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DIRECT PATTERNING OF CONDUCTIVE POLYMER DOMAINS FOR PHOTOVOLTAIC DEVICES

A Dissertation

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Chemical Engineering

by

Suchanun Mounghai

August 2012

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Acknowledgements

First and foremost, I would like to express my sincere gratitude to my advisor, Assistant Professor Gila Stein for the continuous support of my Ph.D study and research, for her patience, motivation, enthusiasm, and immense knowledge. Her guidance helped me in all of my research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D study.

Besides my advisor, I would like to thank Nikhila Mahadevapuram. Much of the work included in this thesis was made possible by her. I am extremely grateful for her assistance, enthusiasm and support. I thank Augustine Rajaendran and Trang Pham for their assistance of the work in chapter 8.

I benefitted from the regular use of the Nanofabrication Facility at the University of Houston, and I thank Dr. Long Chang for providing me with excellent training, support and troubleshooting. I also thank Associate Professor Paul Ruchhoeft and Dr. Azeem Nasrullah for assisting me with the Helium ion system.

I thank my fellow labmates in Dr. Stein's Group: Nikhila Mahadevapuram, Ginusha Perera, Abhijit Patil and Indranil Mitra for the stimulating discussions, assistance and fun we have had. I would like to thank all of my friends, especially Prachya Dowsirirod, for his patience and support.

Last but not the least, I would like to thank my family: Suthep Mounghai, Araya Mounghai and Kopong Mounghai for supporting me spiritually throughout my life.

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Abstract

In the developed world, the demand for energy is increasing tremendously. In this day and age, the main sources of energy are natural resources like oil and coal, and their supply could run out in the near future. In addition, burning fossil fuel produces large amounts of carbon dioxide which are linked to global warming. We need an alternative source of energy that is clean, renewable and sustainable. Photovoltaics are one of the most interesting alternative energy sources for future energy, as this technology could potentially generate clean, efficient, and reliable electricity.

Most products in the marketplace are based on silicon, and these devices require a lot of energy for the fabrication process, driving up their cost and reducing the benefit. Polymer solar cells can be made at a very low cost, and offer additional advantages such as flexible, light weight modules that can be made in a variety of sizes and shapes. A typical polymer solar cell is made from a partially phase-separated polymer/fullerene blend. The main problem for polymer solar cell is their low power-conversion efficiency, which is partly controlled by active layer morphology.

The objective of this work is to develop a system to study the effects of active layer morphology on device function. The approach developed in this work uses electron-beam patterning of polymer semiconductors to build model polymer/fullerene devices. Electron-beam patterning generates conductive nanostructures or microstructures through an in-situ cross-linking reaction, where the size, shape and density of polymer domains are all tunable parameters. Cross-linked polymer structures are thermally-stable and solvent-resistant, so they can be incorporated into devices that require thermal annealing or solution-based processing. This method was validated by building “gradient” and nanostructured poly(3-hexylthiophene)/fullerene

solar cells. These model devices exhibit good power-conversion efficiencies, which are explained by a polymer cross-linking mechanism that largely preserves the π -bonds responsible for light absorption, charge generation, and charge transport. The flexible methodology can be used to study the effects of domains size and interfacial area on optoelectronic function.

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Chapter 1 Introduction

1.1 Introduction

Most of the world's energy is derived from fossil fuels [1]. Concerns about rising oil costs, depleting oil reserves, and climate change have motivated extensive research into renewable energy resources [2]. Solar power is very appealing for long-term electricity generation: harvesting sunlight is environmentally clean, and the power output would greatly exceed any projected energy demands [1–3]. Currently, solar electricity is too expensive to compete with other power sources, which is a consequence of the high production costs associated with traditional photovoltaic modules based on inorganic semiconductors [4, 5]. As a result of these economics, solar energy comprises less than 1% of global energy production [3, 5]. From a cost perspective, solar cells based on polymer semiconductors are very appealing because polymers have large absorption coefficients, synthesis is inexpensive, and modules are produced with simple roll-to-roll technologies [6–8].

Polymer solar cells are attractive for clean energy production because they can be fabricated in light-weight, flexible, durable and inexpensive modules. The most efficient devices are based on the bulk heterojunction (BHJ) design [6, 7]. BHJs are prepared by arresting the phase separation of a polymer-fullerene (donor-acceptor) blend. The resulting structure is a nanoscale, interpenetrating network that offers a large interfacial area for charge generation and a good pathway for charge transport to the electrodes. Currently, it is unclear what aspects of the BHJ structure are controlling device function because it is difficult to control and characterize the formation of these highly non-equilibrium morphologies.

BHJs are usually prepared by spin-casting from volatile solvents and the as-cast

structure is very sensitive to the solvent quality, evaporation rate, solution concentration and ambient temperature. BHJ growth kinetics are controlled by a coupled crystallization diffusion mechanism, so key parameters such as domain size, phase purity, polymer crystallinity and interfacial area cannot be varied independently. Additionally, the BHJ morphology is disordered and anisotropic at both molecular and nanometer length scales and this feature complicates the measurement of the structure with scattering or microscopy [8].

As a result of these challenges, there is wide debate about the optimal design attributes for polymer-based solar cells. It is generally agreed that charge generation is optimized when the phase separation length scale is comparable to the exciton diffusion length, which is approximately 10 nm for most polymer semiconductors. However, even when the average BHJ domain size meets this criteria, the film contains defects such as regions of complete polymer/fullerene miscibility, domains that are larger than the exciton diffusion length, and incomplete paths to the electrodes [8].

These defects are responsible for carrier losses through trapping, recombination or photoluminescence, making it difficult to accurately interpret spectroscopic and optoelectronic measurements. Furthermore, while most works indicate that highly-crystalline polymers will enhance light absorption and carrier transport, there are examples of good optoelectronic function in low-crystallinity systems [9, 10]. This discrepancy is explained by the coupling between crystallinity, domain size and interfacial area in a BHJ device, making it difficult to determine which parameter is controlling the observed photocurrent.

A variety of experimental methods have been developed that offer control over

the nanoscale morphology [11]. Examples include self-assembly of block copolymer semiconductors, [12–14] polymer nanowire growth, [15–17] and imprint lithography [18–25]. Block copolymers provide a simple route to generate dense arrays of nanostructures, but it is difficult to control domain orientations through the film thickness. Furthermore, critical properties such as domain size, interfacial width and crystallinity are all coupled to the copolymer composition and molecular weight [26].

The growth of crystalline polymer nanowires will produce high-mobility nanoscale domains, [15–17, 27] but does not afford precise control over wire diameters, orientations or placement. Recently, several groups have used imprint lithography to build polymer-based heterojunctions with well-defined morphologies [11, 18–20, 23–25]. Such top-down lithographic techniques provide control over domain sizes and interfacial area, which is helpful to understand the effects of active layer structure on optoelectronic function. For example, these studies have demonstrated that matching the domain size to exciton diffusion length can enhance photocurrent generation [24, 25]. However, imprint lithography has a few limitations. First, master stamp fabrication is difficult and expensive, particularly when the desired pattern is a large-area array of sub-20 nm nanostructures. Imprint lithography is an excellent strategy for repetitive printing of a single design, but this approach can be costly and time-consuming when many different designs are under investigation. Second, the thermal and mechanical properties of organic semiconductors are not optimized for imprinting. This means that imprinted nanostructures have limited stability through solvent processing or heat treatments and it is difficult to generate nanostructures with high aspect-ratios (width:height > 2) [25]. Finally, imprinting will induce alignment of the polymer chains within the template, [20] so polymer crystallinity and grain orientations will be coupled to the design of the stamp.

The focus of my PhD research is the development of a flexible approach to control the morphology of polymer/fullerene heterojunctions. Thin films of π -conjugated polymers are directly patterned with electron-beam lithography (EBL) [28–30]. This process initiates a localized, *in-situ* cross-linking reaction that generates conductive nanostructures or microstructures. The image is developed by immersion in an organic solvent and then the cross-linked polymer structures are coated with a soluble fullerene to complete the heterojunction. This protocol allows for the independent variation of domain size and shape, interfacial area and phase purity. The lithographic process is compatible with commercially available materials such as different types of poly(3-alkylthiophene) and poly(phenylene vinylene) [28–30].

Polymer cross-link density can be tuned *on-demand* by varying the exposure dose, providing a simple route to engineer high-performance nanostructures that are stable through solvent and thermal processing. Furthermore, after evaluation the spectroscopic and optoelectronic properties of these devices, the heterojunction morphology can be measured with microscopy by “deconstructing” the active layer. While EBL is too slow for manufacturing, this technology is very valuable for basic scientific research: EBL patterns are defined with Computer-Aided Design (“maskless”), so different types of designs can be rapidly evaluated. State-of-the-art EBL systems require a substantial capital investment, but the data presented in this report was acquired with a scanning electron microscope equipped with a pattern generation system [31]. The materials used in this work are poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), which are benchmark donor and acceptor chemistries, respectively [6,8].

1.2 Overview

This dissertation discusses and underlines the fundamental processes behind the operation of polymer-based solar cells, which are absolutely necessary to further improve the device performance. This dissertation is divided into eight chapters:

Chapter 2 provides an introduction to solar cells. Two types of solar cells, organic and inorganic, are discussed. The main emphasis is on organic solar cells. The chemistry and photophysics of P3HT/PCBM heterojunction are reviewed. Finally, chapter 2 also explains the efficiency calculations and parameters for the electronic measurement.

Chapter 3 discusses device fabrication and characterization. This chapter includes all the details about the fabrication process, starting from the chemicals, material preparation, substrate preparation, device fabrication for bilayer, bulk heterojunction and nanostructure device, and ending with electronic measurement.

Chapter 4 is an introduction to the lithography techniques we used for device fabrication, including photolithography, electron beam lithography, and proximity ion-beam lithography. The photolithography technique is used to pattern device anodes, and is discussed as part of a micropatterning project in Chapter 8. EBL and ion beam lithography are used to pattern polymer semiconductors (to control device morphology). The sensitivity, resolution and contrast of polymer semiconductors are investigated.

Chapter 5 describes spectroscopy characterization of patterned polymer semiconductors. The objective of this study is to evaluate the effects of electron-beam or ion-beam radiation on the structure and properties of P3HT. Ultraviolet-visible

absorption spectroscopy was used to detect changes in absorption coefficient and crystallinity, and Fourier transform infrared spectroscopy was used to look for changes in bond structure.

Chapter 6 reports the electronic performance of patterned polymer film in solar cells. The optoelectronic function of irradiated polymer was determined by fabricating functioning devices and measuring the efficiency. In this chapter, the simple cross-linked bilayer devices were fabricated and compared with graded and bulk heterojunction devices. Furthermore, the performance of nanoline devices were investigated.

Chapter 7 consists of conclusions and outlook. This chapter concludes the current work and gives the overview of future work to improve the device efficiency.

Chapter 8 is entitled “Ordered arrays of polymer droplets with circular, triangular and rod-like shapes.” This chapter is another project separate from the organic solar cell project. The goal of this project is to generate polymer microstructures with controlled size, shape, symmetry and positions by directing the dewetting of polymer films with micropatterned surfaces.

Chapter 2 Introduction to Solar Cells

This chapter gives an overview of inorganic and organic solar cells. Several aspects of polymer solar cell such as power-conversion mechanism and active layer design are introduced. The chemistry of materials used in this work are illustrated. Finally, the principles of efficiency measurement and associated parameters are explained.

2.1 Inorganic solar cell

The extensively-studied silicon (Si) solar cell was first developed in Bell Laboratories in the 1950s with the efficiency of 6%, where efficiency is defined as power out/power in [32]. Since then the efficiency has reached 24% for the silicon solar cell which is close to a theoretical limit of 30% [33]. In inorganic solar cells, the doped inorganic materials are used to form p-n junction. The p-side is doped with material that has less electrons so it has an excess amount of positive charge. On the other hand, the n-side is doped with material that has more electrons so there is an excess amount of negative charge. In the region near the junction called the depletion region, an electric field is formed. Electrons and holes which are generated by light absorption in the bulk silicon, diffuse to this junction where they are directed by the electric field towards the proper electrode. The main problem that prevents photovoltaic technology from providing a large fraction of our electricity is the high cost of manufacturing crystalline silicon. Therefore, to ensure the sustainable technology path for photovoltaic, the development of new materials and device structures are required.

2.2 Organic solar cell

Organic solar cells are promising for the clean, renewable and sustainable alternative energy source with unlimited quantity available. Organic solar cells from

the conjugated polymers are less expensive compared to the inorganic solar cell. The high absorption coefficient, as high as 10^5 cm^{-1} , makes it possible to build thin film devices [34]. Devices can be fabricated using high throughput, low temperature approaches based on roll-to-roll printing. In addition, organic materials can be tuned chemically to adjust properties such as band gap, charge transport and solubility, which make them very interesting.

The first investigation of organic solar cells was in 1959 with an extremely low efficiency based on single (homo-junction) organic material [35]. Although the homo-junction was widely studied, the efficiency remained lower than 0.1% so this design is not practical for applications [36]. The low efficiency is primary due to the fact that the absorption of light generates excitons, which are bound electron-hole pairs instead of free charges as in inorganic solar cells. Due to the low dielectric constant in organic materials (approximately 3), a much higher energy than thermal energy (kT) is needed to dissociate the excitons [37]. A major improvement of solar cell performance came when Tang discovered a much higher efficiency (about 1%) in 1986 [38]. Tang combined the donor and acceptor together in one cell called a *heterojunction*. Using two organic materials which have different electron affinities and ionization potential created a potential difference which acts as a driving force to dissociate the excitons at the interface between donor and acceptor. As a result, heterojunctions create many more free electrons and holes to reach the electrode than do homo-junctions. The highest efficiency of organic solar cells is 5% now. Another obstacle preventing organic solar cells from reaching high efficiency is the short exciton diffusion lengths, which are typically 1-10 nm [39, 40]. The donor/acceptor interface should be within exciton diffusion lengths from where the excitons are generated. Otherwise, the excitons will decay, yielding heat or luminescence instead of a contribution to photo

current.

2.2.1 Mechanism of polymer solar cell

Figure 2.1 explains the mechanism of photocurrent generation in an organic solar cell [40]. Absorption of light by the conjugated polymer (donor) excites an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO), generating the excitons (coulombically-bound electron-hole pair). Excitons diffuse to the interface between donor and acceptor phases. The offset of the energy level in LUMO of the donor and LUMO of the acceptor act as a driving force to dissociate excitons at the interface [41, 42]. Therefore, electrons are transferred from LUMO of the donor to LUMO of the acceptor. Holes are transported in the polymer phase to the anode, and electrons are transported in fullerene-derivative phase to the cathode. Movement of charge-carriers generate a current (or electricity).

To maximize efficiency in polymer photovoltaic cells, the design should have the following aspects.

- Because the polymer has a high absorption coefficient (ca. $\sim 10^5 \text{ cm}^{-1}$), an active layer thickness of approximately 200-300 nm will absorb all the light. However, the charge-carrier mobility in polymers is very poor, so the films are usually around 150 nm thick to optimize the balance between light absorption and charge transport.
- Due to the short diffusion length of excitons (5-10nm), [36] donor-acceptor interfaces must be present within the exciton diffusion length to maximize the probability of exciton dissociation and charge generation.

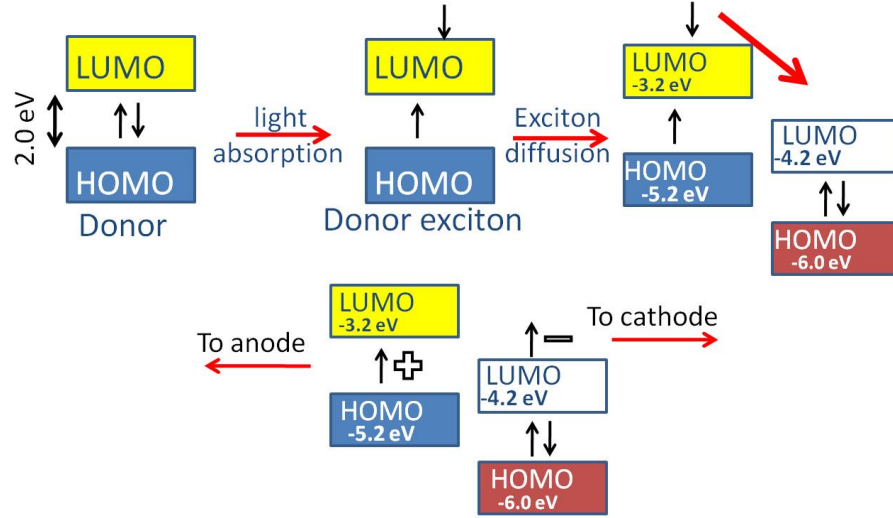


Figure 2.1: Mechanism of Photovoltaic cell.

- Large interfacial area between the donor and the acceptor is needed to maximize the dissociation yield of excitons. This can be achieved by thermal annealing to increase diffusion of one phase to another phase [43–46].
- Direct pathways for charge transport to the electrodes are preferred to minimize losses due to recombination.

2.2.2 Device Architecture

Common designs for the active layer are bilayer and BHJ. Recently, there has been a lot of interest in OHJ where the donor and acceptor domains are "interdigitated" at a scale of 10 nm. Theory and simulations suggest the OHJ design could double the power conversion efficiency [47, 48]. These different designs are shown in Figure 2.2 and compared and contrasted in the following paragraphs.

Bilayer devices: Bilayer devices shown in Figure 2.2 (a) were built in order to provide an interface between the donor (pink) and acceptor (grey) for exciton dissociation [35, 38]. The efficiencies reported were low as exciton dissociation was the

limiting factor. Excitons are likely to decay when generated at a distance from the interface that is larger than exciton diffusion length. The thickness of the layers was maintained to have maximum absorption of light, thus the bilayers had to compromise between light absorption and exciton dissociation [35].

Bulk heterojunction (BHJ) devices: The bulk heterojunction shown in Figure 2.2 (b) is a nanoscale network produced from phase separation of a donor-acceptor blend. A number of studies have been done for this design and the efficiency has reached 5% for P3HT/PCBM [35,47]. The domain size of donor and acceptor is around 10-100 nm, so the design is more efficient than the bilayer because there is more interfacial area between the donor and acceptor and therefore a higher probability that excitons can dissociate. The disadvantages of this design are limited thermal stability, indirect pathway for transportation of the charge to the electrode, [49] and difficulty to control the morphology. Morphology of the devices has significant influence on the device performance and its thorough understanding is essential [24,25].

Ordered heterojunction (OHJ): The ideal structure has the donor and acceptor phases interdigitated at a scale of 5-10 nm, which matches the exciton diffusion length (5-10 nm). Figure 2.2 (c) shows the OHJ device. This design provides a direct path to the electrodes, uniform domain size, large interfacial area, and interfaces distributed within the exciton diffusion length. OHJ should have fewer losses from recombination due to defects in the conduction path [50]. In addition, the electrodes are coated with pure donor or acceptor phase, which minimizes the recombination losses that result from transporting to the wrong type of charge-carrier to the electrodes [41]. Theoretically, the efficiency of this design can exceed 10% [47]. The biggest challenge is fabricating the interdigitated morphology. Several techniques like the imprint nanolithography technique have been adopted to form nanostructure pillars [18–20]. The technique uses a hard mold to form nanopillars. The nanopillar structure improves

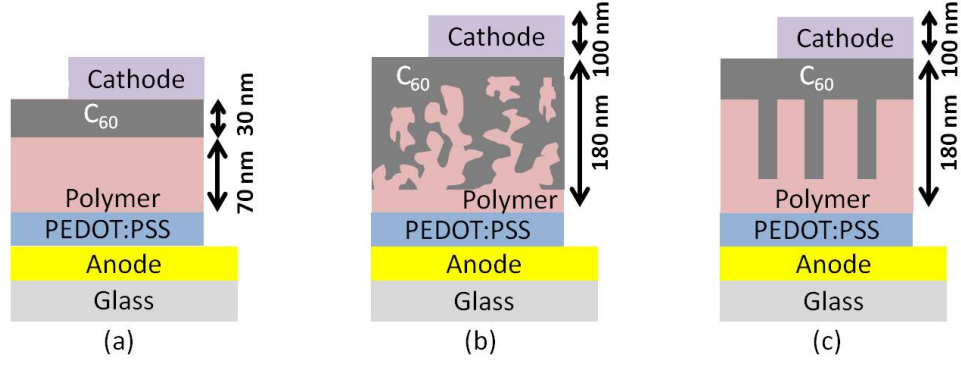


Figure 2.2: Device architecture (a) Bilayer (b) Bulk heterojunction (c) Ordered heterojunction.

the exciton dissociation and charge transport. The device efficiency was improved relative to a bilayer but was less than BHJs based on the same materials. Pillar size was around 25-80 nm which is greater than exciton diffusion length. The stability of these nanopillars through subsequent processing steps, as well effective acceptor filling between the pillars, are issues limiting this technique [24, 25, 51].

2.3 Polymer/Fullerene Chemistry

2.3.1 Poly (3-hexylthiophene) (P3HT)

Regio-regular poly (3-hexylthiophene) (P3HT), shown in Figure 2.3 (a), is used as an electron donor in the active layer of the solar cell device. This semiconductor polymer strongly absorbs visible light in the range of 350 nm to 650 nm, approximately 20% of solar light [6]. Properties like low band-gap and high carrier mobility are favorable for polymer solar cells. P3HT with band-gap of 2 eV and film thickness of 240 nm absorbs approximately 95% of the solar spectrum over 450 - 600 nm [36]. P3HT has a hole mobility as high as $3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) which is good for the hole transport to the electrode [52]. The thiophene ring which have conjugated π bonds are responsible for the absorption of light, charge generation and charge transport. The

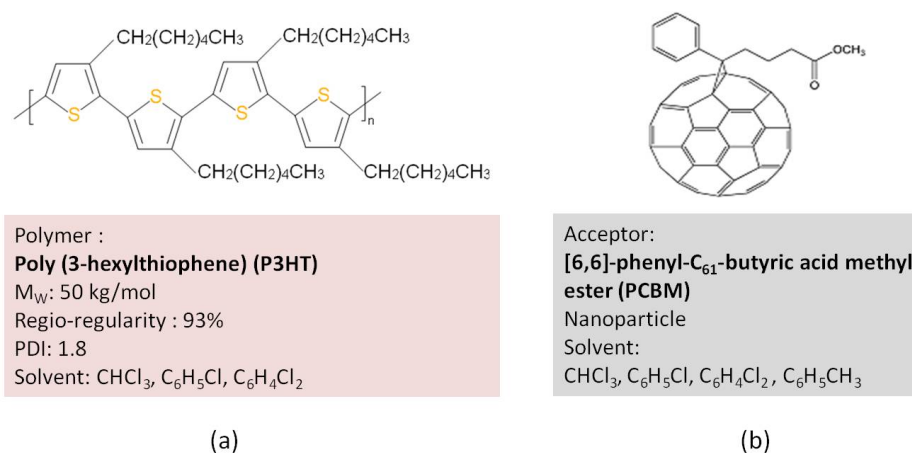


Figure 2.3: Chemical structure and properties (a) P3HT (b) PCBM.

alkyl groups make this molecule soluble in several solvents that include chloroform, chlorobenzene, dichlorobenzene and xylenes.

2.3.2 [6, 6] - phenyl-C₆₁-butyric acid methyl ester (PCBM)

Fullerene derivative [6, 6] - phenyl-C₆₁-butyric acid methyl ester (PCBM), shown in Figure 2.3 (b), is the acceptor. PCBM has a band gap of 1.8 eV, and the lowest unoccupied molecular orbital (LUMO) is 1 eV lower than LUMO of P3HT, which is enough to dissociate the excitons (exciton binding energy is 0.5 eV). Fullerene derivative are excellent acceptors because they have high electron affinity relative to several organic donors. The dielectric constant of PCBM is 3.9 [1]. High dielectric constant make the energy levels in PCBM stabilize the negative charge and contribute to excellent electron transport. These properties are very useful for the polymer solar cell [6]. PCBM is a nanoparticle with a diameter of approximately 1 nm that can diffuse effectively into the polymer matrix.

2.4 Efficiency of Solar Cell

2.4.1 Power conversion efficiency (η)

Power conversion efficiency (η) is the ratio of output power to input power. Usually expressed as a function of short circuit current density (J_{SC}), open circuit voltage (V_{OC}), and fill factor (FF). Each of these parameters relate to the design of the solar cell, so that the design can be adjusted where problems are identified. The relation of the efficiency to J_{SC} , V_{OC} and FF is

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \quad (2.1)$$

The current-voltage characteristics are described by the ideal diode equation. The ideal diode equation is

$$J = J_0(\exp[q\frac{V - IR_S}{nkT}] - 1) + \frac{V - JR_S}{R_{SH}} - J_{PH} \quad (2.2)$$

V is the applied voltage (Volts) and J is the measured current density. J_0 is the dark current. The dark current is the current without illumination which is zero at low applied voltage, because organic semiconductors do not have free carriers at zero illumination. When the applied voltage increases, the electrodes can inject charges and create a current. J_{PH} is the current generated by light (photocurrent). q is the electron charge. R_S is the series resistance. R_{SH} is the shunt resistance. n is an ideality factor. T is temperature, k is Boltzman's constant.

The efficiency of the solar cell is measured by characteristic current density-voltage ($J - V$) curve. The light curve is measured under standard illumination and

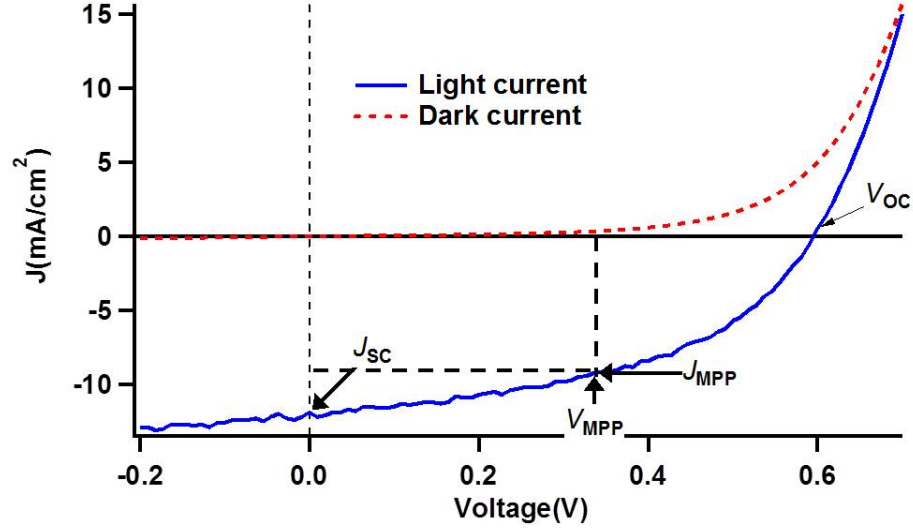


Figure 2.4: Current-voltage ($J - V$) curves of an organic solar cell (dark, - - -; illuminated, -).

the dark curve is measured in dark. From the $J - V$ curve in Figure 2.4, the characteristic intersections with the abscissa and ordinate are the V_{OC} and J_{SC} , respectively. The largest power output (P_{max}) is determined by the point where the product of voltage and current is maximized. Division of P_{max} by the product of J_{SC} and V_{OC} yields the fill factor FF [51]. Shunt resistance (R_{SH}) and series resistance (R_S) can be calculated by fitting the $J - V$ curve to the ideal diode equation (Equation 2.2). The important parameters of solar cell are explained in the following paragraph.

