TUNING FUNCTIONALITY OF PRINTED CONDUCTIVE POLYMERS USING PROXIMITY ION BEAM LITHOGRAPHY

A Thesis

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering University of Houston

> In Partial Fulfillment of the Requirements for the Degree Master of Science in Chemical Engineering

> > by Saeed Ahmadi Vaselabadi

> > > May 2014

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Abstract

Polymer semiconductors are used in low-cost electronics such as plastic solar cells, thin film transistors, and light-emitting diodes. Their performance in these devices is partly dictated by molecular ordering and nanoscale structure, where the latter is particularly difficult to control. We demonstrate a simple approach to control the structure and function of polymer semiconductors by patterning with proximity ion beam lithography (PIBL). The lithographic process generates intermolecular cross-links that render the polymer insoluble in organic solvents. The effects of PIBL exposure dose on optoelectronic properties and molecular ordering were investigated with measurements of ultraviolet-visible absorbance, hole mobility in the space-charge-limited regime, and crystallinity. We find evidence that extensive crosslinking will disrupt intermolecular ordering and introduce electronic trap states that reduce absorbance and mobility.

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Chapter 1 Introduction

1.1 Introduction

Organic semiconductors offer a great set of characteristics which makes them a promising option to be used in electronic devices such as transistors, diodes and solar cells. Organic semiconductors generally have a low-cost synthesis, and manufacturing cost is also low due to the use of roll-to-roll and wet processing techniques. Among organic semiconductors, π -conjugated polymers have been widely investigated since they combine many of characteristics of engineering thermoplastics (such as durability, flexibility) with impressive light absorption properties and charge transport capabilities. Properties including charge transport, solubility and electronic bandgap can be tuned chemically in π -conjugated polymers. These materials intrinsically have wide band gaps (bandgap above 1.4 eV) and subsequently contain a very low charge carrier density in the dark at room temperature. [1–3]

Polymer solar cells can be fabricated in flexible, durable and cheap modules which makes them a potential alternative to fossil fuels for clean energy production. Polymer solar cells consists of acceptor-donor active layer sandwiched between anode and cathode electrodes. In polymer solar cells, photon irradiation creates electronhole pairs in the active layer which need to dissociate at the acceptor-donor interface. After dissociation, electrons ad holes need to be transported to their respected electrodes. π -conjugated polymers have been used commonly as the donor in solar cells. Therefore light absorption and charge transport properties of polymer donor have a great impact on the performance of organic solar cell. Charge carrier mobility is a key parameter in characterizing the charge transport. Consequently it can be used to study physics of charge transport in these materials as well as improve device performance.

The Optical and electrical properties of π -conjugated polymers is dependent on their morphology. These polymer systems have disordered structure and fundamental understanding of the morphology is required to enhance the polymer properties. Conductive microstructures can be printed by direct patterning using electron beam or ion beam lithography. [4,5] Direct patterning of active layer structures using lithographic techniques offers promising features; the size, shape, density, and displacement of the polymer domains can be controlled, therefore the polymer design can be studied systematically. However, we need a better understanding of the structure and function of patterning polymer in order to be able to design a route to low-cost nanopatterning of polymer semiconductors for a variety of applications.

In this work, we report a simple approach to control the morphology of polymer donor mainly applicable in organic solar cells. In this approach, thin films of π conjugated polymers are patterned directly with proximity ion beam lithography. The exposure to high energy atom beams generates free radicals in the polymer, likely at the alpha-carbon (resonance stabilized), and two radicals can undergo cross-linking within the polymer matrix to form conductive microstructures. The cross-linked polymer is then insoluble in organic solvents, so the unexposed material is selectively washed away. This technique can have precise control over size, shape, density and placement of domains in the polymer system. Varying the exposure dose will produce different cross-link densities, which provides a simple approach to investigate the effect of atom beam irradiation on morphology and optoelectronic properties of the polymer. In order to do so, UV-visible spectroscopy and GIWAXS techniques are employed to determine the light absorption and crystal structure of the polymer respectively. Electronic properties of the polymer, i.e. charge carrier mobility, is investigated using current density-voltage analysis of a diode-configuration device. Among π -conjugated polymers, poly(3-hexylthiophene) (P3HT) has been investigated extensively for the use in solar cells and thin film transistors. Many studies to understand the basics of charge transport have been performed with P3HT, which is a hole transporting material. Thin films of P3HT have highly anisotropic and disordered structure, that is determined by processing conditions, molecular weight, and regio-regularity of the hexyl substituents. Commercially available semiconducting polymers such as P3HT are compatible with proximity ion beam lithography. The specific material used in this work is P3HT.

The goal of this thesis is to understand the effects of ionizing radiation on the structure and performance of polymer semiconductors. Thin films of P3HT are cast on substrates such as silicon, glass, or glass coated with indium tin oxide (depending on the type of experiment to be performed). The films are exposed to a range of atom beam doses, from 0 to $2.5 \ \mu C/cm^2$. The effects of irradiation and cross-linking on light absorption is measured with ultraviolet-visible spectroscopy, while hole mobilities are measured from the space charge limited current. Crystallinity is characterized with detailed analysis of grazing-incidence wide-angle X-ray scattering data. Finally, recent X-ray photoelectron spectroscopy studies provide insight into chemical defects introduced by the lithographic process.

1.2 Overview

This thesis consists of 5 chapters. Chapter 1 gives a brief introduction to the project and states the goals and a compact overview of the following chapters.

Chapter 2 gives an introduction to conjugated polymers used in semiconductor industries. Their application in solar cell industry is mainly focused here. A brief discussion of inorganic and organic solar cells, their working principles and respected pros and cons are presented too. Furthermore, basics of charge transport and common mobility characterization techniques in conjugated polymers are discussed.

Chapter 3 describes device fabrication and characterization. This chapter has provided all the experimental details regarding fabrication processes and characterization techniques and instruments used in this project. It begins with materials preparation, substrate and diode-configuration hole-only device fabrication. Furthermore, a general overview of proximity ion beam lithography is given. In the end, structural characterization techniques such as microscopy, UV-Visible spectroscopy and GIWAXS along with electronic characterization technique used in this project are introduced.

In chapter 4, the electronic performance, mainly charge carrier mobility and the result of light absorption and structural analysis performed by UV-Visible spectroscopy and GIWAXS techniques, respectively, are presented and discussed extensively.

Chapter 5 is the conclusion and outlook. This chapter concludes the current work and gives the overview of future work.

Chapter 2 Introduction to Polymer Semiconductors

Polymer semiconductors contain delocalized pi-bonds that can absorb light, generate free charges, and transport free charges. They can be synthesized with soluble side groups, therefore they can be processed from solution to make thin films by using printing production techniques. In addition, their electrical and optical properties can be tuned via chemical synthesis and material design. Polymer semiconductors can be used in variety of applications including light emitting diodes, field-effect transistors, and solar cells.

The first conducting conjugated polymer, Polyacetylene (PA), was synthesized in 1974 and later various doped-types were introduced [6]. These polymers showed an impressive conductivity. The first undoped conjugated polymers were prepared for various applications such as field-effect transistors, light emitting diodes and solar cells in the late 1980s. Since then, numerous researches have been conducted on the performance of π -conjugated polymer in these applications. In this project, we are mainly interested in application of these polymers in solar cells.

This chapter gives a brief introduction of inorganic and organic solar cells and introduces different operating mechanism and device architectures used in each category. Furthermore, charge transport in conjugated polymers will be discussed. Starting with underlying physics of charge transport, carrier mobility and different techniques used for quantifying mobility in organic semiconductors will be introduced. We will be focusing on space charge limited current (SCLC) technique, its theoretical and experimental considerations. Finally, different models incorporated to describe charge transport in SCLC region will be discussed. In here, our focus is to investigate the effect of crystal orientation as a representative of polymer structure on charge transport properties of polymers.

