TEMPERATURE GRADIENT APPROACH TO GROW PREFERENTIALLY-ORIENTED TIPS PENTACENE CRYSTALS FOR ORGANIC THIN FILM TRANSISTORS

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ABSTRACT

As a functionalized pentacene, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) is a $p$-type organic semiconductor with remarkable intrinsic charge carrier transport and stability in ambient conditions. TIPS pentacene is soluble in most organic solvents, making it solution processable. TIPS pentacene, nonetheless, inherently forms acutely anisotropic crystals with large gaps in between the crystals, limiting charge transport and leading to vast variations in organic thin film transistor (OTFT) performance.

Described in this dissertation are crystal growth techniques implemented to overcome these challenges. The presented temperature gradient technique, achieves highly aligned crystal arrays with excellent areal coverage which essentially results in an enhanced OTFT performance.

The technique is firstly utilized to guide the TIPS pentacene crystal growth. An application of a temperature gradient to a TIPS pentacene solution controls the crystallization process to alleviate the intrinsic crystal misorientation and considerably improve film morphology. Employing this method resulted in TIPS pentacene films with uniform crystal orientations and extensive areal coverage. The favorable crystal morphology gave rise to a significant enhancement in OTFT average mobility compared to OTFTs without the temperature gradient. Employing the temperature gradient technique, however, simultaneously introduced thermal cracks in the films due to the occurrence of thermally induced stress during crystallization, which reduced the device performance of the TIPS pentacene OTFTs.
To further improve the performance of TIPS pentacene based OTFTs, TIPS pentacene was blended with polymers to relieve the thermal stress and effectively prevent the generation of thermal cracks. Structural examination of, specifically, TIPS pentacene/Poly(α-methyl styrene) (PαMS) blend films at an optimal weight ratio, revealed a vertical phase segregation with elevated concentrations of TIPS pentacene molecules at the active layer/gate dielectric interface, facilitating charge transport. Thus, OTFTs based on TIPS pentacene/PαMS blends exhibited a dramatic increase in average hole mobility compared to those of pristine TIPS pentacene. In addition, an improved thin film uniformity directly enhanced the device performance consistency.

Following the success of employing the temperature gradient technique concurrently with the insulating polymer, PαMS, studies were extended to build OTFTs on flexible substrates, indium tin oxide (ITO) coated polyethylene terephthalate (PET), to dramatically improve TIPS pentacene/PαMS system. Ultimately, TIPS pentacene/PαMS OTFTs on ITO/PET substrates demonstrated the highest achieved mobility from utilizing the temperature gradient system.
DEDICATION

This dissertation is specially dedicated to my parents Ing. Frederick Asare-Yeboah and Mrs. Mary Asare-Yeboah, and my sisters for their unending support while I completed my Ph.D. program. In addition, I dedicate my work to the rest of my family and the numerous people who assisted, guided and encouraged me through this ambitious undertaking.
LIST OF ABBREVIATIONS AND SYMBOLS

$C_i$  Capacitance per unit area of the dielectric layer

$\mu$  Field-effect mobility

$\lambda$  X-ray wavelength

$K$  Crystallite shape factor
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CHAPTER 1

INTRODUCTION

1.1 Overview of Organic Electronics

Organic electronics materials which are heavily carbon based, include organic small molecule semiconductors and polymer semiconductors. Organic electronics materials have been explored for over 50 years.\textsuperscript{1} They have gained tremendous interest as a field of study due to their tunable electro-optical properties through chemical design and synthesis.\textsuperscript{2} Their low-temperature processability and compatibility with inexpensive, solution-based processes, as well as their wide range functionalities, make them well-suited for applications in flexible, large-area and low-cost devices.\textsuperscript{3,4} The demonstration of an organic light emitting diode (OLED) in 1987 by Ching Tang and Steven VanSlyke at Kodak drove the pursuit of organic electronics in many areas of applications,\textsuperscript{5} such as white lighting, organic thin film transistors (OTFTs) and OLEDs for flexible displays, sensors and photovoltaics.\textsuperscript{6} In general, organic electronics expand the electronic landscape by introducing novel, cost effective, flexible and more accessible electronic devices that are potentially more sustainable than the inorganic, silicon-based electronics.\textsuperscript{7,8}
1.2 Organic Semiconductors

1.2.1 Hybridization, Bonding and Energy Levels

Organic semiconductors are conjugated carbon based materials with electrical conductivity residing between the conductivity of metals and insulators. Conjugated molecules have alternating single and double bonds and a network of p-orbitals with delocalized electrons. The small molecule semiconductor can form crystalline structures which enhances the charge carrier transport. Conjugated polymers on the other hand, are generally semicrystalline with amorphous regions which limit their charge transport property. Unlike the inorganic molecules with strong covalent bonds, weak intermolecular van der Waals forces bond organic molecules and influence their electrical, thermodynamic and mechanical properties.

The electronic configuration of organic semiconductors deviates slightly from energy band models of inorganic semiconductors. Organic semiconductor molecules consist of conjugated π-electron networks of p_z orbitals of sp^2 hybridized carbon atoms. Hybridization unites atomic orbitals of the same atom to form a new one. For carbon, one of the electrons in the 2s orbital fills the unoccupied p orbital creating three identical orbitals and a π-electron. Figure 1.1 illustrates the electronic configuration of sp^2 hybridization. The sp^2 molecular orbital represents an approximation of the linear combination of atomic orbitals (LCAO), 2s and 2p, where the number of p orbitals that are hybridized are described by the superscript in the sp^2
hybrid. The number of hybrid orbitals and unhybridized p-orbitals establish the number of bonds formed.

**Figure 1.1.** Electronic configuration of sp\(^2\) hybridization.\(^{11}\)

The sp\(^2\) hybridization of an organic semiconductor molecule forms a double bond between carbon atoms, one σ bond from the hybridized sp\(^2\) orbitals and one π bond from the fourth valence non-hybridized electron.\(^{12}\) Shown in Figure 1.2(a) is the creation of sp\(^2\) hybrid orbitals and in Figure 1.2(b) an example of the structure of a basic conjugated π-electron system in ethylene. The backbone of the molecules is formed by σ bonds (> 10 eV) which is considerably stronger than the weaker π bonds (< 4eV). σ bonds are nonreactive; they have a strong effect on molecular structure and weak effect on the opto-electronic properties. With an energy gap mostly between 1.5 eV to 3 eV and narrower than σ-σ*, π-π* interactions form the least electronic excitations of conjugated molecules.\(^{13}\)
Figure 1.2. (a) The mixing of atomic orbitals to create sp\(^2\) hybrid orbitals. (b) Ethylene (CH\(_2\) = CH\(_2\)), bonded molecules of two carbon atoms where each carbon atom forms three σ bonds by overlapping the sp\(^2\) orbitals and one π bond by overlapping the p\(_z\) orbitals\(^{12,14}\).

For organic semiconductors, their molecular orbitals are used to explain the energy gap which plays an important role in their optoelectronic properties. When two atomic orbitals interact, two new molecular orbitals are formed: an antibonding orbital (indicated with “*”) and a bonding orbital. Antibonding orbitals develop when similar atomic orbitals combine out-of-phase and in phase combinations produce bonding orbitals. The molecular orbital energy diagram in Figure 1.3 shows the antibonding and bonding orbitals of the ethylene compound. As illustrated in the figure, the energy of the created antibonding orbital is higher than the original orbital and the bonding orbital energy is lower.
Molecular orbitals are more stable when the bonding orbitals are filled with electrons while the antibonding orbitals are empty of electrons. The lowest unoccupied molecular orbitals (LUMO) are formed by $\pi^*$ antibonding orbitals and the highest occupied molecular orbitals (HOMO) are formed by $\pi$ bonding orbitals. The HOMO-LUMO orbitals are also known as the frontier orbitals of the molecules. The difference between HOMO and LUMO is the energy gap of the molecule which is known as the HOMO-LUMO gap.

The optical and electrical properties of an organic semiconductor strongly depend on the HOMO-LUMO energy levels and the gap in between. The efficiency in the charge injection from a metal electrode corresponds to the proximity of the work function to the HOMO or LUMO energy levels. Generally, metals with high work functions ($\Phi$) inject hole charges to the HOMO energy level and those with low $\Phi$ inject electron charges to the LUMO energy level.\(^{15}\) The moderate splitting of HOMO-LUMO $\pi$-orbitals allows for light absorption or emission in...
the visible spectral range as a result of the $\pi-\pi^*$ transitions.\textsuperscript{16} Thus, the significance of the energy level of the HOMO-LUMO gap is realized in the semiconductor’s capability to engage in optical and electrical operations.

1.2.2 Doping

Similar to inorganic semiconductors, the conductivity of an intrinsic semiconductor can be altered by doping. Doping an organic semiconductor with an electron donor or acceptor will respectively produce an $n$-type or $p$-type semiconductor. An electron-transporting semiconductor (majority electrons) falls within the $n$-type category and a hole-transporting one (majority holes) belongs to the $p$-type group. Current organic semiconductor devices, however, are generally based on the intrinsic materials and one of the key reasons for this is the stability challenges associated with doping. Typically, device instability materializes as result of diffusion of dopant ions or very small molecules. The diffusion of these small dopant molecules could cause malfunction of organic electronics devices. To realize device stability, the use of larger aromatic molecules (i.e. ones with strong $\pi$-electron donors or acceptors) are better choices for doping.\textsuperscript{17} Akin to inorganic semiconductor doping, establishing mobile majority charge carriers involves introducing impurities (electron donors or acceptors) into the material. Dopants either accept electrons from the HOMO to create holes ($p$-type doping), as shown in Figure 1.4(a), or donate electrons to the LUMO energy levels to increase the electrons ($n$-type doping), as illustrated in Figure 1.4(b).\textsuperscript{18-20} The figure also depicts the vacant and filled locations in the doped molecule’s HOMO and LUMO levels which allow for increased hole and electron transport, respectively. Compared to $p$-type doping, $n$-type doping is more difficult to achieve due to the fact that the
energy of the \( n \)-type dopant HOMO level needs to be higher than that of the matrix material’s LUMO level, however, this leads to instability in the oxygen-rich environment.\(^7\)

**Figure 1.4.** Organic semiconductor doping mechanism. (a) Molecular \( p \)-type and (b) molecular \( n \)-type doping.

### 1.3 Organic Thin Film Transistors

#### 1.3.1 Organic Thin Film Transistor Architectures

Organic thin film transistors (OTFTs) are the fundamental building blocks for organic materials based integrated circuits and displays. An OTFT is a three-terminal device with drain, source and gate electrodes. In an OTFT, the organic semiconducting layer is positioned between a dielectric layer and the gate contact and bridges the source and drain contacts. OTFTs can be fabricated in different device architectures mainly using four key configurations: (a) bottom-gate/top-contact OTFTs, (b) bottom-gate/bottom-contact OTFTs, (c) top-gate/top-contact OTFTs, and (d) top-gate/bottom-contact OTFTs, as shown in Figure 1.5. For bottom-gate/top-contact and top-gate/top-contact OTFTs, the semiconductor layer is deposited prior to the electrode deposition. Solution processing techniques, such as spin coating, drop-casting, inkjet
printing and dip-coating can be used to form the semiconducting layer. The source and drain contact electrodes, commonly gold (Au), are then thermally evaporated through a shadow mask onto the semiconducting layer. Bottom-gate/bottom-contact and top-gate/bottom-contact OTFTs on the hand, have the source and drain electrodes pre-patterned generally by photolithography on the substrate or dielectric layer before semiconductor layer is deposited. The two types of bottom-gate configurations are used the most because the semiconductor can be directly deposited on the top of the substrate with the insulating layer.

Figure 1.5. Schematic representations of four OTFT configurations (a) bottom-gate/top-contact OTFT configuration, (b) bottom-gate/bottom-contact OTFT configuration, (c) top-gate/top-contact OTFT configuration, and (d) top-gate/bottom-contact OTFT configuration. The main difference between the top-contact and bottom-contact OTFT architectures is the sequence within which the semiconductor layer and contact electrodes are deposited.
Bottom-gate/top-contact OTFTs have been observed to result in better device performances in terms of larger drain currents (orders of magnitude higher) and smaller contact resistances, than bottom-gate/bottom-contact OTFTs. Bottom-contact OTFTs tend to experience a larger potential drop at the semiconductor/contact interface than top-contact ones. The higher potential drop is due to: Firstly, a high contact resistance that is attributed to the small contact region for charge injection/extraction and the existence of larger potential barriers at the interface. Secondly, the poor contact between the semiconductor and electrode layers due to the poor semiconductor layer’s film morphology. Since the fragile semiconductor layer is formed after the source and drain electrodes are patterned on the substrate, a non-uniform film morphology results especially in regions around the electrodes. These issues lead to inferior charge carrier mobilities, on/off current ratios and overall lower device performance.