2.4.2 Open circuit voltage (V_{OC})

Open circuit voltage is the maximum voltage the device could deliver under illumination. This is measured under open circuit conditions, meaning there is no current drawn from the device. In organic solar cells, there are few free charges in the dark. The charge can assume to be zero. The built-in voltage comes from the difference in anode and cathode work function. Work function relates to how easy it is to remove an electron from the solid. The work functions of Aluminum and ITO

(used as electrodes for this work) are approximately 4.2 eV and 4.8 eV, respectively. The work function of Aluminum matches the LUMO of PCBM and the work function of ITO matches the HOMO of P3HT. V_{OC} is observed to be linearly dependent on the highest occupied molecular orbital (HOMO) level of donor ($E^{donor}HOMO$) and the lowest unoccupied molecular orbital (LUMO) level of acceptor ($E^{acceptor}LUMO$). The open circuit of P3HT-PCBM can be estimated by the empirical formula [47] which is

$$V_{OC} = [(\frac{1}{e}) \times (|E^{P3HT}HOMO| - |E^{PCBM}LUMO|)] - 0.3 \quad (2.3)$$

For the P3HT - PCBM BHJ device, the predicted V_{OC} is approximately 0.7 V. but this value has not been achieved and the typical value is 0.6 V. V_{OC} reflects the free charges that build up at the electrodes. If the electrodes are contacted by both *p*-type and *n*-type phases, then electrons and holes could combine and reduce V_{OC} . This is why bilayer devices sometimes exhibit higher V_{OC} than bulk heterojunctions. The OHJ design is expected to have slightly higher V_{OC} than a bulk heterojunction, since OHJ has the correct phase at each electrode.

2.4.3 Short circuit current (J_{SC})

Short circuit current is the maximum current the device can deliver when there is no applied voltage. The short circuit current in the ideal system can be represented by Equation 2.4 [51],

$$J_{SC} = ne\mu E, \quad (2.4)$$

n is density of free charges, e is charge of electron/hole, μ is carrier mobility, E is electric field strength.

J_{SC} is a function of density of charge carriers (n), elementary charge (e), mobility (μ) and electric field (E). The density of free charge carriers that are generated by sunlight (n). Sunlight creates the excitons, so the excitons must dissociate to produce free electrons and holes. So a high J_{SC} means there needs to be a large interfacial area for dissociation and interfaces should be distributed at the length scale of exciton diffusion. The carrier losses due to electron-hole recombination at the electrodes or at defects in the conduction path will minimize the J_{SC} . The mobility (μ) is a device parameter and reflects how easily charges are transported to the electrodes. Defects in the conduction path can reduce mobility. Mobility also depends on how molecules are arranged, because charge-transport in disordered organic semiconductors is very anisotropic [51]. P3HT mobility is highest perpendicular to the conjugated rings which are along the π stacks within the film. In addition, the carrier mobility is also sensitive to molecular weight and annealing conditions.

2.4.4 Fill Factor (FF)

Fill Factor is the ratio between the maximum power delivered to the power the device could potentially deliver. FF can be calculated by

$$FF = \frac{V_{MPP} \times J_{MPP}}{V_{OC} \times J_{SC}}. \quad (2.5)$$

To maximize FF , the photocurrent should increase abruptly when $V \rightarrow V_{OC}$, which means that the number of carriers reaching the electrodes should be maximized. Transport of carriers to the electrodes is primarily limited by mobility (μ), but is also determined by the strength of the electric field (E) and the carrier lifetime (τ). The carrier drift length (L_d) is a function of μ , E and τ and can be calculated by

$$L_d = \mu\tau E. \quad (2.6)$$

The mobility (μ) should be optimized. The hole mobility in P3HT is much smaller than electron mobility in PCBM so hole mobility is a limiting factor [6]. The carrier lifetime (τ) refers to how long the carrier is mobile before recombination. A direct path to the electrode helps optimize the FF by reducing the distance to the electrodes, and removing potential traps for charges. The OHJ device should have better FF because the current is routed to the correct electrode without seeing charges of the opposite sign.

2.4.5 Series Resistance (R_S)

Series Resistance is the resistance to current flow at each point in the device (across the heterojunction interface, across the electrode interface, within each phase, etc). A high series resistance will reduce J_{SC} but has no effect on V_{OC} (see Equation 2.2). In organic solar cells, the series resistance varies considerably as a function of processing [2]. The series resistance strongly impacts FF , since it affects the current through the device.

2.4.6 Shunt Resistance (R_{SH})

The current can flow in other pathways and this create shunt resistance. High shunt resistance is desired. A low shunt resistance means that the device can lose current through an undesired pathway, like a “short-circuit.” “Short” in a bulk heterojunction could result from transporting the charges to the wrong electrode. The shunt resistance can impact the V_{OC} , because if carriers do not reach the right electrode, the V_{OC} will drop. So a high shunt resistance is necessary for a high V_{OC} .

Chapter 3 Device Fabrication and Characterization

This chapter explains the principles of device fabrication, starting from the substrate fabrication, to the material processing by spin-coating, and thermal vacuum evaporation of cathode. The fabrication process of Bilayer Heterojunction, Bulk Heterojunction and Nanostructured Heterojunction are described. In the nanostructure device fabrication, the common problem is how to fill the PCBM in P3HT nanostructure. This steps were experimentally optimized and included in this chapter. Furthermore, the electronic characterization including $J - V$ curve measurement and light source calibration are also described. Finally the measurement of device active area is explained.

3.1 Materials

3.1.1 Substrates

Two substrates used for device fabrication are ITO coated glass slide and Silicon nitride. Glass microscope slides coated with 60-100 nm of indium tin oxide (ITO) and have resistance of 15-25 Ω/Sq were purchased from Sigma Aldrich. The silicon with 100 nm thickness of nitride wafer was purchased from University wafer. Silicon nitride was coated with 170 nm of ITO and has the resistance of 15 - 25 Ω/Sq by THINFILMS Inc.

3.1.2 Active layer

The donor is Poly(3-hexylthiophene) (P3HT). P3HT was purchased from Rieke Metals (90-94% regio-regular, number-average molecular weight of 30 kg/mol, polydispersity index of 1.8). P3HT was dissolved in anhydrous chlorobenzene at a concentration of 0.014 g/mL and filtered three times with a 0.2 μm Teflon mesh. The acceptor is [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was purchased from Nano C. PCBM was suspended in anhydrous dichloromethane at a concentration of 0.005 g/mL and filtered three times with a 0.2 μm Teflon mesh.

3.1.3 Electrodes

PEDOT:PSS was purchased from Baytron (product PH500, 1 wt% aqueous dispersion). The PEDOT:PSS dispersion was diluted with two parts deionized water and then filtered with a 0.45 μm glass microfiber mesh. Indium Tin Oxide (ITO) is used as the transparent anode and Aluminum (Al) as cathode. [49, 50] ITO coated glass slide were purchased from Sigma Aldrich in a form of substrate. The Al pellets (99.999% purity) were purchased from Kurt J. Lesker.

3.2 Substrate fabrication

3.2.1 ITO coated glass slide

ITO etching The ITO etching procedure is shown in Figure 3.1. The ITO coated glass slide was coated with positive tone resist S1813 with the spin rate 500 rpm for 5 seconds followed by spin rate 4000 rpm for 60 seconds to get a thickness of 1 μm and immediately baked at 115 $^{\circ}\text{C}$ for 1 minute to evaporate the solvent. The photoresist film was placed under the shallow mask and exposed by ultraviolet light

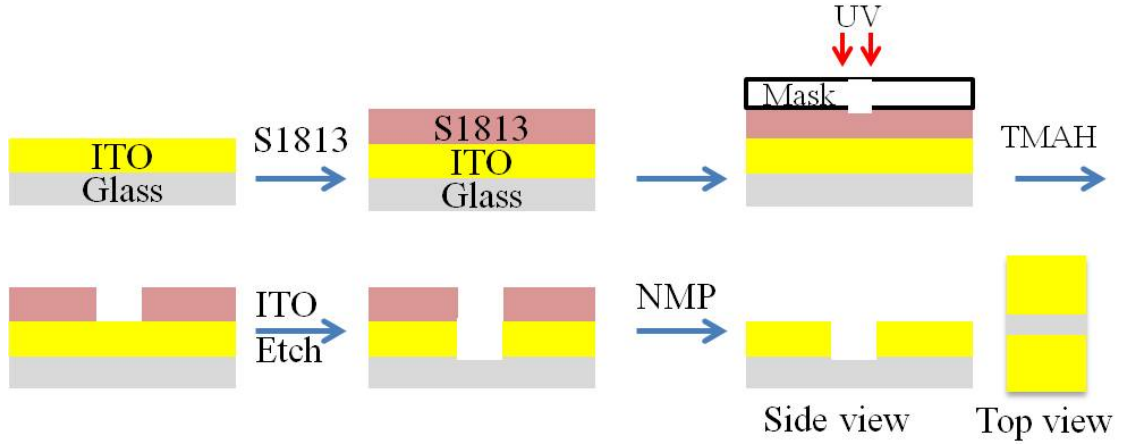


Figure 3.1: ITO etching procedure.

with dose 90 kJ/cm^2 . The exposed film was developed with tetramethylammonium hydroxide (TMAH) for 10 seconds, washed with DI water and dried with nitrogen. The patterned ITO glass slide was etched in ITO etchant which is a mixture of 20% HCl and 5% HNO_3 at 60°C for 120 seconds. The photoresist was washed away by n-methylpyrrolidone (NMP). The etched ITO coated glass will be used to make a device.

3.2.2 ITO coated membrane

Membrane fabrication Silicon nitride coated with ITO was coated with positive tone resist S1813 with the spin rate 500 rpm for 5 seconds followed by spin rate 4000 rpm for 60 seconds to get a thickness of $1 \mu\text{m}$ and immediately baked at 115°C for 1 minute. The photoresist film was placed under the mask which has the pattern shown in Figure 3.2 (a) and exposed by ultraviolet light with dose 90 kJ/cm^2 . The exposed film was developed with TMAH, washed with DI water and dried with nitrogen. The patterned film was etched to generate an opening of nitride film with Oxford Plasmalab 80 RIE Etcher. The recipe for etching was CF_4 25 sccm (standard cubic centimeters per minute) and O_2 5 sccm at pressure 60 mTorr and power 100 W

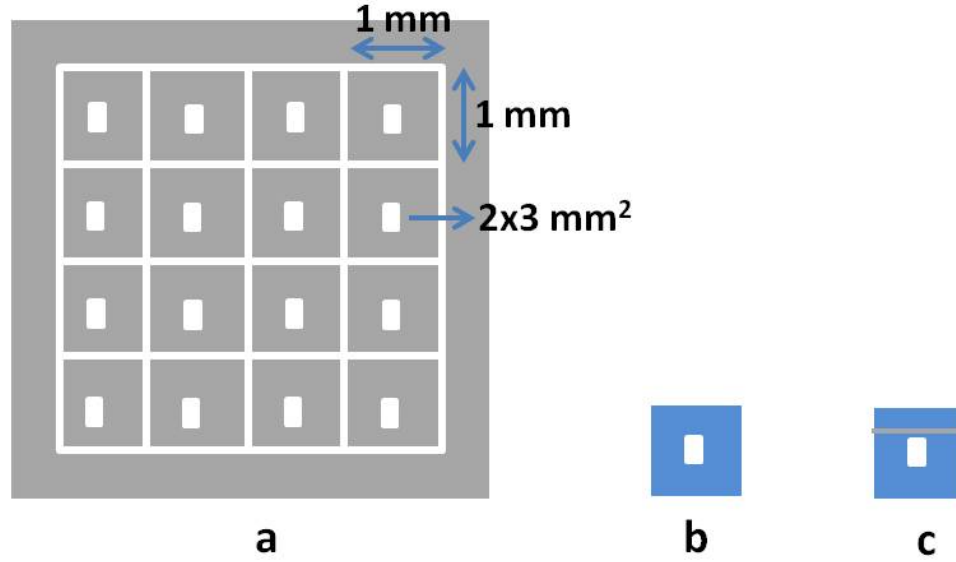


Figure 3.2: a) Mask for membrane fabrication b) ITO coated Silicon chip c) The ITO coated Silicon chip after ITO etching.

for 2 minutes. After etching the opening, photoresist was stripped off using NMP. The substrate was cleaned with DI Water and dried with Nitrogen. The silicon nitride coated with ITO was etched at temperature 60 °C by 30% KOH solution until the silicon layer is etched all the way and see the transparent nitride layer. It takes approximately 20 hours at this condition. The etched ITO coated silicon nitride was washed with DI water and dried with nitrogen before cut it into 16 chips along the groove. Figure 3.2 (b) shows the single chip that will be used for Figure 3.2 (c) shows the image of a silicon nitride chip after ITO etching which create the etch part in the middle of the membrane. The chips were etched in the same way as the ITO glass slide.

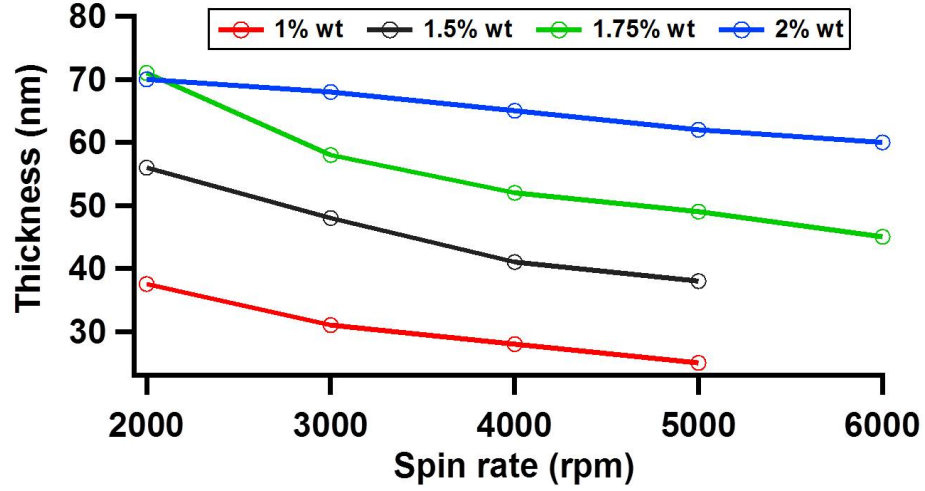


Figure 3.3: The P3HT spin curve for 1.0%wt, 1.5%wt, 1.76%wt and 2.0%wt in anhydrous chlorobenzene.

3.3 Spin curve

3.3.1 P3HT

Spin curve is a plot between the spin rate and thickness of thin film at a specific concentration. It is useful to select the spin rate and concentration for each application to get the desired thickness. In this experiment, both P3HT thickness and concentration is really important for electronic performance of the device. Before proceeding to device fabrication, the spin curve of P3HT layer is created. First, the sticking layer hexamethyldisilazane (HMDS) was spin casted on the silicon wafer substrate. P3HT at concentration of 1.0%wt, 1.5%wt, 1.76%wt and 2.0%wt in anhydrous chlorobenzene was spin casted on top of HMDS at different spin rates of 2000 rpm, 3000 rpm, 4000 rpm, 5000 rpm and 6000 rpm and acceleration of 4000 rpm². The thickness of thin film P3HT at each concentration and spin rate were measured with ellipsometry using the cauchy model to fit the data. The spin curve is shown in Figure 3.3. The film is smoother at a lower concentration and higher spin rate.

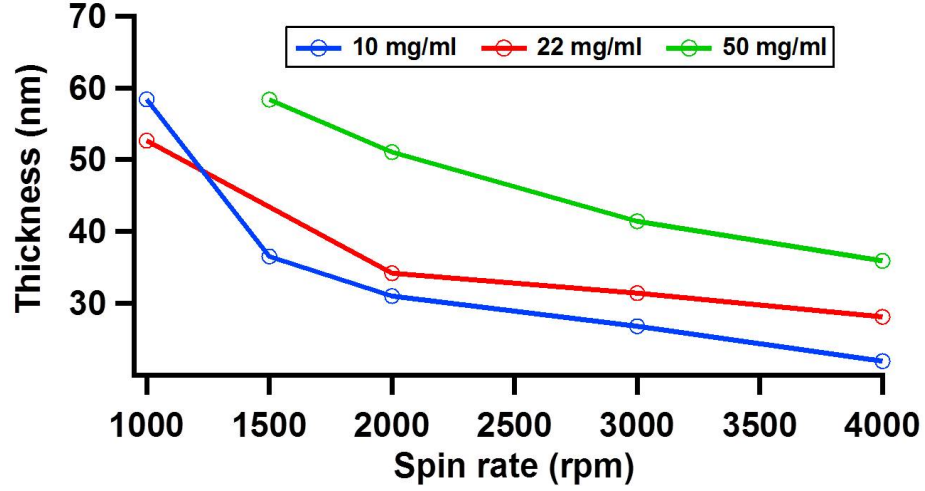


Figure 3.4: The PCBM spin curve for 10 mg/ml, 22 mg/ml and 50 mg/ml in dichloromethane (DCM).

3.3.2 PCBM

PCBM is an acceptor for the solar cell device. The efficiency of the device is also really sensitive to the thickness of active layer which composed of P3HT and PCBM [53]. The spin curve of the PCBM layer is also created. The samples were prepared by spinning different concentrations of PCBM in dichloromethane (DCM) on silicon substrate. The spin rate was varied from 2000-6000 rpm. The thin film PCBM samples were measured by AFM. Figure 3.4 is the spin curve of PCBM.

3.4 Device fabrication

3.4.1 Bilayer Heterojunction

Substrates are cleaned by sonication for 20 minutes in each of the following solutions: 2% Hellmanex II detergent, deionized water and isopropanol. Substrates are then immediately dried in a clean nitrogen stream. PEDOT:PSS films with thickness (25 ± 5) nm are spun-cast in air on top of the ITO anode, then baked for 10

minutes at 140 °C. Substrates are transferred to a nitrogen-purged glove box and the ITO/PEDOT:PSS stack is coated with a (60 ± 5) nm P3HT film. In some cases the P3HT film is pre-baked at 150 °C for 2 minutes (to remove residual solvent and promote crystallization). The active layer is built following the scheme in Figure 3.5 (a). First, samples are transferred to the electron-beam lithography instrument for cross-linking. Second, samples are transferred back to the nitrogen purged glove box for image development. Third, PCBM films with thickness (32 ± 5) nm are spun-cast on top of the patterned P3HT films. Fourth, samples are transferred to a thermal evaporator for deposition of a 100 nm thick Aluminum (Al) cathode. Lastly, samples are returned to the glove box to thermally-anneal the active layer at 170°C for up to 6 minutes. Note that samples are transferred between instruments using a portable chamber that is pressurized with nitrogen.

3.4.2 Nanostructured Heterojunction

Nanostructured heterojunctions are built with the scheme illustrated in Figure 3.5 (b), which is similar to the procedures for bilayer heterojunctions. The key steps that differ for nanostructured devices are as follows: Prior to EBL, the P3HT films are baked at 150 °C for 2 minutes. P3HT nanostructures are developed with *p*-xylene at 35 °C for 25 seconds; the developer is purged with nitrogen to displace dissolved oxygen. Nanostructures are intact after all processing steps. The conditions used to cross-link the donor in both cross-link bilayer and nanostructure devices are beam energy 30 keV and the beam current 12nA.

3.4.3 Bulk Heterojunction

BHJs are prepared with the same anode and cathode as bilayer or nanostructured devices. The only step that differs is the casting of the active layer. Figure 3.5 (c)

illustrates the BHJ device fabrication process. P3HT and PCBM are dissolved in a 1:1 ratio (weight basis) in anhydrous chlorobenzene (concentration of 0.01 g/mL). The solution is filtered three times with a 0.2 μm Teflon mesh, and then a 100 nm thick film is spun-cast on top of the PEDOT:PSS/ITO anode.

3.4.4 Thermal vacuum deposition

Thermal vacuum deposition is the most commonly used method for depositing electrodes on organic photovoltaics. The process is based on the sublimation of a compound from a resistively heated boat or crucible in vacuum reaching from 10^{-6} mbar to 10^{-10} mbar onto a substrate [54]. A schematic picture of an evaporation chamber is depicted in Figure 3.6. The sources are located below the substrate to prevent dust from falling onto the substrate surface. The source materials are held in the boat. The deposition rate is controlled by the source temperature. Typical rates are 10 $\text{\AA}/\text{second}$ to 20 $\text{\AA}/\text{second}$. The shutter is used to control the evaporated film thicknesses. Quartz crystals are used to monitor the actual deposition rate and film thickness. The aluminum cathode of the all devices in this work are evaporated by this technique. The complete device is shown in Figure 3.18 (a).

3.5 Coating PCBM on P3HT nanostructure

The common problem to fabricate ordered heterojunction device is how to fill PCBM in P3HT nanostructure. The goal of this section shown in Figure 3.7 is to find the method to completely coat PCBM on P3HT nanostructure. The dimension of P3HT nanostructure for the device fabrication shown in Figure 3.8 are approximately 148 nm in width, 37.5 nm in height and 400 nm in pitch for line pattern (Figure 3.8 (a)) and 103 nm in diameter, 45 nm in height and 400 nm in pitch for dot pattern (Figure 3.8 (b)). A number of methods were used here.

3.5.1 Spin Coat

The basic technique to coat the thin film is spin coat method. The thickness of the thin film is determined by the concentration of the solution and the spin rate. We initially started with spin coat method at a rotation frequency of 3000 rpm, acceleration 300 rpm². The line and the dot pattern are shown in Figure 3.9 (a) and (b), respectively. The images show that this method can not completely coat the pattern but it fill approximately 20 nm.

3.5.2 Double Coat

We coated the P3HT twice with 0.5% PCBM in DCM. First, the patterns were coated at spin rate 3000 rpm which coated about 20 nm and coat again with the spin rate 1000 rpm. The AFM images of line and dot pattern are shown in Figure 3.10 (a) and (b), respectively. The second coat filled about 10 nm more which still cannot completely cover the pattern.

3.5.3 Capillary Force

Capillary force is the ability of a liquid to flow to narrow spaces without the assistance of, and in opposition to external force like gravity. The set up of this method is shown in Figure 3.11 (a). First, PCBM in DCM solution were dropped on teflon (PTFE) surface. Second, P3HT patterns were put on top of PCBM solution and force were applied on P3HT pattern to make sure that patterns were in touch with PCBM solution. Third, the P3HT patterns were lift off when the solution is dried. Figure 3.11 (a) and (b) show the AFM images of line and dot pattern, respectively after applied capillary force method. Both pattern are not covered.

3.5.4 Drop cast method

Drop cast is the technique to coat the film on the sample. This method generate the thicker film than spin coating. The solution was dropped on top of the sample and dried in a nitrogen environment (glove box environment). Figure 3.12 (a) and (b) are AFM images of the line and dot pattern, respectively after drop cast 0.5% PCBM in DCM. The patterns were covered with PCBM so this method has the possibility to coat the nanopattern. The PCBM film on the pattern shown in Figure 3.12 (c) is really thick, rough and dirty. The thickness of PCBM was around 750 nm which is too thick for the application of solar cell. The dimension of the line and dot pattern were around 40 nm so the optimum thickness of PCBM should be around 60 nm. To reduce the thickness by this method, the concentration, volume were controlled.

3.5.5 Drop cast at slow spin rate and double coat

The drop cast method generate thick, rough and dirty film. To get the thinner and smoother film, the drop cast on the spinner at spin rate 100 rpm was applied. The concentration of PCBM was reduced to 0.125 % to get the thinner film. The AFM image in Figure 3.13 (a) and Figure 3.14 (a) show the line and dot pattern after coated with 0.125% PCBM in DCM by spin coat at 100 rpm. Both patterns were not completely covered so we coated the patterns again with the same method. The line pattern (Figure 3.13 (b) and dot pattern (Figure 3.14 (b)) were still not completely covered with PCBM. The second time coated around 5 nm of PCBM on the patterns.

To get the thicker film to cover the patterns, the concentration of PCBM in DCM was increased to 0.25%wt. We drop cast the solution at spin rate 200 rpm. Figure 3.15 (a) and (b) show the line and dot pattern, respectively after coated with PCBM. The patterns were almost completely covered and smooth. We used this method to

Table 3.1: Electronic performance of P3HT/PCBM solar cells after 4 minutes annealing at 170°C. of bilayer, nanoline and nanopillar with 400 nm pitch.

Design	Dose ($\mu\text{C}/\text{cm}^2$)	Developer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
Bilayer	0	N/A	0.56 ± 0.04	5.10 ± 0.31	0.46 ± 0.03	1.33 ± 0.08
Nanoline	450	C_8H_{10}	0.53 ± 0.02	0.82 ± 0.16	0.30 ± 0.01	0.13 ± 0.03
Nanopillar	450	C_8H_{10}	0.63 ± 0.01	0.87 ± 0.12	0.32 ± 0	0.17 ± 0.01

fabricate the device and compared the efficiency with usual spin coat method. The efficiency decrease 35 % for bilayers (from 2% to 1.35%) and 50 % (from 0.30% to 0.15%) for nanoline devices that fabricate from spin coat method. One possibility that reduce the efficiency is the thick PCBM film which reduces the electron transport to electrode. Although this method can coated the pattern, the efficiency of devices dramatically decrease. This method is not good to fabricate the devices.

3.5.6 Spin cast with high concentration

The drop cast and spin cast at low spin rate (100 rpm or 200 rpm) give the low efficiency devices. The concentration of PCBM is increased from 0.5%wt to 1.0 %wt and the spin rate is decreased from 3000 rpm to 1000 rpm to get the thick and smooth film with spin cast method. Figure 3.16 (a) and (b) show the line and dot patterns, respectively, after spin cast 1% PCBM in DCM at spin rate 1000 rpm. The patterns were almost covered and the film was smooth.

The concentration was increased to 1.5%wt PCBM in DCM. The PCBM solution was coated at 1000 rpm. Figure 3.17 (a) and (b) show the line and dot pattern after spin coated. The P3HT pattern was covered with PCBM but the patterns can be seen. The film was not smooth along the surface and this make the high variation of PCBM thickness.

We fabricated the bilayer and nanopillar device with 1 % and 1.5 % PCBM in

Table 3.2: Electronic performance of P3HT/PCBM solar cells after 4 minutes annealing at 170°C. of bilayer and nanopillar. The P3HT were coated with 1% and 1.5% PCBM in DCM.

Design	PCBM (%wt)	Dose ($\mu\text{C}/\text{cm}^2$)	Developer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Bilayer	1%	0	N/A	0.55	6.72	0.48	1.80
Nanopillar	1%	450	C_8H_{10}	0.58	0.92	0.34	0.18
Bilayer	1.5%	0	N/A	0.60	4.71	0.48	1.35
Nanopillar	1.5%	450	C_8H_{10}	0.59	1.31	0.34	0.27

DCM by spin cast at 1000 rpm. Table 3.2 concludes the efficiency of the bilayer and nanopillar device after 4 minutes of thermal annealing. The efficiency of devices fabricated from 1.5%wt PCBM by spin cast at 1000 rpm are comparable to the device with the usual method which is spin cast 0.5%wt PCBM at 3000 rpm. The efficiency of devices from 1%wt PCBM are lower than 1.5%. The lower efficiency in device fabricated from 1%wt PCBM can be explained by less amount of PCBM and it is not enough to cover the P3HT pattern.