2.1 Solar Cells

The limited sources of carbon-based fuels like oil, natural gas, ethanol and coal have shifted the international tendency toward using sustainable and renewable energies. Solar energy, being the unlimited source of energy supplying the earth, has been the source of attention in the past two decades. However, the real challenge in the pretext of solar energy is to devise reliable and cost-efficient methods to use this type of energy. Another reason for this new tendency is to reduce the emission of greenhouse gases, in search of an environment-friendlier energy.

Photovoltaic solar cell technology, which directly converts solar energy to electricity, has been growing substantially in the market recently. But there are still lots of challenges which should be addressed to improve this technology in terms of cost and power conversion efficiency [7]. Photovoltaic solar cells can be used in different application such as providing power supply in remote locations, space application, and also some consumer products.

2.1.1 Inorganic Solar Cells

Photovoltaic effect was discovered in 19 century by E. Becquerel when he irradiated AgCl solution by light. Later on, first solar cell was built by C. Fritts by using Se as the semiconductor, covered by a layer of Au. Modern solar cells were mainly made in Bell Labs in mid-1940s [8].

In a basic inorganic solar cell, a semiconductor is utilized to absorb light to convert photons to electron-hole pairs. These tightly-bound pairs will get dissociated at a p-n junction. Charge separation normally involves diffusion of carriers through depletion region formed at p-n junction due to an electric field formed. The electric field later on directs the charge carriers to the desired electrodes [8]. Crystalline and multicrystalline silicon, normally referred as the first generation solar cells materials, are the most frequent materials used in building inorganic solar cells. Recently, second generation solar cells which utilize CdTe, Copper Indium Gallium Selenide (CIGS), and amorphous silicon, have gained a decent portion of global market as well. All the aforementioned materials have bandgaps in the range of 1.1- 1.7 eV, which is close the optimum bandgap required for maximum theoretical efficiency [9].

Si panels are brittle, heavy and rigid. In addition, the production cost is high and the issue of availability of raw materials exist. These factors have prevented the Si-based solar cells to be a greater part of today's energy market. Thus, the need for development of new materials and device architectures with a more promising energy-wise future has led researchers exploring other types of materials including organic semiconductors.

2.1.2 Organic Solar Cells

Conversion of light into electricity in organic solar cells can be categorized in the following steps (Figure 2.1):

- (a) Absorption of photon and subsequent exciton formation
- (b) Exciton diffusion to the dissociation interface
- (c) Charge separation at the interface and transport to the electrodes

In organic semiconductors, photoexciation leads to columbically-bound electron-hole pairs instead of free charge carriers. The dissociation of excitons requires strong electric field which can be provided at the interfaces, therefore exciton diffusion length should be enough for pairs to reach the interface. In other words, the diffusion length must be in the same order of magnitude as the donor-acceptor phase separation length. Exciton diffusion length in organic semiconductors is in the order of 10-20 nm. Small molecules such as fullerene can play the role of the electron acceptor and



Figure 2.1: Mechanism of organic solar cell photocurrent generation

provide the necessary interface very well [10].

After charge separation, these charges need to be transported to the respected electrodes through a gradient in chemical potential of electrons and holes formed at the junction. Difference between the highest occupied molecular orbital (HOMO) level of the donor and the lowest unoccupied molecular orbital (LUMO) level of the acceptor forms an internal electric field, the required gradient. Concentration gradient of charges in the respected donor-acceptor regions can also provide a driving force to transport the charges by creating a diffusion current.

In the final step, charge carriers are collected by respected electrodes. The hole extracting electrode, in contact with the donor, should have a work function matching the HOMO of donor, mostly conjugated polymers, while the electron extracting electrode should have a work function close enough to LUMO of the acceptor. In general, Indium tin oxide (ITO) and aluminum have been used frequently for hole and electron contacts (electrodes) respectively in the literature. Figure 2.2 shows the energy levels (work functions) of components of a typical organic solar cell.



Figure 2.2: Energy levels of components of a typical organic solar cell

There are several aspects which should be taken into consideration to maximize efficiency in organic solar cells:

- The conjugated polymer which acts as the absorbing component should be thick enough (almost 100 nm) to maximize the light absorption.
- Dissociation yield of exciton can be maximized provided that a large interfacial area between donor and acceptor exist. Using different device architectures like bulk heterojunction or interpenetrating nanostructured structures can provide the necessary interfacial area. It has been reported that thermal annealing can increase interfacial area by increasing the diffusion of one phase to another.
- Carrier recombination can be alleviated by employing direct pathways for charge carrier transport to the electrodes [11].

Different device structures have been suggested to increase power efficiency of the organic solar cells. (Figure 2.3)

1. **Bilayer**: The simplest design which can provide the necessary donor-acceptor interface. However, exciton decay is the major issue in this type, due to the large thickness of the donor. Thick active layers are needed to insure high light



Figure 2.3: Different architectures of Organic solar cells a)Bilayer b) Bulk Heterojunction c) Ordered Heterojunction

absorption, while thickness has a direct proportionality with the decay rate of excitons due to carrier recombination. Therefore an optimized thickness is required to compromise between exciton dissociation and light absorption [12].

- 2. Bulk Heterojunction (BHJ): The phase separation of a donor-acceptor blend creates a nanoscale network in BHJ architecture. This design has higher efficiency comparing to bilayer, since it provides higher interfacial area between donor and acceptor. Controlling the morphology is a very formidable task in this structure [13, 14].
- 3. Ordered Heterojunction: In this structure, phases are interdigitated ideally in a scale of 5-10 nm to match the exciton diffusion length range. Theoretically, these devices should have the highest efficiency, however, there are still some challenges regarding the fabrication process of this type.

2.2 Charge Transport in Conjugated Polymers

The charge transport characteristics of organic semiconductors are of the utmost importance for improving the performance of the organic optoelectronics such as light emitting diodes and solar cells. Therefore characterization of the charge transport through simplified models and theories is crucial.

2.2.1 Physics of Charge Transport

The coupling between atoms and the long range order in inorganic semiconductors lead to the formation of valence and conduction bands with different electronic states. Free electrons can be generated in the conduction band by photoexciation or thermal activation, while positive holes will be formed in the valence band [15].

This concept is different in case of organic semiconductors. In organic semiconductors, intermolecular interactions are mainly of weak van der Walls and London forces nature while the intramolecular interactions are mostly covalent. Therefore transport bands are narrower comparing to the bands existing in inorganic semiconductors. Similar to valence and conduction bands in inorganic semiconductors, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) bands can be defined respectively in organic materials. Due to the narrow breadth of energetic bands in organic materials, the introduction of disorder in the system of organic nature easily disrupts the band structure [1].

Organic semiconductors have spatially extended $\pi - \pi$ or $\pi - n - \pi$ bonding system, formed by overlap of carbon p_z orbitals. Carbon atom can be hybridized to form the sp^2 -hybrid where the sp^2 -orbitals form a triangle within a plane and the p_z -orbitals are in the plane perpendicular to it (Figure 2.4). In these macromolecules, although σ -bonding forms the backbone and maintains the integrity and mechanical properties of the semiconductor, these bonds don't play any role in electrical charge transport. Charge transport in these materials is mainly due to the delocalization of π -electrons. Different charge carriers like excitons, solitons and polaritons can be formed due to presence of conjugated bonds.

The orbital overlap leads to delocalization of π electrons within the molecule. In



Figure 2.4: (a) Scheme of the orbitals and bonds for two sp^2 -hybridized carbon atoms. (b) Delocalized π -electrons

fact, unlike inorganic semiconductors in which charge is delocalized in large bands, charge is localized to single molecules in case of organic materials. In addition, the energy gap between HOMO and LUMO becomes small due to the overlapping of orbitals. These orbital play the role of valence and conduction bands, respectively.

Charge transport happens through a sequence of charge hopping step from one molecule to another. The localization within single molecules and the hopping transport system which create a couple of flow barriers are the reasons for the relatively low conductivity and low intrinsic carrier density of organic semiconductors. In fact, the transport occurs through barriers which are within and between the molecules, as well as between crystal planes and grains. The hopping process can be described as the quantum mechanically tunneling of charges from one molecule to other adjacent or sometimes far away molecules [1, 10, 16, 17].