1.3.2 Operation Principle of Organic Thin Film Transistors

Organic thin film transistors, also called organic field-effect transistors, work in accumulation regime, unlike metal-oxide-semiconductor field-effect transistors (MOSFETs) which work in inversion bias regime. An external electric field created by the application of a voltage at the gate electrode induces charge carriers at the semiconductor/dielectric interface, forming a conducting channel. For $p$-type semiconductors, such as that of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene), a negative gate voltage is required to accumulate majority carrier holes at the semiconductor/dielectric interface, to create a channel. With a hole channel created from the negative gate bias, an independent negative voltage applied at the drain electrode drives the hole current conduction from the source to the drain. Therefore, current flow in the organic semiconductor channel drifts from the source to the drain with the
gate controlling the charge carrier density. To illustrate the charge carrier injection, the energy diagram of a TIPS pentacene device is depicted in Figure 1.6.24

![Energy Diagram](image)

**Figure 1.6.** Schematic of the energy levels of the gold (Au) electrode’s Fermi level with respect to the HOMO-LUMO levels of the TIPS pentacene organic semiconductor.24

Due to the proximity of the HOMO level of TIPS pentacene to the gold Fermi level, electrons can easily be injected from the source contact into the organic semiconductor, where they then transport through the semiconductor channel and exit through the drain electrode. For n-type semiconductor active layers, the OTFT operates in the electron accumulation regime with an applied positive gate voltage. Since OTFTs operate in accumulation regime, the conducting channel is a few nanometers away from the semiconductor/dielectric interface.25 Charge transport in organic semiconductors mainly occurs as charge hopping between molecules. The hopping efficiency relies on the molecular packing. Charge transport is most effective in organic conjugated semiconductors (small molecules or conjugated polymers) if their molecules are
stacked with their long axes parallel to each other and essentially perpendicular to the substrate. Because of the π-π stacking of the parallel molecules, charge transport from source to drain, through the stacked layer molecules, has demonstrated high mobility in OTFTs. As an example, Chen et al. highlighted the room temperature stacking of TIPS pentacene molecules in the [001] direction, depicted in Figure 1.7.

The TIPS pentacene molecular stacking displays (001) planes parallel to the substrate and acenes almost normal to the substrate plane. The molecular π-π stacking is along the direction of the TIPS pentacene crystal needles, therefore the charge transport is facilitated if source and drain contacts are deposited along the long axis of TIPS pentacene needles.
1.3.3 Characteristics of Organic Thin Film Transistors

At a gate voltage ($V_G$) equal to the threshold voltage ($V_T$ or $V_{TH}$), the OTFT transistor turns on with charge carriers accumulating at the semiconductor/dielectric interface and as the gate voltage increases beyond the threshold voltage more charges accumulate at the interface. Small drain voltages ($V_D$) initiate current flow in the OTFT channel and causes it to operate like a linear resistor with conductivity controlled by the gate voltage. The OTFT operates in the ohmic or triode regime at small drain voltages, see Figure 1.8. An increase in the drain voltage to a value that makes the potential difference between the drain and gate voltage reduce to the threshold voltage, causes the channel to pinch off. The current flow thus becomes independent of higher drain voltages and enters the saturation regime, seen in Figure 1.8(b). The saturation regime of the OTFT is characterized by the square-law model.

$$ I_D = \frac{W}{2L} \mu C_i (V_{GS} - V_T)^2 \quad \text{(1.1)} $$

where $I_D$ is the drain current, $W$ is the channel width, $L$ is the channel length, $\mu$ is the mobility, $C_i$ is the dielectric capacitance per unit area, $V_{GS}$ is the gate voltage referenced to the source voltage. Note that no junction isolation develops at the source and drain electrodes and leakage current is generated by the intrinsic organic semiconductor conductivity. Contact resistance at the source and drain electrode/organic semiconductor interface affect charge injection and become more dominant in low field OTFT operations as well as when the channel length decreases. Contact resistance prevents the OTFT from being able to achieve the full potential of the charge transport in intrinsic organic semiconductors.\textsuperscript{28,29}
**Figure 1.8.** OTFT characteristics in ohmic/triode and saturation regimes. (a) OTFT operating as a linear resistor controlled by the gate voltage with a small drain voltage. (b) Saturation of drain current at drain voltages greater than the saturation voltage, where $V_{D_{\text{Saturation}}} = V_{GS} - V_T$.

### 1.4 Pentacene and TIPS pentacene

A key scientific challenge exists for organic semiconductors when compared to inorganic semiconductors, where they exhibit lower intrinsic carrier mobilities of $10^{-5}-10^{-2}$ cm$^2$/Vs for amorphous organic materials, and up to 43 cm$^2$/Vs for polycrystalline organic materials than the $10^3$-$10^4$ cm$^2$/Vs mobility range of their inorganic counterparts.$^{12,30,31}$ It is expected that high-quality organic crystals can overcome these challenges: their purity and long-range ordered molecular packing will ensure high device performance. Pentacene,$^{32}$ (C$_{22}$H$_{14}$) seen in Figure 1.9, is an example of an organic small molecule which has been extensively studied due to its noted high charge transport capabilities, with measured mobilities of 1–5 cm$^2$/Vs.$^{33-35}$ The conjugated pentacene molecule consists of a polycyclic aromatic hydrocarbon with five linearly fused benzene rings.$^{36}$ Pentacene molecules adopt herringbone crystal structure with edge-to-face and face-to-face molecular packing. Although, they form highly ordered crystalline films, their
lateral $\pi$-$\pi$ overlap interactions are not optimized, which limits charge transport.\textsuperscript{37} Generally, pentacene thin films are formed via thermal evaporation rather than solution processing due to the fact that pentacene is insoluble in most organic solvents. Highly ordered molecules with large grain sizes are necessary for high charge transport; for pentacene, it can be obtained by performing the vapor deposition at an optimal evaporation rate and temperature.\textsuperscript{38,39} The high vacuum requirements needed for vapor deposition can hinder low-cost manufacturing.

![Molecular Structure of Pentacene](image)

**Figure 1.9.** The molecular structure of pentacene which is polycyclic aromatic hydrocarbon with five linearly fused benzene rings.

In order to make pentacene more susceptible to solution processing, Anthony et al., modified the insoluble pentacene by adding bulky alkynyl silyl groups to the aromatic rings to produce the derivative, 6,13-bis(triisopropylsilyl)ethynyl) pentacene (TIPS pentacene),\textsuperscript{40,41} a new organic small molecule semiconductor, as shown in Figure 1.10. The addition of the bulky side groups not only enhanced the solubility but also the oxidative stability.\textsuperscript{25,42} TIPS pentacene is able to dissolve in most organic solvents, and is also more air stable than pentacene. Furthermore, the addition of the side groups changes the molecular packing by breaking up the face-to-edge herringbone packing pattern\textsuperscript{43} and lowering the interplanar spacing from that of pentacene. In principle, the new face-to-face $\pi$-$\pi$ interactions with significantly increased intermolecular $\pi$-orbital overlap enhances charge carrier transport between the individual acene units and can lead to improved overall device performance.\textsuperscript{40} Ultrafast photoconductivity
experiments have suggested that, TIPS pentacene thin films, maintain a band-like charge carrier transport at subpicosecond time scales,\textsuperscript{27} which results in superior charge carrier transport.\textsuperscript{44-47} In summary, the capability of solution processing at room temperature, high charge transport and air stability are the most attractive properties for TIPS pentacene to be applied as the active channel material for \textit{p}-type OTFTs.

\textbf{Figure 1.10}. The molecular structure of TIPS pentacene, a functionalized organic small molecule semiconductor with bulky side groups at the 6,13-position of the pentacene molecule.

\textbf{1.5 Motivation for the Dissertation Research}

The solution processed TIPS pentacene has three major drawbacks: firstly, it intrinsically forms crystal anisotropy which leads to a substantial extent of OTFT device-to-device performance variations, secondly, the rough surface of TIPS pentacene thin film resulting from thickness variations makes subsequent device fabrication on the surface a challenge and finally, TIPS pentacene forms crystal aggregations and dendrites which cause poor film coverage and
decrease the number of operating OTFTs on a substrate. These primary disadvantages limit its applications in large area electronics. The research work included in the dissertation aims to address these TIPS pentacene solution processing issues to improve the performance of TIPS pentacene based OTFTs.

In order to diminish the TIPS pentacene crystal misalignment and device performance inconsistencies, a number of solution processing techniques have been carried out. These methods can essentially be classified into two categories. The first employs an "external force" while the other utilizes a "blend" approach.\textsuperscript{48} External force, as the name goes, refers to applying physical mechanisms to drive crystal alignment from the TIPS pentacene solution. Confined crystallization,\textsuperscript{6,49} zone casting,\textsuperscript{50} and temperature gradient,\textsuperscript{51} the approach developed in this study, are all examples of techniques which apply an external force to attain TIPS pentacene crystal alignment. With confined crystallization, capillary forces pull the deposited solution into the cavities of a flexible stamp and form menisci underneath the stamp as the solvent evaporates. The confinement leads to a well-oriented TIPS pentacene crystalline thin film. The zone casting method and a few other techniques, including the temperature gradient technique utilized to align TIPS pentacene in this work will be discussed in the next chapter.

The blend approach involves combining TIPS pentacene with other materials such as insulating polymers,\textsuperscript{52-54} nanoparticles,\textsuperscript{55,56} or conducting or semiconducting molecules\textsuperscript{57} in order to enhance crystal orientation, areal coverage, and performance. The blending of TIPS pentacene with polymers takes advantage of both the great thin film uniformity of polymers and the high mobility of small molecules. According to Smith \textit{et al.}, thin solid films consisting of two or more components often demonstrate phase separation during the deposition process,\textsuperscript{53} and these blend
films with phase separation, could exhibit a highly crystalline structure. For instance, Kang et al., reported that, when poly(α-methylstyrene) (PαMS) was blended with TIPS pentacene, a trilayer structure with vertical phase separation, PαMS (top)/TIPS pentacene (middle)/PαMS (bottom) was obtained.\textsuperscript{52} He et al. demonstrated that TIPS pentacene blended with silicon dioxide nanoparticles (SiO\textsubscript{2} NPs) resulted in SiO\textsubscript{2} NPs aggregating around the edges of the grain boundaries of TIPS pentacene crystals which confined the crystal growth and reduced the crystal misalignment. In addition, since most of the SiO\textsubscript{2} NPs were distributed at the edges of the grain boundaries rather than the interface between TIPS pentacene and oxide dielectric layer, they did not have a detrimental effect on the charge transport. Due to the improved crystal alignment, TIPS pentacene/SiO\textsubscript{2} NPs blends demonstrated a great improvement in average mobilities and performance consistency when compared to pristine TIPS pentacene OTFTs.\textsuperscript{56}

Since both the external force techniques and blending approaches have demonstrated to be effective in achieving good crystalline films as well as device performance, as noticed from the above examples, the work performed in this dissertation utilizes both approaches in TIPS pentacene deposition to attain a film morphology with well-aligned crystals and large areal coverage leading to enhanced OTFT device performance.
2.1 Introduction

Processing of organic semiconductor materials into thin films require either vacuum or solution deposition (a wet chemical technique). Vacuum deposition involves evaporation or sublimation of the materials. Small molecules which are generally insoluble employ vacuum deposition. To fully take advantage of low-cost organic electronics on flexible substrates, solution processing of organic semiconductors is preferred. It is also a widely used approach to deposit films of soluble small molecules, such as TIPS pentacene, and semiconducting polymers. There are numerous techniques that fall within the solution deposition category, such as drop-casting, meniscus-guided coating, spin-coating and printing. A few solution processing approaches that have also been utilized for TIPS pentacene crystal growth and alignment are briefly introduced and reviewed in this chapter.
2.2 Solution Processing Methods for Crystal Alignment by Controlling Solvent Evaporation

Controlled solvent evaporation is a typical physical mechanism used for crystal alignment in solution processing techniques, such as dip-coating, solution shearing, zone-casting, and spin-coating.