3.5.7 Conclusions

The usual problem in fabricating OHJ device is coating P3HT nanostructure with PCBM. Several methods which are capillary force, drop casting, spin casting and increasing PCBM concentration have been studied. The possible method to coat PCBM on P3HT nanostructure are drop casting at slow spin rate and increasing the PCBM concentration. The drop casting at slow spin rate generate the dirty, rough and thick film and these factors decrease the efficiency of the device so this is not a good way to fabricate the devices. Coating the P3HT with 1.5%wt PCBM can coat the nanostructure and the efficiency of the devices are comparable to the usual method so this method will be used to fabricate the future device.

3.6 Electronic Characterization

3.6.1 Light source calibration

The lamp power is calibrated to 100 mW/cm² using a silicon reference solar cell equipped with KG5 filter (certified by the National Renewable Energy Laboratory, VLSI Standards) [55]. First, the lamp is focused and all of the probes from the source meter are connected to the reference cell. Second, the lamp power is set to 100 mW/cm² and current-voltage characteristic curve is measured. Third, the lamp power is adjusted accordingly to get the V_{OC} and J_{SC} equal to certified value at the lamp power of 100 mW/cm². The certified value for this reference cell are 0.49 mA/cm² for J_{SC} and 0.59 V for V_{OC} .

3.6.2 Current-voltage curve measurement

The sketch of the top and side view of the completed solar cell device is shown in Figure 3.18 (a) and Figure 3.18 (c), respectively. The ITO in the middle of the device is etched to separate the electrode. The active layer (pink) of the devices are partly wiped off to generate the contact between the measurement probes and the electrode. Anhydrous chlorobenzene is used to remove the active layer and ethanol is used to remove PEDOT:PSS layer. The devices were fixed into the base and the four probes were in contact with the device electrodes. Figure 3.18 (b) shows the probes position on solar cell device. The probes on the top part of the device are for ITO anode and the probes on the bottom part of the device are for Al cathode. All electronic measurements are conducted in a nitrogen-purged glove box at 28 °C. Devices are illuminated with a 150 W solar simulator (Oriel) equipped with an air mass 1.5 global filter. The lamp power is calibrated to 100 mW/cm². Current-voltage

characteristics are recorded with a Keithley 2601A source meter.

3.7 Measurement of active area

After electronic characterization, the devices were taken off from glove box to measure the active area. The device active area is determined from the cathode area that have the active layer underneath. The sketch in Figure 3.18 (b) shows the active area of the device. The active area of the actual device is measured by a Nikon Eclipse LV100 optical microscope (bright-field optics) with 2.5 magnification. Figure 3.19 is the optical image of cross-linked bilayer device. The measured active area for this device is 4.51 cm².

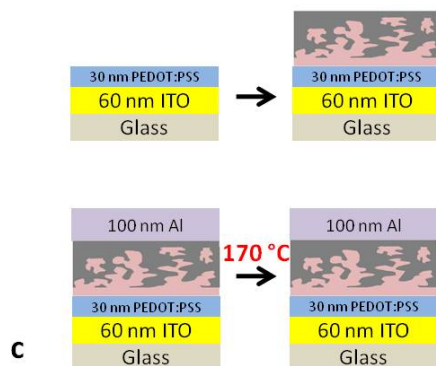
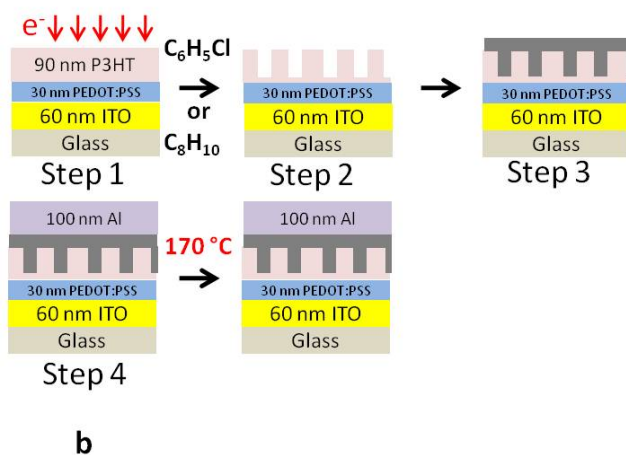
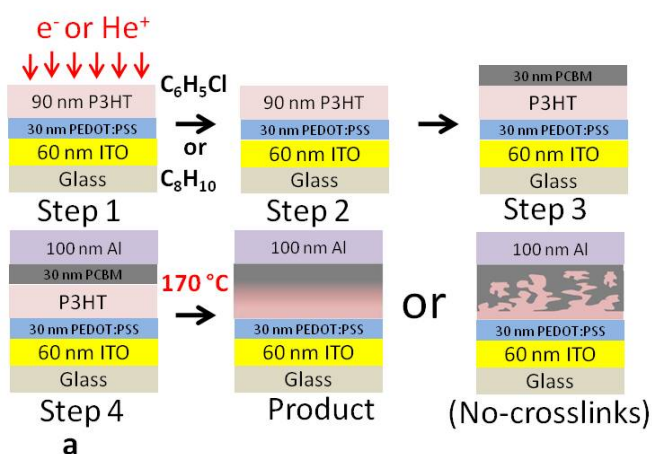


Figure 3.5: (a) Bilayer Heterojunction Device Fabrication; (b) Nanos-structured Heterojunction Device Fabrication; (c) Bulk Heterojunction Device Fabrication.

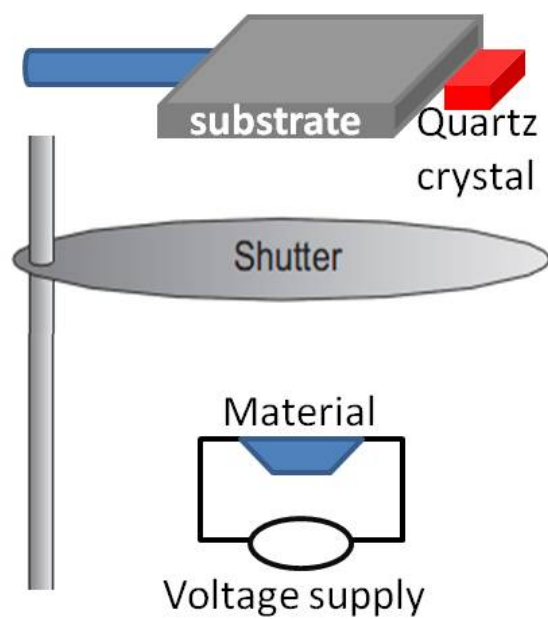


Figure 3.6: Schematic picture of an evaporation chamber.

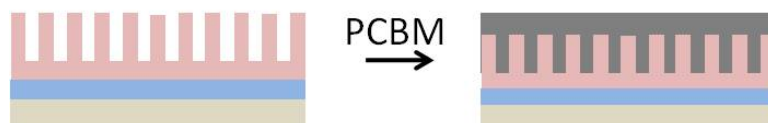


Figure 3.7: Filling PCBM in P3HT nanostructure.

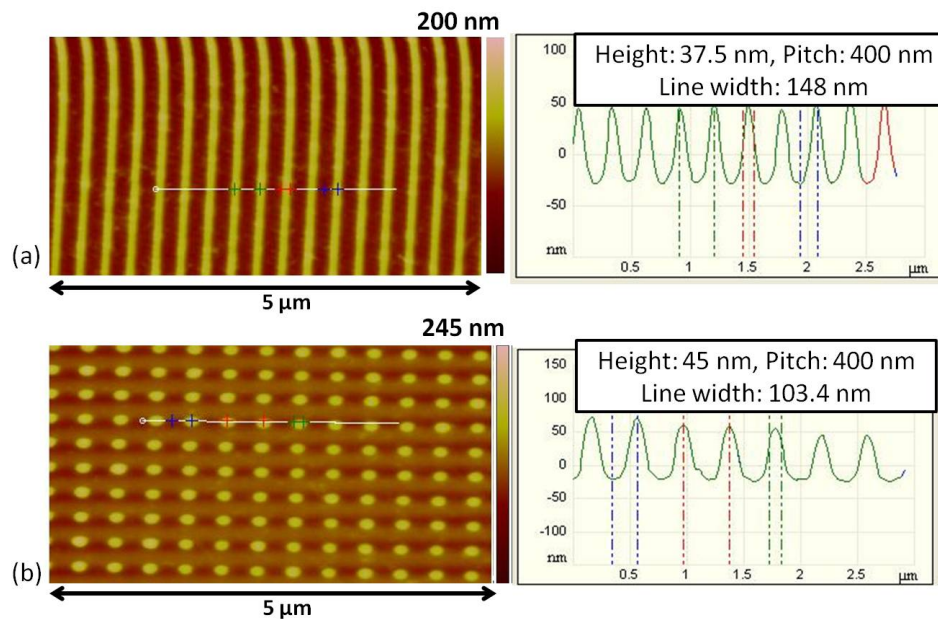


Figure 3.8: AFM images of (a) Line pattern on P3HT for the device fabrication (b) Dot pattern on P3HT for the device fabrication.

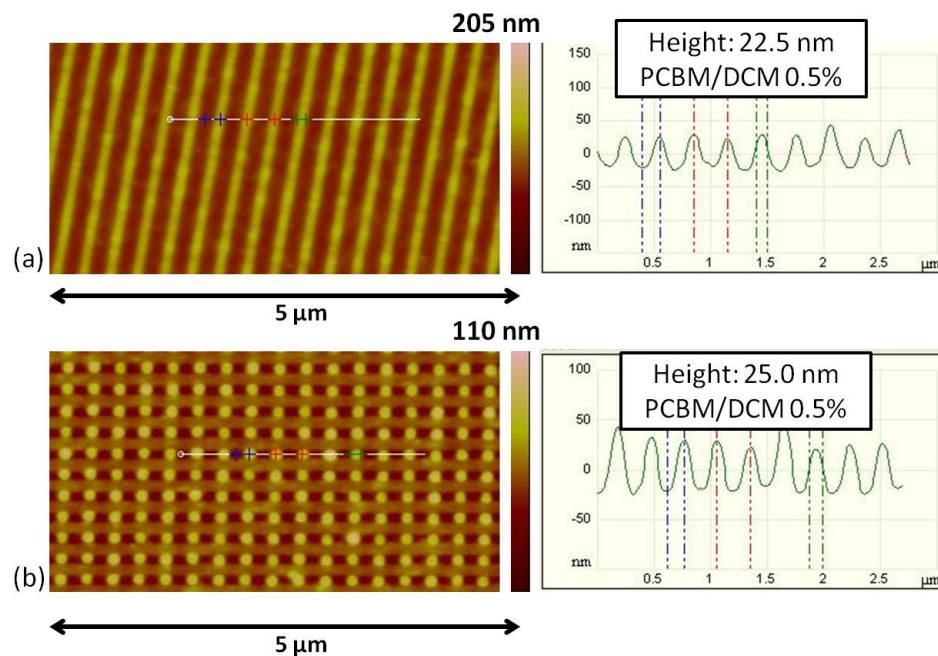


Figure 3.9: (a) AFM image of line pattern after spin coat with 0.5% PCBM in DCM at spin rate 3000 rpm (b) AFM image of dot pattern after spin coat with 0.5% PCBM in DCM at spin rate 3000 rpm.

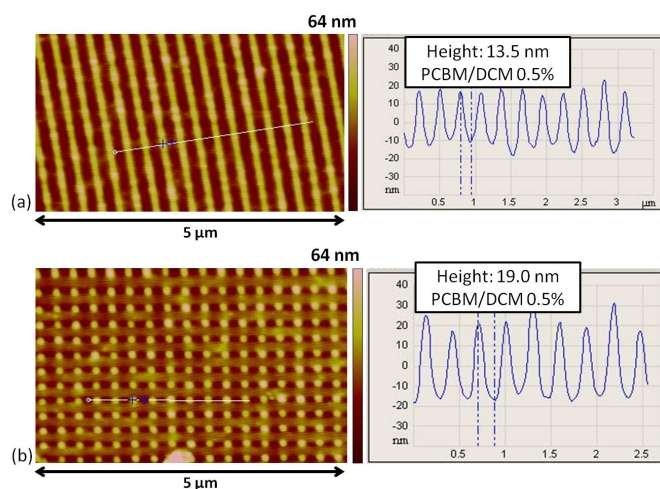


Figure 3.10: (a) AFM image of line pattern after spin coat with 0.5% PCBM in DCM at spin rate 3000 rpm and 1000 rpm (b) AFM image of dot pattern after spin coat with 0.5% PCBM in DCM at spin rate 3000 rpm and 1000 rpm.

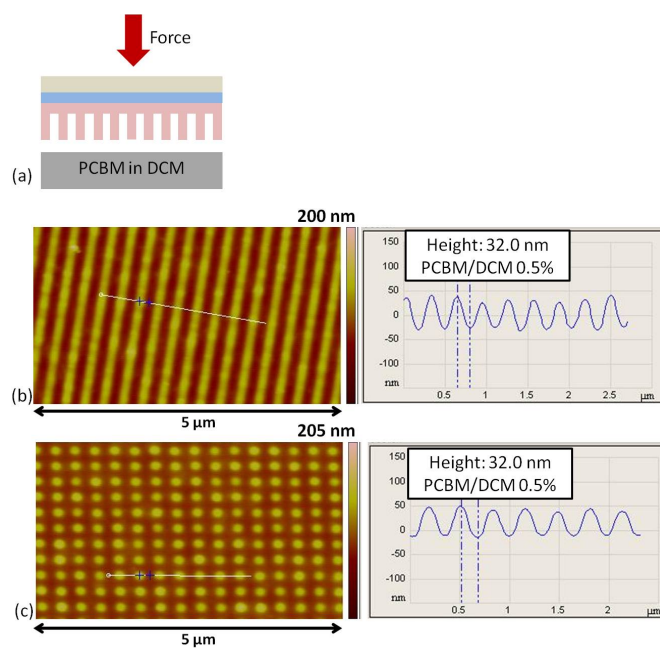


Figure 3.11: a) The set up of experiment for capillary force method (b) Line pattern after coated with 0.5%wt PCBM in DCM with capillary force method (c) Dot pattern after coated with 0.5%wt PCBM in DCM with capillary force method.

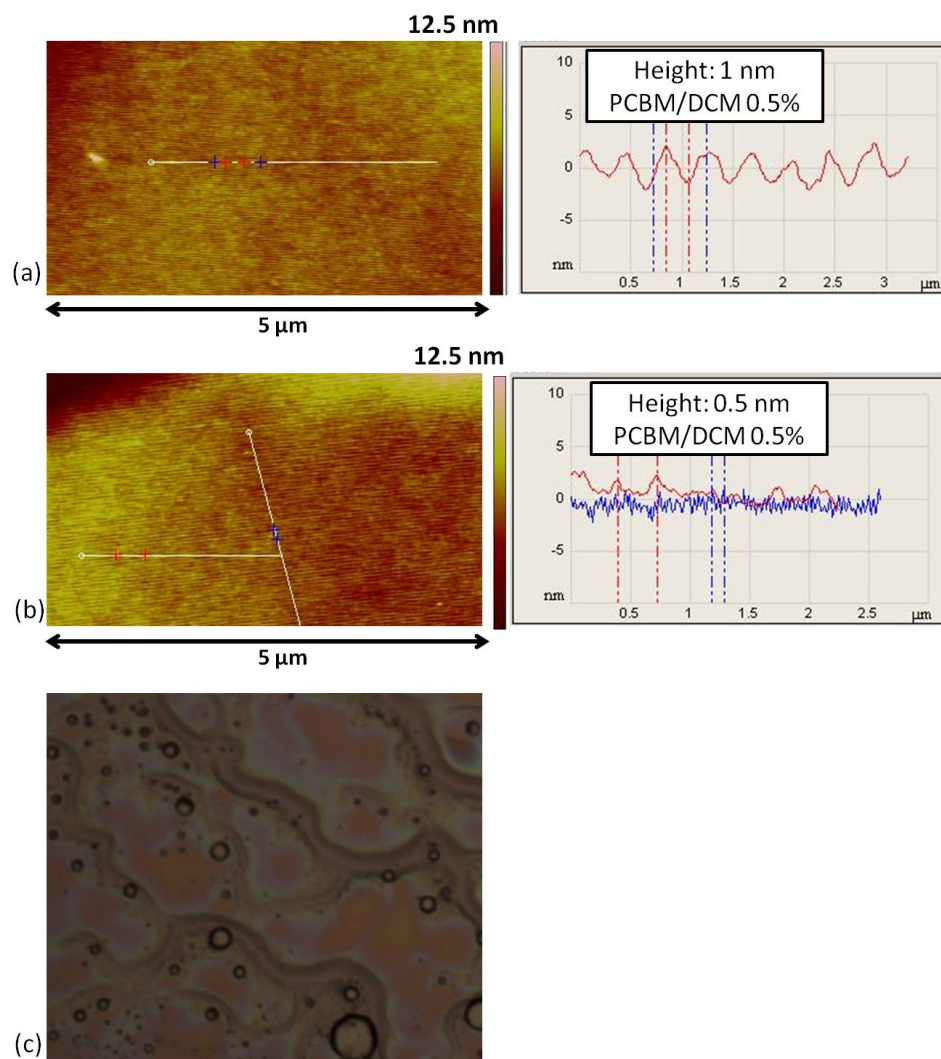


Figure 3.12: (a) Line pattern after coated PCBM in DCM with drop cast method (b) Dot pattern after coated with 0.5%wt PCBM in DCM with drop cast method (c) PCBM film after drop cast method.

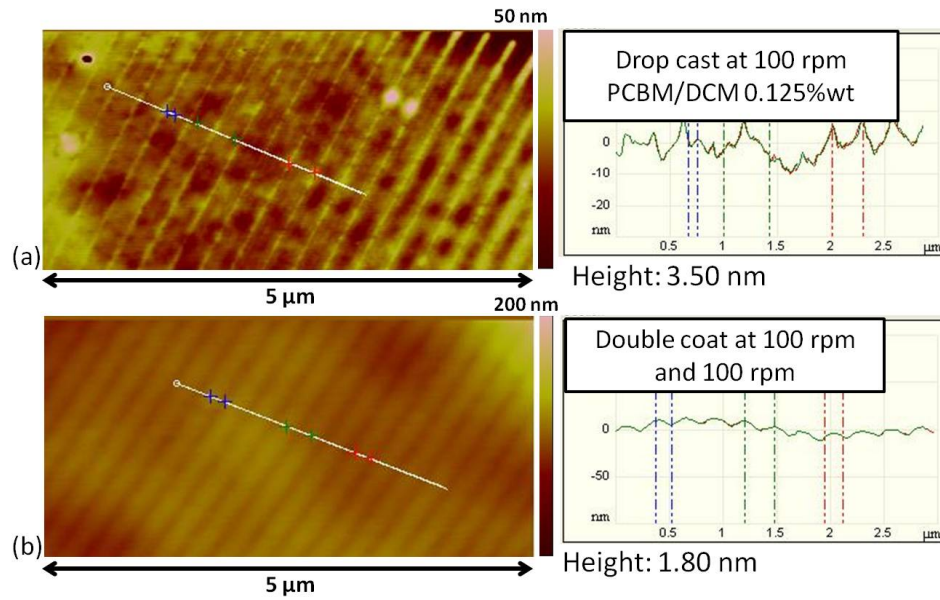


Figure 3.13: (a) AFM image of line pattern after spin coat at 100 rpm with 0.125%wt PCBM in DCM (b) AFM image of line pattern after spin coat with 0.125%wt PCBM in DCM twice.

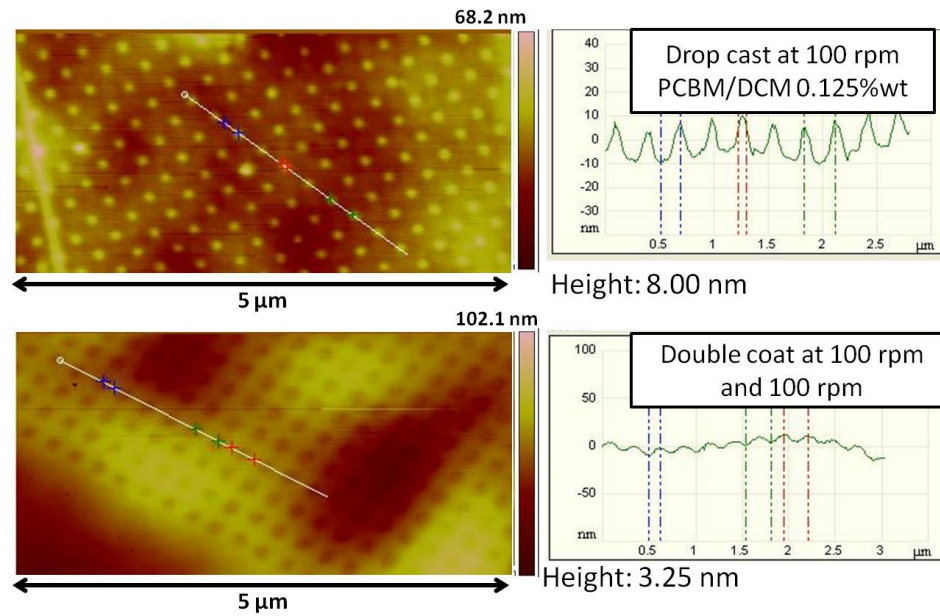


Figure 3.14: (a) AFM image of dot pattern after spin coat at 100 rpm with 0.125%wt PCBM in DCM (b) AFM image of dot pattern after spin coat with 0.125%wt PCBM in DCM twice.

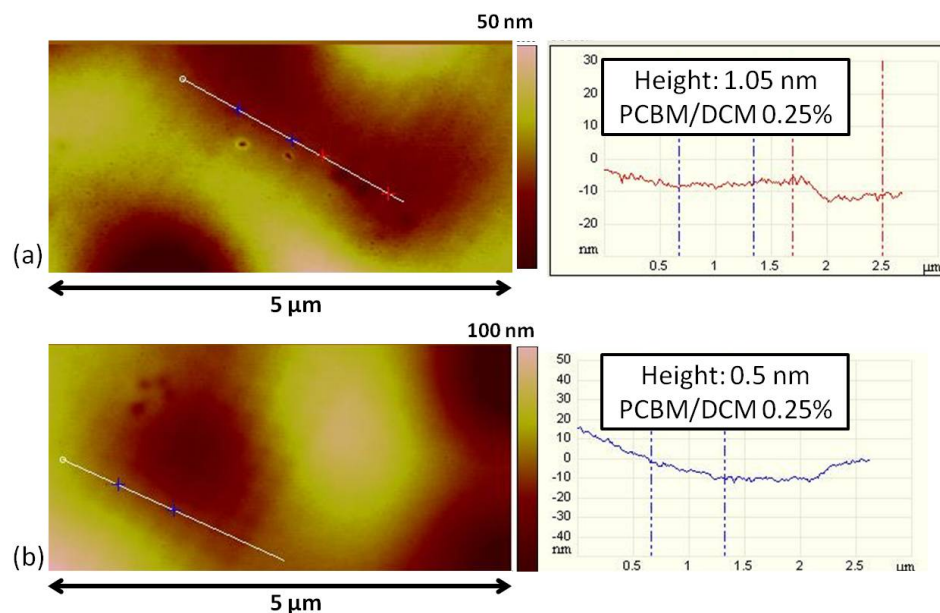


Figure 3.15: (a) AFM image of line pattern after spin coat at 200 rpm with 0.25%wt PCBM in DCM (b) AFM image of dot pattern after spin coat with 0.25%wt PCBM in DCM.

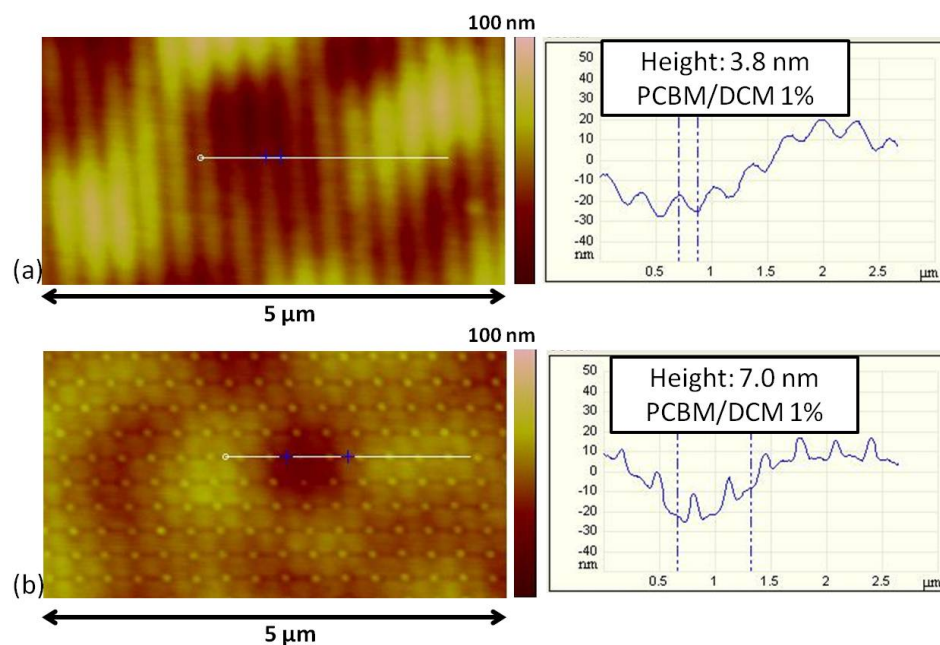


Figure 3.16: (a) AFM image of line pattern after spin coat at 1000 rpm with 1%wt PCBM in DCM (b) AFM image of dot pattern after spin coat at 1000 rpm with 1%wt PCBM in DCM.

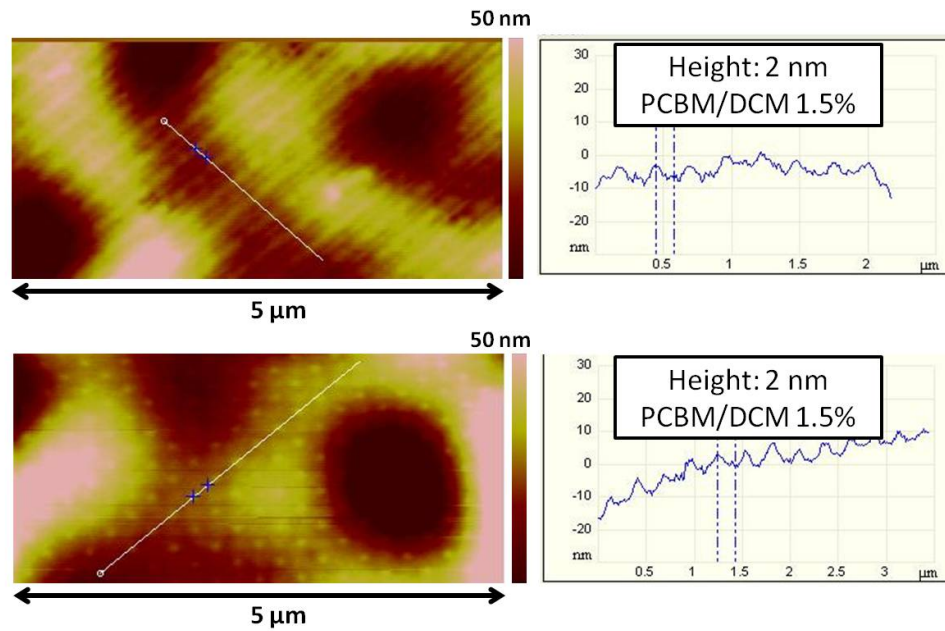


Figure 3.17: (a) AFM image of line pattern after spin coat at 1000 rpm with 1.5%wt PCBM in DCM (b) AFM image of dot pattern after spin coat at 1000 rpm with 1.5%wt PCBM in DCM.