The position of HOMO and LUMO levels and the bandgap value of conjugated polymers basically determine their electronic and spectroscopic properties. There are couple of factors playing important roles in determining the exact position of these level. On the structural level, chain regularity is one factor which have great influence on band structure and charge carrier mobility of conjugated polymers. High regio-regularity insures a more ordered molecular structure and higher charge carrier mobility. Polydispersity is another factor. High polydispersity of molecular mass has negative effect in structural order of the polymer [10].

2.2.2 Charge Carrier Mobility

Charge carrier mobility is the main quantity used for characterizing charge transport. Charge transport is solely based on diffusion in the absence of external potentials. In here, diffusion is attributed to local transport of charges around a specific position. In this case, charge carrier mobility (μ) can be calculated via Einstein-Smoluchowsky equation (Eq. 1.1) which relates mobility to diffusion coefficient (D):

$$\mu = \frac{qD}{k_B T},\tag{2.1}$$

where q is the electron charge and k is the Boltzmann constant.

In case of existence of an external electric field, a drift of charge carrier will be formed which dominates the transport of charge carriers across the organic layer. Drift current displaces the average position of charges. Therefore, mobility is defined as the following:

$$\mu = \frac{\nu}{E},\tag{2.2}$$

in which ν is the velocity of charges and E is the electric field [18].

Charge carrier mobility depends on couple of factors including type of carrier, being hole or electron, charge carrier density, temperature, electric field, molecular structure and morphology, disorder and molecular weight of organic material. The effect of electric field will be discussed when introducing space charge limited current method. In the next section, the effect of temperature and crystal orientation and molecular packing on charge transport will be discussed [18].

As mentioned earlier, charge transport basically happens through hopping in

organic semiconductors. This process is thermally active therefore an increase i temperature will drive it faster. In fact, disorder in these systems creates energetic barriers preventing charge transport which can be overcome by applying high temperatures. It is been reported that structural order of $\pi - \pi$ stacking is in a close correlation to electronic properties, especially charge carrier mobility, of conjugated polymers. There has been numerous studies considering the correlation between crystal structure and charge carrier mobility of conjugated polymers. For instance, Kline et al. [18,19] has investigated the effect of molecular weight on both crystal structure and in- plane hole mobility of P3HT thin films in a field effect transistor configuration.

2.2.3 Mobility Measurement Techniques

Organic semiconductors contain small amount of intrinsic charge carriers and subsequently a relatively lower mobility in comparison with inorganic semiconductors. As a result, different set of techniques have been developed to characterize the mobility in organic materials. In general, factors such as sample thickness, energy levels of the semiconductor and the configuration of electrodes in addition to cost and availability of instruments determine the most suitable technique. In the following, a brief introduction of the most common techniques will be given.

Time of Flight (ToF) This method is one the most common techniques currently used for mobility measurement. In this method, the carrier transit time, which is the time that charge carrier drift from one electrode to another, is the basis to measure mobility. In general, a diode configuration in which organic semiconductor is sandwiched between two electrodes are employed. The charges are produced by irradiation a laser pulse on the material. Based on the bias direction and magnitude of electric field, generated holes or electron move to the respected electrodes. Mobility can be calculated by recording the current as a function of time based on the following equation:

$$\mu = \frac{\nu}{E} = \frac{d^2}{V t_{tr}},\tag{2.3}$$

in which E is the electric field, d is the distance between electrodes, V is the voltage and t is the carrier transient time. In ToF, thick samples in range of several micrometers should be used in order to have considerable and precise measurement of transient time [16, 20].

Carrier extraction by linearly increasing voltage (CELIV) This technique has become popular recently. In CELIV, which very similar to ToF in terms of geometry and energy level requirements, the organic materials mobility can be measured directly. In this technique, an electric field is applied on one electrode while the current transient due to charge carriers is being measured. The applied electric field is increased linearly and mobility is calculated directly from the measured current transient. In comparison with ToF, thinner films can be used in CELIV and also lower electric field is required [21, 22].

Field-effect Transistor (FET) This technique is generally used to characterize the mobility in the direction parallel to the film plane. FETs are similar to thin-film transistors in terms of configuration. A typical FET has the following components :

- Semiconductor thin layer, separated from gate electrode by an insulator
- Source (S) and drain (D) electrodes
- Gate (G) electrode

In a basic configuration of FET, the current is injected from source electrode and collected at the drain electrode. Gain electrode controls the current flow through semiconductor layer. In this technique, charge carrier mobility can be calculated based on the characteristic curves. Characteristic curves are the plots of drain-source current versus drain voltage while gate voltage is changing [23, 24]. The reported mobilities based on FET method are normally several order of magnitude higher than the values reported by other methods due to the fact that this technique measures the mobility parallel to the substrate. Other method measure the charge transport perpendicular to the substrate [19].

Space Charge Limited Current (SCLC) The charge carrier mobility can also be measured by space charge limited current(SCLC) method. This technique utilizes the analysis of current density vs. voltage characteristics of the sample in dark condition. This techniques is particularly useful to measure the mobility of single charge carriers separately, i.e., holes and electrons. The criteria to choose the electrodes determines whether hole or electron are injected through the semiconductor. This method can also be utilized to extract useful information such as trap distribution in semiconductor bandgap and position of Fermi level in case presence of traps is verified. Detailed discussion is provided later [16, 18, 21, 25]. SCLC requires a sample including thin film of organic semiconductor connected to two different electrodes, namely anode and cathode. This configuration is very similar to the diode configuration. In diode configuration, i.e. metal-organic semiconductor-metal configuration, conduction mechanism has been explained by two models based on the magnitude of energy barrier between metal-semiconductor interfaces [26–28]:

- Injection limited conduction (ILC)
- Space charge current limited current (SCLC)

It is been shown that ILC mechanism is dominated if the barrier height is more than 0.3 eV where charge carriers will be transported through jumping or tunneling across the metal-semiconductor interface and the injection is not enough to create space charge withing the semiconductor. In case of energy barriers lower than 0.3 eV, transport is not injection limited anymore and is bulk limited instead. This results to high rate of injection of carriers into the semiconductor even in low voltages.

A space charge region is formed near the interface when the number of injected carriers are greater than the carrier intrinsic capacity of the material in thermal equilibrium. At some point, the number of injected carriers reach a maximum value in which the electrostatic potential created by them will prevent the further injection of carriers and limits the current. This results to a higher charge density near the interface and a nonuniform charge density across the thin film.

As mentioned, SCLC can happen if one contact, referred as ohmic contact, is able to inject carrier charges higher than the capacity of the material. The current density-voltage relation is ohmic at low voltages with ohmic contact, since the field due to the applied voltage is so larger than the field associated with the injected charge carriers. Equation 2.4 is used to correlate these parameters in ohmic region:

$$J_{ohm} = q n_P \mu \frac{V}{d},\tag{2.4}$$

where n_p is the charge carrier density, μ is the carrier mobility, V is the voltage, d is the sample thickness and q is the electronic charge. This condition is dominant until the electric field due to injected carriers prevail the space charge condition [29]. SCLC mechanism can be divided into two different categories based on sample purity and magnitude of electric field: trap free SCLC or trap filling SCLC.

Trap free SCLC In the absence of traps and at low electric fields, current density has a quadratic correlation to voltage. Therefore SCLC can be characterized by Child's Law [30] :

$$J = \frac{9}{8}\varepsilon_0\varepsilon\mu\frac{V^2}{d^3},\tag{2.5}$$

where ε is the relative permittivity (or dielectric constant) and and ε_0 is the permittivity of free space. In this equation the effect of diffusion is neglected and current is independent of electric field. At high electric fields, normally an increase in charge carrier mobility is observed. Murgatroyd [30] proposed an analytical solution to measure mobility considering the effects of electric field. This effect is known as Poole-Frenkel (PF) effect. Murgatroyd proposed the following equation which is known as modified Mott-Gurney equation:

$$\mu(E) = \mu_0 \exp\left(\beta\sqrt{E}\right),\tag{2.6}$$

therefore :

$$J = \frac{9}{8} (\varepsilon \varepsilon \mu \frac{V^2}{d^3}) \exp\left(\beta \sqrt{E}\right), \qquad (2.7)$$

where μ_0 is the zero-field mobility, E is the electric field and β (or γ in some articles) describes the field activation coefficient which is the field dependence of mobility as a function of temperature. Gill [31] reported that the field activation is dependent on temperature in the following form based on a set of time of flight experiments:

$$\beta = B(\frac{1}{k_B T} - \frac{1}{k_B T_0}), \tag{2.8}$$

in which k_B is the Boltzmann constant, $T_0 = 600K$ and $B = 2.9 \times 10^{-5}$ eV. B and T_0 values are the same for a large variety of organic semiconductors.