Dip-coating is one of the first solution deposition methods used for crystal alignment. It is a quick and simple technique which orients the crystals primarily by controlling the vertical regression. In the process, a substrate is dipped into the organic semiconducting solution bath and retreated at a controlled velocity, as demonstrated in Figure 2.1(a-c). The method operates near equilibrium where the nature of the substrate/solution interface, such as temperature and substrate removal speed strongly influence the saturation variation, fluid motion and film formation. Since solvent evaporates faster at the top than at the bottom, the top solution supersaturates first and initiates crystallization. The resulting crystal growth is then uniformly oriented from top to bottom, as illustrated in Figure 2.1(d). Solvents used in dip-coating play a critical role since they affect evaporation rate. The combination of the evaporation rate, substrate removal velocity and a balance of forces at the substrate/solution interface affects the crystal growth and thus final film morphology. Dip-coating is capable of generating thin films with uniform morphology, however, only a decent level of substrate coverage can be attained. In addition, the dip-coating method wastes material and produces a doubled sided substrate coating. Merging the dip-coating process with other techniques, like azeotrope solvent mixtures, has been employed to attain highly ordered crystalline TIPS pentacene films.
Figure 2.1. Schematic of the dip-coating process. (a) The substrate is dipped into a bath of organic semiconductor solution to commence the deposition process and, (b) withdrawn at a controlled speed. (c) The solvent evaporates to produce (d) aligned crystalline domains in the thin film.

Solution shearing is another method used to attain uniform crystal orientations. A shearing plate gradually moves across a temperature-controlled substrate at a constant speed where a greater portion of the solution is held between the shearing plate and heated substrate, as shown in Figure 2.2. Since solvent evaporation mainly occurs at the exposed edges of the solution, as the shearing plate moves relative to the substrate, the uncovered solution at the forefront quickly evaporates to create a seeding layer with many nucleation sites, leading to unidirectional crystallization along the shearing direction. In the shearing process, volatile
solvents are used, and the solutions deposited typically have low concentrations, i.e. highly diluted solutions.\textsuperscript{64} As the shearing speed increases, the thickness of the resulting film decreases. An increased transfer of fluid to the growth front leads to a higher evaporation rate, thereby rapid crystallization. The kinetic feature of the rapidly generated crystals produces metastable molecular packing.\textsuperscript{65,66} The solution shearing process exhibits crystal defects, such as dendrites and gaps in the thin film resulting from the streamline flow which affects mass transport during deposition, a typical occurrence in rapid deposition methods.

\textbf{Figure 2.2.} Schematic of the solution shearing technique demonstrating a moving plate relative to the fixed temperature-controlled substrate. The solvent evaporating at the exposed forefront of solution leads to an oriented crystalline film along the shearing direction.\textsuperscript{47,64}

Similarly, zone casting is another of a solution deposition method utilizing controlled solvent evaporation to attain large area highly ordered crystalline films.\textsuperscript{67} The process involves dispensing the organic semiconductor solution, like TIPS pentacene through a stationary flat nozzle onto a thermally controlled moving substrate,\textsuperscript{50} as the schematic depicts in Figure 2.3. The thermally regulated semiconductor solution is continuously supplied through the nozzle to the evaporation zone as the substrate moves underneath the nozzle.\textsuperscript{68} A stationary concentration gradient is established at the meniscus of the solution at the proper solvent evaporation and
solution supply rates, leading to the deposition of well-aligned crystalline stripes in the casting direction.\textsuperscript{69} A challenge of the zone casting process is the stick-slip motion of the three-phase contact line on the moving substrate, which simply is the pinning and unpinning feature that occurs during solvent evaporation. The stick-slip process leads to deposition lines of the solute perpendicular to the casting direction as opposed to large continuous crystals.\textsuperscript{70}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{zone_casting_schematic}
\caption{Schematic of the zone casting technique illustrating the crystal growth and alignment with a continuous flow of solution through the fixed nozzle onto a temperature controlled moving substrate.\textsuperscript{68}}
\end{figure}

Spin-coating is a high throughput, reproducible and widely used solution deposition technique generally employed to obtain continuous and uniform organic semiconductor thin films.\textsuperscript{71} The organic semiconductor solution is spread on a rotating substrate with a centrifugal force by quickly ramping up the rotation to a specified angular speed for a period of time. The solvent is then expelled by evaporation resulting from the elevated rotation speeds. The final thin film thickness (typically tens of nanometers to microns) depends on controllable parameters such as the solution viscosity, concentration, spin speed, ramping rate, and time. The spin-coating process produces highly uniform and extremely thin films in minuscule time compared to other
processes like dip-coating and vacuum deposition. Nonetheless, spin-coating is uneconomical with materials since it spins off a greater portion of the deposited solution. Additionally, the quick deposition can generate films with less molecular ordering, and post-deposition thermal annealing is often needed to improve the molecular ordering and crystallinity of the films. Spin-coating of multilayers, like dielectric and semiconductor materials for OTFTs, introduces some level of complexity, as solvents used for subsequent layers could possibly dissolve previously deposited thin films, altering the desired structure. Oriented crystalline films or patterned films in confined regions are difficult to attain with the spin-coating process described above. An alternate method which achieves crystal alignment is off-centered spin-coating, where the centrifugal force is applied, practically in a single direction on the entire rotating substrate, see Figure 2.4. The centrifugal force causes the contact line to recede in the radial direction. The radial shearing of the solution, created by the friction of solution against air and substrate, is essential to the crystal alignment, and the spin-coating rate influences the continuity of the aligned crystal domains. The relationship between the receding velocity and critical alignment velocity control the contact line recession alignment. So, a slow receding velocity (determined by solution viscosity and evaporation rate) lower than the critical alignment velocity, possibly results in extensive solute concentration gradients, and drives the crystallization rate to match the receding velocity of the contact line to result in well-oriented crystals. These stripped crystal long axes growth are parallel to the radial direction. On the other hand, a receding velocity greater than the critical alignment velocity causes solvent evaporation to dominate, creating discontinuous crystal alignments and cracks in the metastable thin film morphology.
Figure 2.4. Schematic of the off-centered spin-coating process. (a) The organic semiconductor solution is cast on the substrate. (b) The spin-coater accelerates (ramp-up), spreads and radially spins off the solution while the solvent evaporates simultaneously to achieve the resulting thin film.\textsuperscript{31}

2.3 Drop-casting and Temperature Gradient for Crystal Growth and Alignment

Drop-casting is a simple pseudo-equilibrium solution deposition process where crystallization occurs as the solvent of a cast organic semiconductor solution evaporates and results in a thin film or single crystal; Figure 2.5 illustrates the process. In drop-casting, organic semiconductors with strong self-organizing properties can easily crystallize. However, this technique is not appropriate for depositing continuous large-area thin films since solvent evaporation is not uniformly controlled during crystallization.\textsuperscript{75} Solvent evaporation is therefore an influential and sometimes limiting factor in drop-casting. Although drop-casting is an efficient method for saving materials, it leads to undesired heterogeneous thin film morphology
in terms of poor aerial coverage, subpar uniformity, and uncontrollable crystal thickness due to its stochastic nature.

![Figure 2.5](image)

**Figure 2.5.** Drop-casting technique used for the deposition of organic semiconductor materials. (a) Organic semiconductor solution is drop-cast on a substrate. (b) The solvent evaporation leads to solution supersaturation, and (c) crystallization ensues from the nucleation sites to form single crystals or a film.

Numerous deposition processes build on this method to improve the morphology of the drop-cast solutions. One such process is to control solvent evaporation rate. Slower evaporation rates lead to better crystallization as the solutes have more time to self-organize. Other examples include: tilting substrates to improve the crystal orientation and quality. In such a system, a solution droplet pinned at the elevated end of the substrate travels towards the lower pinned side,
and since evaporation is faster at the top, crystallization initiates in that region. The crystallization continuously moves in an oriented form towards the bottom end as the contact line recedes.\textsuperscript{77,78} Air-flow,\textsuperscript{48} pinned solution crystallization,\textsuperscript{79,80} ultrasound-assisted crystallization,\textsuperscript{81} sealed and solvent-rich environments for annealing,\textsuperscript{82} surface treatments\textsuperscript{83,84} and azeotropic mixtures\textsuperscript{61,85} are also reformed drop-cast techniques that tune thin film morphology or orient single crystals. The developed temperature gradient approach used in this study builds on drop-casting by incorporating a temperature gradient during crystallization.

The solution deposition methods mentioned above deliver some promising results. However, there are many limitations to these techniques. Drop-casting especially, results in films with crystal aggregations, acute anisotropy and display vast gaps between the crystals. The variability in the drop-cast crystals lead to inconsistent OTFT electrical characteristics. Despite the fact that many methods have been utilized to address the TIPS pentacene crystal misalignment, a temperature gradient technique assisting TIPS pentacene film crystal growth and alignment has not been explored. Owing to a technique used in inorganic semiconductor crystal growth, the Czochralski process,\textsuperscript{86} the developed temperature gradient approach in this study achieves TIPS pentacene crystal films with larger individual crystal sizes (measured along the crystal short axis), widespread areal coverage, and more uniform crystal orientation compared to other deposition methods. Figure 2.6 shows the process of the temperature gradient approach applied to TIPS pentacene for its application in OTFTs.
Figure 2.6. Schematic of (a) temperature gradient technique setup for TIPS pentacene crystalline growth. (b) Preferentially oriented TIPS pentacene crystals grown from the low to high temperature end. (c) Bottom-gate/top-contact OTFT with source and drain electrodes aligned perpendicular to the long axis of the TIPS pentacene crystals.
A temperature gradient applied to a drop-cast solution of TIPS pentacene generates a concentration gradient in solution along the gradient direction since TIPS pentacene dissolution is greater at the higher temperature end than the lower end. Supersaturation arises at the lower temperature end with solvent evaporation and the increased nuclei density promotes crystal growth along the temperature gradient direction leading to a preferential directional growth (low temperature to higher temperature end) of uniformly oriented crystals. Toluene solvent annealing employed during crystallization creates a solvent-rich environment and decelerates the rate of solvent evaporation to facilitate the formation of high quality TIPS pentacene crystals. Thus, well-oriented TIPS pentacene crystals with a high percentage of areal coverage result from the temperature gradient method. OTFTs based on the generated crystals demonstrate a significant improvement in average mobility and performance consistency when compared to simple drop-cast films.
CHAPTER 3

TEMPERATURE GRADIENT APPROACH TO GROW LARGE, PREFERENTIALLY ORIENTED 6,13-BIS(TRIISOPROPYLISILYLETHNYL) PENTACENE CRYSTALS FOR ORGANIC THIN FILM TRANSISTORS

3.1 Introduction

In this chapter, details of all the experimental procedures used in the dissertation will be presented. The description entails developing three different deposition approaches (listed below) with the application of the temperature gradient technique.

a. In the first approach, the temperature gradient method was used to deposit pristine TIPS pentacene on rigid silicon substrates.

b. The second method involved the deposition of TIPS pentacene blended with a polymer on silicon substrates via the temperature gradient system.

c. For the final approach, TIPS pentacene/polymer blends fabricated via a temperature gradient was taken a step further by depositing TIPS pentacene/PαMS blends on flexible ITO/PET substrates.

The temperature gradient experimental setup, which is universally shared among the three approaches for the TIPS pentacene deposition, and a summary of the material preparations and
as well as procedures for each method will be discussed. In addition, techniques, which include optical microscopy, atomic force microscopy (AFM), surface profilometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM), adopted to investigate the thin film morphology, crystallinity, and phase separation will be detailed. Lastly, the electrical characterization carried out to study the charge carrier transport will be outlined.

