C8-BTBT films by spin and blade-coating.
These conclusions are probably valid for experiments performed at a substrate temperature of 90°C, which has thus far given us the best film quality and OTFT performance. We therefore changed the substrate temperature and kept all other parameters such as solution concentration and coating speed unchanged. Figures 7.21a-e show the comparison of in-plane and out-of-plane texture development during spin-coating and blade-coating experiments performed at different temperatures. In the case of spin-coating, the crystallization appears to be initiated from the bulk of the solution, as we previously discussed. Interestingly, we find that in blade-coating at lower temperatures, 50°C, the formation of the LC phase coincides with solvent scattering, suggesting it forms directly from solution. However, the LC phase is still an intermediate phase from which the final crystalline phase forms and thus may be considered a form of two-step nucleation. Blade-coating experiment at 70°C show rapid loss of the solvent prior to formation of the lamellar diffraction feature, thus indicating an intermediate amorphous phase forms prior to LC phase formation. Spin-coating and blade coating at room temperature (25°C) behave similarly (Figure 7.21a & b), proceeding through a direct crystallization route from solution directly to the final crystalline form. There are no liquid crystalline phases involved at these conditions. In situ GIWAXS during blade coating at 70°C reveals formation of the LC$_1$ phase prior to formation of the final crystalline form. We did not observe the LC$_2$ phase previously observed at 90°C (Figure 7.18a&b), but we observed the (112) Bragg peak belonging to the LC$_2$ phase for a very short duration of 100 ms at the 1 s mark, after formation of the LC$_1$ phase (Figure 7.22c, top).
Figure 7.21 Evolution of in-plane and out-of-plane Bragg peaks during (a) spin coating (b-d) blade coating at 25°C, 50°C and 70°C respectively.

Figure 7.22 2D-GIWAXS maps recorded during blade coating of C8-BTBT at different temperatures and fixed speed of 25mms⁻¹

These results indicate that the intermediate LC states play a pivotal role in the formation of high quality films achieving very high-performance OFETs. Figure 7.23&24 show the
POMs and corresponding BGTC field effect mobility of blade coated C8-BTBT films at different temperatures, respectively. We observed better field effect mobility at high temperatures which involved LC phases during phase transformation of these films.

**Figure 7. 23** POMs of blade coated C8-BTBT films at different temperatures.

**Figure 7. 24** Field effect mobility of BGTC based on blade-coated C8-BTBT films at different temperatures.
**In situ HSPOM**

We also looked into intermediate states by *in situ* HSPOM. Figures 7.25a-e show HSPOM snapshots taken during blade coating of C8-BTBT at 90°C. The blade leaves behind the trailing bulk solution which is transformed into an amorphous intermediate state, then to presumably LC$_1$ phase. Figure 7.25d shows the nucleation and growth of LC$_2$ which subsequently transforms into final crystalline form. The cracks appear during transition from LC$_2$ to final crystalline form. The intermediate phase looks dense, similar to what we observed for blade-coated diF-TES-ADT and TIPS-pentacene. Closer examination of POM images (Figure 7.25c) reveals that there are some features present, perhaps indicative of the LC$_1$ phase formation.

![Figure 7.25 In situ HSPOM snapshots taken during blade coating of C8-BTBT at 90°C](image)

*In situ* GIWAXS showed the (001) Bragg sheet appears very quickly after bulk solution scattering fades away. This first (001) Bragg sheet belongs to LC$_1$. The intermediate state observed using *in-situ* HSPOM as shown in Figures 7.25c therefore belongs to the LC$_1$. Then, we see nucleation and growth of C8-BTBT crystallites belonging to LC$_2$ (Figure 7.25d) which we also noted earlier by *in situ* GIWAXS (Figure 7.19b).

As was discussed earlier, the thickness of OSC influences morphology, including cracking and related defects, which are prominent in thicker films. We can see clear evidence of
cracks in Figure 7.25, so we coated a thinner C8-BTBT film using a smaller ink volume and obtained films without cracking, as shown in Figure 7.26. We see the same sequence of crystallization as in Figure 7.25 and show that no cracks appear during thin film crystallization. The crystallite growth in both thick and thin films proceeds via the LC$_2$ phase, as we observed from in situ GIWAXS.