Trap filling SCLC Traps present in band gap of conjugated polymers can be either due to structural defects or molecular perturbation in the lattice. The distribution of traps in the band gap determines the J-V characteristics of the system. Couple of models have been suggested to correctly explain the distribution of trap states. One of the most widely used models, suggested by Mark and Helfrich [32], states that traps are distributed exponentially within the bandgap. In TF-SCLC model discussed earlier, power law follows the simple form of $J \propto V^2$ while exponential traps distribution model shows that the J-V behavior is expressed by $J \propto V^{l+1}$, where l > 1. If we suppose a exponential trap energy distribution, the density of traps can be defined as a function of energy (E) in the following form:

$$H(E) = \frac{H_t}{lkT} \exp\left(-\frac{E}{lkt}\right).$$
(2.9)

According to this equation, if all the traps are filled lkt must be equal to zero. Therefore characteristic energy can be defined as $E_t = klT$ After some mathematical modification, the exponential trap distribution is given by Equation 2.9. [25]

$$J = q^{l-1} \mu_p N_{\nu} \left(\frac{2l+1}{l+1}\right)^2 \left(\frac{l\varepsilon\varepsilon_0}{(l+1)N_{total}}\right)^l \frac{V^{l+1}}{d^{2l+1}},$$
 (2.10)

where N_{total} is the total density of traps and N_{ν} is the density of states in the valence band. l is an energy parameter which is equal to $T_c/T = E_t/kT$ where T_c is the characteristic temperature of the traps. In addition, as can be seen from Equation 2.8, if E = klT, the exponential term will have the value of 1/e thus lkT can be considered as the characteristic width of the exponential distribution. Consequently the value of l can be used as a criteria to compare the magnitude of the width of trap energy distribution. The value of l can be extracted from the slope $\log(J)$ vs. $\log(V)$ plot which is l + 1 [25, 27, 33].

Chapter 3 Device Fabrication and Characterization

3.1 Materials

3.1.1 Substrate

ITO-coated glass slides were used as the substrate for the diode configuration hole-only device fabrication. Glass microscope slides coated with 60-100 nm of indium tin oxide(ITO), a transparent conductive oxide, was purchased from Sigma Aldrich. These slides have resistance in the range of 15-25 Ω/Sq , and the work function of ITO is 4.9 eV. In order to prepare samples for UV-Visible spectroscopy measurements, transparent glass slides were used as the substrate to insure that no extra absorption is being collected from the substrate.

Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is a hole transport layer which is common in organic solar cell fabrication. (Figure 3.1) PEDOT:PSS is a conducting conjugated polymer which improves the charge extraction properties of ITO and P3HT films interface. PEDOT:PSS was purchased from Baytron (product PH500, 1%wt aqueous dispersion). The PEDOT:PSS dispersion was diluted with 2 parts deionized water. Solution was then filtered with a 0.45 μ m glass microfiber mesh.

3.1.2 Active Layer

The polymer used for the active layer is Poly(3-hexylthiophene) (P3HT). Due to its high light absorbing and hole transporting properties, use of P3HT in active layer of organic solar cells is very common. P3HT strongly absorbs a vast range of visible light(350-650 nm)

P3HT has a thiophene backbone ring in which carbon atoms are sp^2 -hybridized, forming π -bond with neighboring carbons. The thiophene ring is responsible for



Figure 3.1: Chemical structure of PEDOT:PSS

absorption of light, charge generation and subsequent transport. The alkyl group attached to the thiophene ring has enabled P3HT to dissolve in several organic solvents including chlorobenzene, dichlorobenzene, chloroform and xylenes. Figure 3.2 shows the P3HT chemical structure.

The LUMO level of P3HT is 3.2 eV and the HOMO level is at 5.1 eV, therefore it has bandgap of around 2 eV [34]. P3HT was purchased from Rieke Metals. The properties of P3HT is shown in Table 3.1 . P3HT was dissolved in anhydrous chlorobenzene (Sigma Aldrich) at a concentration of 0.019 g/mL and filtered 3 times with 0.2 μ m Teflon mesh.

3.1.3 Electrodes

Indium Tin Oxide (ITO) is used as the transparent anode and Aluminum (Al) as the cathode. The Al pellets (99.99% purity) were purchased from Kurt J. Lesker.

3.2 Substrate Fabrication

Photolithography and acid etching are used to prepare the substrate for device fabrication. First, a rectangular pattern of 2 mm \times 12.5 mm is needed to be transferred onto the ITO-coated glass slide as the pattern for acid etching. ITO-coated glass slide was spin coated by positive tone photoresist SU1813 (thickness of 1 μ m).



Figure 3.2: Chemical structure of P3HT

The thin film was baked on a hot plate at 150° C for 1 min immediately after spin coating to evaporate the solvent. The photoresist film was irradiated with UV light using an ABM Mask Aligner. The aim dose is 90 mJ/cm². The exposed film was developed with Microposite MF 319 developer for 60 sec that washes away the exposed portion of the photoresist. The patterned ITO glass slide was etched at 60°C for 120 sec in an acidic ITO etchant which is a mixture of 20% HCl and 5% HNO₃. Later, the remaining photoresist was washed away by n-methylpyrrolidone (NMP).

3.3 Diode-configuration Device Fabrication

Substrates are cleaned by sonication for 20 minutes in each of the following solutions: 2% Hellmanex II detergent, deionized (DI) water and isopropanol alcohol (IPA). They are dried with nitrogen immediately. Then, clean substrates are transported into Nitrogen glove box in which a thin film of PEDOT:PSS is spun cast onto them. The thickness is 35 ± 5 nm. The sample is being heated at 140 °C for 10 min to evaporate PEDOT:PSS solvent. P3HT films (thickness of 100 ± 5 nm) are coated on ITO/ PEDOT:PSS stack later and pre-baked at 150 °C for 2 min in order to remove residual solvent and promote crystallization.

Afterward, the samples are either transferred to a thermal evaporator to deposit a 100 nm thick Al layer as the cathode or transferred to He ion beam system to be exposed to different He atom beam doses. Exposure to high energy beams initiates the cross-linking in P3HT films. In the latter case, the cross-linked P3HT films are

Table 3.1: Properties of P3HT polymer

Regio-regularity	90-94%
M_n	$30 \mathrm{kg/mol}$
Polydispersity (PDI)	1.8

transferred back to thermal evaporator for cathode deposition. In the end, devices were returned to glove box to perform the post-baking step in which the devices were heated at 170 °C for 2 mins to enhance the active layer-cathode contact. The device fabrication procedure is shown in Figure 3.3. Note that samples are transferred between instruments using a portable chamber that is pressurized with nitrogen.

The Al cathode for diode-configuration devices are deposited using thermal deposition. The evaporator uses tungsten conical basket as the filament. Typical rates of evaporation are 0.1-1 nm/s. Deposition rate and film thickness of deposited Al are monitored using Quartz crystals. The Al thickness used is 100 ± 5 nm.