3.2 Temperature Gradient Setup

To setup the temperature gradient, a temperature controller set to a specified temperature was used to heat up a metal plate over a 3 hour period in a controlled environment. The heat source was kept stationary beneath the metal plate to provide constant heat to the sample for the duration of crystallization. Once thermal stability was attained on the plate, one end of the petri dish was placed on the heated metal plate and the other end on a support in ambient, to establish the temperature gradient on the petri dish. The petri dish rested on the metal plate and support for 30 minutes to allow it to also reach thermal constancy. After the 30 minute heating period, a substrate was carefully positioned in the region of the petri dish where the temperature gradient had been established. The temperatures were measured using a type-K thermocouple beaded probe. For the three types of TIPS pentacene crystallization studies that were performed, the temperature gradients established ranged from 2.5–6 °C/cm for temperatures that fell within 29–50 °C temperature limits. In addition, the minimum and maximum temperature boundaries increased as the temperature gradient increased due to the constraints of the setup. Tilt on the petri dish was eliminated in all directions to ensure that the obtained crystal alignment did not result from substrate tilting.
3.3 Pristine TIPS Pentacene Materials Preparation and Deposition

To form pristine TIPS pentacene crystals, TIPS pentacene solution in toluene (anhydrous, 99.8%) was prepared at a concentration of 7 mg/mL. The solution was placed in an ultrasonic bath for 25 minutes to ensure complete dissolution of the TIPS pentacene powder in toluene. A volume of 250 μL of TIPS pentacene solution was drop-cast onto a pre-cleaned heavily doped n-type silicon wafer (with a 300 nm SiO₂ dielectric layer thickness) placed in a petri dish. As detailed in section 3.2, both the substrate and petri dish were subject to a temperature gradient prior to the solution being dispensed, see Figure 3.1. Approximately 0.8 mL of toluene used for solvent annealing was deposited onto the petri dish, circumventing the sample inside the petri dish. Sealing of the petri dish with a few layers of parafilm was implemented to reduce the rate of solvent evaporation and aid the crystallization process.

![Temperature Gradient Technology](image)

**Figure 3.1.** Temperature gradient technology applied to a drop-cast TIPS pentacene solution for crystallization.

The temperature gradient (ranging from 2.5 °C/cm to 6 °C/cm) used during TIPS pentacene deposition determined the time needed for crystallization. The temperature gradient
established a solubility difference of the dissolved solutes in the solution along the substrate, inducing crystal growth and driving crystallization from the lower temperature end to the higher temperature end of the substrate. The long axes of the resulting TIPS pentacene crystals were oriented in the temperature gradient direction, while the short axes (the crystal size or width) were perpendicularly to the direction of the temperature gradient.

To fabricate bottom-gate/top-contact OTFT, 60 nm gold electrode contacts were thermally evaporated via a shadow mask following the TIPS pentacene film deposition. The gold source and drain contacts were deposited perpendicular to the long axis of the TIPS pentacene crystals in order to maximize the charge transport in the channel. The heavily doped n-type silicon substrate was used as the bottom gate electrode.

### 3.4 TIPS Pentacene/Polymer Blends Materials Preparation and Deposition

TIPS pentacene, poly(4-vinylphenol) (PVP) (Mw = 25k), poly(methyl methacrylate) (PMMA) (Mw = 350k), poly(triarylamine) (PTAA) and PαMS (Mw = 108k) with a number average molecular weight (Mn) of 106 kDa, and a polydispersity index (PDI) of 1.02 were the semiconductor and polymer materials used in the second study of the temperature gradient technique. TIPS pentacene/polymer blend films were also attained by drop-casting the blend solutions (with toluene (anhydrous, 99.8%) as the solvent) on silicon substrates under the influence of a temperature gradient. Prior to deposition, the substrates were cleaned in acetone and isopropyl alcohol (IPA) ultrasonic baths for 15 minutes each. 1:1 weight ratios of TIPS pentacene/polymer blend solutions at 5 mg/mL, as well as 2:1 and 3:1 weight ratios solely of TIPS pentacene/PαMS blend solutions at 5 mg/mL concentrations were prepared for subsequent crystallization. The TIPS pentacene and polymer solutions were individually agitated by
sonication for 20 minutes, and the sonication was repeated for the TIPS pentacene/polymer blend solutions for 5 minutes to create a homogeneous mixture. Preceding the TIPS pentacene/polymer blend deposition, a silicon substrate placed on the petri dish as part of the setup described in section 3.2, rested for 15 minutes to reach a stable temperature gradient. A volume of 280 μL was drop-cast onto the silicon substrate and toluene deposited on the petri dish for solvent annealing. The petri dish was sealed in order to maintain the favorable solvent-rich environment for crystallization. For the optimum TIPS pentacene/polymer film morphology results, the temperature gradients chosen were between 3 °C/cm and 5.5 °C/cm.

To form the active layer, 1:1, 2:1 and 3:1 TIPS pentacene/PαMS blend weight ratios were deposited on heavily doped n-type silicon wafers with 3000 Å thermally grown silicon dioxide (SiO₂) insulating layers with a capacitance of 11.50 nF/cm². Gold layers 50 nm thick, were deposited and patterned as source and drain electrodes via thermal evaporation through a shadow mask onto the active layer to complete the bottom-gate/top-contact OTFT. The device channel width was fixed at 1000 μm while the lengths included 40 μm, 50 μm, 75 μm and 100 μm.

3.5 TIPS Pentacene/Poly(a-methylstyrrene) Blends on Flexible Substrates Preparation and Deposition

The final study utilizing the temperature gradient technique focused on the fabrication of TIPS pentacene/PαMS blend films on flexible substrates. Low-cost polymeric indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrates were adopted for the study. To form the gate dielectric layer, PVP and a cross-linking agent, poly(melamine-co-formaldehyde) methylated solution (PMF), were combined at a 1:1 weight ratio and dissolved in propylene glycol monomethyl ether acetate (PGMEA ≥ 99.5%) at a concentration of 8 wt%. The PVP-PMF
in PGMEA solution was stirred for 24 hours and spin-coated onto pre-cleaned ITO/PET substrates at 2000 rpm for 60 seconds, after which, the substrates were cured at 180 °C in a vacuum oven for 30 minutes to generate thermal cross-linking in the PVP layer. The thickness of the PVP-PMF dielectric layer was measured to be 280 nm using an SEM (JEOL 7000 FE SEM). 130 µL of 2:1 TIPS pentacene/PαMS weight ratios in toluene solutions were crystallized at the optimum temperature gradient range of 3–3.5 °C/cm. As the final step, gold was thermally evaporated onto the TIPS pentacene/PαMS blend films deposited on the ITO/PET flexible substrates to complete the OTFT fabrication. The gold source and drain electrodes were patterned with a thickness of 100 nm to accommodate the active layer’s surface roughness. The OTFT channel dimensions were 1000 µm for the width and a range of channel lengths 40 µm, 50 µm, 75 µm and 100 µm.

3.6 Film Characterization

To examine the effect of using the temperature gradient technique to deposit TIPS pentacene and TIPS pentacene/PαMS blend films, the film morphology, microstructure properties and electrical performance were characterized with a variation of techniques. The techniques used are detailed in this section.

3.6.1 Characterization of the Film Morphology

Since the organic semiconductor crystalline film plays a key role in the device performance, studying its morphology is essential. The morphology of the TIPS pentacene films were observed using a Zeiss Axioplan 2 microscope in polarized optical mode. In addition, vital properties of the film morphology, which are the crystal width (size), areal coverage, crystal
orientation, and crystal thickness, were examined further, as they primarily make up the features of the morphology that strongly affect the OTFTs device performance.

The TIPS pentacene crystal width (or size), is the length of the crystal short axis [120] and is also known as the grain width (WG). In the study, the grain width of the thin film crystals were measured using an optical microscope. The measurements were used to determine the crystal sizes achieved for the temperature gradient applied. Temperature gradients that exhibited larger crystal grain widths generally lead to a better the areal coverage on the substrate.

The areal coverage which is the ratio of the substrate area covered by crystals to the area of the whole substrate was acquired by performing line scans on the surface of the film using surface profiliometry. Vecco Dektak Series V profilometer was employed to scan the film. In its operation, topography data of the film’s surface is measured electromechanically by scanning a diamond-tipped stylus across the sample mounted on a high precision moving stage. The stylus which is coupled mechanically to a Linear Variable Differential Transformer (LVDT) is directed by user defined inputs such as: scan length, speed and stylus force. As the sample’s surface is scanned, the stylus experiences vertical displacements when it encounters height feature variations. The movement of the stylus leads to displacements of the core position of the LVDT, which is realized proportionally as analog electrical signals. The analog signal is converted to digital signals through an integrating analog-to-digital converter and stored for data acquisition and display. For this study, after performing the scans, measurements attained were used to compute the ratio of the total widths of the peaks in a single line scan to the scan length. The computation was repeated for all scans on the entire substrate to result in the areal coverage.
As mentioned previously, crystal orientation is one of the parameters that influences the quality of the film morphology. It can adversely affect device performance if the crystal alignment of the thin film is not uniform and accurately directed in the channel regions. Misaligned crystals contribute extensively to performance variations of OTFTs. Figure 3.2 presents a general depiction of the TIPS pentacene crystal misalignment that can occur at different regions on the substrate. To obtain better performance of the TIPS pentacene films, the misalignment angle, $\theta$ (located between two adjacent long axes [210]), as well as the number of misalignment angles, are required to be low. The low number indicates that there is good crystal alignment and uniform array of crystal orientations.

![Figure 3.2. TIPS pentacene crystal misalignment, with misalignment angle, $\theta$, defined as the angle between two adjacent long axes [210] of TIPS pentacene crystals.](image)

In the study, the number of crystal orientations of a sample was acquired by accounting for the different crystal directions present in the TIPS pentacene film. The varying crystal directions were obtained by performing ten systematic line scans using an optical microscope. Upon acquisition of the orientations, the total number of directions was computed for all the line
scans performed on the entire substrate. This process was repeated on more TIPS pentacene films deposited specifically under the same temperature gradient conditions. The values were averaged to characterize the total number of crystal orientations for each temperature gradient.

On occasion, films with excessively high thickness values could have the crystal thicknesses resulting from unfavorable crystal aggregations, which can hinder charge transport. For this reason, the surface topographies of the TIPS pentacene and TIPS pentacene/PαMS films were examined. The surface profile measurements previously obtained from the Dektak profilometer scans were employed to determine and analyze the general film surface roughness and film thickness. Digital Instruments Dimension 3100 AFM equipped with a Nanoscope IV controller was additionally adopted to scan the vertical features of the TIPS pentacene/PαMS films. As a very high-resolution type of scanning probe microscopy, AFM was well suited to characterize the thin film’s surface topography as well as its surface roughness for the various deposition and treatment conditions. The film surface was scanned with the AFM operating in tapping mode. In this mode, a sharp nanoscale AFM tip attached to the end of a cantilever, raster scans over the sample’s surface. During the scanning process, the cantilever oscillates in the vertical direction at/or close to its resonant frequency with the aid of a small piezoelectric component fixed in the AFM tip holder. The cantilever tip is typically constructed out of silicon or silicon nitride due to its hardness and generally oscillates at a high frequency (hundreds of kilohertz) while operating the AFM to prevent the tip from being seized by any surface tension forces on the sample. When the tip is moved close to the surface during operation, the cantilever deflects in agreement with Hooke’s law, where the tip’s deflection, associated with the thickness variations of the sample, is proportional to the resulting force. Depending on the type of AFM used, the force measured, can be a mechanical contact force, capillary force, electrostatic force,
or magnetic force, among others. Usually, a laser spot positioned on top of the part of the cantilever directly above the tip, reflects the laser rays into a group of photodiodes. If constant height scanning is performed, it poses a hazard to the tip as it could be destroyed when it strikes the sample surface. Hence, in this study, a constant force between the tip and sample where a feedback loop regulates the gap between them to conserve the force, was used. When the tip drew close to the sample (i.e. TIPS pentacene/PαMS film), the forces that act on the cantilever controlled the oscillation amplitude by reducing it as it drew nearer the sample’s surface to mitigate the probability of damaging the surface or tip. The thickness and height variations associated with the oscillation amplitude were extracted from the TIPS pentacene/PαMS scanned measurements. An extracted small degree of surface roughness indicated a good surface uniformity.

3.6.2 Characterization of the Crystal Structure

X-ray diffraction was carried out to characterize the molecular structure of the TIPS pentacene crystals as it gives the most definitive structural information. A Philips X'pert Diffractometer with the commonly used target material, Cu Kα radiation (wavelength = 1.5418 Å) was employed for the analysis. The crystalline structure, lattice position and atomic spacing of the temperature gradient TIPS pentacene films were individually compared with the pure TIPS pentacene films and with literature. The full width half max (FWHM) values and the average interlayer spacing of the films were extracted and calculated respectively to assist with the comparison.