![Figure 7.26 In-situ HSPOM snapshots taken during blade coating of C8-BTBT at 90°C](image)

7.6 Crystallization of other BTBT derivatives

We have tested and investigated a newly developed BTBT derivative by our collaborator Prof. Yves Geerts at Brussels (ULB). They modified the BTBT core by attaching tert-butyl groups at both ends of BTBT core and named as 2,7-di-tert–butylBTBT (ditBu-BTBT). It showed an impressive field effect of mobility of 17 cm$^2$V$^{-1}$s$^{-1}$ in single crystal form. We used our optimized coating conditions for C8-BTBT and fabricated BGTC devices. The figure 7.27a&b shows the POMs, and corresponding transfer and output characteristics of spin and blade coated films respectively. The spin-coated devices showed an average
mobility (15 devices) of 5.29 cm²V⁻¹s⁻¹ (±0.7) while blade-coated devices resulted in average mobility (25 devices) of 10.9 cm²V⁻¹s⁻¹ (±1.3). We performed static GIWAXS experiments similar to what we did for C8-BTBT to understand the differences in device performance. The Figure 7.28a&b shows the GIWAXS data of spin and blade-coated films. The zoomed-in views reveal that Bragg peak (11L) position is same for both films. We show the azimuthal integrated intensity versus $q_{xy}$ plots of in-plane (113) Bragg peak for a spin and blade-coated films in the Figure 7.28c. It can be seen in the inset that the corresponding FWHM extracted from azimuthally integrated peaks for blade coated films decreases to 4.4° in comparison to 14.5°. It suggests massively improved in-plane order in blade coated films leading to better charge transport properties. These results are similar to what we observed for C8-BTBT.

**Figure 7.27** POM images, transfer and output characteristics of ditBu-BTBT (a) Spin-coated (b) Blade-coated
7.6.1 In situ Investigations

We asked ourselves how phase transformation proceeds for this new BTBT derivative. We performed in situ GIWAXS measurements during spin-coating and blade-coating. We have investigated the time-evolution of out-of-plane as well as in-plane scattering peaks during blade coating of ditBu-BTBT at 50°C and 90°C. Figures 7.29a-b shows the comparison of in-plane and out-of-plane texture development during blade-coating experiments. Both of these experiments reveal similar results as we previously observed for C8-BTBT. We find that in blade coating at 50°C, the formation lamellar diffraction feature (001) coincides with solvent scattering, suggesting it forms directly from solution. The plot at 90°C shows the solution scattering feature disappearing and the (001) Bragg sheet appearing after loss of the solution. The (001) Bragg sheet appears after 65 ms and saturates by 140 ms. Higher
order (00L) and in-plane Bragg peaks appear much later, after 0.7 s. We observe loss of the solvent prior to formation of the lamellar diffraction feature, thus indicating an intermediate amorphous phase forms prior to crystallization at 90°C.

**Figure 7.29** Evolution of in-plane and out-of-plane Bragg peaks during blade coating at (a) 50°C and (b) 90°C

**Figure 7.30** (a) Intensity versus qz plots of (001) Bragg sheet recorded in situ during blade coating of ditBu-BTBT at at (a) 50°C (b) 90°C
Figure 7. 31 2D-GIWAXS maps recorded during blade coating of ditBu-BTBT at two different temperatures and fixed speed of 25 mms\(^{-1}\).

We show the integrated intensity plot belonging to the out-of-plane Bragg sheet (001) in Figure 7.30a&b at two different stages during the blade-coating experiments. The peak is located at \(q_z = 2.16 \text{ nm}^{-1}\) initially and broadens after appearance of the LC phase after 1.5 s, shifting its center to 2.22 nm\(^{-1}\). This suggests a decrease in the inter-planar spacing from 2.90 nm to 2.8 nm, assuming the peak is associated to a single phase. It is worth noting that there is no meaningful shift in the out-of-plane \(q_z\) values of the in-plane Bragg peaks through the coating process (Figure 7.31a). The formation of this LC phase coincides with solvent scattering, suggesting it forms directly from solution.