3.3.1 Proximity Ion Beam Lithography (PIBL)

Optical lithography has been used extensively during the past decades, but there are some disadvantages to this technique. The most important one is that there are diffraction resolution limits set by wavelength which reduces the precision substantially. Therefore Proximity techniques including electron beam and ion beam lithography have attracted great interest among researchers.

electron beams have been used to produce very high resolution patterns due to the low wavelength of electrons since 1970s. Electron beam lithography is maskless, cheap and is capable of patterning sub 10 nm features. However, this techniques has a lower throughput relative to ion beam lithography. Furthermore, use of atom/ion beams instead of electron has showed some other benefits; for example, atom/ion



Figure 3.3: Direct patterning of polymer and diode-configuration device fabrication for mobility measurements. The device consists of layers of indium tin oxide (ITO), PEDOT:PSS, poly(3- hexylthiophene)(P3HT), and aluminum (Al)

beams don't suffer or show a very little amount of forward or back scattering. This technique has a very high throughput and also enables us to make large size patterns easily. In PIBL, a mask held in close proximity of the substrate is being irradiated with a beam of atom/ions [35]. Figure 3.4 shows a schematic of a basic PIBL used in making exposed P3HT films.

We used a custom in-house proximity ion beam system to irradiate P3HT samples. In this system, a saddle field ion source, enabled to pattern high resolution features, is used. The system is being flushed with helium constantly to ensure that it is oxygen free. To create required vacuum, a turbo pump aligned with a rotary mechanical pump have been used. The beam current density is being measured using an ion secondary electron detector. The exposure dose can be calculated by this simple correlation:

$$Dose = \frac{I \times t}{A},\tag{3.1}$$



Figure 3.4: Basic schematic of a PIBL system

where I is the beam current, A is the area and t is the exposure time.

Samples can be mounted on a piezo x-y stage, which is controlled by a LabView program. This program enables the automatic current measurements as well. The beam line consists both ions and neutralized atom beams, therefore the beam column is equipped with a set of electrostatic deflector plates to deflect energetic ions in a certain direction leaving only atom beams. Consequently the remaining high energy atom beams will be hitting the sample surface mounted on the stage in this system [36]. An outline of the He ion beam system is shown in Figure 3.5.

After pre-baking step, P3HT thin films are transferred to He ion beam system described earlier for irradiation. Samples were patterned with 10 keV, 0.3 mA atom beams. Exposure doses were varied based on the exposure time. The used doses range from 0.3 to 2.5 μ C/cm². The samples are flood exposed without the use of any masks. Afterward, irradiated samples were either taken for Al deposition in case of diode-configuration devices or otherwise sent for UV-Vis spectroscopy and X-ray scattering characterization purposes.

PMMA Contrast Curve PMMA contrast curves are used as a calibration tool for the He ion beam system. These curves were constructed in a 3 month interval during the period of experiments in order to calibrate the system exposure dose and maintain a constant reference for all set of experiments. The doses were corrected accordingly before reporting for any deviation from the previous set of experiments.



Figure 3.5: Diagram of He ion beam system

Poly(methyl methacrylate) (PMMA) contrast curves were generated by irradiating a thin film of PMMA with a thickness in the range of 250-350 nm. Doses were varied in the range of 0.3 to 2.5 μ C/cm². PMMA is a positive tone photoresist. The PMMA films are prepared by spin coating a 1:5 solution of PMMA:anisole onto an already cleaned Si substrate. samples were heated at 180 °C for 60 mins to remove the solvents before irradiation. Irradiated patterns were created by using a 1 cm in diameter aperture mask and were developed in a 1:3 solution of MIBK:IPA for 30 sec and in pure IPA for another 30 sec consecutively. By developing, the cross-linked PMMA were washed away. Contrast curves were constructed based on measuring the normalized residual thickness of each pad separately.

3.4 Electronic Characterization

The most frequent method of charge transport characterization is to apply an external voltage to the device through electrodes and measure the outgoing current. A Keithley 2610 source meter was used to characterize current-voltage curves. The final schematic of the diode-configuration device is shown in Fig 3.6. The device was fixed on a base and four gold probes attached to Keithley source meter was used to measure the electronic characteristics.

As shown in the figure 3.6, ITO layer has been etched before to provide two separate parts used as electrodes connections. In addition, the P3HT layer and PE-DOT:PSS layer have been wiped off separately with anhydrous chlorobenzene and IPA respectively to generate the contact between probes and electrodes. The lower part of ITO provides the cathode connection and also used as the position to attach cathode probes while the top part has the same function for anode probes. Note that all measurements are done in nitrogen-purged glove box.

To characterize the current density, we need to measure the efficient active layer



Figure 3.6: Diode-configuration device architecture

area of each device. After electronic characterization, devices are removed from glove box to measure the area by the microscopy technique. The devices' active area values are in the range of 0.08-0.14 cm². Figure 3.7 shows a 2.5X microscopy image of the surface area of a diode-configuration device. The active area consists the P3HT layer underneath the Al cathode which is in contact with lower layers of PEDOT:PSS and ITO. (Figures 3.6 and 3.7)

3.5 Structural Characterization

3.5.1 Microscopy

Patterned P3HT films is measured with Atomic Force Microscopy (AFM) using a MultiMode 3 (Veeco) in Tapping Mode for film thickness. AFM probes are silicon with a spring constant of 40 N/m, and these tips are most effective when functionalized with hexamethyldisiloxane (to minimize adhesive interactions with the polymer). The structures of microscale and millimeter-scale features are evaluated with a Nikon Eclipse LV100 optical microscope (bright-field optics).



Figure 3.7: 2.5X microscopy image of diode-configuration device.

3.5.2 UV-Visible Spectroscopy

Theory

Ultraviolet-visible spectroscopy is used to evaluate the absorption properties of as-cast and irradiated P3HT samples. This technique provides useful information about the length and structure of P3HT π -conjugation.

UV-visible spectroscopy detects the absorbance of electromagnetic radiation caused by the excitation of bonding or non-bonding electrons. The electromagnetic spectrum between 190-900 nm are considered to account for the majority of electron transitions. There are three types of orbitals containing valence electrons:

- 1. single, or σ bonding
- 2. π bonding (double or triple)
- 3. non-bonding (lone pair electrons)

The orbitals are arranged in the increasing order based on energy, which makes the non-bonding orbitals, the highest. Electron transitions normally occurs from



Figure 3.8: Electron transitions in UV-Visible spectroscopy

these orbitals to an anti bonding orbital, σ^* or π^* . Common transition are $\pi \to \pi^*$ and $n \to \pi^*$ and $n \to \sigma^*$ (Figure 3.8).

The absorption wavelengths (mainly the wavelength at which maximum absorption occurs- λ_{max}) are used to obtain qualitative information about the structure of the molecule or ion while Beer-Lambert law is used for quantitative analysis. Beer-Lambert law (Eq. 3.2) shows the relationship between absorbance and concentration of material.

$$A = \log\left(\frac{I_r}{I_s}\right) = \varepsilon cl, \qquad (3.2)$$

where I_r = reference beam intensity, I_s = sample beam intensity, c = sample concentration, l = path length of light through the cell, ε = the molar absorptivity (or molar extinction coefficient) of the sample. Molar absorptivity (ε) is a measure of how strong the sample absorbs light at that wavelength [37].

Experimental Procedure

UV-Vis spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrophotometer (250-850 nm). Samples are prepared by spin-casting thin films on glass slides. P3HT film thickness is approximately 95 ± 5 nm. P3HT films were pre-baked at 150 °C for 2 min after spin casting. P3HT films were then irradiated for the dose series of 0.3 to 2.5 μ C/cm². The as-cast and exposed films were measured for light absorbance using the aforementioned spectrophotometer. All data are collected in transmission mode at normal incidence (approximately). The signal from a clean glass slide was also measured and subtracted from the spectra.

Film thicknesses of P3HT on glass slides were measured by AFM. Absorptivity (μ) were reported and calculated using the Beer-Lambert Law for an absorbance (A), film thickness (t) of P3HT films sample concentration (c) is given by:

$$\mu = \frac{A}{C \times t}.\tag{3.3}$$

3.5.3 Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) Theory

X-ray scattering techniques are commonly used to analyze the crystal structure of the materials. Two major types of scattering experiments are small angle Xray scattering (SAXS) and wide angle X-ray scattering (WAXS). SAXS probes the domain size of materials over a long distance while WAXS mainly focuses on smaller distances and shorter range order. In WAXS, the incident beam is either at the specular direction or at grazing incidence. The former configuration enables the probing of parallel planes of the surface while the latter probes the normal planes to the surface. The latter is known as the grazing incidence wide angle X-ray scattering (GIWAXS) [38]. GIWAXS has been frequently used to characterize the morphology of conjugated polymers. It provides useful information about the in-plane packing of thin films. One of the main advantages of grazing incidence XRD over the traditional XRD is that a small volume of sample is needed in this method to perform characterization. In addition, this technique is able to collect significant information while operating on a very small incident angle.