In operating the X-ray diffraction, a precisely focused monochromatic incident X-ray beam generated by a cathode ray tube bombarded the TIPS pentacene sample mounted on a
goniometer which rotated the sample such that it was situated at preferred crystal orientations. The beam was scattered by features in the crystal lattice and diffracted in defined directions at regularly located spots. The diffracted rays are also referred to as reflections since they are reflected from regularly spaced planes in the crystal. For the detector to register and count peak intensities of a reflection, coherent scattering of the incident X-ray should satisfy the constructive interference criteria, which occurs when the distance the X-ray beam travels is equal to an integer multiple of the wavelength of the radiation, satisfying Bragg's Law:

\[ n\lambda = 2d_{hkl} \sin \theta \]  \hspace{1cm} (3.1)

where \( n \) is an integer value defining the diffraction order, \( \lambda \) is the electromagnetic radiation (i.e. X-ray wavelength), \( d \) is the distance between atomic lattice planes (also known as interlayer spacing or \( d \)-spacing), \( hkl \) are the Miller indices of the planes being analyzed and \( \theta \) is the angle of incidence with the lattice plane (i.e. the scattering plane). The law defines the relationship between the X-ray wavelength, the reflected angle and the interlayer spacing of the TIPS pentacene crystalline sample. Figure 3.3 depicts the conditions that satisfy Bragg’s Law, where the crystalline lattice planes are represented by the set of horizontal lines. As illustrated in the figure, the source and the detector are located at points where the angle between them and the reference sample surface are the same. There are different types of XRD scans that are performed; however, for the study, 2\( \theta \)-omega and omega scans were performed on TIPS pentacene films, where omega is the angle of incidence, \( \theta \). The geometry of the 2\( \theta \)-omega scan is such that the source remains stationary while the sample rotates at an angle of \( \theta \) in the path of the X-ray beam and the detector rotates at an angle of 2\( \theta \). The detector’s 2\( \theta \) angle scan range allows for full detection of all probable diffraction directions.
Figure 3.3. Geometry of Bragg diffraction showing two X-ray incident beams with the same wavelength and phase. The incident beams are reflected off two different atoms in the crystal where the angle of incidence, $\theta$, is the same as the angle of reflection. The lower beam travels an additional distance of $2d\sin\theta$, where $d$ is the distance between the crystallographic planes.

As the TIPS pentacene sample and detector were rotated, the detector registered the intensity of the reflected diffracted rays, processed and converted the signal to count rate. The resulting $2\theta$-omega scans gave information on the composition of the corresponding molecular layers in the TIPS pentacene structure. From the acquired peak intensities, the interlayer spacing was extracted. The determined interlayer spacing was compared to documented values in literature during analysis. For the omega scan, also referred to as rocking curve, both the source and detector were fixed in their positions but the TIPS pentacene sample was rotated at small angles encompassing a specific diffraction peak. Thus, the sample was rocked around a diffraction peak; hence, the name rocking curve. An omega scan is mainly used to get details about the crystalline quality and size. The FWHM values (i.e. the natural width of a diffraction peak) for different temperature gradients were determined from the omega scans of 3 diffraction peaks. A schematic of a diffraction peak indicating the FWHM position is illustrated in Figure
3.4. A mathematical curve fitting function, such as the Gaussian function, was used to fit each diffraction peak to extract the FWHM values.

![Diagram of a diffraction peak with FWHM labeled as \( \frac{1}{2}I_{\text{max}} \) and peak position at \( 2\theta_1 \).](image)

**Figure 3.4.** Schematic of a diffraction peak showing the FWHM, the full width of the diffraction peak at half the maximum intensity, \( I_{\text{max}} \), at a \( 2\theta_1 \) Bragg angle.

For this study, the fitting was done in first approximation, where fairly ideal case assumptions were made; for example, the instrument, the X-ray beam, and other elements were assumed to not influence the final value. Information about the quality of the TIPS pentacene crystals were obtained from extracting the details of the diffraction peak. This was determined by using the knowledge that, the calculated FWHM value is inversely proportional to the crystallite size, according to Scherrer’s equation:\(^{88}\)

\[
D_{hkl} = \frac{K\lambda}{B_{hkl} \cos \theta} \tag{3.2}
\]
where $D_{hkl}$ is the crystallite size directed perpendicular to the lattice planes, $K$ is a constant value generally referred to as the crystallite shape factor, $\lambda$ is the incident X-ray wavelength, $B_{hkl}$ is the FWHM value expressed in radians and $\theta$ is the Bragg angle (angular position of the peak).

The vertical phase separation along with the percentages of material composition of each of the phases of the TIPS pentacene/PαMS films were studied using a JEOL 7000 FE SEM. Images of the phase separation, energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS) data were acquired from the equipment. The JEOL 7000 FE SEM used is fitted with an Oxford detector to detect emitted X-rays. In the qualitative and quantitative analyses, point mode, line, and area scans were all performed to determine the composition and percentages of the individual elements located in the layers of the TIPS pentacene/PαMS sample.

SEM is a nondestructive tool that utilizes the complex interactions between a focused electron beam and atoms of the sample to generate different signals to be detected. These signals give information about the surface formation and composition. The SEM tool is composed of an electron gun unit, electromagnetic lenses and apertures, a vacuum system and a specimen state. For the widely used SEM tools, including the one utilized here, the electron gun unit generally consists of a tungsten filament (cathode), Wehnelt cylinder, and an anode plate. A voltage difference generated between the cathode and anode plate produces the accelerating voltage (typically about 0.2 keV to 40 keV) of the system and the movement of the electrons (electron beam) is attained by thermionic emission. Two types of lenses, the condenser and objective lenses, make up the electromagnetic lenses of the SEM. These electromagnetic lenses combined with the apertures were used to focus the primary electron beam on the TIPS pentacene/PαMS samples. The final lens which deflects the beam in the x-y direction raster scanned the surface of
the sample in a rectangular form during operation. When the electron beam hit and excited the sample, a teardrop-shaped interaction or emission volume was created and elastic and inelastic electron scattering occurred. The depth and width of the interaction volume depends on the beam energy and the sample’s atomic number density. The signals generated by an electron beam sample interaction are, secondary electrons (SE), backscattered electrons (BSE), characteristic and continuum X-rays, cathodoluminescence (visible, ultraviolet and infrared wavelengths), auger electrons, specimen current and transmitted electrons, as depicted in Figure 3.5. Surface structure information is obtained from SE, and BSE gives topographical contrast and compositional or atomic number contrast details. Characteristic X-rays provide elemental composition while continuum X-rays which generate the Bremsstrahlung radiation forms part of the background (which gives no useful information). Cathodoluminescence yields specifics on impurity concentration, whereas auger electrons produce surface composition information. Specimen current provides atomic number contrast details, and transmitted electrons deliver information on the internal ultrastructure of the sample. Each of these signals are detected by their own dedicated detectors. SE detectors are customary equipment in all SEMs, however it is uncommon to find detectors for all the types of generated signals in a single equipment. SE and BSE detectors were used to form TIPS pentacene/PtαMS images by converting the generated radiation into an electrical signal. The signals were amplified by different types of electronic amplifiers and displayed as variations in brightness, where every pixel corresponded with the position of the beam on the sample. Thus, the image was a projection of the intensity of the emitted signal from the scanned area of the sample.
Figure 3.5. Cross-sectional schematic of the interaction volume created when an SEM electron beam strikes a sample.

Acquisition of EDS and WDS spectra depended on emitted characteristic X-ray signals of the TIPS pentacene/PαMS films. X-ray signals were emitted when the electron beam dislodged a low energy inner shell electron of the TIPS pentacene/PαMS sample. The dislodged electron energy was released as an X-ray signal, as the higher energy outer shell electron immediately filled the vacancy. These X-rays not only had energies characteristic of the elements in the TIPS pentacene/PαMS sample, they also had an associated wavelength which were detected with the energy dispersive or wavelength dispersive spectrometers, respectively.
3.6.3 Electrical Characterization

Electrical characterization was performed on the TIPS pentacene and TIPS pentacene/PaMS using a semiconductor parameter analyzer (Agilent Technologies B1500A) in ambient air, at room temperature. The source and drain contacts were aligned with semiconducting active layer crystals in the direction where maximum charge transport in the channel could be reached. Typical $I_{DS}$–$V_{DS}$ output characteristics were acquired at gate voltages varying from 0 to $-20$ V in $-5$ V increments. The field-effect mobility in the saturation regime ($V_{DS} = -20$ V), as well as the threshold voltage, were determined from the fitted line of the $(−I_{DS})^{1/2} − V_{GS}$ transfer characteristics.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter will theoretically explain the temperature gradient technique and its effect on TIPS pentacene crystal growth. Detailed discussions of the results attained from employing the temperature gradient technique to crystallize TIPS pentacene, TIPS pentacene/polymers and TIPS pentacene/PαMS on flexible ITO/PET substrates will be presented. Analysis of the various characterizations performed on the TIPS pentacene films will elucidate as well as demonstrate the essence and influence of the temperature gradient technique on film growth.

4.2 Temperature Gradient Approach to Grow Large, Preferentially Oriented 6,13-bis(triisopropylsilylethynyl) Pentacene Crystals for Organic Thin Film Transistors

In this study, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) crystalline growth was enhanced by applying a temperature gradient across the substrate during deposition. Traditional deposition methods, such as drop-casting, have generally been used to attain polycrystalline TIPS pentacene thin films. However, their resulting thin films are acutely anisotropic with large gaps in between the crystals, leading to vast variations in OTFT performance. While many techniques have been utilized to address this issue, a temperature
gradient applied during deposition not only achieves excellent TIPS pentacene crystal alignment and reduced thin film roughness but additionally produces crystal films with larger individual crystal sizes, extensive areal coverage, and more uniform crystal orientation. Thus, the temperature gradient method induces a preferential crystal orientation which alleviates the intrinsic crystallization anisotropy and controls film morphology.

In the approach, a temperature gradient was applied to the drop-cast solution of TIPS pentacene to allow unidirectional growth of the crystals. Since the dissolution of TIPS pentacene in the toluene solvent is greater at higher temperatures, the temperature gradient causes a solubility difference along the substrate to preferentially drive crystallization from the lower temperature end to the higher temperature end. During TIPS pentacene crystal growth, solvent annealing with toluene was used to create a solvent-rich environment to slow down the solvent evaporation, and, thus, achieve high quality TIPS pentacene crystals. Characterization and analyses performed on the resulting TIPS pentacene films are detailed next.

4.2.1 Analysis of Film Morphology

Figure 4.1 presents the polarized optical images of the TIPS pentacene crystals. The variant colors shown in each image is due to the change of crystal orientation and thickness. Crystals resulting from simple drop-casting deposition show random crystal orientation and large gaps, as depicted in Figure 4.1(a). The application of temperature gradients generate plate-like TIPS pentacene crystals with more uniform crystal orientation, larger individual crystal sizes, and greater areal coverage on the substrates [Figures 4.1(b)–4.1(f)]. It was observed that the crystal size varied depending on the temperature gradient. With an increase in the temperature gradient from ~2.5 to ~3.5 °C/cm [Figures 4.1(b)–4.1(d)], the individual crystal sizes increased,
reducing the gaps between the crystals, thereby enhancing the film coverage. The largest individual crystal size of \( \sim 1158.6 \) \( \mu \text{m} \) was obtained from a 3.5 \( ^\circ \text{C/cm} \) temperature gradient. Additional increases in the temperature gradient to 5 and 6 \( ^\circ \text{C/cm} \), still produced excellent areal coverage, but individual crystal sizes were reduced, as seen in Figures 4.1(e) and 4.1(f), respectively. Solvent annealing with toluene employed during TIPS pentacene crystal growth promoted an increase the individual crystal size, as well as the quality.\(^{41,92,93}\) In a solvent-rich environment, the rate of solvent evaporation decelerates, granting the crystals more time to develop in size and quality.\(^6,59\) Large sized crystals curtails the occurrence of gaps between the crystal grains, and thus enhance the areal coverage. The mechanism for the improved crystal orientation as well as the crystal size variations at different temperature gradients can be explained with the illustrations in Figures 4.1(g) and 4.1(h). Since solubility increases with temperature, as the solution at the high temperature end approaches its solubility limit, the solution at the low temperature end would be supersaturated. Supersaturation is what drives crystal nucleation and growth. At a low nucleation density, crystallization from nuclei is randomly oriented. However, the orientation of the crystal growth can improve at a higher nucleation density, which occurs when a balance between the nucleation and growth rate is achieved.\(^94\) The supersaturated low temperature end has a high nucleation density which drives crystal growth in the direction of low to high temperature along the temperature gradient, thereby creating highly oriented crystals. For small temperature gradients, within a \( \sim 2.5–3.5 \) \( ^\circ \text{C/cm} \) range, both the low and high temperature boundaries are low, e.g., \( T_1 \) and \( T_2 \) in Figure 4.1(g), leading to a low supersaturation. This low amount of supersaturation falls within region I of Figure 4.1(h). As the temperature gradient increases, the supersaturation increases, producing
large crystals. At large enough temperature gradients, (5–6 °C/cm), both the low and high temperature limits increase to, $T_3$–$T_4$, due to the constraints of the experimental setup.