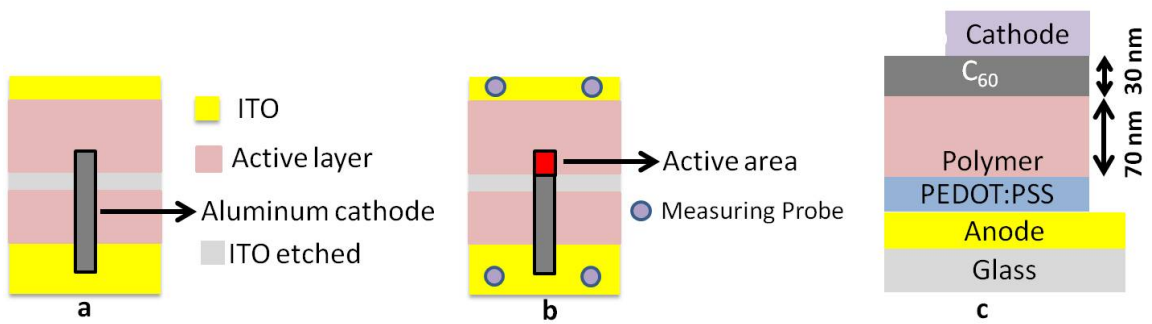


Figure 3.18: a) Solar cell device b) Solar cell device measurement c) Side view of solar cell device.

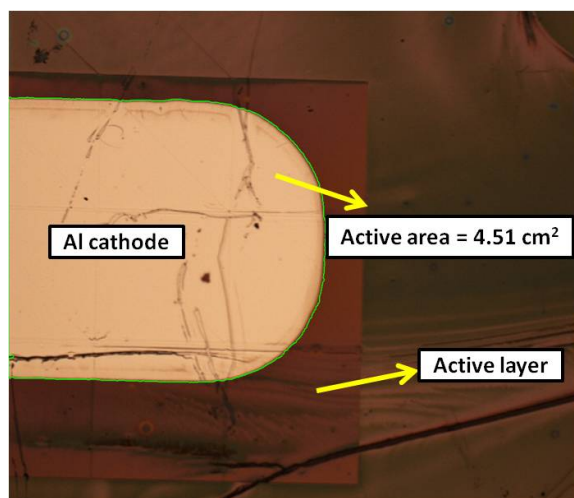


Figure 3.19: Optical image of active area for cross-link bilayer device.

Chapter 4 Introduction to Lithography Principle

In this chapter, the lithography techniques used in solar cell fabrication and directed dewetting of polymer thin films are reviewed. The photolithography technique is used for both solar cell and directed dewetting of polymer thin film projects to transfer the pattern to the substrate. The Electron Beam Lithography (EBL) technique is used to control the morphology of the solar cell active layer. There are two instruments used for EBL which are Scanning Electron Microscope (SEM) equipped with Nanometer Pattern Generation System (NPGS) and JBX 5500 e-beam writer. The sensitivity and resolution of the EBL technique with both SEM and JBX 5500 e-beam writer are described. The patterning conditions for the devices fabrication were optimized and included. In addition to the EBL technique, the Ion Beam Lithography technique was used to cross-link the active layer of the solar cell. The P3HT polymer is more sensitive to the ion beam so this process can cross-link a large area of polymer in a short period of time. The sensitivity of Ion Beam Lithography technique is explained.

4.1 Photolithography

The photolithography technique is mainly used in the microelectronics industry because it provides both resolution and high throughput. This technique is used to transfer the pattern from the mask onto a substrate coated with photoresist. Figure 4.1 shows the mask replication process with an imaging lens. The light passed through the condenser, mask, imaging lens and was exposed to the photoresist generating the latent image. The relief image is produced after development. The pattern on the photoresist can be transferred to the substrate by a subsequent process such as etching, lift off, or ion implantation. There are different ways to transfer the pattern from the mask to the resist which are contact printing, proximity printing

and projection lithography. All of the photolithography steps in this work use contact printing which means the mask directly contacts the photoresist. This will damage the mask if it is used many times. So this method is not used for industry but mainly used in university research. The contact aligner shown in Figure 4.2 has broadband light ($\lambda = 436, 405$ and 365 nm). The intensity of the lamp is constant so the dose is controlled by exposure time. The joystick is used to align the substrate with mask. The microscope is used to see the mask and substrate during the alignment. Proximity printing is the print that has a small gap between the photo mask and the sample. This method creates no damage for the mask but creates a blur on the pattern image. The projection lithography uses the lens to project the image. There is no damage to the mask and it creates minimal blur. This method is mainly used in the microfabrication industry. The resolution limit (R_{min}) is given by

$$R_{min} = \frac{k_1 \times \lambda}{NA}, \quad (4.1)$$

where λ = wavelength of light source, k_1 = process parameter, NA = numerical aperture of the optics. Basically, for high resolution printing, k_1 and λ need to be small. The shortest wavelength of the light source being used in industry is Argon fluoride (193nm). The process parameter (k_1) depends on the instrument and materials. Numerical aperture is the property of the optic lens which is preferred to be large for high resolution printing.

4.1.1 Photoresist

Photoresists are light sensitive materials. The chemical structure and property change upon light exposure. Figure 4.3 shows the process flow diagram for photolithography and illustrate the positive and negative tone resist. The following steps

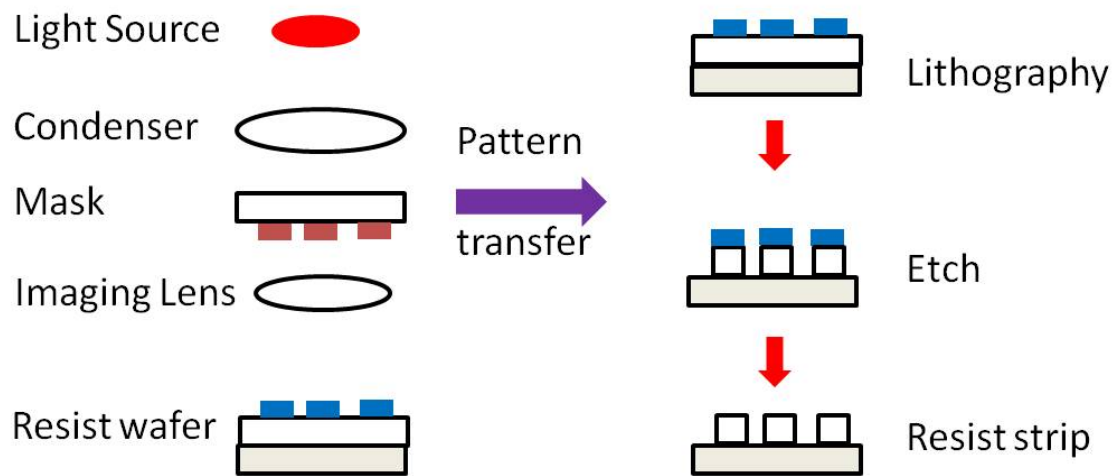


Figure 4.1: Optical lithography replicate the mask pattern through the imaging lens and a pattern transfer to substrate.

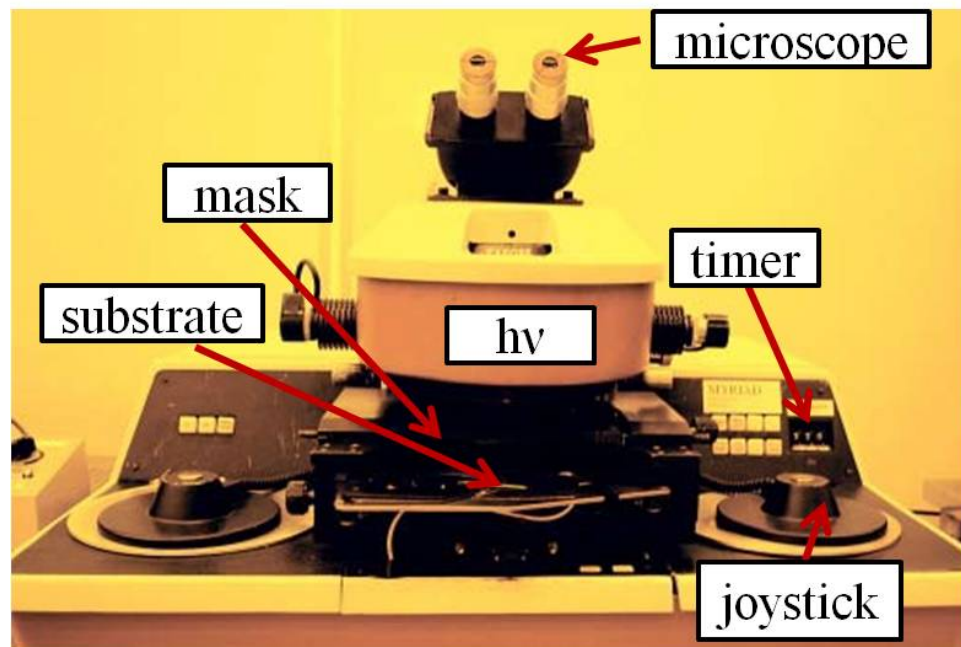


Figure 4.2: Contact aligner for contact printing lithography.

are applied to use the photoresist.

- Spin coating the resist on the substrate: The film thickness is determined by spin speed and resist concentration, and solvent type.
- Bake after coating: The objective of this step is to evaporate the solvent out of the resist film.
- Exposure: Exposure will change the resist chemistry
- Post exposure bake: This step depends on the type of the resist. Some resist requires this step to trigger the deprotection reaction.
- Development: This step will wash away the soluble part of the resist after exposure so the latent image appears. For negative tone resist, the exposed resist will intact with the substrate and the non-exposure part will be washed away. Conversely for positive tone resist, the exposure part will be more soluble and washed away.

The resist that is mainly used for this work is S1813 which is a positive tone resist. The developer for S1813 is aqueous tetramethylammonium hydroxide (TMAH), 0.26N concentration.

4.1.2 Resist contrast

Contrast in lithography is estimated by plotting the normalized residual film thickness as a function of the logarithmic exposure dose, the slope of this semilog plot is defined as a contrast (γ) which can be calculated by,

$$\gamma = |\log(\frac{D_2}{D_1})|^{-1}, \quad (4.2)$$

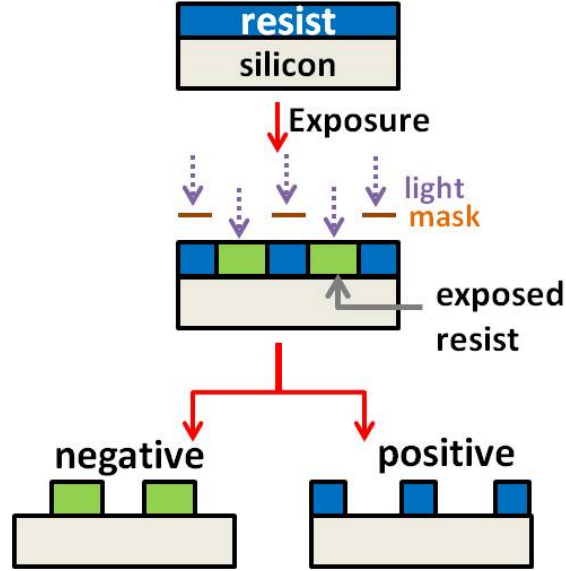


Figure 4.3: The process flow diagram for photolithography with positive and negative tone resist. S-1813 is positive tone.

where D_1 is the largest dose at which no film is lost (actually, the extrapolation of the linear portion of Figure 4.4 to 100%) and D_2 is the dose at which all of the film is lost (again, actually the extrapolation of the linear portion of Figure 4.4). The higher contrast is preferred to get the sharp pattern with minimal blur. Figure 4.4 (a) and (b) show a typical logarithmic response or contrast plot for positive and negative resists, respectively.

4.2 Electron Beam Lithography

It has been recognized since the early 1970's that a focused beam of electrons can be accelerated at a resist surface to produce very high resolution patterns since the wavelength of electrons are three orders of magnitude smaller than ultraviolet photons [56]. The calculated wavelength of the electrons that have an energy of 30 keV by de Broglie wavelength equation is 0.0071 nm. EBL is used for photomask production, imprint template manufacturing and device prototyping. The advantages

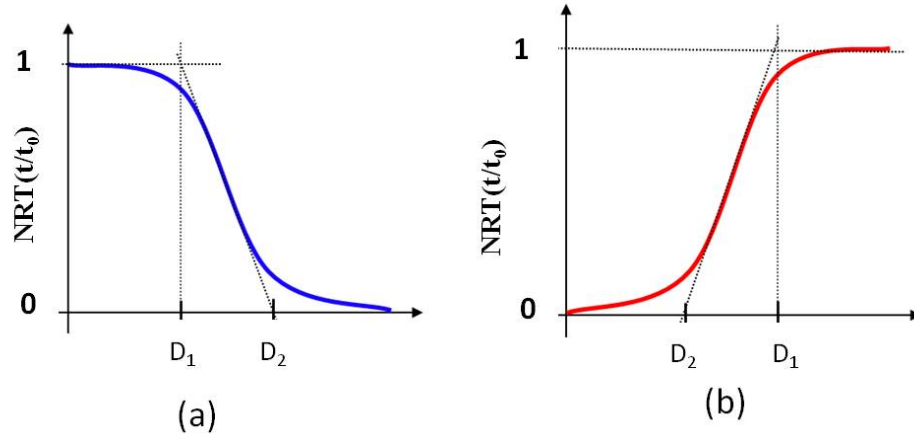


Figure 4.4: Typical logarithmic response or contrast plot for (a) positive resists and (b) negative resists.

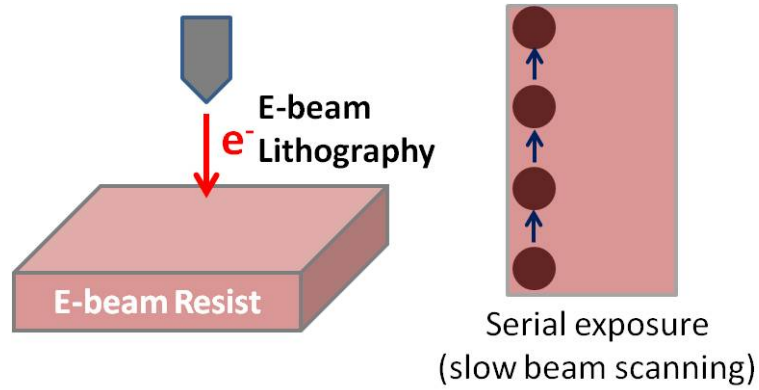


Figure 4.5: Electron Beam Lithography.

of EBL are high resolution (sub 10nm), mask less, and capital cost is much cheaper than an optical stepper. The major disadvantage of EBL is the slow speed so this system is not appropriate for manufacturing. Figure 4.5 illustrates the EBL system. The slow speed is due to the point by point exposure.

4.2.1 Scanning Electron Microscope

The EBL system is ideal for patterning small area devices with nanometer resolution. This work was done by a 30 keV electron beam using a FEI XL-30FEG field

emission scanning electron microscope (SEM) equipped with a 5 MHz Nanometer Pattern Generation System (NPGS) [31]. Exposures are implemented with a square grid based on a 30 nm pixel size. In this EBL system, the beam spot size depends on acceleration voltage and beam current. Figure 4.6 shows a schematic of SEM. Electrons are generated from heating the filament cathode and emitted from the electron gun as high energy electrons. These electrons travel downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. At the bottom end of the column, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. SEM is controlled externally through NPGS which directs a tightly focused electron beam to the desired locations on the resist surface by deflecting and tuning the beam on and off according to the pattern.

This SEM system does not have dynamic focus correction so the resolution of the pattern depends on the focus and the flatness of the samples. Other factors that control the resolution are type of resist, resist thickness, exposure dosage, the beam current level, proximity effect (electron scattering) and the development process.

4.2.2 Electron beam writer

The JBX 5500 e-beam writer is a new instrument in facility. In the future, this instrument will mostly be used for patterning because this system operates at higher voltage ($V_{max} = 50$ kV) which produces more uniform exposures. In addition the JBX 5500 e-beam writer has dynamic focus correction which will generate the high resolution feature. This instrument can resolve the line width of 10 nm.

4.2.3 Electron Beam Resist

As the incident electrons interact with the sample, the latent image is generated. Latent image formation in the electron beam processes are most commonly

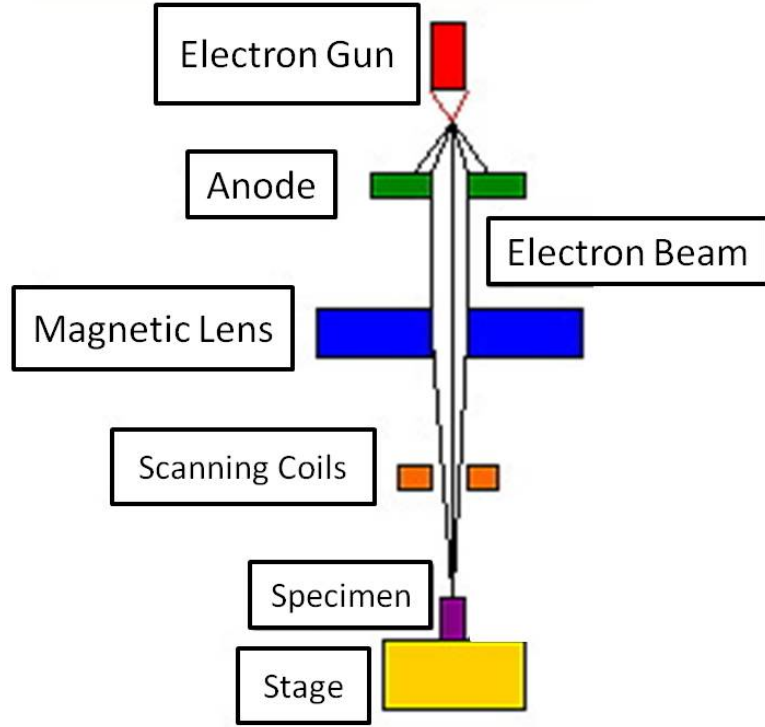


Figure 4.6: Schematic diagram of Scanning Electron Microscope.

realized through chain scission that causes fragmentation of high molecular weight polymer into smaller chains (positive tone resist). In the opposite case, a latent image is formed by cross-linking the exposed polymer (negative tone resist). Therefore, distinction between exposed and unexposed regions in both case is obtained by modifying molecular weight distributions within the patterning film. The latent image can be developed into a relief pattern in an organic solvent due to the different solubility in exposed and unexposed regions. The mechanism of positive and negative tone resist when exposed to the electron beam and after the developing process as illustrated in Figure 4.7 [57].

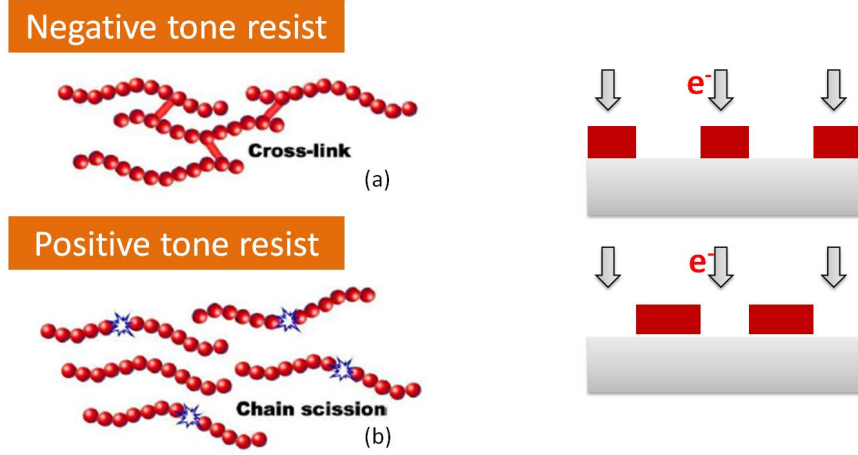


Figure 4.7: The mechanism of positive and negative tone electron beam resist: [57].

4.2.4 Resolution

Theoretically, the resolution limit of an electron beam lithography system is defined by the diffraction of electrons. For the Gaussian beam system the beam diameter d is defined by [58],

$$d^2 = \left[\frac{i}{B} + (1.22\lambda)^2 \right] \frac{1}{\alpha^2} + (0.5C_s)^2 \alpha^6 + \left(\frac{\Delta E}{E_0} C_c \right)^2 \alpha^2, \quad (4.3)$$

where i is a beam current, B is a brightness of an electron source, α is the convergence half-angle of an electron beam, C_s , C_c are the spherical and chromatic aberration coefficients of the final lens, and E_0 and ΔE are the average energy and the energy spread of the electrons in the beam accordingly.

Practically, the resolution is not limited by beam diameter. Other factors such as forward scattering, backscattering, beam focus, and the resist chemistry will ultimately determine the resolution.

4.2.5 Proximity effect

When primary electrons interact with the sample, they slow down and energy is dissipated in the form of secondary electrons. Secondary electrons undergo small angle scattering which are responsible for most of the exposure. Since secondary electrons do not have enough energy to travel very far, they contribute to the effective spreading of the electron path along with the forward scattering of the primary electron. However, some of the primary electrons can penetrate the resist and collide with the nucleus of the substrate atom. Since the nucleus is heavier, the scattering event is mostly elastic and results in a large scattering angle. This type of scattering is called back scattering which generate the backscattering electron. The backscattering electron returns at a distance significantly far away from the incident beam, and leads to additional exposure in the resist. The combination of forward scattering and backscattering make the exposure area larger than the scan area and this effect is called proximity effect [59]. Figure 4.8 illustrates the forward and backscattering which generate the proximity effect. The proximity effect can be modeled with the double Gaussian function [60] which is

$$f(r) = \frac{1}{\pi(1 + \eta)} \left[\frac{1}{\alpha^2} \exp\left(\frac{-r^2}{\alpha^2}\right) + \frac{\eta}{\beta^2} \exp\left(\frac{-r^2}{\beta^2}\right) \right], \quad (4.4)$$

where α and β are the characteristic widths of forward and backward scattering, and η is the ratio of the backscattered energy to the forward-scattered energy. The combination of exposed pattern and the proximity function is the final exposing energy incident on the resist.

There are different methods to minimize the proximity effect. If the pattern has uniform density, the dose can be adjusted accordingly until it comes out to be

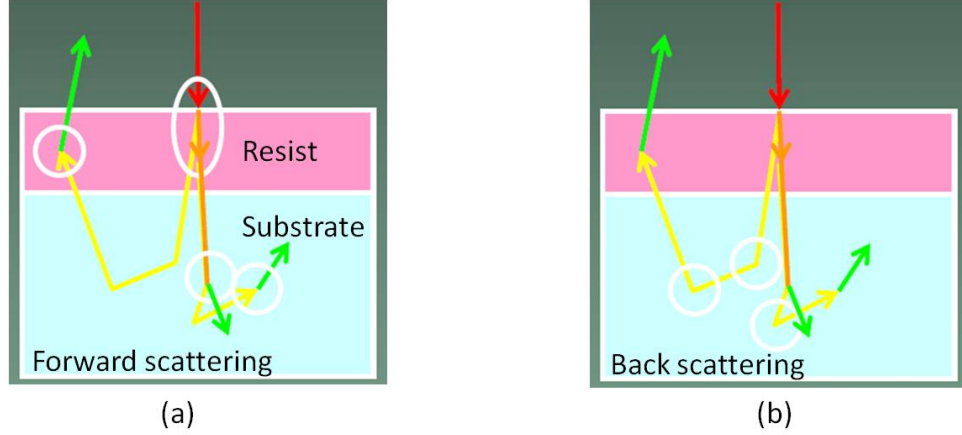


Figure 4.8: (a) Forward Scattering (b) Backscattering.

the proper size. Interestingly, many EBL tools come with proximity effect correction software. Patterning at higher beam energy or higher voltage will minimize the forward scattering range and the backscattering will be averaged over a larger area. Conversely, patterning at low voltage (<2 keV), the backscattered electron range is smaller than the feature size. In addition, backscattering can be eliminated by patterning on a low density material like a silicon nitride membrane. The beam will go straight through the nitride, and an absorbing material like graphite can be put underneath to prevent any backscatter. The Monte Carlo calculation of the backscattered electron in different materials is shown in Figure 4.9 [61]. The backscattering is minimized with the substrate that has a low atomic number (z).

4.2.6 Speed

EBL is very slow compared to optical lithography because of point by point exposure illustrated in Figure 4.5. The amount of time used to make the pattern depends on dose, beam current, step size and the area of the pattern. The total time to write the pattern can be estimated by

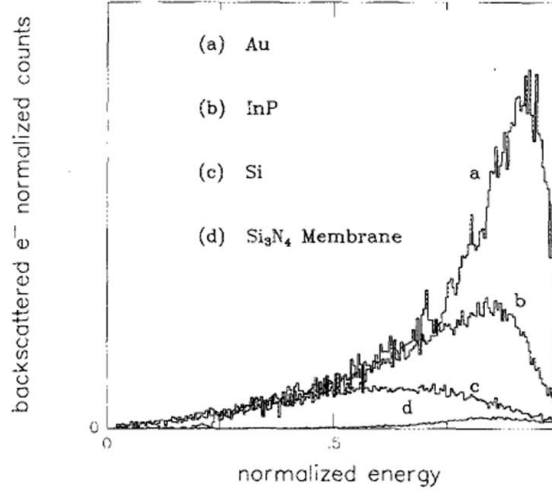


Figure 4.9: Monte Carlo calculated backscattered electron energy spectra for 40 kV beam.

$$Time = \frac{Dose \times Area}{current}. \quad (4.5)$$

The unit for time is in seconds, Dose is in $\mu\text{C}/\text{cm}^2$, Area is in cm^2 and current is in μA .

For example, the typical exposure time to pattern $3 \text{ mm} \times 3 \text{ mm}$ at a beam current of 10,000 pA and a dose of $600 \mu\text{C}/\text{cm}^2$ is 1.5 hours. There is a trade-off between the minimum resolution and exposure time. The minimum resolution is a function of beam current. To get a smaller feature size, a lower beam current is required. At high currents, the beam loses focus so the feature size is bigger.

4.3 Contrast, Sensitivity and Resolution of P3HT by EBL

Contrast, sensitivity and resolution are important parameters used to describe resist properties. Contrast is a measure of the ability of a resist to distinguish between

light and dark portion. Sensitivity describes how quickly the resist responds to radiation. The resist which requires a lower exposure dose has higher sensitivity. Usually, the higher sensitivity is preferred because it saves both cost and exposure time. The resolution determines how small the pattern can be created. Most of the applications, especially in the microelectronic industry, require a high resolution pattern to create a more efficient device.