Furthermore, collecting scattering data from polymers are difficult in XRD due to the weak scattering signal caused by the relative small number of molecules as well the existing disorder in the polymers, therefore high exposure times or high flux of X-ray source is needed. Synchrotron sources provide the necessary high fluxes of Xrays. As a result, GIWAXS performed in accordance with synchrotron source is very desirable technique to characterize the organic semiconductor in-plane structures. In GIWAXS, adjusting the incident angle controls the depth of beam penetration which allows different depth profiling of the surface [19,38,39].

It is noticeable to mention that GIWAXS is not able to characterize the structure of amorphous regions. Other techniques like Near-edge x-ray absorption fine structure (NEXAFS)can be used to give insight into effects of amorphous regions of conjugated polymers on charge transport [40].

Experimental Procedure

In this set of experiments. we are interested to obtain detailed information about the molecular ordering, crystallite size and crystal orientation and degree of crystallinity of as cast and irradiated P3HT thin films. Samples are prepared by spin-casting thin films of P3HT on Si wafers. P3HT film thickness is approximately 95 ± 5 nm. Film thicknesses of P3HT on glass slides was measured using a JA Wollam M-2000 spectroscopic ellipsometer. P3HT films were pre-baked at 150 °C for 2 min after spin casting. P3HT films were then irradiated for the dose series of 0.3 to 2.5 μ C/cm² with He ion beam system. The samples were later sent to Argonne National lab to perform GIWAXS analysis.

GIWAXS experiments were conducted at beam line 8-ID-E at the Advanced Photon Source of Argonne National Laboratory. Samples were placed in a vacuum chamber and illuminated with 7.35 keV radiation at incident angles in the range of 0.1-0.24; the off-specular scattering was recorded with a Pilatus 1MF pixel array detector (pixel size = $172 \ \mu$ m) positioned 204 mm from the sample. Acquisition times were approximately 10 sec per frame. Each data set is stored as a 981 × 1043 32-bit tiff image (Pilatus, with 20-bit dynamic range). In order to fill gaps in the image due to the detector, two images with a vertical offset were collected. Gapfilled images are corrected for flat field, solid angle and displayed as intensity maps in q-space with the GIXSGUI package for MATLAB.

Chapter 4 Results and Discussion

4.1 P3HT Contrast Curve

P3HT contrast curves are constructed to evaluate the sensitivity of P3HT film to He atom beams as well as to determine lithographic contrast of cross-linked P3HT films. In case of negative tone photoresists, contrast curves basically show the ratio of retained thickness after development to the initial thickness versus the exposure dose. microscale P3HT pads (1 cm diameter) are patterned with a 10 keV, 0.3 mA atom beam with varying exposure times which results in different exposure doses (0.3- $2.5 \ \mu C/cm^2$) using PIBL. A 1 cm in diameter aperture mask was used to create the patterned pads. The relief images were developed with chlorobenzene, dichlorbenzene (both at room temperature) and p-xylene (at 35 °C).

Figure 4.1 (a) shows the optical micrograph of cross-linked P3HT pads on a silicon substrate. Irradiation doses are marked inside each pad in units of μ C/cm². Figure 4.1 (b) shows the normalized residual thickness (t/t_0) as a function of exposure dose for p-xylene (square), chlorobenzene (line) and dichlorobenzene (triangle) developers. We confirm that P3HT is a negative tone resist since, e.g. an exposure dose of 1μ C/cm² retains around 80% of the film after development.

4.1.1 Cross-linking Mechanism

When π -conjugated polymers are exposed to high energy beams in proximity ion beam lithography, cross-linked molecules will be formed. These polymers generally have aliphatic side chains which in case of being irradiated to high energy beams like electron or ion beams, charged and excited molecules will be generated. These species subsequently lead to formation of free radicals [5].

In case of P3HT molecules, irradiation leads to formation of free radical on



Figure 4.1: (a) Optical micrograph of cross-linked P3HT pads on Si substrate. Doses are in units of $\mu C/cm^2$. (b) Normalized residual thickness as a function of dose for different developers.

 α -carbon as shown in Figure 4.4 which are resonantly more stable. We have hypothesized that these unstable free radicals tend to form intramolecular cross-links by reacting to adjacent charged molecules in the polymer matrix. Change of exposure dose leads to different cross-link density which is verified by performing the contrast curve, as shown in Figure 4.1 As discussed in elsewhere, the newly formed cross-links are thermally and mechanically stable and their resistance to different organic solvent such as chlorobenzene, dichlorobenzene and p-xylene have been reported [11].

4.2 UV-Visible Spectroscopy

The as-cast and irradiated samples' volume is large enough to be characterized by UV-Vis spectroscopy. The irradiation dose used is from 0.3 to 2.5 μ C/cm². Total of 8 samples plus two unexposed samples, one labeled as "as-cast" and the other labeled as "control" have been made. "As-cast" sample plays the role of reference for other devices. The sample "control" follows the same procedure as irradiated samples with exposure time of 0 seconds. Collected absorbance data for different dose series are normalized to account for variation in film thickness. Figure 4.3 (a) shows the spectra of absorptivity (μ) for different doses series and Figure 4.3 (b) reports the



Figure 4.2: Proposed chross-linking mechanism. We postulate the minor products are the final products since they are resonantly more stable.

maximum absorptivity (μ) and vibronic shoulder collected at wavelength of 600 nm for the dose series.

Considering only the spectrum of as-cast P3HT thin film, absorption peaks are observed at 520, 550 and 600 nm which are nearly the same as for all the irradiated films. Therefore no significant shifts in peaks are observed after exposure of P3HT to ion beams. As Sundberg et. al, [41] suggested the difference between adjacent peaks of 520 and 550 is due to the coupling of one C = C stretching phonon with the π - π * transition. Peak at 600 nm, generally referred to "vibronic shoulder" corresponds to π - π stacking interchain interaction.

The UV-Vis spectra of as-cast and irradiated P3HT films are nearly similar at lower doses where the cross-linking density is very low. Absorptivity drops gradually as the exposure dose increases. This can be due to the disruption of intermolecular ordering at high doses which results to the loss of the fine structure of the polymer



Figure 4.3: (a) Absorptivity (μ) measured by UV-Vis and (b) Absorptivity (μ) at maximum and at vibronic shoulder are plotted.

film. Gearba et al. [42] also showed that there was no significant change in UV-Vis absorbance of low-to-moderate cross-link density. In their article, They were investigating the the thermally cross-linking of P3HT films with a peroxide radical initiator.

It is observed that the absorptivity of vibronic shoulder also decreases with exposure dose, which indicates that the light absorption capability of π - π stacking drops. This can be attributed to the introduction of disorder in the system and the relative decrease of degree of crystallinity in (010) plane direction. However, in overall UV-Vis spectra show that the cross-linked P3HT retain π -bonds which are responsible for light absorption, charge generation and their subsequent transport.

4.3 Polymer Structure

Due to the anisotropic nature of P3HT films, the crystal orientation and molecular packing play crucial roles in determining the electrical and optical properties of P3HT and correlating the structure to these properties. GIWAXS experiments along with certain analysis methods were performed on the as-cast and irradiated P3HT samples to investigate the ion beam irradiation effect on the structure of cross-linked P3HT films.