**Figure 4.1.** Polarized optical micrographs of deposited TIPS pentacene films obtained from: (a) simple drop-casting, displaying misoriented crystals with large gaps, and (b)–(f) the temperature-gradient technique (temperature gradients: $b \approx 2.5$ °C/cm, $c \approx 3$ °C/cm, $d \approx 3.5$ °C/cm, $e \approx 5$ °C/cm, and $f \approx 6$ °C/cm) demonstrating uniform crystal alignment, large and single plate-like crystal sizes, and enhanced areal coverage. Schematic drawings depicting (g) the effect of temperature on solubility, and (h) the influence of supersaturation on crystal size, growth rate, and nucleation rate.
The temperature zone shift from $T_1$–$T_2$ to $T_3$–$T_4$ leads to a greater supersaturation [Figure 4.1(g)], which could be located in region II in Figure 4.1(h). In region II, crystal sizes reduce as supersaturation increases due to the competition between the nucleation rate and growth rate in the solution.\textsuperscript{95,96} This may also explain the reduction in crystal size at slightly higher temperature gradients of 5–6 °C/cm. Furthermore, the increase in temperature for the higher temperature gradients, promotes solvent evaporation. This rapid evaporation deprives the crystallization process the time needed to attain desired crystal sizes. Therefore, it may also lead to a reduction in crystal sizes.\textsuperscript{97}

To further investigate the effect of temperature gradients on crystal morphology, the areal coverage and orientation as a function of temperature gradients, as well as the surface topography were analyzed, and are shown in Figure 4.2. The areal coverage was determined by performing line scans over the entire film on the substrate using the Vecco Dektak Series V profilometer. The percentage coverage was calculated by determining the ratio of the overall length of crystal coverage to the total scan length. The plot shown in Figure 4.2(a) reveals a steep rise in the coverage for the lower temperature gradients due to a significant increase in crystal sizes. With additional increases in the temperature gradient, more gaps between individual crystals are bridged, leading to minimal increases in areal coverage. Figure 4.2(b) shows the number of crystal orientations determined for each temperature gradient. Crystal alignment benefits from a low number of crystal orientations, hence, the lower the number of crystal orientations the better the crystal alignment. The number of crystal orientations was computed by totaling the varying crystal directions on a single line scan. The lines scans were performed for ten total rows and averaged to characterize the crystal orientations on the entire substrate for each temperature gradient.
Figure 4.2. (a) Areal coverage (%) of TIPS pentacene film. (b) Crystal orientations as a function of temperature gradient, indicating the influence of temperature gradient on crystal alignment. (c) Comparison of surface topographies of the TIPS pentacene film obtained from simple drop-cast and a temperature gradient of 5 °C/cm.
As shown in Figure 4.2(b), the sharp decrease in the number of orientations signifies that the temperature gradient technique can substantially improve crystal alignment. It can be observed that the reduction in the number of orientations becomes less prominent at temperature gradients of 3.5–5 °C/cm. The minute increase in the number of orientations at the 6 °C/cm temperature gradient is due to the elevated nucleation rate at higher temperature gradients, as previously mentioned. Figure 4.2(c) exhibits the vast improvement in the surface topography of the TIPS pentacene film deposited with a 5 °C/cm applied temperature gradient, compared with that from simple drop-casting. The TIPS pentacene film attained using a temperature gradient produced a more uniform surface profile and much lower film thickness than that obtained from simple drop-casting, and it contributed to the improved morphology. Specifically, the application of a temperature gradient lead to a significant reduction in film roughness and enhancement in areal coverage.

4.2.2 X-ray Diffraction

Figure 4.3(a) shows X-ray diffraction spectra of TIPS pentacene films from simple drop-casting (without temperature gradient) and with applied temperature gradients of 2.5–6 °C/cm. The diffraction patterns corresponding to the varying temperature gradients are vertically shifted to enable visual differentiation. The consistently strong reflections from the (00l) planes match well with previously reported results. The peak intensity ratios (peak\(_{(00l)}\)/peak\(_{(001)}\)) shown in Figure 4.3(b) are higher for the temperature gradient TIPS pentacene films than for the simple drop-cast films, which suggests that the film crystallinity may also be slightly enhanced with the application of the temperature gradients.
Figure 4.3. (a) X-ray diffraction patterns of TIPS pentacene films obtained with and without a temperature gradient (TG). (b) The slight increase in peak intensity ratios (peak\textsubscript{(001)}/peak\textsubscript{(001)}) of the temperature gradient films indicate that the film crystallinity is enhanced by applying a temperature gradient.

The full width half max (FWHM) values of the (001) peaks were also extracted from Gaussian fitting curves. The comparable FWHM values further indicate that film crystallinity is at least maintained when temperature gradients up to at most 6 °C/cm are applied. A marginal
shift in the two-theta values was observed for the crystals obtained using a temperature gradient compared to those obtained without a temperature gradient. Based on the Bragg formulation of X-ray diffraction (see Equation (3.1) for Bragg’s Law), the average interlayer spacing was calculated. The TIPS pentacene films obtained using the temperature gradients showed an average interlayer spacing of 16.6 Å, which is a slight decrease compared to films grown with simple drop-casting (16.7 Å). A probable reason for this reduction is that the crystals grown with the temperature gradient method are more compact with less lattice strain.99

4.2.3 Device Characterization

Organic thin film transistors were fabricated using TIPS pentacene films grown by the temperature gradient method. Figure 4.4 shows typical $I_{DS}$–$V_{GS}$ transfer and $I_{DS}$–$V_{DS}$ output characteristics. The highest hole mobility of $3.5 \times 10^{-2}$ cm$^2$/Vs was attained from a device using films grown with a 5 °C/cm temperature gradient. The device’s threshold voltage was $\sim$6.2 V and the current on/off ratio was $>10^3$. The subthreshold swing also was extracted from the log ($I_D$) versus $V_{GS}$ characteristic curve. The average subthreshold swing at the 5 °C/cm temperature gradient was 2.1 V/dec, which is less than the averaged 5.63 V/dec from the simple drop-cast samples. The steeper subthreshold slopes in the subthreshold region from the samples obtained with applied temperature gradients indicate fewer grain boundaries and interface traps in comparison with those from simple drop-casting.100 The high performance achieved by the 5 °C/cm temperature gradient sample was due to the film’s excellent crystal coverage and crystal alignment.
Figure 4.4. (a) Typical transfer and (b) output characteristics from OTFTs with the TIPS pentacene active layer obtained with an applied temperature gradient.

Figure 4.5 shows the average mobility ($\mu_{\text{Avg}}$) and standard deviations ($\mu_{\text{Stdev}}$) as a function of temperature gradient. The average mobility increased as the temperature gradient increased from 3.5 to 5 °C/cm, due to the improved film coverage and enhanced crystal alignment. However, with a further increase in the temperature gradient to 6 °C/cm, the average mobility slightly decreased because of the increased number of crystal orientations. Since charge carrier
transport is most efficient when the long axis of TIPS pentacene crystals are aligned along the source and drain contacts, a rise in the number of crystal orientations results in a drop in the average mobility. Nevertheless, compared with simple drop-casting, the average mobilities attained from the temperature gradient samples were consistently higher. Specifically, the average mobility of $3 \times 10^{-2}$ cm$^2$/Vs from the 5 °C/cm temperature gradient OTFTs demonstrated about a 15-fold enhancement compared to that of simple drop-casting (about $2 \times 10^{-3}$ cm$^2$/Vs). This signifies that the temperature gradient approach is an effective way to grow TIPS pentacene crystals with extensive areal coverage and notable crystal alignment, which results in improved OTFT performance.

![Graph showing average mobility and standard deviation of TIPS pentacene films](image)

**Figure 4.5.** Average mobility ($\mu_{\text{Avg}}$) and standard deviation ($\mu_{\text{Stdev}}$) of TIPS pentacene films obtained by applying 3.5 °C/cm, 5 °C/cm, and 6 °C/cm temperature gradients.

It should be noted that there were no surface treatments performed on the oxide substrates before TIPS pentacene growth with the temperature gradient method because of solution
Charge carrier transport in OTFT devices substantially depends on the gate dielectric surface. The absence of surface treatments is considered to be one of the reasons that the extracted mobilities were lower than previously reported values. In addition, thermal cracking was observed in the TIPS pentacene films when temperature gradients were applied, as shown in Figure 4.6. An increment in the generation of thermal cracks occurred as the temperature gradient increased. These thermal cracks were mostly perpendicular to the long axes of the needle-shaped TIPS pentacene crystals. According to the studies of Chen et al., thermal cracks in TIPS pentacene films could cause a 50%–80% drop in mobility. It is deduced that the cracks that were created at higher temperature gradients (such as 6 °C/cm) are accountable for the large standard deviations in field-effect mobilities.

![Figure 4.6](image.png)

**Figure 4.6.** TIPS pentacene crystals with thermal cracking. The short and long axes of the needle-shaped TIPS pentacene crystals are indicated by the short rods and long arrows, respectively.

In conclusion, a methodical investigation of TIPS pentacene crystal morphology dependence on temperature showed that well-oriented TIPS pentacene crystals with a high
percentage of areal coverage are achieved through the temperature gradient approach. OTFTs based on the generated crystals demonstrate a significant enhancement in average mobility when compared to OTFTs using films grown without the temperature gradient. X-ray diffraction characterization revealed that the film crystallinity is not sacrificed with the application of a temperature gradient. The TIPS pentacene films, however, displayed thermal cracks. To prevent the development of thermal cracks while employing the temperature gradient technique, further studies which include blending TIPS pentacene with polymers, as well as performing TIPS pentacene/polymer depositions on a flexible substrate with a polymeric dielectric layer (ITO/PET substrate) were carried out and will be discussed in subsequent sections.

4.3 Temperature Gradient Controlled Crystal Growth of TIPS Pentacene/Poly(α-methyl styrene) Blends for Improving Performance of Organic Thin Film Transistors

The preceding study detailed that, a simple yet unique solution processing method, the temperature technique, was utilized to address the intrinsic crystal misorientation and poor areal coverage of TIPS pentacene films. Based on the resulting film morphology, where large crystal sizes and substantial areal coverage were demonstrated, the effectiveness of the method was shown to eliminate the intrinsic crystallization anisotropy and result in a uniform orientation of crystals. The approach, however, simultaneously introduced thermal cracks due to the thermally induced stress during crystallization. These thermal cracks accounted for a significant reduction of charge transport, thereby impacting the device performance of TIPS pentacene based OTFTs. Therefore, eliminating the thermal cracks in the TIPS pentacene films in order to realize high-performance OTFTs is imperative.
The long chains of polymers are anticipated to provide a strong but flexible matrix to the TIPS pentacene semiconductor, which could relieve the thermal stress, and prevent the occurrence of thermal cracks associated with the temperature gradient technique. In addition, various polymer additives, particularly poly(α-methyl styrene) (PαMS),\textsuperscript{105} have demonstrated a vertical phase segregation within the TIPS pentacene active layer, improving charge transport.\textsuperscript{52,106} Therefore, incorporating polymers into TIPS pentacene could result in a significant enhancement of OTFT performance by taking advantage of both the prevention of thermal cracks from the flexible matrix characteristic of the polymers, and the high charge transport from the vertical phase segregation.\textsuperscript{107,108}

In this work, the temperature gradient technique was employed to reduce the crystal anisotropy and enhance areal coverage of the TIPS pentacene film, and insulating polymers, PαMS, poly-4-vinylphenol (PVP), poly(methyl methacrylate) (PMMA), and poly(triarylamine) (PTAA) were independently blended with the TIPS pentacene as additives to eliminate the thermal cracks and improve charge transport through vertical phase segregation. Discussions on analyses performed on the results follows.

4.3.1 TIPS pentacene/polymer Film Morphology

Figure 4.7 presents optical microscopy studies performed to examine the morphology of the TIPS pentacene/polymer blends. The TIPS pentacene/PVP film morphology shown in Figure 4.7(a) depicts randomly distributed dendritic crystals. Since PVP dissolves mainly in polar solvents, it forms an immense level of solute residue in toluene. The residue solutes cause spontaneous nucleation throughout the solution.\textsuperscript{109} This stochastic nucleation leads to dendritic
crystal growth of TIPS pentacene/PVP with regions of spherulite film morphology, as seen in the figure.