The contrast and sensitivity can be determined by the contrast curve. The contrast curve is the relation between the dose and the thickness of photoresist after patterning and developing (normalized by initial thickness). The contrast curve is used to determine the optimum dose for the patterning of the resist. Figure 4.10 shows the procedure to make the contrast curve by the electron beam or ion beam lithography. The resolution can be determined by the nanopattern on the resist. In this project, we patterned the nanopillar which will be used for the ordered heterojunction device.

EBL with SEM The contrast curve are made by following the procedure shown in Figure 4.10. First, the 0.014 g/ml of P3HT in anhydrous chlorobenzene was spin casted on a silicon chip which has a dimension of $1\text{ cm} \times 1\text{ cm}$ at spin rate 3000 rpm for 60 s. The thickness was measured by AFM to be 70 nm. Second, P3HT sample was patterned by the electron beam from SEM. The pattern was the $45\text{ }\mu\text{m} \times 45\text{ }\mu\text{m}$ box array. There were 25 boxes in the array and each box was exposed to different doses of the electron beam. The SEM was operated at a voltage of 30 kV, current 12 nA and step size 40 nm. The area doses were varied from $60\text{ }\mu\text{C}/\text{cm}^2$ to $2000\text{ }\mu\text{C}/\text{cm}^2$ with equal increments. Third, the exposed films were developed in chlorobenzene at room temperature or *p*-xylene at 35°C for 25 seconds. Note that *p*-xylene is purged with nitrogen to displace dissolved oxygen. Fourth, the images of the box arrays were

taken with the optical microscope and the thickness of each box was measured by AFM.

The optical image of the micro box are shown in Figure 4.11 (a). Figure 4.11 (c) reports the normalized residual thickness as a function of exposure dose for each developer. We find that P3HT is a negative-tone electron-beam resist. P3HT starts to cross-link between dose $141 \mu\text{C}/\text{cm}^2$ and $221 \mu\text{C}/\text{cm}^2$. The critical exposure dose at 30 keV is approximately $400 \mu\text{C}/\text{cm}^2$, which is slightly lower than poly(methyl methacrylate) or hydrogen silsesquioxane electron-beam resists [62,63]. The contrast parameter (γ) is 0.9 for chlorobenzene and 1.0 for *p*-xylene. The resolution of P3HT with the EBL by SEM is also determined using the same procedure as the contrast curve. The difference was the pattern. Instead of box array, the dot pattern was printed by a highly focused electron beam from SEM. The dot pattern was printed using the same beam energy but lower current at 40 pA and step size 100 nm.

We found that P3HT is a high resolution negative tone resist. Figure 4.11 (b) shows the AFM image of nanodots patterned with an area dose of $225 \mu\text{C}/\text{cm}^2$ (point dose of 90 fC). The average pillar diameter and height are 50 nm and 60 nm, respectively. The image was acquired with an atomic force microscope operating in tapping-mode. It is difficult to evaluate the resolution limit for P3HT because our EBL system does not have instrumentation for dynamic focus corrections. However, we found the nanodots with 30 nm widths are reliably resolved using a low beam current, and we anticipated that even smaller features can be printed with a more sophisticated EBL system and an optimized development protocol [62,64]. Figure 4.4 (d) shows the relation between the dot size as a function of doses. The smaller dose resolved the higher resolution of nanopillar because the proximity effect increased with the dose. The sensitivity of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

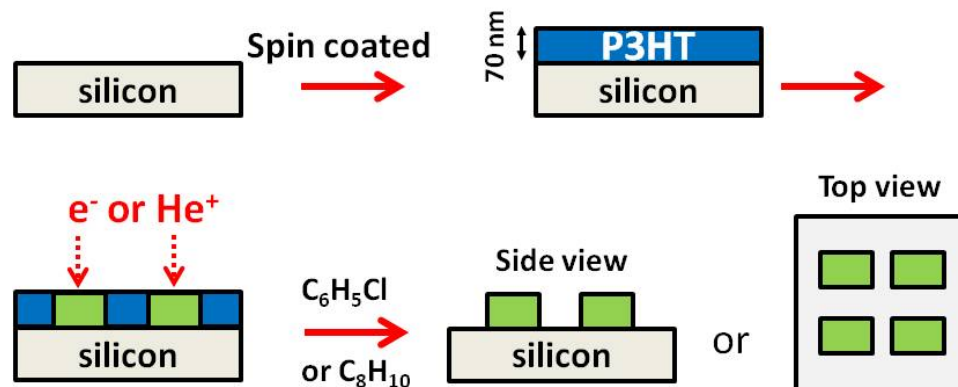


Figure 4.10: The procedure to make a contrast curve by electron beam or Ion beam lithography.

(PEDOT:PSS) to electron-beam radiation is evaluated. This material is used as a hole-injection layer at the anode and is therefore irradiated during the fabrication process. Figure 4.12 show the optical micrograph of PEDOT:PSS (30nm) pads on a silicon substrate. Irradiation doses are marked below each pad in units of $\mu C/cm^2$. These images were developed by immersion in deionized water for 25 seconds at room temperature. PEDOT:PSS is also a negative-tone material, but with a low critical exposure dose of $200 \mu C/cm^2$ for development in water.

EBL with JBX5500 e-beam writer The contrast curve of EBL using the JBX5500 e-beam writer is made with the same way as SEM, but with different operation conditions. The beam energy was 50 kV and the current was 1 nA. The area doses were varied from $200 \mu C/cm^2$ to $1400 \mu C/cm^2$ with equal increments. Figure 4.13 (a-b) includes examples of microscale and nanoscale P3HT patterns, and Figure 4.13 (c) reports the normalized residual thickness as a function of exposure dose for the chlorobenzene developer. The critical exposure dose at 50 keV is approximately $500 \mu C/cm^2$ which is slightly higher than EBL from SEM. The dose required for the

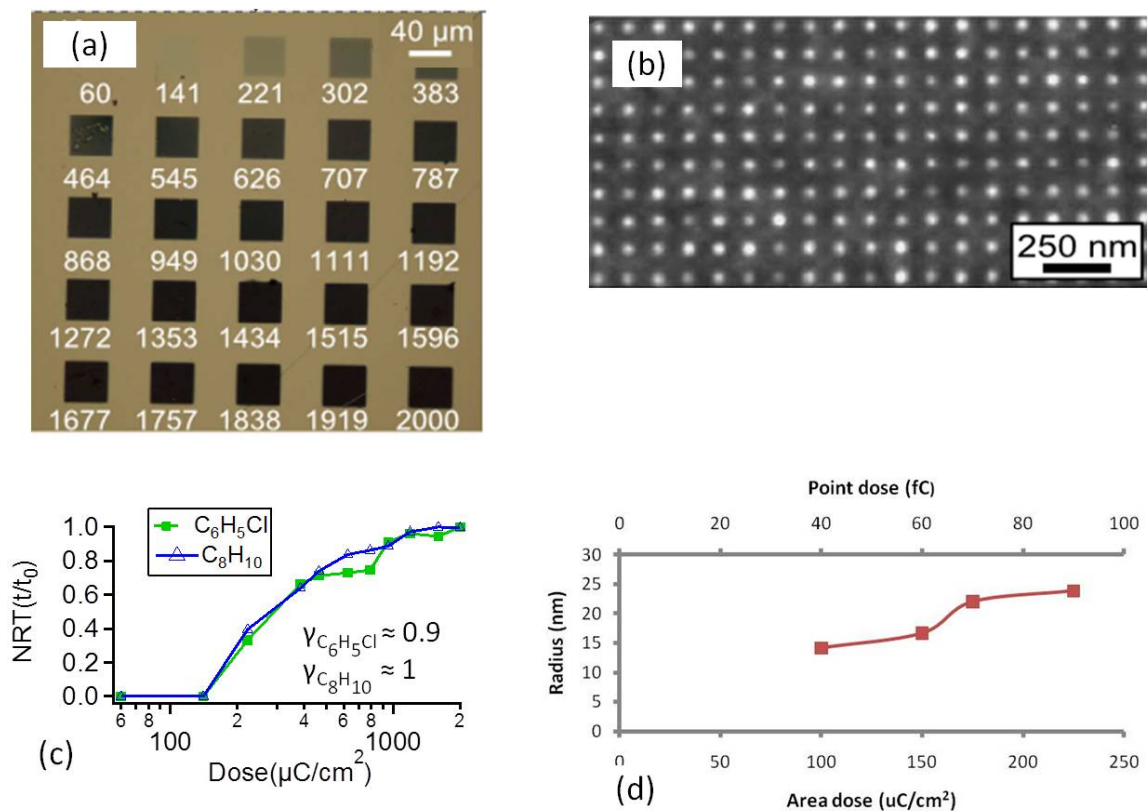


Figure 4.11: (a) Optical micrograph of cross-linked P3HT pads on a silicon substrate (The dose unit is $\mu\text{C}/\text{cm}^2$); (b) P3HT nanopillar arrays; (c) Contrast curve of P3HT; (d) Resolution as a function of dose.

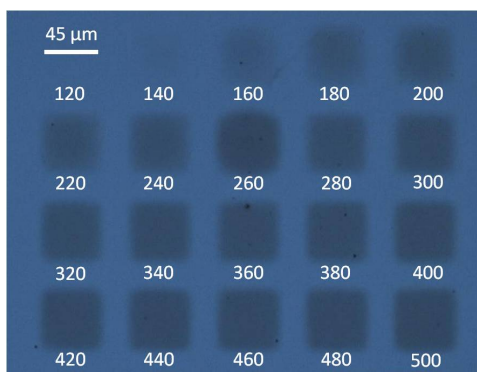


Figure 4.12: Sensitivity of PEDOT:PSS to electron-beam radiation (The dose unit is $\mu\text{C}/\text{cm}^2$).

pattern is directly proportional to the beam energy that is why this instrument requires a higher dose than SEM ($V=30$ keV). The contrast parameter (γ) is 1.43 for chlorobenzene.

The JBX5500 e-beam writer is a new instrument. We are in the process of setting up the parameter for this instrument for EBL with P3HT resist. The results shown here are the first attempt. The current resolution is not high. The diameter of the nanopillar is around 200 nm with the height of 75 nm. The JBX5500 e-beam writer has dynamic focus correction. We anticipate that after the system is set up, the resolution will be higher than the resolution from SEM.

4.4 Optimize the EBL condition for Device fabrication

EBL is used to nanopattern P3HT for nanostructured devices. Although EBL generates high resolution structures, the patterning process is slow. The minimum area for the device fabrication is around $2\text{ mm} \times 3\text{ mm}$ which is large for EBL so the patterning conditions have to be optimized. In this section, the parameter was the magnification when patterning. Another process that is important for patterning is x-y focus correction.

Magnification The patterning process is faster at lower magnification because a larger area can be exposed in a single field, meaning the sample stage does not need to be moved as frequently. The magnifications in this experiment were 180x and 1000x. At 180x magnification, a maximum area of $1000\text{ }\mu\text{m}^2$ can be patterned. To pattern the device ($2\text{ mm} \times 3\text{ mm}$), it requires 6 boxes of $1000\text{ }\mu\text{m}$ on each side. In comparison, maximum area of $175\text{ }\mu\text{m}^2$ can be patterned at 1000x. It requires 205 boxes to pattern the area of $2\text{ mm} \times 3\text{ mm}$. As the number of boxes are increased, the total time to move the stage will also increase. As a result, 1000x magnification

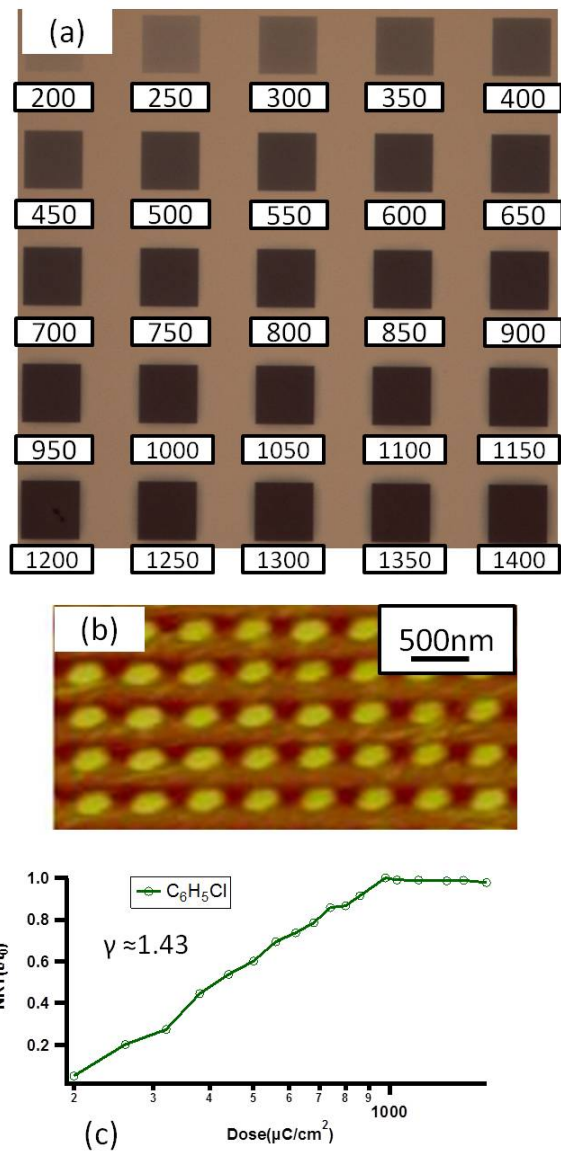


Figure 4.13: (a) Optical micrograph of cross-linked P3HT pads on a silicon substrate; (b) P3HT nanopillar arrays; (c) Contrast curve of P3HT with JBX5500.

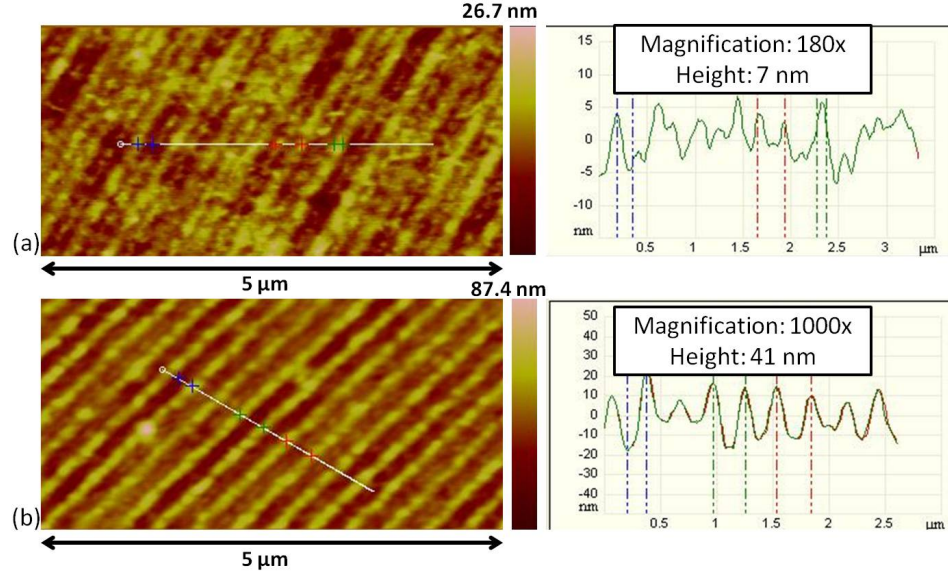
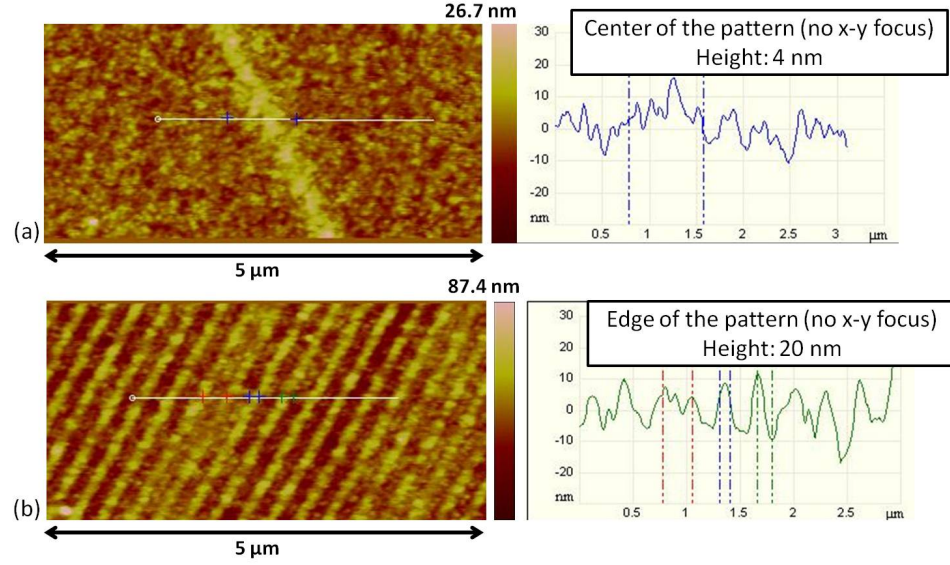


Figure 4.14: (a) AFM image of line pattern at patterning magnification 180x. (b) AFM image of line pattern at patterning magnification 1000x.

takes 1 hour more to pattern than at 180x for the same size of the area. In this experiment 60 nm of P3HT film on ITO glass slide was patterned at 180x and 1000x and then developed with *p*-xylene. Figure 4.14 (a) is the line pattern at patterning magnification 180x. The lines were not properly resolved and height of the lines were approximately 7 nm. In contrast to magnification 1000x (Figure 4.14 (b)), the line pattern was there and the height of the lines was approximately 41 nm. In conclusion, the magnification at 1000x will be used for device patterning.

x-y focus The SEM used for device fabrication does not have dynamic focus correction. As the stage is moving to a different area of the resist, the focus will be changed according to the height variation of the sample. To get the uniform pattern, the x-y focus is necessary. The sample was 60 nm P3HT film patterned with SEM at magnification 1000x and developed with *p*-xylene at 35 °C. The total pattern area was 3 mm × 2 mm. Figure 4.15 (a) and (b) are the AFM images of line pattern



**Figure 4.15: (a) AFM image of line pattern at the center of the sample
(b) AFM image of line pattern at the edge of the sample.**

at the center and the edge of the pattern, respectively. The P3HT was patterned without x-y focus. One could see that the pattern came out properly at the edge (Figure 4.15 (b)) but not the center of the pattern area (Figure 4.15 (a)). Figure 4.16 illustrates the line patterns at the center and edge with x-y focus. The line patterns were developed properly at the center (Figure 4.16 (a)) and edge of the pattern area (Figure 4.16 (a)). From this experiment, we conclude that the x-y focus is needed to pattern the nanostructure device.

4.5 Proximity Ion Beam Lithography

In this project, ion beam lithography is used to cross-link a large area of polymer resist because the process is much faster than electron beam lithography with the same cross-linking mechanism (Figure 5.9) in chapter 5. The resist is much more sensitive to the ion beam than the electron beam due to the higher stopping power of the ions. The stopping power determines the amount of energy loss in the process.

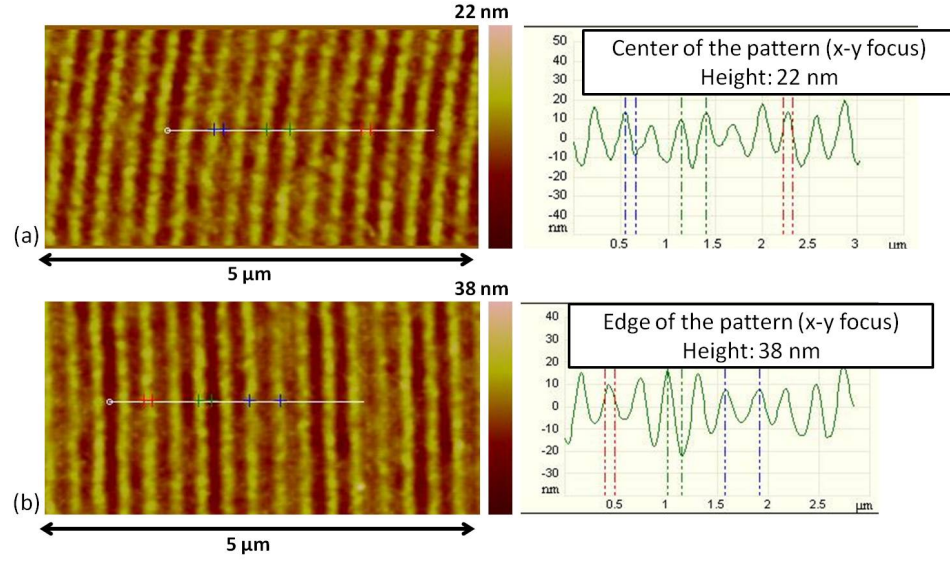


Figure 4.16: (a) AFM image of line pattern at the center of the sample with x-y focus (b) AFM image of line pattern at the edge of the sample with x-y focus.

High stopping power means high energy loss and generates more secondary electrons which are mainly responsible for cross-linking the resist. Electron and ion stopping powers are different in their behavior because the charged particle interactions are not energy dependent but velocity dependent [65]. Helium is 7300 times the mass of an electron so at the same energies level a factor of 0.0123 times slower than an electron. Another advantage of the ion beam over the electron beam is the proximity effect. The proximity effect is negligible in the ion beam because there is minimal backscattering.

The samples were prepared the same way as EBL but the P3HT film were exposed with the ion beam instead of the electron beam. The irradiated P3HT samples were developed with *p*-xylene. Figure 4.17 (a) show the optical image of cross-linked P3HT on a microscope glass slide substrate. Figure 4.17 (b) reports the normalized residual thickness as a function of exposure dose for *p*-xylene developers.

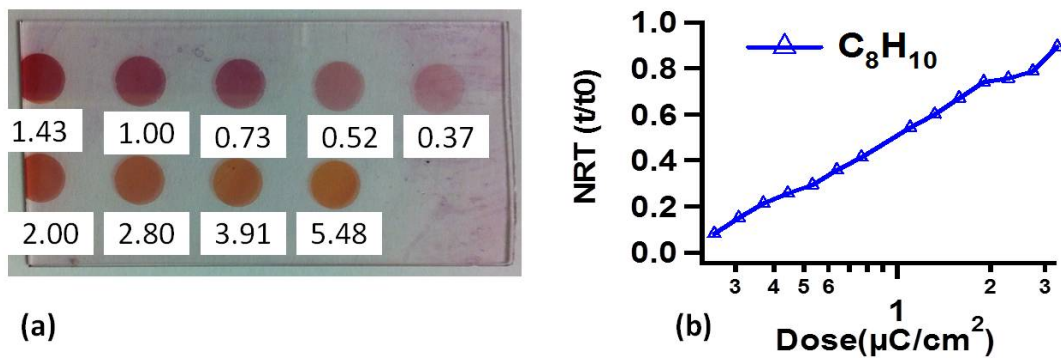


Figure 4.17: (a) Optical image of cross-linked P3HT pads on microscope glass slide substrate (The dose unit is $\mu\text{C}/\text{cm}^2$); (b) Contrast curve of P3HT with ion beam.

The contrast is not high but the sensitivity is a lot better than EBL. The doses required to cross-link P3HT with the ion beam is approximately 200 times lower than the electron beam. The ion beam is used to prepare spectroscopy samples which are UV-Vis, FTIR and device because this technique provides a fast way to cross-link the polymer.

Chapter 5 Spectroscopy Characterization

The P3HT semiconducting polymer used as a donor in the organic solar cell is a conjugated polymer that can absorb light, generate charges and transfer charges. All of these properties are really important for the application of the solar cell. As the polymer film is exposed by the electron beam during the device fabrication process, the properties of the irradiated polymer are determined by the spectroscopy technique. The irradiated sample volume is very small which prevents a detailed characterization of the bond structure with nuclear magnetic resonance or x-ray photoelectron spectroscopy. Instead, Ultraviolet-visible (UV-Vis) spectroscopy and Infrared (IR) spectroscopy are used to evaluate the properties of un-exposed films, irradiated films, and irradiated films after immersion in developer.

In this chapter, the UV-Vis and IR principle and application to the thin film polymer are reviewed. The P3HT donor, PEDOT:PSS as hole injection layer and PCBM acceptor are characterized with these two techniques. The UV-Vis and IR data of irradiated P3HT are used to determine if there is any loss of conjugation due to exposure, and to propose a cross-linking mechanism. The post-exposure annealing condition was optimized based on the UV-Vis result, and is included in this chapter.

5.1 Spectroscopy techniques

Spectroscopy techniques are useful for both qualitative and quantitative investigations of samples. These techniques are non-destructive and can be applied to small sample volumes. The absorption spectroscopy is the measurement of the amount of light absorbed by a compound as a function of the wavelength of light. Generally, the sample is irradiated by the light source and the detector measures the amount of transmitted light at various wavelengths. In this work, the UV-Vis and IR are used to determine the spectroscopy properties of the polymer.

5.1.1 Ultraviolet-Visible spectroscopy

Ultraviolet-Visible spectroscopy (UV-Vis) detects the electronic transition of conjugated systems and provides information about the length and structure of the conjugated part of a molecule. UV-Vis spectroscopy investigates the absorption of the different substances between the wavelength limits 200 nm and 800 nm. In this wavelength the absorption of the electromagnetic radiation is caused by the excitation of the bonding and non-bonding electrons of the ions or molecules. Figure 5.1 shows the energy diagram of light absorption with the type of the bond in the molecule. The UV-Vis absorption wavelength is for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ so any molecules that have π bonds can be detected with this instrument. P3HT, PEDOT:PSS and PCBM in the active layer of the solar cell have the conjugated π bond so UV-Vis is useful for both quantitative and qualitative analysis of this polymer. The absorption wavelength is used for qualitative analysis. The combination of UV-Vis and other techniques can be used to determine the chemical structure. Quantitative measurements are based on Beer's Lambert Law which is

$$A = \log\left(\frac{I_r}{I_s}\right) = \varepsilon cl = \alpha l, \quad (5.1)$$

where I_r = intensity of reference beam, I_s = intensity of sample beam, c = sample concentration in moles per liter, l = path length of light through the cell in centimeters, ε = the molar absorptivity (or molar extinction coefficient) of the sample. Molar absorptivity (ε) is a measure of how strongly the sample absorbs light at that wavelength and α = Absorption coefficient (cm^{-1}).

For the application of thin film measurement, the absorption coefficient (α) is calculated to compare between the samples because this number does not depend on

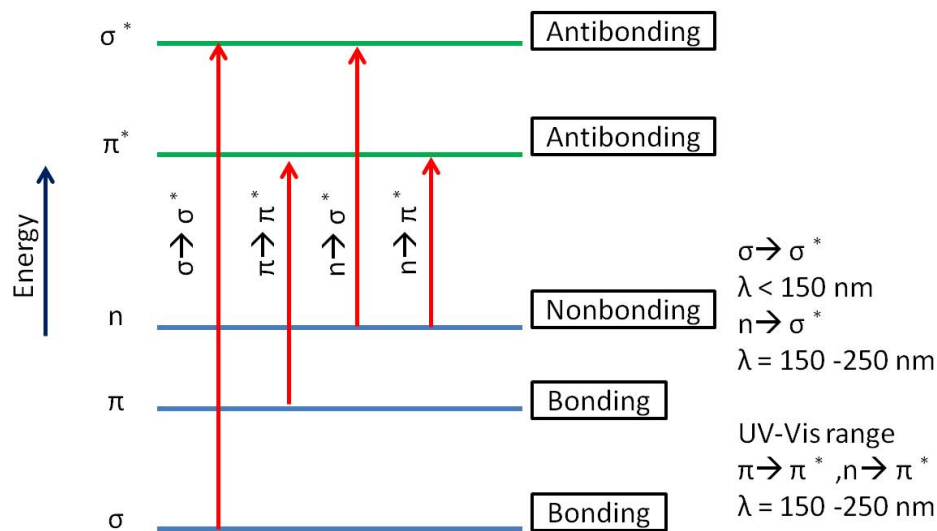


Figure 5.1: Energy diagram of electronic excitation for organic molecules [66].

the thickness of the thin film. The absorbance (A) is measured from the instrument and converted to the absorption length by divided thickness of the thin film.