4.3.1 Crystal Orientation

As mentioned in detail in chapter 3, the GIWAXS data were obtained for all samples and the corresponding images were corrected for flat field and solid angle after being gapfilled. The corrected GIWAXS pattern of As-cast and irradiated P3HT thin films are shown in Figure 4.4 (a). These images correspond to pre-baked P3HT films of as-cast and irradiated samples at 0.3 μ C/cm², 0.7 μ C/cm² and 0.9 μ C/cm². The patterns are function of q_z , the vertical projection of scattering vector (q) and q_{xy} , the horizontal projection. These axes correspond to in-plane and out-of-plane scattering directions respectively. Four peaks of (100), (200), (300) and (010) can be observed clearly, therefore we can see that the density of crystallites are considerable. The nomenclature used for defining the observed peaks are based on Miller indices (hkl).

Figure 4.4 (b) shows the one dimensional scattering intensity (I) curves obtained by averaging the azimuthal integration of intensity over the the total azimuthal polar angle range ($\phi = 0.90^{\circ}$) verses scattering vector (q) for as-cast and irradiated P3HT films at 0.3 μ C/cm², 0.7 μ C/cm² and 0.9 μ C/cm². Broad observed peaks correspond to disordered orientation of crystals in both as-cast and irradiated P3HT films.

P3HT has a thiophene ring which acts as a rigid backbone attached to an alkyl



Figure 4.4: (a) Corrected grazing-incidence X-ray scattering data for as-cast and exposed P3HT films. (b) Azimuthal average of intensity (I) verses scattering vector (q) for as-cast and exposed P3HT films.

chain. It is highly anisotropic due to chain packing in the crystallites. As-cast P3HT films is made of crystallites in the size order of 10-30 nm separated by amorphous regions. The geometrical variance of these thiophene and alkyl chains drive the formation of two major crystal orientations for P3HT polymers, namely "face on" and "edge on" orientations [19,43]. Figure 4.5 shows the different crystal orientations in P3HT thin films.

- "Face on" Orientation: this orientation is most favored for the out-of-plane charge transport direction, esp. in solar cell applications. The out-of-plane $\pi \pi$ stacking of aromatic thiophene ring forms face on orientation which corresponds to (010) plane direction in P3HT microstructures.
- "Edge on" Orientation: In this orientation, the alkyl chain direction is perpendicular to the substrate. This orientation is particularly useful in FET applications where the in-plane $\pi - \pi$ stacking improves charge transport substantially. In P3HT, edge on orientation corresponds to (100), (200) and (300)



Figure 4.5: Different crystal orientation in P3HT thin films

planes [44].

4.3.2 Degree of Crystallinity

Analysis of pole figures can give quantitative information about the distribution of alignment of the ordered lattice planes [38,45]. These pole figures were constructed for (100) peak of as-cast and irradiated samples at 0.3 μ C/cm², 0.7 μ C/cm² and 0.9 μ C/cm² using the procedure described by other groups [45,46] Wedge cuts of angular breadth 2° were taken for various detector angles from corrected GIWAXS images. Peak intensities at (100) peak position were fitted with a Lorentzian function considering the background. Intensities were corrected for angular resolution limit.

Figure 4.6 (a) shows the pole figures for (100) peak where logarithm of peak intensity was plotted as a function of orientation angle (χ) for as-cast and exposed P3HT films. The data and fit were given an offset for simplification in comparison purposes. Integrated peak intensity (I_{intg}) for (100) peak was evaluated from the fits to the pole figure intensities. I_{intg} for all irradiated P3HT films was compared to integrated peak intensity of as-cast sample (I_{intg_0}). Figure 4.6(b) shows the integrated peak intensities relative to as-cast P3HT films. Degree of crystallization (DOC) is directly related to integrated peak intensity. As can be observed from the plot, DOC decreases for about 50% when polymer is exposed to radiation.



Figure 4.6: (a) Pole figures for (100) peak where logarithm of peak intensity was plotted as a function of polar angle. Fits for the data is shown as a solid line (b) Integrated peak intensity of exposed films relative to as-cast P3HT film.

4.3.3 Crystallite Size Calculation

Peak intensities were fitted with Lorentzian function to estimate full width half maximum (FWHM) for (100) and (010) peak positions. FWHM is inversely related to crystallite size in polymer system. Crystallite size in exposed polymer were compared to unexposed polymer, therefore the reported values are relative values of the size. Figure 4.7 (a) shows the full width half maximum (FWHM) evaluated from the fits. FWHM for as-cast films is lower when compared to exposed films. This can be clearly seen from the crystallite size corresponding (100) and (010) directions. Figure 4.7 (b) shows crystallite size in exposed films relative to as-cast film. As the exposure dose increases, the relative crystallite size along (100) and (010) direction reduces. In the next section, the charge carrier mobility data, as an index of charge transport phenomenon in out-of-plane as-cast and cross-linked P3HT films will be discussed. We anticipate that the results from polymer structure as well as mobility measurements



Figure 4.7: (a) FWHM evaluated from peak intensities at (100), (200), (300) and (010) peak positions in as-cast and exposed P3HT thin films. (b) Relative crystallite size (ϕ) for (100) and (010) in exposed P3HT films relative to as-cast.

could be coupled to give us a full understanding of the correlation between molecular structure and charge transport and the corresponding effect of irradiation on both in π -conjugated polymers.

4.4 Mobility Measurements

Total of 10 set of devices were made following the scheme presented in chapter 3 (Figure 3.3) for current density (J)-voltage (V) analysis of diode-configuration devices in the dark condition. They include as-cast, control and irradiated doses ranging from 0.3 to 2.5 μ C/cm². For each set of devices, a minimum of 3-4 devices were made to confirm the the accuracy of experimental results. It was observed that in case of devices made in different batches, even though the absolute current values were different from sample to sample, values of hole mobility were comparable and of the same order of magnitude.

J-V analysis were performed using a Keithley 2610 source meter. As discussed

extensively in chapter 3, the slope of $\log(J)-\log(V)$ plot can distinct different conductivity regimes according the values of slope (m) in SCLC technique. Figure 4.7 (a) shows the $\log(J)-\log(V)$ plot of as-cast P3HT films. Three different regimes are observed: ohmic, trap-filling, and SCLC.

- In ohmic region (V < 1V), the ITO-P3HT interface barrier is able to prevent high rate injection of holes, since the applied electric field is relatively small in low voltages. Therefore the number of injected positive charge carriers are less than the intrinsic charge carriers. As a result, the conduction is mostly due to intrinsic carriers and the system follows an ohmic behavior with the slope of J-V double logarithmic equal to 1 (m ≈ 1).
- Second region (1V < V < 8V) starts off after the threshold voltage has been reached. At this point, charge carrier density increases rapidly due to the high rate of hole injection. Thus the slope starts to increase suddenly and shows values of greater than 2. This region is labeled as trap filling region. It is assumed that the intrinsic energetic traps present in P3HT films inhibits the charge within themselves leading to a higher current throughout the thin film. Exponential trap distribution model shows that the J-V behavior is expressed by the form of J ∝ V^m where m = l + 1 and l > 1. Meanwhile, value of l (subsequently m) corresponds to the characteristic width of the traps' energy states [25, 47]. In this case, high slope means a abrupt distribution while the low slope corresponds to an extended distribution.
- Third region denotes to trap free SCLC region in which the charge injection comes to a halt ($\mathbf{V} > 8V$). In this state, all the traps are filled with holes and the current starts to drop. The number of remaining charge carriers are still greater than the intrinsic capacity of thin film, therefore space charge starts



Figure 4.8: (a) log(J)- log(V) characteristics of as-cast diode-configuration P3HT devices. (b) m in the SCLC region was plotted for all devices studied. Error bars correspond to measurements for 3-4 devices for each exposure dose.

to accumulate throughout the film. An opposite direction electric field will be formed due to these charge carriers which will prevent further injection through the ITO-P3HT interface. The J-V behavior is shown in the form of $J \propto V^m$, corresponding to slope $m \leq 2$.

Figure 4.7 (b) shows the plot of slope of the SCLC region as a function of exposure dose. In overall, by increasing the exposure dose, the slope increases gradually which shows that width of energetic trap distribution extends. In other words, a broader exponential distribution is observed. Trap free SCLC behavior ($m \leq 2$) is observed for low to moderate doses ($<1 \ \mu C/cm^2$). For doses $>1 \ \mu C/cm^2$, the slope passes the m = 2 threshold. This behavior indicates that more trap states are introduced in the polymer system for high exposure doses.