For the case of 90°C, we have marked the final (11L) Bragg peak \(q_{xy}\) position corresponding to the final crystalline form with a white line as a guide to the eye (Figure 7.31b). We observe some in-plane diffraction features, highlighted by the black line, which appear during the coating and before formation of the final crystalline form (white line).
We ascribe these features to an intermediate liquid crystalline (LC) phase of ditBu-BTBT. In Figure 7.31b we show the in-plane (11L) Bragg peaks observed at 1.12 s. These peaks of the LC phase (red line) have a lower $q_{xy}$ (13 nm$^{-1}$) and $q_z$ values than the crystalline (blue line) Bragg peak ($q_{xy} = 13.25$ nm$^{-1}$). The weak signature of Bragg peaks belonging to the final crystalline phase appear by the 1.32s mark. By 2.4 s mark, the crystalline phase appears to be completely formed while the LC diffraction signature fades away, leaving only the crystalline phase in the film. No further changes are seen beyond this point. These results indicate that the phase transformation for ditBu-BTBT is similar to C8-BTBT case and we also observed high performance under such conditions which involve amorphous intermediate and multiple LC phases.

We also looked thin film formation process by *in situ* HSPOM. Figures 7.32a-e show HSPOM snapshots taken during blade coating of ditBu-BTBT at 25 mms$^{-1}$,90$^\circ$C. The blade leaves behind the trailing bulk solution which is transformed into an intermediate liquid crystalline state. This sequence is also similar to what we observed for C8-BTBT.

![Figure 7.32 In situ HSPOM snapshots taken during blade coating of ditBu-BTBT at 90$^\circ$C](image-url)
7.7 Conclusions

In this study, we show that high-quality thin films of C8-BTBT can be blade coated at industrially compatible coating speeds (>100 mms⁻¹). These films show massive single-domains with very few apparent defects. We achieve average field-effect mobility from BGTC TFTs of ~10 cm²V⁻¹s⁻¹ from as-cast blade coated films. The optimized spin coated conditions result in decent quality films having islands with molecular terraces. Though these films are free of pin-holes and any apparent grain-boundaries or cracks yet show lower mobilities of ~ 5 cm²V⁻¹s⁻¹. The in-situ GIWAXS reveal that the C8-BTBT crystallization during blade-coating is a very complex phenomenon under certain coating conditions. It is also very different from previously investigated TIPS-pentacene and diF-TES-ADT. The in situ GIWAXS reveal that spin and blade-coated films at room temperature directly crystallize to final form. But blade-coated films at ≥ 50°C showed a liquid crystalline phase (LC₁) which leads to final crystalline form. The in situ GIWAXS also reveals a second liquid crystalline phase (LC₂) during blade-coating of C8-BTBT at 70°C and 90°C. We find that crystallization via two intermediate liquid crystalline phases (LC₁ & LC₂) resulted in improved in-plane molecular texture in C8-BTBT films. The better in-plane texture and high-quality defect-free films showed highest mobilities at >70°C. The device performance of OSC films suggest that crystallization pathway involving liquid crystalline intermediate states is a key to achieve better functional properties. GIWAXS also showed that C8-BTBT films which showed lower field effect mobility always have mixture of polymorphs whether it is spin-coated or blade-coated. The metastable polymorph leads to closer in-plane packing and thus high charge carrier mobility in OSC films. We find similar results for another BTBT derivative, ditBu-BTBT. In situ GIWAXS
showed that ditBu-BTBT also crystallizes via intermediate liquid crystalline states at 90°C and has pure metastable polymorph (similar behavior as of C8-BTBT). These ditBu-BTBT films (BGTC OFETs) showed an average mobility of \( \sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and maximum reaching to \( \sim 14 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \).
Chapter 8

Conclusions and Future Perspectives

8.1 Summary

In this thesis, we have shed light on the importance of the process-structure-property-performance relationship in small molecule OSCs. We have used a suit of both *ex* and *in situ* characterization techniques to develop a deeper understanding of solution-to-solid phase transformation phenomenon in lab-based coating methods (drop casting & spin coating) and roll-to-roll compatible methods such as blade coating. This in-depth study allowed us to develop the sound knowledge necessary to make the transition from traditional solution coating methods to industrially desired methods in the context of small molecule OSCs thin film fabrication as active layers for OFETs. Our investigations highlight that controlling the thin film quality holds the key to achieve high-performance OFETs. Our understanding of small molecule OSCs solution processing has led to the development of successful protocols to control OSCs thin film quality during scalable and industrially compatible fabrication.