For this project, UV-Vis is used to measure the absorption property of the polymer which are P3HT, PEDOT:PSS and PCBM. The main polymer that we want to evaluate is P3HT but the PEDOT:PSS layer is the layer underneath P3HT so this polymer is also exposed to the electron beam or ion beam. PCBM is also measured with UV-Vis. We compared the properties of as-cast polymer, irradiated polymer with electron beam, and irradiated and developed polymer. All data is collected in transmission mode at normal incidence. UV-Vis spectrum were recorded with a UV-2401PC (UV-Vis recording spectrophotometer-Shimadzu).

5.1.2 Infrared Spectroscopy

Infrared spectroscopy measures the frequencies of infrared light absorbed by a compound. The absorption frequency of each molecule depend on the vibration of the bond in the molecule. The vibration depends on the mass of atoms and stiffness

of the bond. The heavy atom vibrates slower than the light atom so it appears at a lower frequency region. The stronger bond is more stiff than the weaker bond so it appears at a higher frequency region. There are also different modes of vibration in the molecule such as stretching, bending, wagging, and rocking. Even the simple compound, IR contain many different absorptions for each bond. So it is unlikely that two molecules will have the same IR absorption. The specific IR absorption peak for each molecule is called a finger print. The finger print is used for qualitative analysis for Infrared spectroscopy. The IR spectra is the plot between the absorption and the wavenumber instead of wavelength. The wavenumber is the reciprocal of wavelength and has a unit of cm^{-1} . IR absorbance is measured with a Nicolet 6700 spectrometer.

5.2 Spectroscopy Analysis

5.2.1 PEDOT:PSS

The PEDOT:PSS molecule shows the absorption at 856 cm^{-1} and 991 cm^{-1} from C-S bond in thiophene ring. Vibration at 1155 cm^{-1} originated from C-O-C bond stretching in the ethylene dioxy group. The vibration around 1556 cm^{-1} due to stretching of the thiophene ring [67].

Electron Beam UV-Vis absorbance spectroscopy of 30 nm PEDOT:PSS films is illustrated in Figure 5.2 (a). Films were baked at 140°C for 10 minutes to remove residual water, and then one film was irradiated at $450 \mu\text{C}/\text{cm}^2$ and was immersed in deionized water for 25 seconds. Irradiation slightly increased the UV-Vis absorbance at 437 nm, while no clear changes were detected in IR absorbance in Figure 5.2 (b). Other works suggest that low-energy electrons (ca. 3 eV) can induce oxygen and sulfur loss from PSS and disrupt carbon-oxygen bonds in PEDOT, [68] while the thiophene rings are unaffected by irradiation. We find that irradiated PEDOT:PSS

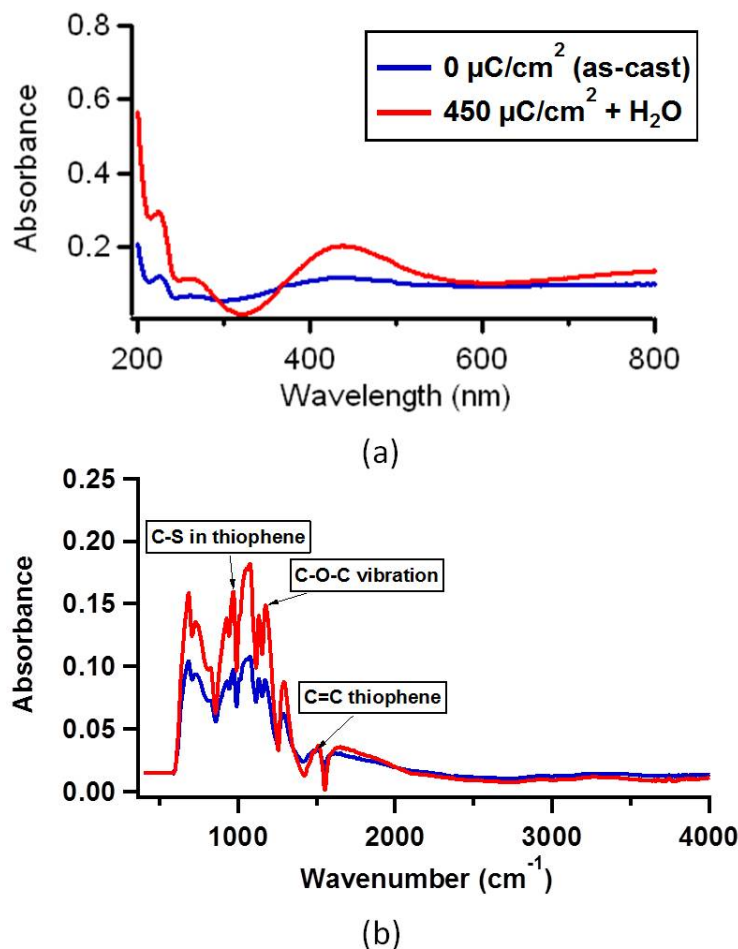


Figure 5.2: (a) UV-Vis absorbance spectroscopy of as-cast and irradiated film; (b) IR absorbance spectroscopy of as-cast and irradiated film with electron beam.

films are insoluble in water, which is consistent with a reduction of PSS solubility due to sulfonate damage and/or intermolecular cross-linking through ionization of the polymers.

Ion Beam UV-Vis and IR absorption of PEDOT:PSS as cast film, irradiated with ion dose 0.6 $\mu\text{C}/\text{cm}^2$ and 2 $\mu\text{C}/\text{cm}^2$ are included in Figure 5.3. Note that the PEDOT:PSS film were exposed with the ion beam without development. There is no change of absorption from UV-Vis (Figure 5.3 (a)). The IR data in Figure 5.3 (b)

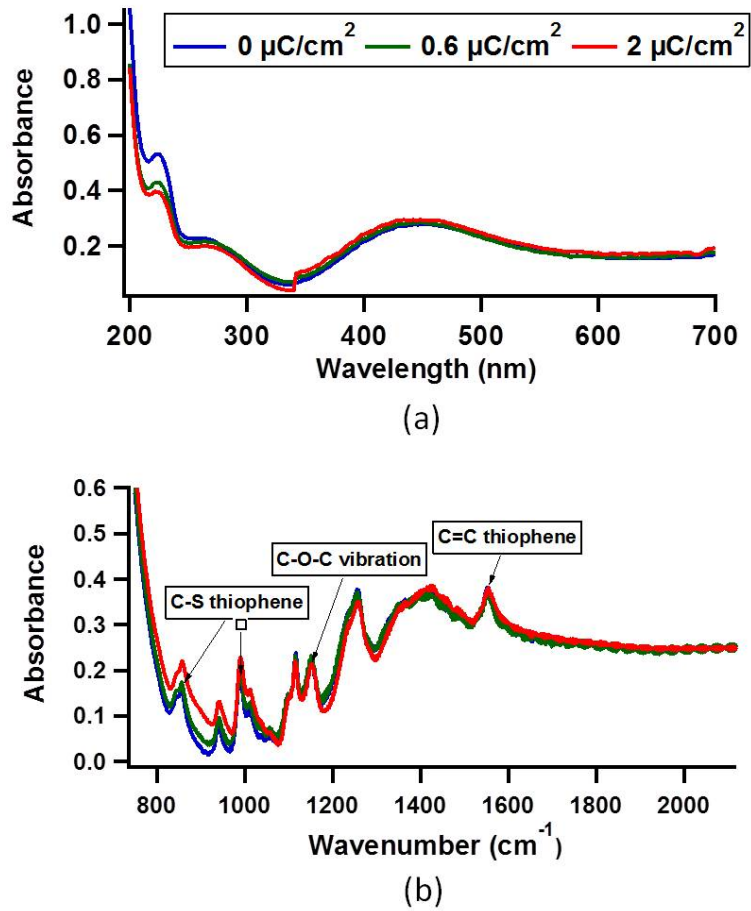


Figure 5.3: (a) UV-Vis absorbance spectroscopy of as-cast and irradiated film; (b) IR absorbance spectroscopy of as-cast and irradiated film with ion beam.

do not detect additional or loss of functional group in both irradiation doses. In conclusion, we cannot detect any changes in PEDOT:PSS properties after exposure to ion-beam radiation.

5.2.2 P3HT

P3HT has a broad absorption band due to the delocalization of π -electron. The UV-Vis of P3HT shows the maximum at 520 nm. There are two shoulders at 550 nm and 600 nm [69]. The shoulder at 600 nm can assigned to inter-chain absorption

coming from a highly ordered domain [70]. The IR spectrum of P3HT appears in two regions. The thiophene ring shows the finger print at wavenumber 1370 - 1560 cm^{-1} and the hexyl group has a finger print at wavenumber 2850 -3050 cm^{-1} [69].

Electron Beam Representative UV-Vis and IR absorbance data are included in Figure 5.4 for five samples: An as-cast P3HT film that was irradiated at 450 $\mu\text{C}/\text{cm}^2$ and then immersed in chlorobenzene or *p*-xylene. First, the linear absorption coefficients (μ) for as-prepared and irradiated P3HT films are nearly identical. This finding is consistent with work from Gearba et al., where thin P3HT films were thermally cross-linked with a peroxide radical initiator, and there was no change in UV-Vis absorbance at low-to-moderate cross-link densities [71]. However, we do find evidence of photobleaching when irradiated films are immersed in the developer. The wavelength at peak absorbance is (515 ± 2) nm, (513 ± 2) nm, and (509 ± 2) nm for as-prepared, irradiated, and developed films, respectively (average values and standard deviations are calculated from measurements of five to ten samples at each step in the process).

In addition to this blue-shift, developed films absorb less light and exhibit weaker vibronic shoulders [70, 72]. The loss of fine structure suggested that development disrupts the intermolecular ordering. This conclusion is supported by preliminary grazing-incidence wide-angle X-ray scattering (GIWAXS) data that are in Figure 5.5. P3HT films were measured with grazing-incidence wide-angle X-ray scattering (GIWAXS). These films were irradiated with low-energy helium ions at a dose of 0.6 $\mu\text{C}/\text{cm}^2$. At this dose, the P3HT is largely insoluble in organic solvents so the cross-link density should be similar to the results of EBL. From Figure 5.5 (a), the (100), (200), and (300) reflections are clearly resolved. This data demonstrates that irradiated films (at low to moderate doses) retain some or all of the native crystallinity, but the crystalline domains vanish after development in *p*-xylene (Figure 5.5 (b)).

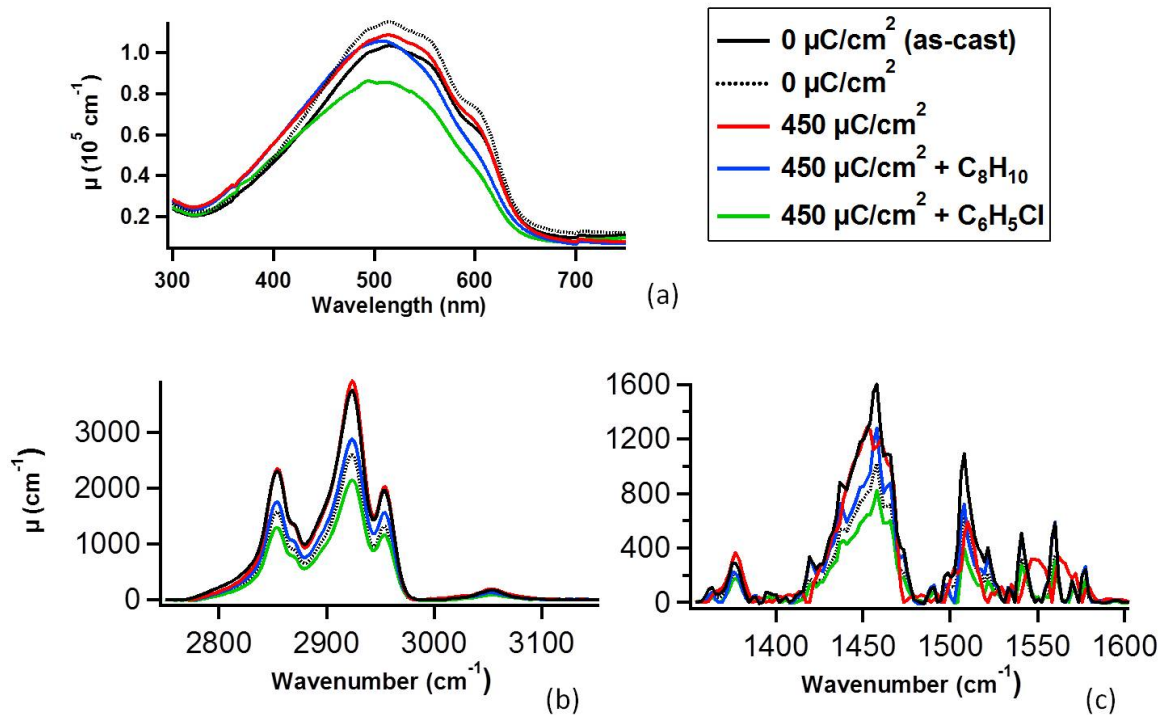


Figure 5.4: (a) Linear absorption coefficient (μ) measured by UV-Vis and (b) IR absorbance spectra of P3HT films at different stages in the lithographic process.

Second, the IR spectra for as-prepared and irradiated films are nearly identical. Peaks associated with hydrocarbon and the aromatic functional group are resolved in the ranges 2850 - 3050 cm^{-1} and 1370 cm^{-1} , respectively, although the latter fingerprint region is quite noisy. All peak intensities are weaker after development, which is expected based on the reduced film thickness, but this finding is also consistent with polymer degradation [69, 73].

Ion Beam The UV-Vis and IR absorbance data are included in Figure 5.6 and Figure 5.7, respectively, for different exposure doses of the ion beam and some are developed with chlorobenzene. The UV-Vis sample of different exposure doses 0.6, 2 and 3 $\mu\text{C}/\text{cm}^2$ are shown in Figure 5.6 (a). The UV-Vis for reference sample (0 $\mu\text{C}/\text{cm}^2$) is the same as the irradiated sample with ion beam dose 0.6 $\mu\text{C}/\text{cm}^2$. There

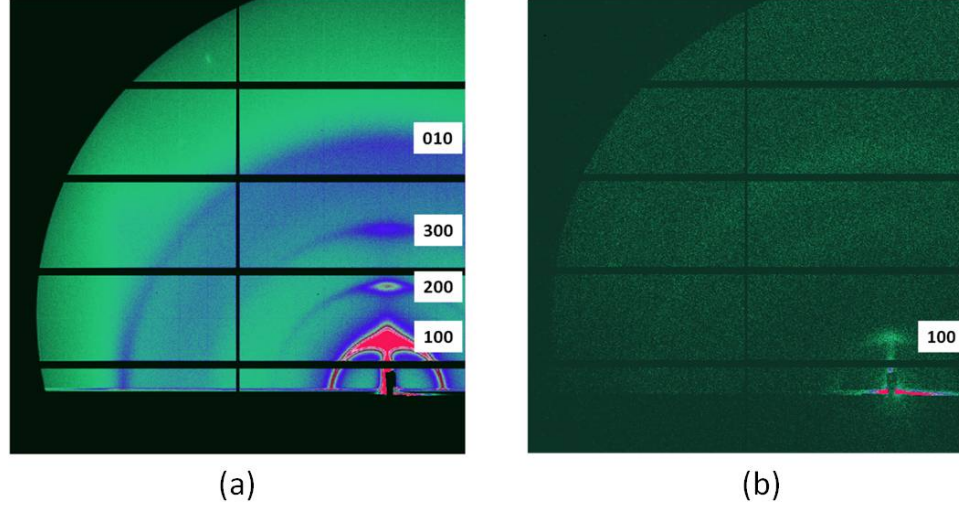


Figure 5.5: (a) GIWAXS data from irradiated P3HT films; (b) GIWAXS data from irradiated P3HT films after development with *p*-xylene.

is a little blue shift of the curve at the higher exposure dose, 2 and 3 $\mu\text{C}/\text{cm}^2$. This data concludes that the absorption property of P3HT preserved after being exposed to the ion beam. Figure 5.6 (b)-(d) shows the comparison of the control, to the exposed and developed data. We found the drop of the absorption and the photobleaching when the exposed film was immersed in the developer. The wavelength of the absorbance shift from 515 nm for no expose sample to 509 nm in the developed sample. This UV-Vis data from the ion expose are consistent with the UV-Vis exposed with the electron beam. The IR data of P3HT exposed to the ion beam dose 2 $\mu\text{C}/\text{cm}^2$ is shown in Figure 5.7. The IR data of the control sample and irradiated sample are similar but the absorption drop after being developed in chlorobenzene. There are no other products detected after development. These IR data of the samples exposed to the ion beam are consistent with the one that was exposed to the electron beam.

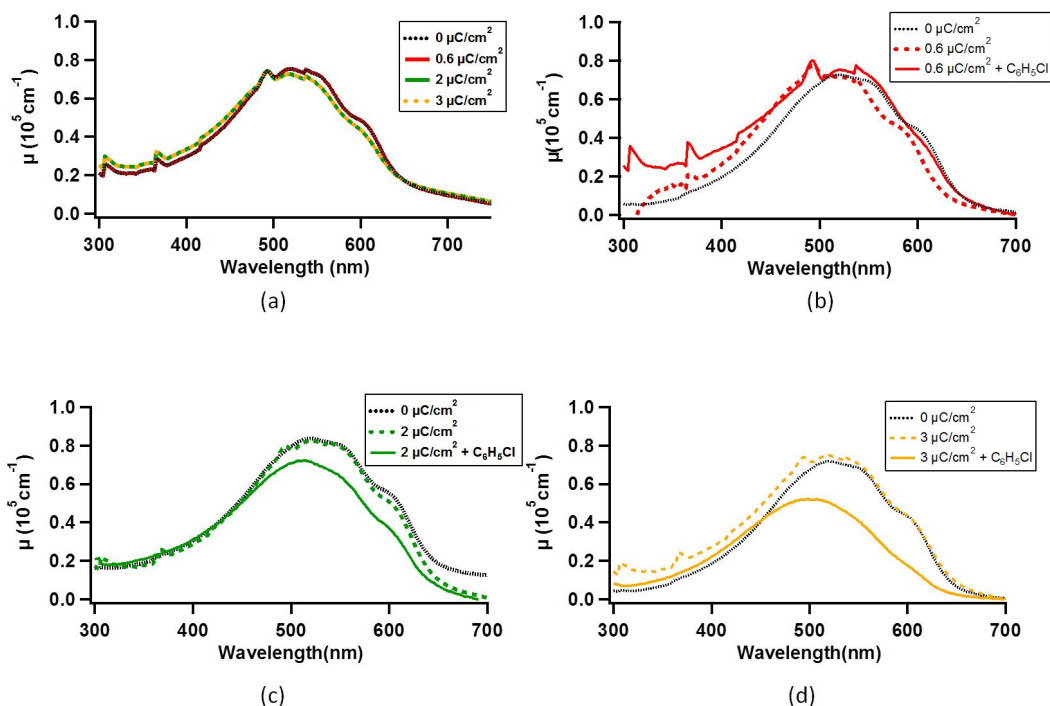


Figure 5.6: UV-Vis data of (a) Irradiated P3HT with doses 0.6, 2 and 3 $\mu\text{C}/\text{cm}^2$ of ion beam. (b)-(d) Irradiated and irradiated and developed of P3HT in chlorobenzene with dose (b) 0.6 $\mu\text{C}/\text{cm}^2$, (c) 2 $\mu\text{C}/\text{cm}^2$ (d) 3 $\mu\text{C}/\text{cm}^2$, respectively.

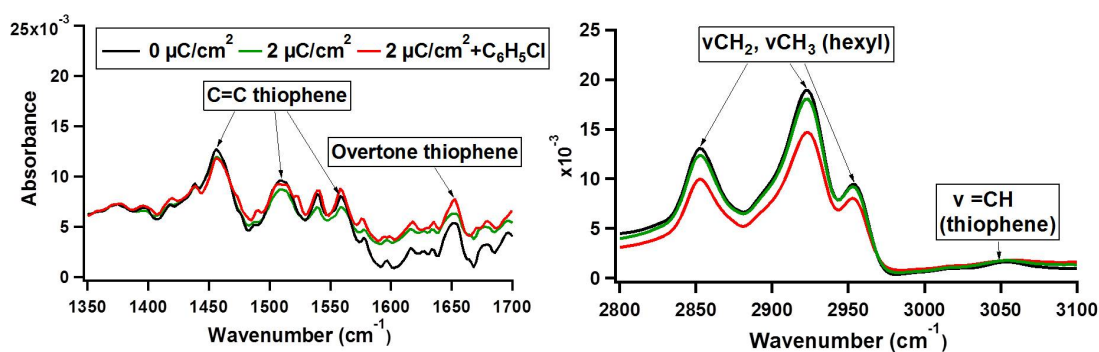


Figure 5.7: IR data of Irradiated and irradiated and developed of P3HT in chlorobenzene of P3HT with dose 2 $\mu\text{C}/\text{cm}^2$.

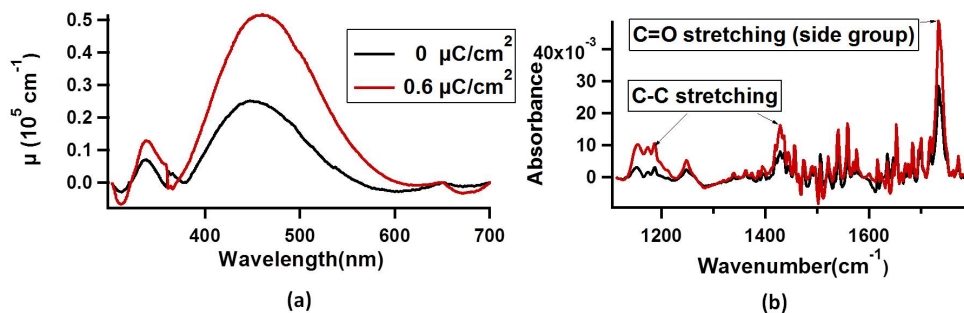


Figure 5.8: (a) UV-Vis of PCBM and exposed PCBM to ion dose $0.6 \mu\text{C}/\text{cm}^{-1}$ (b) IR of PCBM and exposed PCBM to ion dose $0.6 \mu\text{C}/\text{cm}^{-1}$.

5.2.3 PCBM

PCBM has the absorption at 1182 and 1429 cm^{-1} for C-C stretching [74]. The side group which is ester shows the signature at 1733 cm^{-1} . The UV-Vis in Figure 5.8 (a) show that PCBM can absorb visible light so the excitons are generated from the PCBM layer as well as P3HT. Although the PCBM can generate excitons, the exciton diffusion length in PCBM is 5 nm [75] which is relatively small. Most of the excitons generated from PCBM will recombine before splitting to be free charges at the interface. UV-Vis and IR data of PCBM included in Figure 5.8 show the same signature before and after exposed with the ion dose $2 \mu\text{C}/\text{cm}^2$. Even though the signal after exposure is higher than before exposure, which we do not know the reason for this. PCBM will not be exposed to the electron or ion beam in the device fabrication process.

5.3 Cross-linking mechanism

Based on these measurements of UV-Vis and IR absorbance, we propose a cross-linking mechanism for P3HT. Electron-beam radiation ionizes the α -carbons on hexyl substituent, producing the resonance-stabilized radicals that are illustrated in Figure

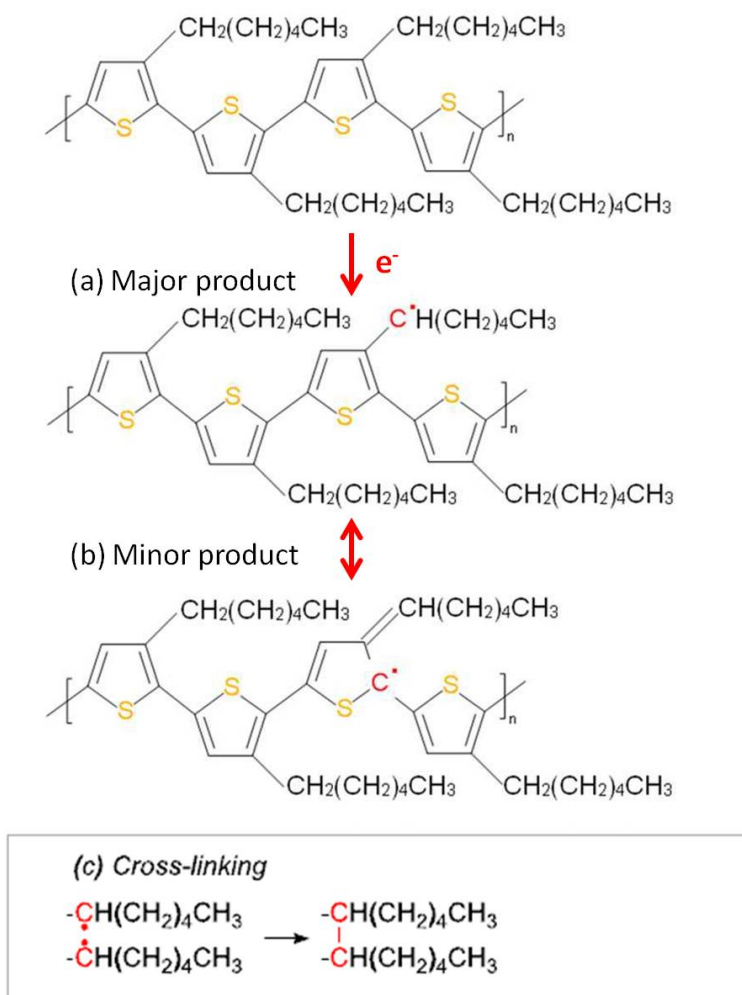


Figure 5.9: Proposed cross-linking mechanism for P3HT (in vacuum).

5.9 [30,73]. The major and minor products of this ionization reaction are the aromatic and anti-aromatic structures, respectively. The radicals can then react to form inter-molecular cross-links, where steric effects favor coupling of the more stable aromatic products over other potential pathways. The formation of cross-links at the α -carbon would not change either UV-Vis or IR absorbance, so this mechanism explains why the spectra in Figure 5.9 are similar for as-prepared and irradiated films.

5.4 Reaction in Development Process

5.4.1 Trapped radical

The changes in UV-Vis and IR absorbance after immersion in chlorobenzene or *p*-xylene point to a subsequent reaction during development. P3HT is a semi-crystalline polymer with a glass transition temperature near 12 °C, [76] although this number is widely debated, [77,78]; cross-links are most likely formed in the amorphous regions where the polymer has greater segmental mobility. There is a high probability that some radicals remain trapped in the polymer and can undergo further reactions during development that disrupt the native crystallinity. Indirect evidence of trapped radicals is illustrated in Figure 5.10.