Hole mobility (μ_h) values can be extracted from Trap free SCLC region by fitting the linear J-V curves to modified Mott-Gurney equation which account s for the effect of electric field (Equation 4.1)



Figure 4.9: Hole mobility (μ_h) of as-cast, control, 0.3, 0.5, 0.7 and 0.9 μ C/cm² devices as a function of exposure dose. μ_h of as-cast and control devices are denoted at an exposure dose 0 μ C/cm². Error bars correspond to measurements from 3-4 devices for each exposure dose.

$$J = \frac{9}{8} (\varepsilon \varepsilon \mu \frac{V^2}{d^3}) \exp\left(\beta \sqrt{E}\right). \tag{4.1}$$

Figure 4.8 shows the plot of hole mobility (μ_h) as a function of exposure dose for low to moderate doses (doses $<1 \ \mu C/cm^2$). The modified Mott-Gurney equation is not applicable for doses $>1 \ \mu C/cm^2$. μ_h of unexposed devices is of the order 2×10^{-4} (cm²/V.s), which is consistent with results from other groups [48,49]. Hole mobility in patterned devices drops by almost 50% when compared to unexposed devices. At high exposure dose, trap states are introduced which can reduce the charge-carrier mobility.

In addition, the calculated field activation coefficients are negative and in the order of 1×10^{-3} eV. This indicates that the hole mobility of unexposed and low to moderate exposed P3HT films have a negative field dependence. Mozer and Sariciftci [50] postulated that this trend is due to the large spatial disorder present in P3HT

films.

In conclusion, it can be noted from analysis of GIWAXS data that the crystallite size and degree of crystallization of cross-linked P3HT drop significantly at low-tomoderate doses compared to as-cast films. Intermolecular cross-links generated in π -conjugated polymers can disrupt the crystallite formation and thus reduced crystal orientations. This may be couple to reduced charge-carrier mobility in exposed P3HT films which is consistent with the trend observed for hole mobility of cross-linked P3HT.

Chapter 5 Conclusion and Outlook

5.1 Conclusion

In this project, we have studied the effects of radiation on polymer system structure and charge transport properties. We have tried to establish an approach to be used as a model system for structure-property studies in organic devices. P3HT, a π -conjugated polymer, was used as the case-study material in this project. P3HT forms cross-links after exposure to atom beam irradiation.

UV-Vis spectroscopy was used to characterize the light absorption properties of cross-linked P3HT. The results showed that cross-linked P3HT films retain light absorption properties upon exposure. P3HT molecular structure and crystallinity was studied by grazing-incidence wide angle X-ray scattering technique. Degree of crystallinity and crystallite size were shown to have decreased by half in cross-linked polymer. Mobility measurements were performed to evaluate hole mobility. Measurements showed that the positive charge carrier mobility measured from space charge limited current (SCLC) region drops by 50% after P3HT exposed to low-to-moderate doses. On higher exposure doses, trap states are introduced in the system which can significantly reduce carrier mobility. Based on the results, we can postulate that the intermolecular cross-links generated in π -conjugated polymers disrupt the crystallinity and reduce the optoelectronic properties.

5.2 Outlook

5.2.1 X-ray Photoelectron Spectroscopy (XPS) Studies

X-ray Photoelectron spectroscopy is a surface-probing technique which can provide valuable information about chemical composition and electronic state of the materials. In a basic XPS instrument, the sample surface is irradiated with X-rays,



Figure 5.1: XPS survey scan of as-cast and exposed P3HT at dose of 2.5 μ C/cm²

hitting the core electrons of atoms. The spectra is collected based on number and kinetic energy of electrons ejecting out of the depth of the material. The applicable signals are due to a depth of 1-10 nm. XPS spectra are plots of number of electron counts as a function of binding energy of that electron. Each core electron has a specific binding energy. Therefore, XPS can be used to find different electronic states of elements and chemical bonds in a material. In order to fully understand the cross-linking mechanism in these polymer system, further studies including XPS are required.

As pointed out earlier, the irradiation of π -conjugated polymers with high energy beams like electron or atom/ion beams can generate free radicals which leads to crosslinking of polymer molecules in the system. These radicals are chemically very active and may react with the oxygen in the atmosphere during the cross-linked polymer formation. Therefore in order to test our postulation about the existence of oxygen atoms, XPS studies on as-cast and exposed P3HT films are currently done. We are expecting that this set of experiment can be used as a tool to study the oxidation pathways in the cross-linked polymers.

Figure 5.1 shows the XPS survey scan of as-cast and exposed P3HT at two doses



Figure 5.2: (a) Raw high resolution spectrum of carbon edge and (b) sulfur edge for as-cast P3HT and exposed P3HT at dose of 2.5 μ C/cm². (c) Shifted high resolution spectrum of carbon edge and (d) sulfur edge for as-cast P3HT and exposed P3HT at dose of 2.5 μ C/cm².

of $0.5 \ \mu\text{C/cm}^2$ and $2.5 \ \mu\text{C/cm}^2$. In both as-cast and exposed samples, the sharp peaks of carbon and sulfur are observed clearly. Furthermore, It is observed that $2.5 \ \mu\text{C/cm}^2$ sample shows a peak at binding energy (B.E.) of 530 eV, which is due to the presence of small amount oxygen ($\simeq 1\%$) in the cross-linked P3HT. While oxygen peak is not observed in other spectra. The high resolution XPS scans of carbon and sulfur edges normalized based on the maximum peak and their corresponding shifted spectra have been shown in Figure 5.2. The C edge peak is located at B.E.= 282.87 eV for as-cast P3HT while it is at B. E. = 282 eV and B.E. = 282.68 eV for $0.5 \ \mu\text{C/cm}^2$ and 2.5 $\ \mu\text{C/cm}^2$ P3HT samples respectively in Figure 5.2 (a). The sulfur edge peaks of ascast, $0.5 \ \mu\text{C/cm}^2$ and $2.5 \ \mu\text{C/cm}^2$ samples are at the binding energies of 161.64 eV, 160.76 and 160.86 eV respectively (Figure 5.2 (b)). Parts (c) and (d) of Figure 5.3 show the offset spectra of C and S edges respectively. The offset has been applied relative to as-cast spectrum. Since the calibration of absolute energy on polymers is difficult, offsetting the spectra helps us gain a better understanding of the changes in the spectra.

It is observed that C edge peaks in the cross-linked P3HT samples are broader than the peak in the as-cast P3HT (Figure 5.3 (c)). In addition, we have observed from survey scan that oxygen molecules are present in 2.5 μ C/cm² sample. Therefore we can attribute the relative change of breadth of C peaks to either the change in carbon structure and formation of C-O or C=O bonds or formation of dangling bonds in cross-linked P3HT samples. In case of sulfur edge (Figure 5.2 (d)), offsetting results to overlapping of all three spectra nearly perfectly, thus we can speculate that the C-S bonds are probably unchanged. [51,52]. These experiments are at a preliminary stage, therefore it is difficult to pinpoint the validity of the results and justifications at this point. More experiments need to be conducted to confirm the reliability and accuracy of the data.

5.2.2 Solvent Chemistry

In our studies, we constructed P3HT contrast curves to evaluate the sensitivity of P3HT films to He atom beams as well as to determine lithographic contrast of crosslinked P3HT films. The patterned P3HT were developed with organic solvents and since P3HT is a negative tone resist, the cross-linked portion was retained. Therefore the effect of solvent might be a factor that could be used to gain better understanding of underlying chemistry in formation of cross-linked polymers.

Another short-term goal of our studies will be to understand the changes in chemistry of polymer induced by development step of the process. Studies in our group [11] have already shown that the retained cross-links are stable through thermal annealing and solution-based processing. We are planning to study the effects of irradiation on the light absorption, molecular structure and charge transport properties of cross-linked P3HT after development with organic solvents such as chlorobenzene, dichlorbenzene, and p-xylene.

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