As detailed in Chapter 2, solution processing of OSCs to manufacture high-quality single-crystals or polycrystalline thin films is a very complicated phenomenon. The functional properties of OSCs in the solid state are strongly coupled to the complex solution to the solid phase transformation process. Figure 8.1 has been constructed to summarize important factors influencing directly the solidification of OSCs. At the start of this Ph.D. (2013), few publications surfaced highlighting the massive gains in solution manufacturing of OSCs by blade coating and related meniscus guided methods.
However, there was no research available, which involved in-depth understanding of crystallization mechanism during spin and blade coating. This encouraged us to perform an exhaustive investigation to develop the necessary understanding of the subject by using modern in situ characterization tools, which we discussed in Chapter 4. We found that
crystallization of small molecular OSCs happens from the bulk of OSC liquid during drop-casting, spin-coating and very low-speed blade-coating (Ribbon-like crystallites). This type of crystallization behavior follows the direct nucleation model (classical nucleation theory). Interestingly, we found that OSC molecules aggregate to form a dense amorphous intermediate state during blade coating under a wide window of coating conditions. The nucleation and growth of OSC crystallites proceed from this intermediate state. This phenomenon resembles the so-called two-step nucleation model. The thin films of OSCs manufactured by this two-step pathway showed superior figures of merit in comparison to direct nucleation when used as active layers in BGB and TGB field effect transistors. We developed a map to highlight the two-step coating window on a coating speed versus substrate temperature plot. The OSC films prepared in two-step nucleation window show uniform texture and morphology, resulting in improved OFET figures of merit. We used insulating polymer binders to further improve the thin film quality and OFET device performance and reproducibility.

In Chapter 5, we developed protocols in the context of polymer: OSC blends, leading to the formation of very high-quality OSC thin films. These blended polycrystalline thin films based on high molecular weight amorphous polymer resulted in well-connected grains and domain boundaries. It helps small molecules to crystallize uniformly on large areas with bilayer vertical phase separation between small molecule and polymer. This study revealed that thin layer of PS stratified on bottom surface modifies the SiO2 dielectric surface and becomes part of the dielectric. This high quality interface leads to massive reduction in interfacial trap states density from $10^{13}$ cm$^{-2}$eV$^{-1}$ (neat) to $10^{11}$ cm$^{-2}$eV$^{-1}$ (blend). The blend films also have lower threshold voltages (close to 0) and high on/off ratios of $10^5$-$10^6$ as
compared to neat films lower on/off ratios of $10^3$ and massive positive threshold voltage. The charge carrier mobility is also improved to the average values of 2 cm$^2$/Vs and maximum reaching to 4 cm$^2$/Vs. On the other hand, neat films showed carrier mobility < 0.5 cm$^2$/Vs under all processing conditions. Furthermore, using appropriate solvent mixtures such as mesitylene and anisole also improved the quality of OSC crystallites and it yielded sheet-like polycrystalline thin films of diF-TES-ADT: PS. These blend films showed average carrier mobilities of 3 cm$^2$/Vs and maximum reaching to 6.7 cm$^2$/Vs along with lower threshold voltage of 0.1 V and high on/off ratios of $10^5$-$10^6$. We also found that it was mandatory to crystallize blend films in two-step coating window to achieve high quality and high OFET performance. We concluded that optimized coating speed in two-step nucleation window, Mw of the binder polymer, blending ratio, choice of solvents and crystal growth rate are key factors influencing thin film quality and eventually charge carrier mobility.

As our studies involved OFETs based on bottom contacts, it was important to probe the interaction of bottom contacts under different surface treated conditions with OSCs in large area compatible blade coating process. In Chapter 6, we found that film formation in blade coating in two-strep nucleation regime is sensitive to bottom surface conditions. The SAM-modified contacts acted as templates for heterogeneous nucleation. This behavior changes the regular bilayer vertical stratification of OSC: Polymer blend thin films to trilayer with polymer sandwiched between the top and bottom OSC layers. The heterogeneous nucleation leads to the formation of small crystals with larger grain boundary density, which eventually serves as a bottleneck to charge transport. To solve this problem, we developed protocols to use O$_2$-plasma treatment that led to the formation of Au$_2$O$_3$
monolayer on Au electrodes. We believe that this gold oxide monolayer might be acting as charge injection monolayer similar to PFBT and other SAMs used for work function modifications of the electrodes. The O₂-plasma treated electrodes did not show any alteration to the crystallization mechanism during blade coating of OSCs, thus resulting in superior OFET performance than halogenated treatment case.