The concept of trapped radicals is demonstrated with the following experiment: A 60 nm thick film of P3HT is patterned with electron-beam lithography at a dose of 450 $\mu\text{C}/\text{cm}^2$. The substrate is a clean silicon wafer. We compared the line width of P3HT nanostructures in two cases: Figure 5.10 (a) report the line width of P3HT nanostructures after the process of EBL exposure and development in solvent. Figure 5.10 (b) reports the line width of baked P3HT nanostructure. In this case, after EBL exposure of P3HT film, the film was baked at 150°C for 2 minutes. It was then developed in solvent for P3HT nanostructure. The structure at each stage was imaged with atomic force microscopy. The line width of the cross-linked P3HT nanostructure with post exposure bake increases by 15 %. This indicates that the trapped radicals further cross-link P3HT chains on baking and thus increases the line width of the nanostructure. One possibility is that trapped radicals can react with dissolved oxygen in the solvent. The IR measurements do not detect any oxidation products such as carbonyl and hydroxyl moieties, but the UV-Vis spectra suggests that purified

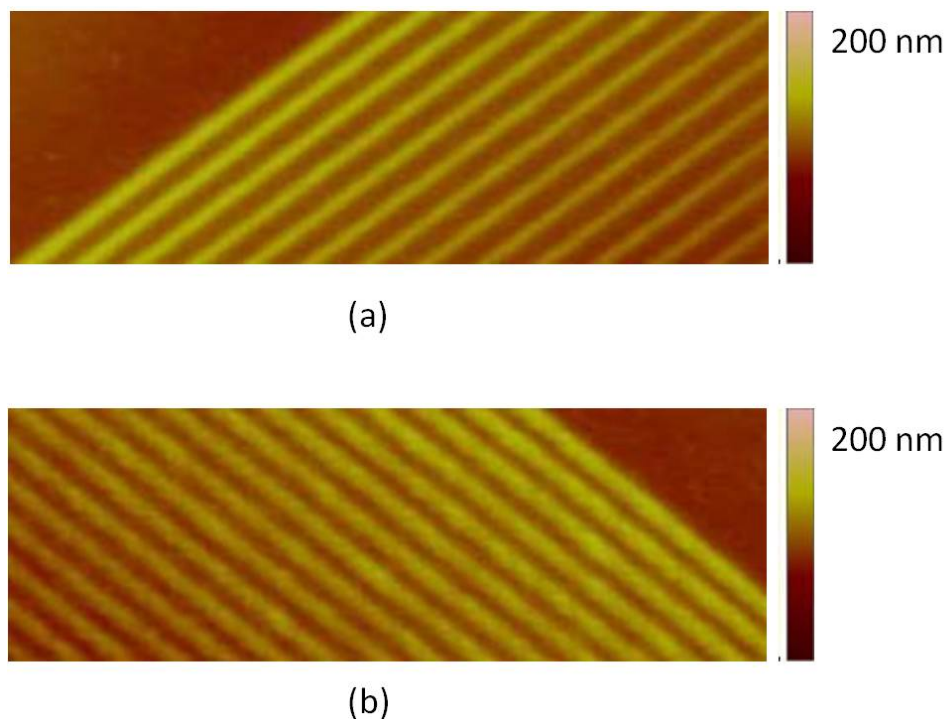


Figure 5.10: (a) Cross-linked P3HT nanostructure (b) Cross-linked P3HT nanostructure with bake after EBL exposure.

p-xylene can minimize photobleaching compared with the out-of-the-bottle chlorobenzene. Another possibility is that residual iron catalyst from the polymer synthesis is sensitized by electron-beam radiation, generating free radicals that could attack the thienyl ring and reduce the extent of conjugation. This explanation is consistent with UV-Vis and IR absorbance spectra. Further investigations are underway to identify the photobleaching mechanism and address this challenge.

5.4.2 Oxidation reaction in developing process

From the previous section, the trapped radicals from EBL can react with oxygen. We designed the tests in the table of Figure 5.11 to minimize the oxygen in the developing process. Parameters in this set of experiments were type of beaker (glass or Teflon (PTFE)), developer (chlorobenzene (C_6H_5Cl) or *p*-xylene (C_8H_{10}) and the

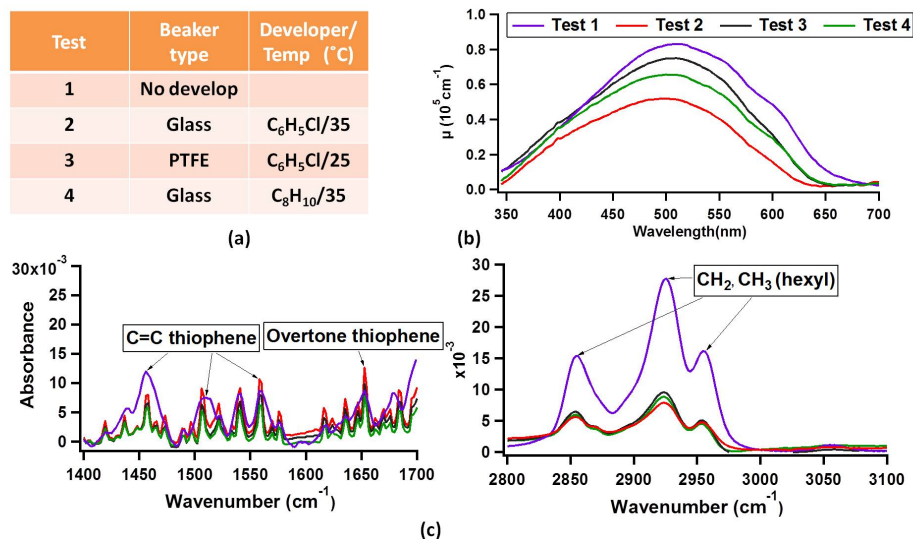


Figure 5.11: (a) Oxidation test table, (b) UV-Vis, (c) FTIR data for different tests.

temperature of the developer (25°C or 35°C). Test 1 idea was increasing the developer temperature to minimize the oxygen dissolved in solvent. The assumption for the test 2 was absorption of oxygen in glassware, so the PTFE beaker was used instead of the glass beaker. Test 3 was changing the developer from chlorobenzene to *p*-xylene. The FTIR data show the drop of the absorption peak after pattern development in every test. Comparing the different method of developing pattern, there is a slight difference in peak intensity in each experiment. However, the absorption in UV-Vis shows that development in the PTFE beaker with chlorobenzene at room temperature (25°C) gave the best absorption and development in *p*-xylene at 35°C with the glass ware (test 4) gave better absorption compared with chlorobenzene developer at 35°C in the glass ware (test1). In conclusion, *p*-xylene is a better developer compared with chlorobenzene and the Teflon (PTFE) beaker is better compared with the glass beaker.

Another experiment set was designed in the table of Figure 5.12. Based on the

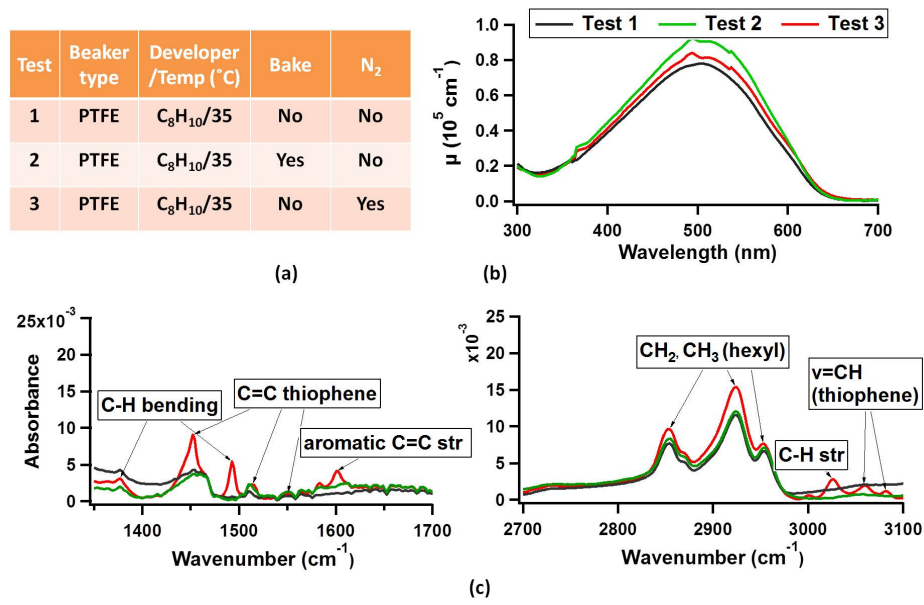


Figure 5.12: (a) Oxidation test table, (b)UV-Vis, (c) FTIR data for different tests.

previous experiment, *p*-xylene and the Teflon beaker were chosen to be developer and beaker type, respectively. Test 1 was the control sample. The assumption for test 2 was baking the sample before development will cross-link the remaining radical species after patterning so the idea is to get rid of radical (active species) before the development process. Test 3 was designed to substitute oxygen dissolved in solvent with nitrogen by bubbling the nitrogen through the solvent before developing the sample. A high intensity of thiophene and hydrocarbon signal was observed in test 3. The same intensity of IR signal was observed from the annealing sample (test 2) and control sample (test 1). Based on UV-Vis data, the highest absorption is from the baked sample, which is better than nitrogen bubbling (test 3) and the control sample (test 1), respectively. Although the spectroscopy data suggest that developing in PTFE beaker with nitrogen bubbling through the xylene developer with baked sample will be the best way to avoid the oxidation reaction, the electrical measurement on the real device should be tested to confirm spectroscopy data.

5.5 Optimized annealing condition

The device fabrication process conditions affect the efficiency of the device. Thermal annealing can increase the performance of P3HT:PCBM transistor by increasing the crystallinity of P3HT and generate better contact between P3HT and the electrode [79]. The process condition optimized here is the annealing condition, pre-exposure and post-exposure bake.

Pre-exposure bake The annealing polymer above glass transition temperature can increase the crystallinity of P3HT which effects the charge transport in the device [79]. In this experiment, as-cast P3HT film was baked at different temperatures and times to optimize the UV-Vis absorption intensity. The UV-Vis absorption is shown in Figure 5.13 (a). All of the P3HT samples show the same absorption at wavelength 520 nm and the shoulder around 600 nm. The difference between the samples is the absorbance. P3HT annealing at 150 °C for 2 minutes shows the highest absorbance. The pre-bake sample at 170 °C for 2 minutes show the same absorption as P3HT with no anneal and all other conditions gave less absorption of light. From this experiment, annealing at 150 °C for 2 minutes is selected to be the pre-exposure bake condition for device fabrication because the absorbance is highest.

Post-exposure bake Another parameter is the post-exposure bake. Figure 5.13 (b) show the absorption length of the pre-exposure bake of P3HT at 150 °C for 2 minutes then exposed to the electron beam dose 450 $\mu\text{C}/\text{cm}^2$ and developed in *p*-xylene (green) compare with the pre-exposure bake of P3HT at 150 °C for 2 minutes then exposed to the electron beam dose 450 $\mu\text{C}/\text{cm}^2$, the post-exposure bake at 150 °C for 2 minutes and developed in *p*-xylene (red). The additional post-exposure bake step decreased the absorption length of P3HT so this post-exposure bake step was

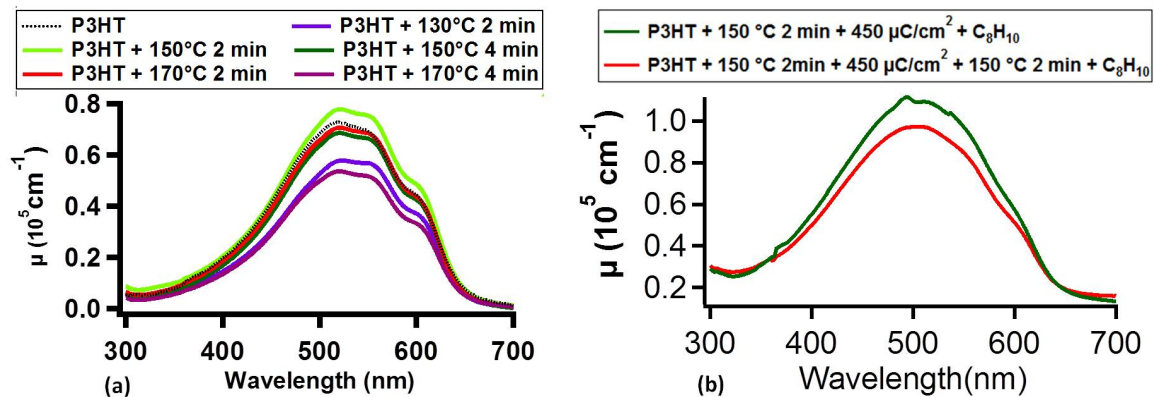


Figure 5.13: (a) UV-Vis of pre-exposure bake P3HT at various temperature and time; (b) UV-Vis of P3HT at different pre and post-bake condition.

not applied for the device fabrication process.

Chapter 6 Electronic Performance of Patterned Polymer Films in Solar Cells

The electron beam lithography technique is used to control the structure of P3HT/PCBM heterojunction solar cell device. In the device fabrication process introduced in Chapter 3, the P3HT donor is directly exposed with the electron or ion beam to cross-link the polymer. In chapter 5, the light absorption properties and chemical functional group of the irradiated polymers are determined by UV-Vis and IR spectroscopy. In this chapter, we characterize the electronic performance of lithographically-patterned P3HT films in P3HT/PCBM solar cells. For the proof of concept, we started with simple cross-link bilayer design and determined the efficiency. We also fabricated graded and bulk heterojunction (BHJ) P3HT/PCBM device to be control samples for the patterned device. We further built nanoline devices which are the ideal design for the organic solar cell device. The electronic performance of graded heterojunction, bulk heterojunction, cross-linked bilayer and nanoline devices are compared in this chapter.

6.1 Graded Device

The graded device is a bilayer device that has a nanoscale, interpenetration network between the donor and acceptor due to thermal annealing at the temperature which is higher than the glass transition temperature. Thermal annealing at a high temperature make both P3HT and PCBM diffuse so the structure of the graded device become similar to the bulk heterojunction device. Efficiencies of this devices are in the range of 1-3%. J-V characteristic curve of the bilayer device is shown in Figure 6.1 (a). The triangle symbols represent the J-V in dark illumination and the circle symbols represent the J-V in light illumination. Open and closed symbols mark the

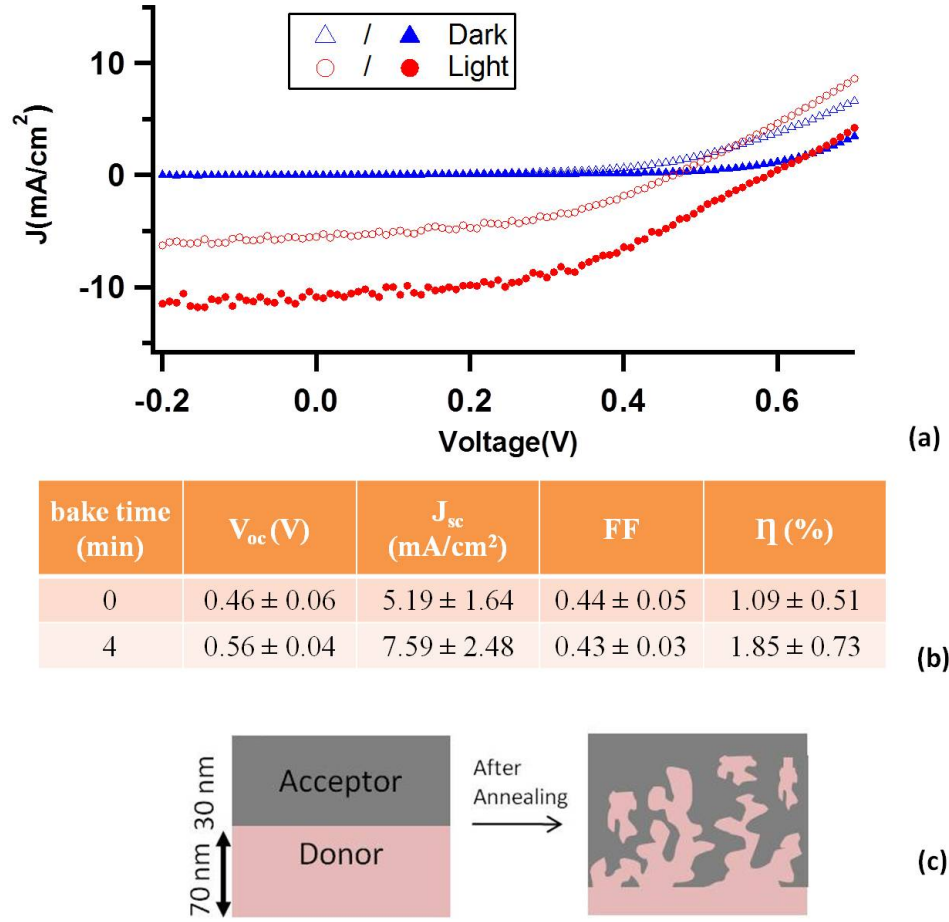
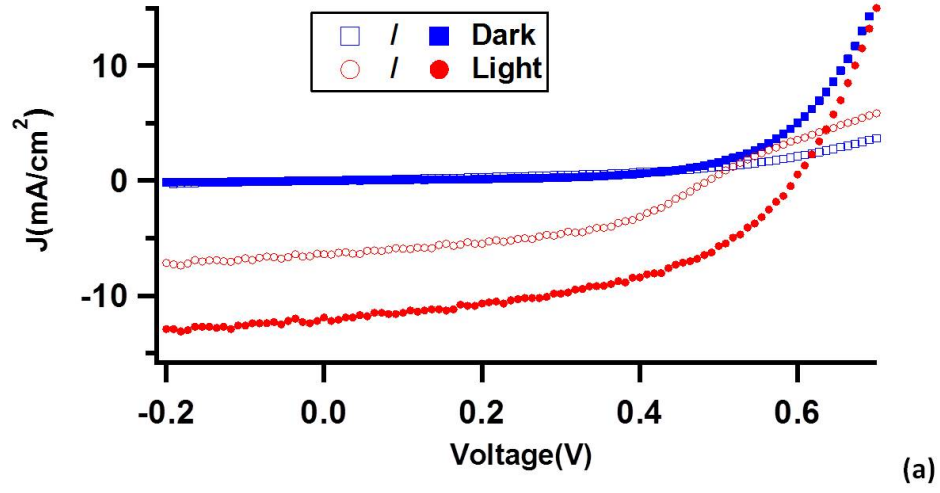


Figure 6.1: Bilayer Devices (a) J-V curves (b) Cartoon for the active layer structure before and after annealing (c) Table of electronic performance before and after 4 minutes annealing.

performance before and after 4 minutes of thermal annealing. Figure 6.1 (b) shows the V_{OC} , J_{SC} , FF and percent efficiency (η). The errors are based on an average of 5 samples. The increasing of V_{OC} , J_{SC} and efficiency after annealing the device are mainly due to the increasing of interfacial area between the donor and acceptor. The cartoon in Figure 6.1 (c) illustrates the improved efficiency presumably because both constituents are able to diffuse and increase the interfacial area upon annealing at 170 °C. V_{OC} was substantially increasing after annealing because of the better contact

between the active layer and electrodes.



bake time (min)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
0	0.54 ± 0.07	6.05 ± 0.52	0.44 ± 0.04	1.43 ± 0.05
4	0.60 ± 0.01	8.86 ± 3.01	0.46 ± 0.06	2.45 ± 0.85

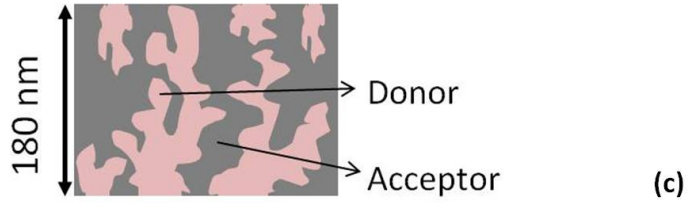


Figure 6.2: Bulk Heterojunction Devices (a) J-V curves (b) Cartoon for the active layer structure (c) Table of electronic performance before and after 4 minutes annealing.

6.2 Bulk Heterojunction Device

The bulk heterojunction device shown in Figure 6.2 (c) is the blended nanoscale structure between P3HT (donor) and PCBM (acceptor). BHJ has a large interface area and small domain which makes this design really efficient. The efficiency of bulk heterojunction (BHJ) devices were around 2.5 - 3.5 %. Figure 6.2 ((a) and (b)) show

the J-V curve and illustrate the electronic performance of BHJ devices. The errors are based on an average of 2 samples. The J_{SC} increase after thermal annealing the device due to more interfacial area between P3HT donor and PCBM acceptor. The increasing of V_{OC} is due to the better contact between electrode and active layer. The electronic characteristics of BHJ and bilayer devices are very similar. This finding indicates that the bilayer device generates a bicontinuous morphology during thermal annealing which is shown in Figure 6.1 (c) [80–82], which is expected based on the well-documented miscibility of P3HT and PCBM and fast inter-diffusion rates [83–85].

6.3 Cross-linked Bilayer Device

Both the electron beam and ion beam are used to cross-link the P3HT donor in the device fabrication process. The same cross-linking mechanism for both systems is proposed in Figure 5.9. The advantage of the ion beam over the electron beam is the fast patterning speed. The ion beam can cross-link the large area of the polymer in a short period of time. For example, it takes the electron beam approximately 2 hours to cross-link $3 \times 3 \text{ mm}^2$ with dose $450 \text{ } \mu\text{C}/\text{cm}^2$ and beam current 10 pA. Conversely, the ion beam can do the same thing in 60 seconds with the dose $2 \text{ } \mu\text{C}/\text{cm}^2$ and source current 4 mA. In this section, the devices for both systems are illustrated.

There are two significant differences between this work and others in the literature. First, the device active areas are small (ca. $0.02\text{-}0.05 \text{ cm}^2$), so edge effects could inflate the measured short-circuit current density [86,87]. Second, the cathode is Al rather than the optical LiF/Al design, and this leads to inferior power-conversion efficiency [88,89]. With these factors in mind, the device characteristics in this dissertation should be compared against each other rather than other works.

Table 6.1: Electronic performance of P3HT/PCBM solar cells after 4 minutes annealing at 170°C. Bi = Bilayer, NP = Nanopillar with 400 nm pitch.

Design	Dose ($\mu\text{C}/\text{cm}^2$)	Developer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
Bi	300	C ₆ H ₅ Cl	0.56 ± 0.01	2.67 ± 1.32	0.36 ± 0.03	0.55 ± 0.33
Bi	450	C ₆ H ₅ Cl	0.57 ± 0.04	3.07 ± 1.25	0.35 ± 0.01	0.61 ± 0.27
Bi	600	C ₆ H ₅ Cl	0.58 ± 0.02	1.51 ± 0.66	0.34 ± 0.01	0.30 ± 0.15
Bi	300	C ₈ H ₁₀	0.58 ± 0.03	1.47 ± 0.32	0.34 ± 0.01	0.29 ± 0.08
Bi	450	C ₈ H ₁₀	0.59 ± 0.02	1.24 ± 0.30	0.36 ± 0.03	0.33 ± 0.10
Bi	600	C ₈ H ₁₀	0.60 ± 0.02	1.38 ± 0.02	0.35 ± 0.02	0.29 ± 0.01
NP	600	C ₈ H ₁₀	0.60 ± 0.01	1.79 ± 0.13	0.42 ± 0.04	0.45 ± 0.04

Electron Beam

The cross-linked bilayer device with electron beam is the device that the P3HT donor is cross-linked with the electron beam before cast with PCBM donor. The variable in these experiments were exposure dose and type of developer; Patterns were defined with an area dose of 300, 450 or 600 $\mu\text{C}/\text{cm}^2$, and then developed with either chlorobenzene or *p*-xylene. There are two types of control samples that were not exposed to electron-beam radiation: BHJ based on P3HT/PCBM blends, and bilayer devices that were prepared by sequential casting of P3HT and PCBM layers from orthogonal solvents. [81, 82, 90] Table 6.1 summarizes the average photovoltaic response for all devices after annealing for 4 minutes at 170 °C

The power-conversion efficiencies (PCE) of lithographically-defined gradient active layers range from 0.3 - 0.6 %, while PCE of control samples prepared by sequential casting is approximately 2%. This difference stems from smaller fill factors (FF) and short-circuit current densities (J_{SC}) when the active layer is built with EBL. The open-circuit voltage (V_{OC}) is not affected by the lithographic process. There are two likely causes for diminished electronic performance of electron-beam patterned heterojunctions. First, the patterned P3HT films are slightly photobleached during

development, so the polymer absorbs less light (Figure 5.4). Photobleaching could also reduce the carrier mobility. Second, cross-linking the P3HT film will prevent the formation of a nanoscale P3HT/PCBM network during thermal annealing. The smaller interfacial area in gradient devices will reduce the density of photo-generated charges. We note that other studies of P3HT-PCBM interdiffusion, [25,80] although it is difficult to compare these data against ours due to the differences in device layout and processing methods.

The spectroscopy data in Figure 5.4 suggest that purified *p*-xylene is more effective at suppressing photobleaching than chlorobenzene. However, as summarized in Table 6.1 and Figure 6.3, development with chlorobenzene can yield higher values of PCE than *p*-xylene. This finding might suggest that chlorobenzene is the better developer, but there are three observations that lead us to select *p*-xylene. First, there is less sample-to-sample variability when developing with *p*-xylene compared with chlorobenzene. Figure 6.3 shows that the error bar for the devices developed with *p*-xylene is much smaller than the devices developed with chlorobenzene and these statistics are also included in Table 6.1. Second, the PCE of the cross-linked bilayer device developed with *p*-xylene are independent with exposure dose. Figure 6.3 shows that there is less variation of PCE with the exposure dose when developing the cross-linked device with *p*-xylene compared with chlorobenzene. Third, development with *p*-xylene yields heterojunction with better thermal stability than chlorobenzene.

Figure 6.4 reports the current-voltage (J - V) characteristics of a few gradient devices, both before and after thermal annealing for 4 minutes at 170 °C. Figure 6.5 (a) shows that the J - V characteristic of the control device (blue) is changing as a function of time but for the cross-link device (red) the J - V parameters are constant after annealing for 2 minutes. Open/partially filled/closed symbols correspond with

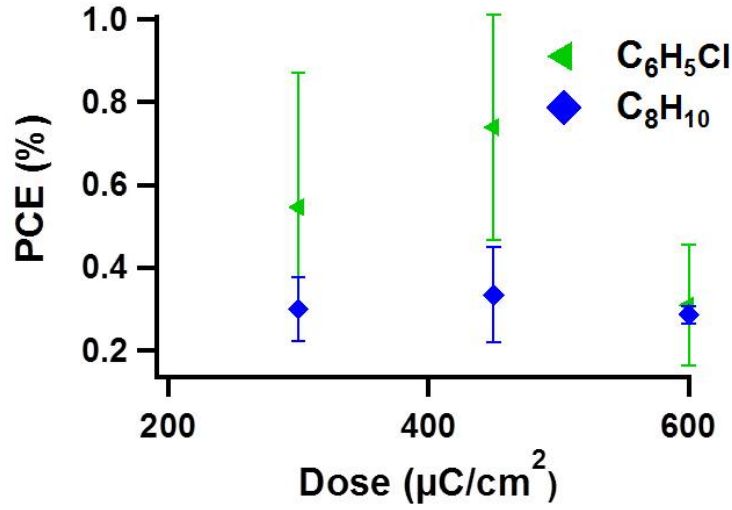


Figure 6.3: Power-conversion efficiency (PCE) of bilayer P3HT/PCBM devices as a function of exposure dose in chlorobenzene (green) and *p*-xylene developer (blue) developer.

no annealing, 2 minutes and 4 minutes thermal annealing at 170 °C, respectively. This implies that the active layer structure of cross-linked devices are thermally stable at a very high temperature (170 °C).