![Optical micrographs of blend films](image)

**Figure 4.7.** Optical micrographs of blend films of (a) TIPS pentacene/PVP showing dendritic crystal film morphology, (b) TIPS pentacene/PMMA with thin crystal widths, (c) TIPS pentacene/PTAA exhibiting good crystal alignment but small crystal sizes, and (d) TIPS pentacene/PαMS displaying uniform crystal orientation and excellent areal coverage.

The dissolution of PMMA in toluene superseded that of PVP, however, residue solutes were still present. The highly supersaturated solution resulted in a brush-like crystallite film morphology (i.e. extremely thin crystal widths) with fairly aligned crystals, Figure 4.7(b). Evident from Figures 4.7(c) and 4.7(d), both TIPS pentacene/PTAA and TIPS pentacene/PαMS blend films respectfully illustrate exceptionally uniform crystal alignment. However, TIPS
pentacene/PTAA blend films displayed slightly more grain boundaries due to its smaller crystal sizes compared to TIPS pentacene/PaMS blends. In addition, PTAA is a light sensitive material, making it the less desirable material to work with. Hence, TIPS pentacene/PaMS blend films were chosen as the material composition to investigate further.

In Figure 4.8, application of the temperature gradient method for crystallization of the TIPS pentacene/PaMS blend films is illustrated. Figure 4.8(a-c) highlights the initial growth stages of the TIPS pentacene crystals.

**Figure 4.8.** (a-d) Schematic of TIPS pentacene/PaMS crystal growth using the temperature gradient technique. (e) A digital image of the resultant TIPS pentacene crystals from the combination of the temperature gradient technique and addition of the PaMS polymer.
As seen in the figures, the commencement of the TIPS pentacene crystallization ensues at the lower temperature region, with crystal growth towards the higher temperature region when the solution at the low temperature end reaches supersaturation. Illustrated in the cartoon of Figure 4.8(d) is the improved film uniformity achieved by the incorporation of the PaMS polymer, which eliminates the thermal cracking that could have developed in the crystalline film during crystallization, and also featured, is the exceptional crystal alignment and enhanced areal coverage achieved by crystallization of the blend film using the temperature gradient technique. A digital image of the TIPS pentacene/PaMS blend film with a complete substrate coverage is shown in Figure 4.8(e). The image demonstrates the improved results from the pure TIPS pentacene crystalline film by utilizing the combination of the temperature gradient technique with the addition of the PaMS polymer.

For comparison, Figure 4.9(a) shows the morphology of a TIPS pentacene thin film from simple drop-casting, which is without the application of the temperature gradient nor the addition of the PaMS polymer. This simple deposition leads to a nonuniform film with poor areal coverage and crystal misorientations. The application of a temperature gradient at 5 °C/cm overcomes the anisotropic crystal formation, however, it also causes the development of undesired thermal cracks in the film. In order to address the cracking issue, PaMS was blended with TIPS pentacene in solution. Figures 4.9(b-d) show the morphologies of the TIPS pentacene film with the addition of the PaMS polymer and application of a temperature gradient, where the TIPS pentacene to PaMS blending ratios are 1:1, 2:1 and 3:1, respectively. As anticipated, the long polymer chains likely provided a strong yet flexible matrix within the TIPS pentacene film, thereby relieving the thermally induced stress and effectively preventing thermal cracks during crystallization. The stripes seen between the well-oriented TIPS pentacene crystals result from
TIPS pentacene/PαMS molecules that were not fully crystallized but deposited onto the substrate. Among the films of TIPS pentacene/PαMS at different blend ratios, there are no significant differences in the morphology in terms of crystal size, areal coverage and crystal orientation.

**Figure 4.9.** Polarized optical micrographs of (a) TIPS pentacene film from simple drop-casting, and (b-d) TIPS pentacene/PαMS blend films at 1:1, 2:1 and 3:1 ratios, respectively, with an applied 5 °C/cm temperature gradient.

The surface profiles of TIPS pentacene/PαMS at 1:1 weight ratio and pristine TIPS pentacene films acquired using the Dektak profilometer are illustrated in Figure 4.10. The figure demonstrates the improvement in surface topography of the TIPS pentacene/PαMS film compared with that of pristine TIPS pentacene. The TIPS pentacene/PαMS blend film shows a more uniform surface profile contributing to the enhanced film morphology.
Figure 4.10. Comparison of the surface profile of TIPS pentacene/PαMS blend film with that of pristine TIPS pentacene.

4.3.2 Device Characterization

Bottom-gate/top-contact OTFTs were fabricated to test charge transport in the TIPS pentacene/PαMS blend film. Figures 4.11(a) and 4.11(b) show the typical transfer and output curves of the TIPS pentacene/PαMS based OTFTs, respectively. The highest hole mobility of 0.3 cm²/Vs was attained from OTFTs based on a blend ratio of 2:1 and temperature gradient at 3.5 °C/cm. Also, a threshold voltage $V_T$ of -3.5 V and current on/off ratio $I_{On/Off} > 5 \times 10^4$ were obtained. It is worth mentioning that, although hexamethyldisilazane (HMDS) treatment has been employed in most literature work to passivate the silanol groups on the silicon dioxide surface to enhance charge transport, this treatment was not utilized in the study, since the TIPS pentacene/PαMS solution suffered from severe dewetting on the HMDS treated surface, which considerably reduced the film areal coverage.
To more accurately study the effect of the PaMS polymer additive on the performance of TIPS pentacene OTFTs, the average mobilities ($\mu_{\text{Avg}}$) were plotted against each of the TIPS pentacene/PaMS blend ratios, demonstrated in Figure 4.11(c).

![Graphs showing transfer and output characteristics of TIPS pentacene/PaMS OTFTs](image)

**Figure 4.11.** (a) Typical transfer and (b) output characteristics of bottom-gate/top-contact TIPS pentacene/PaMS OTFTs on Si/SiO$_2$ substrate. (c) Average hole mobility and (d) corresponding performance consistency at different TIPS pentacene to PaMS loading ratios. The performance consistency is defined as the ratio of average mobility to the standard deviation of mobility.

As indicated in the figure, pristine TIPS pentacene based OTFTs present an average mobility of $0.06 \pm 0.05$ cm$^2$/Vs. The addition of the PaMS polymer at a 1:1 weight ratio greatly enhances the average mobility to $0.09 \pm 0.03$ cm$^2$/Vs, due to the significant improvement in
crystal orientation and elimination of thermal cracks. A maximum average mobility of $0.17 \pm 0.06 \text{ cm}^2/\text{Vs}$ was achieved at the 2:1 weight ratio of TIPS pentacene to PαMS. However, the average mobility dramatically declined to $0.05 \pm 0.03 \text{ cm}^2/\text{Vs}$ at a 3:1 ratio. The reasons for the mobility variations will be addressed in a later section. The addition of the PαMS polymer not only enhances the average mobility but also improves the OTFT performance consistency. The performance consistency, which is defined as the ratio of the average mobility ($\mu_{\text{Avg}}$) to the standard deviation of mobility ($\mu_{\text{Stdev}}$), is plotted against each TIPS pentacene to PαMS blend ratio, as illustrated in Figure 4.11(d). The pristine TIPS pentacene based OTFTs exhibit $\mu_{\text{Avg}}/\mu_{\text{Stdev}}$ of 1.2, whereas TIPS pentacene/PαMS OTFTs at 1:1, 2:1 and 3:1 weight ratios show $\mu_{\text{Avg}}/\mu_{\text{Stdev}}$ of 3.1, 2.8 and 2.0, respectively, indicating effectively improved and constantly higher performance consistency.

4.3.3 Crystal Structure Analysis

In order to understand the mobility variations at different TIPS pentacene to PαMS weight ratios, the vertical composition profile, particularly the concentration of TIPS pentacene molecules adjacent to the semiconductor/dielectric interface, was examined by performing wavelength-dispersive spectrometer (WDS) analysis. Since the OTFT charge transport channel is at the semiconductor/dielectric interface, a higher concentration of TIPS pentacene near the interface results in a larger average mobility. Due to the presence of silicon element from the silyl group of TIPS pentacene and its absence in PαMS, the silicon element is used to discern the relative amount of TIPS pentacene molecules at the semiconductor/dielectric interface by WDS analysis. In WDS characterization, the silicon element weight percentage is measured, and used to determine the TIPS pentacene molecular weight percentage (concentration). As indicated in
Table 4.1, a much higher TIPS pentacene concentration of 22.43% is found adjacent to the interface in the TIPS pentacene/PαMS blend film at 2:1 weight ratio as compared to 3.68% and 2.26% at 1:1 and 3:1 weight ratios, respectively. Therefore, the elevated concentration of TIPS pentacene at the 2:1 TIPS pentacene/PαMS loading contributes to the highest average OTFT mobility.

<table>
<thead>
<tr>
<th>Film with TIPS pentacene:PαMS ratio</th>
<th>Silicon element weight percentage from WDS measurements</th>
<th>Molecular concentration of TIPS pentacene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>8.05%</td>
<td>3.68%</td>
</tr>
<tr>
<td>2:1</td>
<td>49.14%</td>
<td>22.43%</td>
</tr>
<tr>
<td>3:1</td>
<td>4.95%</td>
<td>2.26%</td>
</tr>
</tbody>
</table>

Table 4.1. WDS measurements of silicon element weight percentage and calculated TIPS pentacene molecular concentration adjacent to the active layer/dielectric interface.

Figure 4.12 shows a cross-sectional SEM image of the 2:1 TIPS pentacene/PαMS blend film, revealing a vertical bilayer structural phase separation with TIPS pentacene adjacent to the silicon substrate and PαMS on top of TIPS pentacene.

**Figure 4.12.** Cross-sectional SEM image of a 2:1 weight ratio TIPS pentacene/PαMS blend film showing a bilayer vertical phase separation of TIPS pentacene and PαMS in the microstructure of the film.
In summary, for the temperature gradient technique combined with insulating polymer additives, TIPS pentacene/PαMS blends ultimately displayed the best morphology. Optical images indicated that the addition of PαMS not only prevents the generation of thermal cracks, but also enhances film uniformity with exceptional crystal alignment. Further analysis of the TIPS pentacene/PαMS blend film revealed that, at the optimal loading 2:1 weight ratio, the film exhibits a vertical phase segregation with an elevated concentration of TIPS pentacene at the active layer/SiO_2 dielectric interface, favoring charge transport. As a result, the temperature gradient technique combined with the PαMS additive effectively enhances the hole mobility, showing that the highest average value was about 3 times greater than that of pristine TIPS pentacene. The method also improves device performance consistency of TIPS pentacene based OTFTs.

Following the success of simultaneously employing the temperature gradient technique along with the insulating polymer, PαMS, to dramatically improve TIPS pentacene film’s morphology, including the prevention of thermal cracks introduced by the applied temperature gradient, studies were carried a step further by depositing the TIPS pentacene/PαMS blends on flexible ITO/PET substrates, and are recounted next.

4.4 Temperature Gradient Processed High Performance Tips Pentacene/Poly(α-methylstyrene) Flexible Organic Thin Film Transistors

The potential of the solution processed TIPS pentacene/PαMS film via the temperature gradient approach for flexible applications, was demonstrated by fabricating OTFTs on flexible ITO/PET substrates. Transitioning from silicon to the flexible ITO/PET substrate required optimization of the temperature gradient due to the thermal conductivity of the substrate and
surface roughness, since they influence the film forming properties of the TIPS pentacene/PαMS active layer. The optimum TIPS pentacene/PαMS blend morphology was attained with a temperature gradient of 3.5 °C/cm, at a loading ratio of 2:1 (TIPS pentacene/PαMS). Cross-linked PVP-PMF was used as the gate dielectric because it is chemically inert against the toluene solvent used to dissolve the TIPS pentacene/PαMS blends. In addition, PVP has a well matched surface energy with TIPS pentacene, thereby promoting the adhesion of the hydrophobic silyl groups of TIPS pentacene to the substrate.

Figure 4.13(a) displays a schematic of the spin-coated PVP-PMF dielectric on an ITO/PET substrate.