In chapter 7, we developed protocols to fabricate high-quality thin films of BTBT based OSCs by blade coating at industrially compatible coating speeds (>100 mms⁻¹). These films showed massive single-domains with very few apparent defects. We achieved average field-effect mobility from BGTC TFTs of ~10 cm²V⁻¹s⁻¹ from as-cast blade coated films via two-step coating pathway in comparison to ~5 cm²V⁻¹s⁻¹ via direct crystallization by spin coating. The in-situ investigation revealed that the C8-BTBT crystallization during blade-coating is a very complex phenomenon. We found that spin and blade-coated films at room temperature directly crystallize to final form but blade-coated films at ≥50°C showed a liquid crystalline phase (LC₁) before conversion to final form. Furthermore, blade-coated films at ≥70°C showed a second liquid crystalline phase (LC₂). We find that crystallization via two intermediate liquid crystalline phases (LC₁ & LC₂) resulted in improved in-plane molecular texture in C8-BTBT thin films. The better in-plane texture and high-quality defect-free films showed highest mobilities at >70°C. The device performance of OSC films suggests that crystallization pathway involving liquid crystalline intermediate states is a key to achieve better functional properties. We also found that low performing thin films of BTBT based OSCs had a mixture of polymorphs (equilibrium and metastable) whether it is spin or blade-coated. The metastable polymorph leads to closer in-plane packing and thus high charge carrier mobility in OSC films.
To sum up, this thesis has aimed at developing an understanding of the formation of solution-processed OSC thin films and using this knowledge in developing efficient protocols to improve thin film quality by adopting beneficial crystallization pathways, solvent mixtures, polymer binders, device manufacturing conditions with a key goal to demonstrate scalable, reproducible and industry-compatible manufacturability of high performance OFETs. We successfully provide the necessary understanding of crystallization mechanism and the protocols to use it to boost OFET figures of merit.

8.2 Future directions

Two-step nucleation pathway enabled us to manufacture high-quality small molecule OSC thin films but this had not been investigated or applied in the context of polymers. This crystallization pathway can potentially improve the lamellar quality of crystalline/semi-crystalline polymers, eventually leading to high-performance devices. We have only focused on OSCs that find their use in OFETs. This two-step nucleation pathway can also be tested and applied to crystallizable small molecule OSCs that are being used in OPVs.

Although we have used this so-called two-step nucleation pathway to improve OFET figures of merit, still it requires further in-depth studies to develop rate equations. This exercise will certainly help to control important characteristics of polycrystalline thin films.

In this thesis, we provide understanding related to the role of bottom contact treatment in the context of blade-coating and its impact on OFET figures of merit. To further strengthen this knowledge, there should be a detailed study that must describe the impact of O2-plasma and halogenated SAM treatments on the contact resistance, gate voltage dependence of a
wide range of small molecule and polymer OSC based FETs. This will help to understand the role of Au$_2$O$_3$ on charge injection properties in these OFETs.

This thesis has provided protocols to manufacture reproducible defect free millimeter-scale domains of BTBT based OSCs, and we have achieved $> 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the BTBT based OFETs by blade coating in top-contact bottom-gate configuration. However, we noticed gate-voltage mobility dependence in these devices. Sirringhaus H. et al. has recently published the important protocols that must be followed to assess the true performance of OFETs. Therefore, we suggest that there should be a study to establish the impact of different device configurations on figures of merit (especially carrier mobility and its dependence on gate-voltage). This will certainly help to realize the true standing of high-performance BTBT derivatives.

We focused on solution processing of OSC active layers on rigid silicon or glass substrates. An effort needs to be made to test the protocols developed in this thesis to realize high-performance OFETs on flexible plastic substrates. We can physically bend or fold thin films on plastic substrates to test whether it is possible to change the level of strain in unit cells of certain OSCs that possess strained metastable polymorphs in their solid state thin films such as TIPS-pentacene and BTBT derivatives.

Finally, we believe that developments reported in this dissertation have placed small molecule OSCs on a firm ground with respect to the understanding of solution-to-solid phase transformation mechanism, high-quality thin film fabrication by scalable and industry-compatible solution processing method for realization of high-performance OFETs in a reproducible manner.
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