**Figure 4.13.** (a) Cartoon of spin-coated blend of PVP-PMF as the dielectric layer on the ITO/PET flexible substrate. (b) AFM image indicating the PVP-PMF surface roughness as 0.662 nm. (c) Device configuration of bottom-gate/top-contact TIPS pentacene/PαMS blend based OTFTs. (d) A digital image showing the OTFTs on ITO/PET flexible substrate.
with a surface roughness of 0.662 nm shown in the AFM image of Figure 4.13(b). The small degree of PVP-PMF dielectric surface roughness is an indication of a fairly uniform surface which was appropriate for the subsequent deposition of TIPS pentacene/PαMS. TIPS pentacene/PαMS blend based OTFTs on ITO/PET substrates with a PVP-PMF insulating layer were developed upon achieving high quality crystal morphology. The device configuration of bottom-gate/top-contact TIPS pentacene/PαMS OTFTs with PVP-PMF dielectric on the ITO/PET substrate is depicted in Figure 4.13(c) and the corresponding digital image of patterned OTFTs is presented in Figure 4.13(d).

4.4.1 Device Characterization

In order to extract the mobility and other TIPS pentacene/PαMS OTFT parameters, parallel plate capacitors (ITO–(PVP-PMF)–Au) were fabricated and capacitance-voltage measurements were performed to determine the capacitance. The maximum capacitance density measured in accumulation regime with a bias voltage of -20 V was determined as 10.75 nF/cm². Figure 4.14(a) and 4.14(b) show the typical transfer and output characteristics acquired from the TIPS pentacene/PαMS OTFTs fabricated on ITO/PET substrates, respectively. The maximum field-effect hole mobility was extracted to be 0.5 cm²/Vs using the measured capacitance, which is essentially the highest mobility achieved by employing the temperature gradient technique for TIPS pentacene and TIPS pentacene/PαMS crystallization. The average mobility along with the standard deviation of mobility was calculated to be 0.37 ± 0.12 cm²/Vs, based on the measurement of five OTFTs. Compared with mobilities from pristine TIPS pentacene, the mobility increased by an order of magnitude, from 10⁻² cm²/Vs,⁵¹ to about 10⁻¹ cm²/Vs, due to the elimination of thermal cracks from the TIPS pentacene/PαMS blend.
Figure 4.14. Typical transfer (a) and output (b) characteristics of top-contact TIPS pentacene/PαMS OTFTs on the ITO/PET flexible substrate with at a loading ratio of 2:1 and a temperature gradient of 3.5 °C/cm.

In addition, the average mobility of the OTFTs based on ITO/PET flexible substrates was higher compared to that based on silicon substrates. The higher mobility is attributed to the hydrophobic nature of PVP-PMF dielectric surface, which promotes the adhesion of silyl group from TIPS pentacene and molecular stacking.\textsuperscript{110}
The subthreshold swing of OTFTs based on the flexible substrate shown in Figure 4.14(a) was calculated to be 3.3 V/dec. For comparison, a subthreshold swing of 2.6 V/dec from the OTFT with the highest mobility of 0.3 cm²/Vs on silicon substrate was also extracted. The subthreshold swing is an indicator of the trap density \( N_{\text{trap}} \) in the charge transport channel, which can be calculated based on the following equation:\(^{111}\)

\[
N_{\text{trap}} \approx \left[ S \times \frac{1}{kT} \times C_i \times \log e \right] - \frac{C_{\text{ox}}}{q}
\]

(4.1)

where \( S \) is the subthreshold swing, \( k \) is the Boltzmann’s constant, \( T \) is the temperature in Kelvin, \( C_i \) is the capacitance of the SiO₂ or PVP-PMF dielectric per unit area, \( e \) is the base of natural logarithm, and \( q \) is the elementary charge.

The trap density, \( N_{\text{trap}} \), of the ITO/PET flexible substrate with the PVP-PMF dielectric was calculated as \( 3.71 \times 10^{12} \) cm\(^{-2}\), whereas that of the silicon substrate with the SiO₂ dielectric was determined to be \( 3.08 \times 10^{12} \) cm\(^{-2}\). The higher subthreshold swing of the OTFTs on the flexible substrate indicates that there are slightly more defects and trap centers at the interface between TIPS pentacene/PaMS and PVP-PMF dielectric than at the oxide surface.\(^{111}\)
CHAPTER 5

SUMMARY AND FUTURE WORK

5.1 Summary

The investigated study of this dissertation focuses on the crystallization of a solution processed small molecule crystalline organic semiconductor, TIPS pentacene. Two approaches, external force and blend approach, are utilized in this work to diminish TIPS pentacene crystal misalignment, and improve the performance inconsistencies of TIPS pentacene based OTFT devices. The methods employing the external force, and blend approaches, consist of: utilizing a developed temperature gradient technique and adding insulating polymers, respectively to crystallize TIPS pentacene thin films to produce excellent film morphology, which subsequently leads to high performing OTFT devices. A summary of the chapters and the results of this study are detailed as follows:

Chapter 1 presents a general overview of organic semiconductors with TIPS pentacene as the material of interest; since TIPS pentacene is an attractive organic semiconductor due to its superior charge carrier transport, solution processability at room temperature, and air stability. The operation principle of organic thin film transistors and TIPS pentacene as the active channel material were also discussed.
Chapter 2 summarizes some solution deposition processing methods for crystal growth and alignment of organic small molecule semiconductors, particularly those used in the crystallization of TIPS pentacene such as, drop-casting, dip-coating, solution shearing, etc. In addition, it introduces the first approach used in this study, the temperature gradient technique, as a method that generates a concentration gradient in solution along the gradient direction to preferentially orient the TIPS pentacene crystals from the low to high temperature region and improve crystal coverage on the substrate.

Chapter 3 reports all the experimental procedures used in the study and summarizes the operation of the equipment used to characterize the results. The experimental discussion consists of a description of the temperature gradient setup and the three TIPS pentacene crystallization approaches performed employing the application of the temperature gradient technique. These include: firstly, applying the temperature gradient method to deposit pristine TIPS pentacene on rigid silicon substrates, secondly, depositing TIPS pentacene/polymer blends on silicon substrates via the temperature gradient system and lastly, depositing TIPS pentacene/polymer blends on flexible ITO/PET substrates while utilizing the temperature gradient technique.

Chapter 4 presents all the results attained from the characterization of the TIPS pentacene and TIPS/polymer blend films. Below is a summary of the conclusions.

First and foremost, temperature gradients were applied to substrates with TIPS pentacene solutions to achieve well-aligned and preferentially oriented TIPS pentacene crystals with high percentages of areal coverage. Exceptional morphology of the TIPS pentacene films were attained across the entire substrate demonstrating the effectiveness of the temperature gradient technique. Compared with OTFTs based on simple drop-cast TIPS pentacene films, those
acquired via the temperature gradient technique present a significant improvement in average mobility. Nonetheless, thermal cracks were detected in the temperature gradient films which could cause mobility reduction and OTFT device-to-device performance variations.

As a result of the thermal cracks, a second study employing the temperature gradient technique coupled with the addition of insulating polymers was carried out. The most favorable insulating polymer, PαMS, in combination with the temperature gradient technique, reduced the crystal anisotropy even further and enhanced areal coverage of the TIPS pentacene film. It also concurrently eliminated the thermal cracks introduced by the application of temperature gradient. By optimizing the loading ratio between TIPS pentacene and PαMS, an effective vertical phase segregation with an elevated concentration of TIPS pentacene at the active layer/SiO$_2$ dielectric interface was achieved. Such favorable vertical composition profile promotes charge transport and contributed to a high hole mobility up to 0.3 cm$^2$/Vs. With the incorporation of PαMS polymer, the OTFT performance was consistently higher compared to those based on pristine TIPS pentacene. Additionally, the average mobility from the TIPS pentacene/PαMS devices at the optimal ratio was about 3 times higher than that of pure TIPS pentacene based OTFTs.

Lastly, the effectiveness and versatility of the temperature gradient method with the PαMS additive was demonstrated on a flexible ITO/PET substrate with PVP-PMF dielectric layer, and a high hole mobility of 0.5 cm$^2$/Vs was obtained; the maximum TIPS pentacene organic semiconductor mobility attained for the study in this dissertation.
5.2 Future Work

The results of this dissertation present a number of promising directions for future work. One proposed direction is to utilize the temperature gradient method to deposit and uniformly orient other solution processable organic small molecule semiconductor materials and small molecule semiconductor/polymer blends over a large area, like 5,6,11,12-tetraphenylnaphthacene (Rubrene).

Rubrene single crystals in orthorhombic phase has demonstrated high OTFT hole mobilities up to 20 cm$^2$/Vs via physical vapor transport (PVT).\textsuperscript{112,113} However, solution processing of rubrene has experienced much less success. Stingelin-Stutzmann et al. demonstrated solution processing of rubrene via drop-casting. In the study, a glass-inducing diluent (5,12-diphenylanthracene), that permitted controlled crystallization from an initial vitreous state of rubrene, and a high molecular weight polymer (polystyrene), were blended with rubrene prior to deposition. Thermal annealing and crystallization performed above the eutectic temperature but below the melting temperature resulted in polycrystalline rubrene based OTFTs reaching the highest mobility of 0.7 cm$^2$/Vs.\textsuperscript{114} Another study performed by Jo et al., presented rubrene/polystyrene blend OTFT mobilities up to 0.52 cm$^2$/Vs, where the active layers were spin-coated. The rubrene/polystyrene blend active layers in the study showed a bilayer vertical phase separation which contributed to the high charge transport of the OTFTs.\textsuperscript{115}

Although, solution processing of rubrene has been demonstrated to work, their mobilities can still be improved. Studies performed on solution processed rubrene, like the examples presented previously, suffer from achieving large area crystal alignment. The importance of crystal alignment is realized in OTFT mobilities, as it plays an essential role in attaining the
highest possible charge transport. Thus, the temperature gradient method can be employed to crystallize rubrene/polymer blends to address this challenges. Based on the mechanism of the temperature gradient method, crystal nucleation and growth commence at the low temperature end due to supersaturation, and orient the crystallization towards the higher temperature end; hence, solution deposition of rubrene/polymer blends with the application of temperature gradients is expected to present a crystalline morphology with uniform alignment over a large area and excellent areal coverage. A vertical phase separation of rubrene and the polymer is expected to be present in the blend film. The combination of a large area of uniformly aligned crystals, extensive areal coverage and the vertical phase separation of the temperature gradient crystallized rubrene/polymer blend film will lead to even higher OTFT mobilities.

Another potential study proposed here is to blend TIPS pentacene with graphene as a way to further improve the electronic conductivity of the temperature gradient grown TIPS pentacene crystals. Accordingly, the combined properties of highly crystalline graphene with TIPS pentacene organic semiconductor should yield higher performing OTFTs.

The temperature gradient technique can be employed to the blend solution of a TIPS pentacene-graphene composite to orient the crystal direction during crystal growth from solution. Graphene is combined with TIPS pentacene mainly due to the extremely high mobility it possesses. Graphene is expected to form an interpenetrating network with TIPS pentacene when combined. Although high charge transport is a property of graphene, its zero band nature does not allow for semiconducting capabilities which could cause a difficulty in switching devices off. Based on this reason, minute amounts of graphene flakes will be added to TIPS pentacene to improve the mobility but not adversely degrade the current on-off ratio. The graphene flakes in
TIPS pentacene should not interrupt the molecular π-π stacking of the TIPS pentacene.\textsuperscript{57} The morphology of the TIPS pentacene/graphene film is expected to have good uniformity and better crystal orientation due to the highly ordered nature of the graphene structure. The TIPS pentacene crystals modified with graphene are predicted to increase the charge carrier transport within the active layer without resulting in undesirable current on-off ratios. That is, there will be an enhancement with the TIPS pentacene hole mobility without degrading the switching capabilities of the OTFTs.

The last future study proposed here is to extend the scope of the temperature gradient processed TIPS pentacene/PαMS based OTFTs on flexible ITO/PET substrates.

Since organic semiconductor based flexible devices need to demonstrate excellent electro-mechanical stability to compete with inorganic semiconductor flexible devices, such as ultra-thin single crystal silicon OTFTs,\textsuperscript{78} examining the dependence of electrical performance of the TIPS pentacene/PαMS blend based flexible OTFTs on mechanical bending is essential. Therefore, an investigation of the performance reliability of the fabricated flexible devices under mechanical bending needs to be characterized. The degree of electrical stability of TIPS pentacene/PαMS blend flexible devices will be tested through multiple cycles of device bending to a selected set of small radii (\(\mu\)m range). Electrical measurements will be carried out while the devices are under mechanical stress, and succeeding the removal of the applied stress. The resulting stability performance will determine the robustness of the OTFTs developed from temperature gradient grown TIPS pentacene/PαMS blend films on flexible ITO/PET substrates.
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