Figure 6.5 (b)-(c) reports the power-conversion efficiency as a function of annealing time for all gradient devices. Control PCE (diamonds) refer to 0 $\mu\text{C}/\text{cm}^2$, and EBL PCE (circles, triangles, square) refers to lithographically-defined bilayer devices. The same trends are observed for control samples and patterned samples that were developed with chlorobenzene: after annealing, the PCE is doubled due to improvements in V_{OC} , FF and J_{SC} . In contrast, samples that were developed with *p*-xylene are nearly unchanged by subsequent thermal annealing (approximately 10% improvement in PCE).

The electronic characteristics of lithographically-defined gradient heterojunctions are independent of exposure dose. This result is consistent with the proposed cross-linking mechanism in Figure 5.9: If the ionization reaction generates cross-links

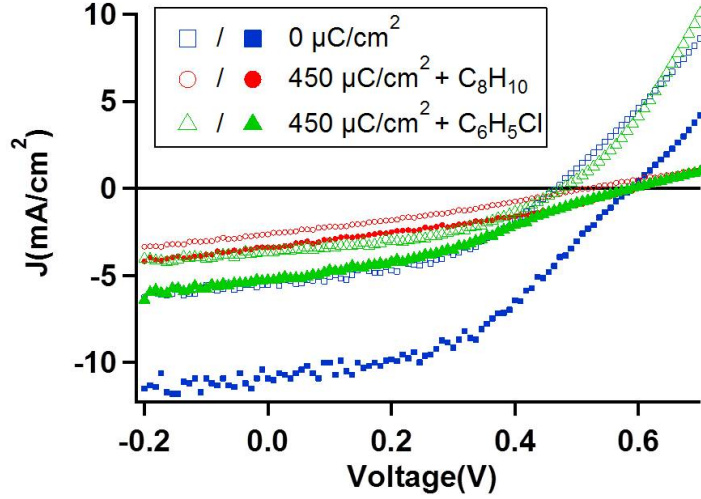


Figure 6.4: J - V characteristics of bilayer P3HT/PCBM solar cells compared with graded device ($0 \mu\text{C}/\text{cm}^2$). Open/closed symbols correspond with no annealing and 4 minutes thermal annealing at 170°C , respectively.

at the α -carbon on hexyl substituent, then increasing the exposure dose should not affect the optoelectronic function. We do find that sample-to-sample variability in PCE is minimized by increasing the exposure dose (Figure 6.3). Such improvement in reproducibility are explained by the lithographic contrast curve in Figure 4.11 (c). The slope of the contrast curve is a maximum when the exposure dose is between 200 and $500 \mu\text{C}/\text{cm}^2$, which means that a slight variation in beam current or development time will change the residual thickness of the P3HT film. The contrast curve is flat when the dose exceeds $500 \mu\text{C}/\text{cm}^2$, so the process is less sensitive to human error above this threshold. Other studies have demonstrated that PCE in gradient P3HT/PCBM heterojunctions is very sensitive to the thickness of P3HT films, and variations at the scale of 10 nm can change J_{SC} by a factor of 2 [91]. This sensitivity to film thickness can explain why J_{SC} seems to vary with the type of developer, because the residual film thickness will differ for chlorobenzene and *p*-xylene.

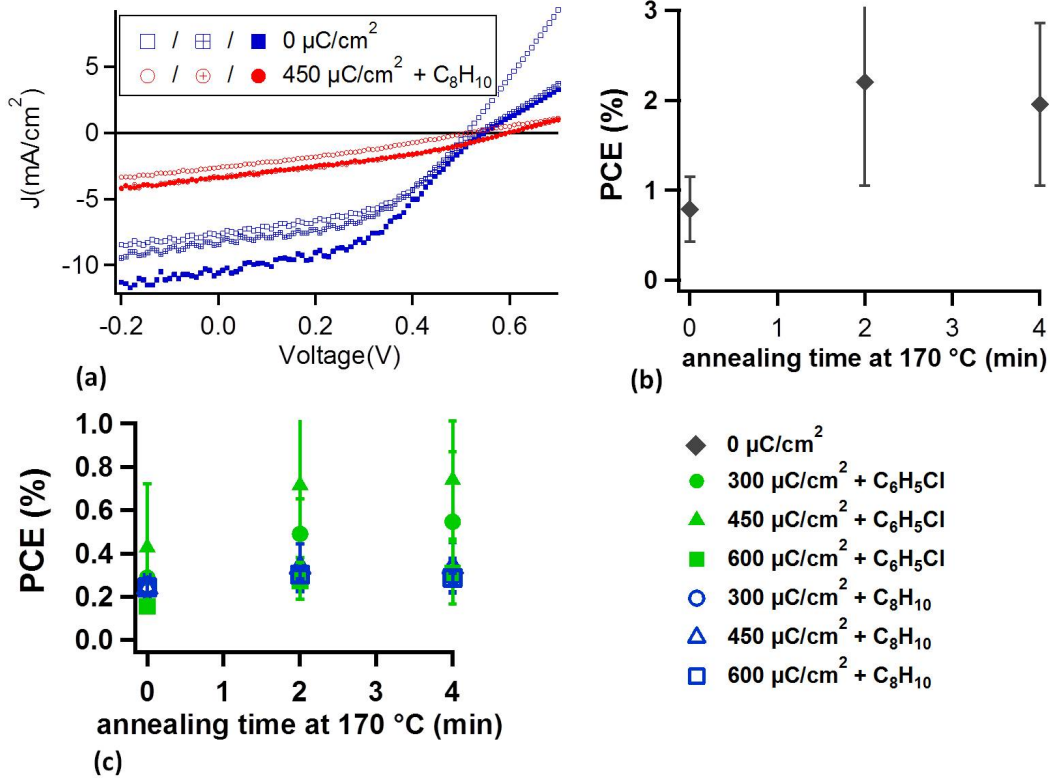


Figure 6.5: (a) J - V characteristics of bilayer device (b) Efficiency of bilayer devices as a function of annealing time (c) Efficiency of cross-linked bilayer devices as a function of annealing time.

Ion Beam

From Figure 6.6, the circle symbols represent the device which P3HT donor were cross-linked with an ion beam dose $0.6 \mu\text{C}/\text{cm}^2$ and spun cast PCBM on top without developing the P3HT film. The open and closed symbols stand for the data before and after thermal annealing, respectively. The efficiencies of the cross-linked device without development are a little bit lower than the control sample. The decreasing of the efficiency could be attributed to the beam-induced damage in the patterned film, or cross-linking might change the active layer structure by limiting inter-diffusion (decreasing interfacial area). The triangle symbols represent the devices which P3HT

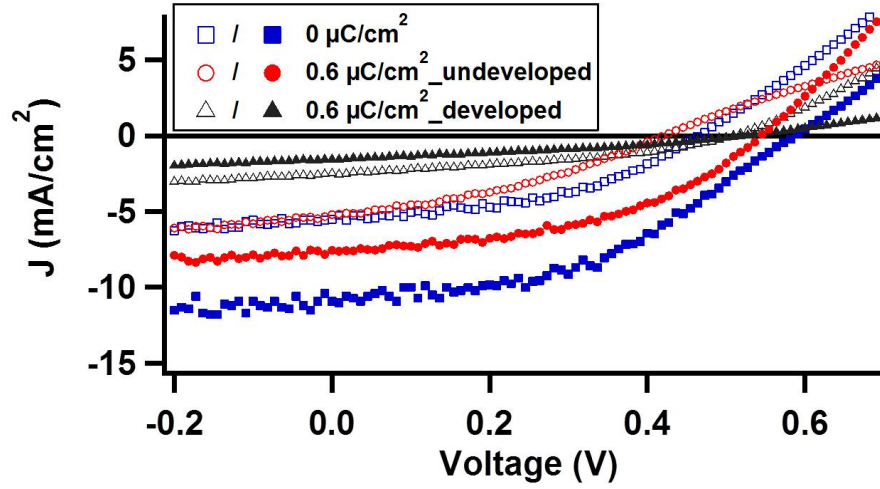


Figure 6.6: J - V characteristics of cross-linked bilayer P3HT/PCBM solar cells. Open/closed symbols correspond with no annealing and 4 minutes thermal annealing at 170 °C, respectively.

Table 6.2: Electronic performance of cross-linked bilayer P3HT/PCBM solar cells after 4 minutes annealing at 170°C

Dose ($\mu\text{C}/\text{cm}^2$)	Developer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
0	N/A	0.56 ± 0.04	7.59 ± 2.48	0.43 ± 0.03	1.85 ± 0.73
0.6	N/A	0.52 ± 0.03	8.80 ± 0.20	0.41 ± 0.07	1.90 ± 0.50
0.6	$\text{C}_6\text{H}_5\text{Cl}$	0.51 ± 0.03	1.70 ± 0.50	0.33 ± 0.01	0.30 ± 0.10

donor were cross-link with ion dose $0.6 \mu\text{C}/\text{cm}^2$ and developed with chlorobenzene. The low efficiency can be explained by the thickness loss of the donor after development. From the contrast curve (Figure 4.17), only 38% of the donor thickness remains after development so there is a small number of generated excitons.

6.4 Nanopillar device

The electronic property of P3HT is at least partly preserved through the electron beam patterning process during device fabrication which is confirmed by the working cross-linked bilayer device. The final goal is to make the ideal nanostructure design

which has the domain size smaller than exciton diffusion length. In this section, the nanopillar device is fabricated. We used electron-beam patterning to build nanostructured heterojunctions based on P3HT. The width and height of these P3HT pillars are approximately 200 nm and 40 nm, respectively, and the pitch is 400 nm. This domain size is much larger than the exciton diffusion length (~ 10 nm) so it is not ideal, but represents a first step in establishing the methods.

The patterns were exposed with an area dose of $450 \mu\text{C}/\text{cm}^2$ and then developed with *p*-xylene. This process leaves approximately 40 nm of residual P3HT between the pillars, so the anode is coated with a continuous P3HT film (see Figure 3.5 (a)). The J - V characteristic is shown in Figure 6.7. The open and closed symbols correspond with no annealing and 4 minutes thermal annealing at 170°C , respectively. Nanopillar devices show the same thermal stability with annealing time as a cross-linked bilayer. The average PCE for these nanopillar devices is approximately 30% larger than lithographically-patterned P3HT/PCBM bilayer heterojunctions. This improvement stems from larger values of J_{SC} and FF due to the increase in interfacial area. The average PCE of these nanopillar devices is inferior to the BHJ design, but this is not surprising since the 200 nm pillar width is much larger than the exciton diffusion length [92]. Uniquely, after measuring the J - V characteristics for these nanopillar devices, the morphology can be inspected with microscopy by deconstructing the active layer. Deconstruction is a simple, two-step process shown in Figure 6.8 (a) and the results are included in Figure 6.8 (b)-(c). First, the Aluminum cathode is removed with a drop of aqueous potassium hydroxide solution and then the active layer topography is measured with atomic force microscopy (AFM). A faint dot pattern is detected in these images, demonstrating that the thickness of the PCBM coating is slightly modulated by the underlying P3HT grating. Second,

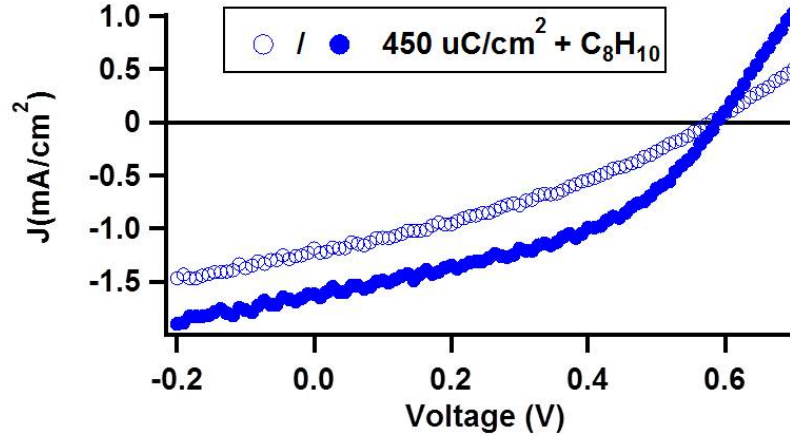


Figure 6.7: J-V characteristics of 400 nm pitch nanoline P3HT/PCBM solar cell. Open/partially filled/closed symbols correspond with no annealing and 4 minutes thermal annealing at 170 °C, respectively.

the PCBM phase is washed away with dichloromethane, and then the P3HT phase is imaged with AFM. The P3HT nanostructures are still intact after multiple thermal annealing, solvent-based processing and electronic characterization steps.

Stability of Nanostructure device The nanoline device is proved to be thermally stable and solvent resistant by the experiment in Figure 6.9. First, the P3HT was cross-linked with EBL and developed in solvent to get the nanoline in Figure 6.9 (a). Second, PCBM was coated on the cross-linked P3HT nanostructure and the image is shown in Figure 6.9 (b). Third, PCBM on the nanostructure was removed by dichloromethane. The image in Figure 6.9 (c) show that the nanoline are there so the cross-linked P3HT nanostructures are stable through the solution-based processing. This cross-linked nanolines are solvent resistant. Fourth, PCBM was coated on P3HT nanostructures and the model heterojunction was baked at 170 °C for 2 minutes and 4 minutes. The image in Figure 6.9 (d) shows that the nanolines were coated. Fifth, PCBM was removed by dichloromethane. The cross-linked P3HT nanostructure are stable after the bake process at 170 °C for 2 minutes (Figure 6.9 (e)) and 4 minutes

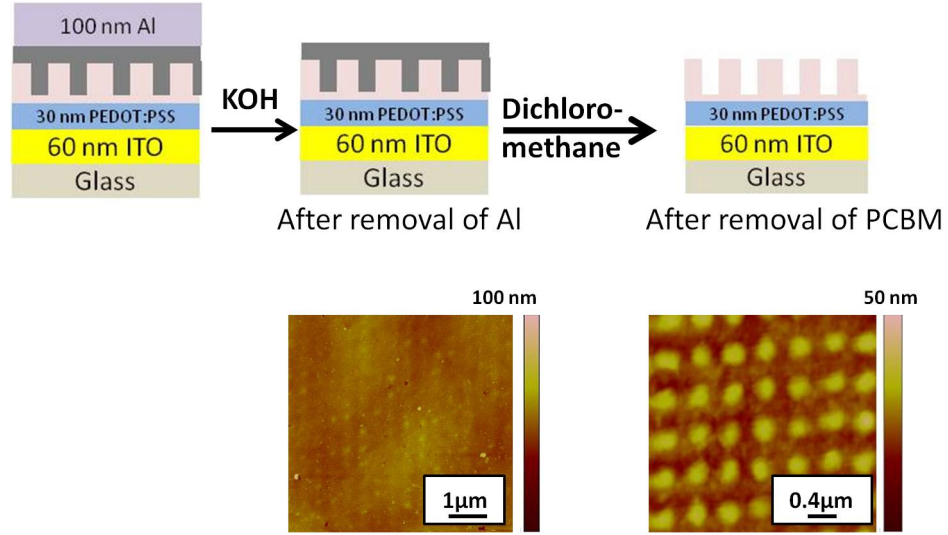


Figure 6.8: (a) Device deconstruction procedure. Surface of the nanostructured P3HT/PCBM composite (b) after removal of Al cathode and (c) after immersion in dichloromethane.

(Figure 6.9 (f)).

Polymer-based electronics have limited stability through thermal or solution-based processing, and this challenge is usually addressed by synthesizing polymer semiconductors with crosslinkable side groups [91,93–96]. In our approach, polymer cross-linking is inherent to the lithographic process. Cross-link density is controlled by exposure dose, so properties such as thermal stability, mechanical stability, and solvent resistance are easy to optimize for a specific application.

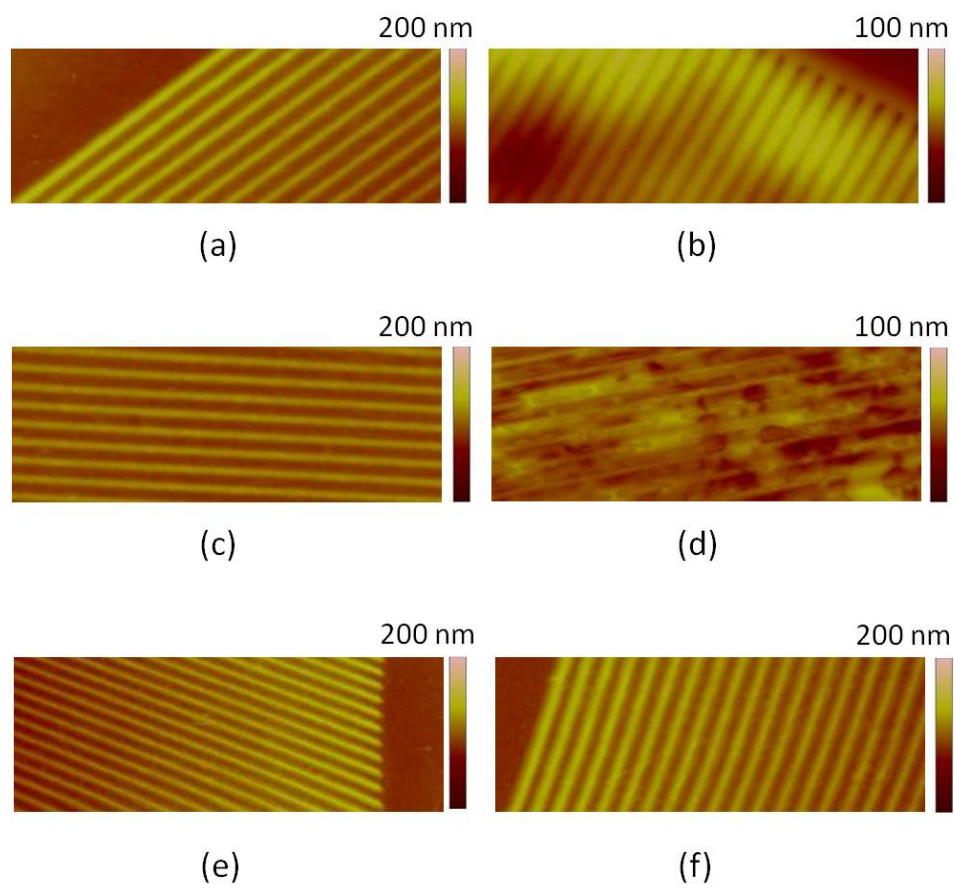


Figure 6.9: The procedure for the test of P3HT nanostructure heat/solvent resistant.

Chapter 7 Conclusions and Outlook

7.1 Conclusions

We developed a simple, two-stage approach to control the morphology of polymer/fullerene solar cells based on direct-write lithography of polymer semiconductors. First, thin films of poly(3-hexylthiophene) (P3HT) are cross-linked into conductive nanostructures or microstructures with electron-beam lithography. Second, the polymer structures are coated with a soluble fullerene to complete the heterojunction. This methodology offers several features that are very valuable for fundamental structure-property investigations. First, the lithographic process is compatible with commercially-available materials. Second, the cross-linked polymer structures are stable through thermal annealing and solution-based processing. Third, different designs can be studied systematically because nanostructure size, shape, density and placement are all controlled with computer software. Finally, after measuring the optoelectronic characteristics of these model devices, the active layer can be deconstructed to measure the morphology.

We have verified that patterned P3HT films can absorb light, generate charges and conduct charges. The optoelectronic properties of irradiated P3HT films are surprisingly good and this finding is attributed to a cross-linking mechanism that preserves the thienyl groups. Further studies are needed to fully evaluate the effects of irradiation and their development on molecular structure, crystallinity and charge-carrier mobility. The basic principles could be extended to a variety of solution-processable organic semiconductors.

Electron-beam lithography is too slow for large-scale production of polymer-based optoelectronic devices. However, like electrochemical nanopatterning and other scanning-probe techniques, [97–100] direct-write lithography could be very valuable

for basic scientific investigations. For example, when nanoscale polymer devices are generated *in-situ* with lithography, their positions are precisely controlled for integration into circuitry. This attribute is very useful for testing the function of nanoscale optical and electrical sensors [96, 101, 102]. The cross-linking reaction is advantageous for devices that require sequential casting of different layers, such as multi-color light emitting diodes [94] or tandem solar cells [93]. Other lithographic tools based on ionizing radiation may be appropriate for manufacturing. For example, we have shown that ion beams effect the same cross-linking reactions as electrons, but at much lower doses. Proximity ion beam lithography systems can provide high-throughput (square meters per hour), [103–106] offering a route to low-cost nanopatterning of polymer semiconductors for a variety of applications.

7.2 Outlook

Ordered Heterojunction (OHJ) device The cross-link bilayer devices with EBL proved that optoelectronic properties of the polymer are largely preserved through the fabrication process. In addition, spectroscopy data, IR and UV-Vis, support that thiophene ring which responsible for absorption of light and all electronic properties still functioning. The average power conversion efficiency for nanoline devices is approximately 20% larger than lithographically-patterned P3HT/PCBM gradient heterojunctions. Future studies will focus on the OHJ device. OHJ devices will be studied and will optimize the efficiency by three parameters.

1. Domain Size: Theoretical prediction shows that the efficiency of the solar cell improves with smaller domain size of the donor in order to dissociate the excitons [24, 25]. In the current work, a nanoline device has approximately 200 nm in diameter which is about 10 times larger than exciton diffusion length. The

domain size can be controlled with the focus of the electron beam. The new EBL instrument can resolve smaller features.

2. Ratio of donor to ratio of acceptor: To maximize efficiency of OHJ, the ratio of P3HT:PCBM has to be optimized. Based on the studies in BHJ devices, the 4 to 1 mass ratio of P3HT:PCBM has the highest efficiency. The mass fraction can be controlled by the domain size of patterned P3HT and the pitch between the pattern.
3. Interfacial width: P3HT-PCBM interfacial width can be varied by thermal annealing, solvent quality and cross-link density. Thermal annealing allows the diffusion of PCBM to P3HT layer so the degree of diffusion can be controlled by temperature and time of annealing. Good solvent will swell polymer and assists in greater diffusion of PCBM to P3HT. The cross-link density of the polymer depends on electron beam exposure. The cross-link density of polymer can be studied by a swelling experiment of cross-linking P3HT with different solvent using ellipsometry. The cross-link density and swelling can be related using Flory-Rehner theory.

Optimize the developing process The absorption in UV-Vis and IR data are significantly decreasing after the patterned P3HT immersed in chlorobenzene or *p*-xylene. In chapter 5, we minimized the oxidation process by changing the developer, changing the beaker and bubbling nitrogen through the developer. With this method, the UV-Vis and IR data still show the evidence of photobleaching of P3HT. Another possibility is that residual iron catalyst from the polymer synthesis is sensitized by electron-beam radiation, generating free radicals that could attack the thienyl ring and reduce the extent of conjugation. This explanation is consistent with UV-Vis

and IR absorbance spectra. Further investigations are underway to identify the photobleaching mechanism and address this challenge.

Series Resistance and Shunt Resistance Series resistance (R_S) is the resistance to the current flow at each point in the device. High R_S will reduce J_{SC} and lower the efficiency of the device. On the other hand, high shunt resistance (R_{SH}) is desired. A low R_{SH} means that the device can lose current through an undesired pathway. For an ideal device R_S is zero and R_{SH} is infinity. The R_S and R_{SH} are the important parameters for solar cell devices which can be modeled by fitting the J-V curve of each device to ideal diode equation (equation 2.2).

Ideally, the nanoline design should have higher R_{SH} compared with BHJ because of direct pathway of charge transport to the electrode. The low J_{SC} in nanoline device might due to the high R_S . Knowing this, both R_{SH} and R_S will be useful to adjust the device design to maximize the efficiency.

Chapter 8 Ordered arrays of polymer droplets with triangular, circular, and rod like shapes

This chapter demonstrates that the topographically-patterned oxide surfaces can direct the dewetting of an overlying polystyrene film and produce triangular, circular, or rod-like droplets. Thin films of polystyrene on oxide surfaces are unstable and will rupture by spinodal dewetting. We demonstrate that spinodal dewetting can be suppressed with topographically-patterned surfaces. Dewetting is initiated at specific points on the surface by modulating the film curvature, and this drives the formation of unstable polymer rims that break apart into discrete droplets. The symmetry of oxide patterns controls the direction of polymer flow during dewetting, and these dynamics determine the locations and shapes of polymer droplets. Patterns with two-fold symmetry generate drops shaped like rods or bullets, and patterns with three-fold symmetry will produce triangles, distorted circles, or perfect circles.

8.1 Introduction

The instability of thin polymer films has been studied extensively through theory, simulations, and experiments [107,108]. When a thin polymer film is cast on a non-wettable surface, microscale polymer droplets are formed by a three-stage process. First, holes are formed in the film through capillary instability, thermal nucleation, or heterogeneous nucleation. Second, the holes will grow and coalesce into ribbons. Finally, the ribbons will break apart into discrete circular droplets. These studies of film rupture are partly motivated by applications in coatings, adhesives, and lubrication, where the polymer film must be stable for optimal performance. On the other hand, *unstable* polymer films can be very valuable for large-area micropatterning. Compared with optical lithography, the spontaneous formation of microscale

polymer droplets is very simple and inexpensive. However, the sizes, shapes, and positions of polymer droplets must be controlled for most patterning applications.

Recently, there have been many studies of polymer thin film dewetting on topographic patterns, [77, 109–116] on chemical patterns, [111, 117–121] and in confined geometries [122–128]. These reports demonstrate that simple templates can direct the dewetting process and provide some level of control over the locations of polymer droplets. The exact rupture and dewetting mechanisms will differ according to the type of template. For example, corrugated surfaces initiate dewetting by physically modulating the film curvature, [109, 114] while chemical contrast drives mass transfer towards to the more wettable regions of the substrate [117, 120]. Droplets are ultimately formed at the more stable sites, provided the dimensions of these sites are commensurate with the dominant instability modes [117]. Usually, the droplets are shaped like circles (spherical caps), which is the expected equilibrium profile for liquid wetting on a solid surface. However, with three-dimensional confinement or complex chemical patterns, it is possible to produce transient anisotropic droplets such as "bullets" or distorted circles [122, 124, 129]. In such instances, it is very likely that dewetting dynamics are generating unusual droplet profiles, [130] suggesting that droplet shapes can be tuned by controlling the direction of polymer flow.

In this report, we use topographically-patterned oxide surfaces to direct the dewetting of an overlying polystyrene film. The symmetry of the patterned surface controls the direction of polymer flow during dewetting, so the locations and shapes of polystyrene droplets are both tunable parameters. We use this approach to generate triangular, circular, and rod-like polystyrene droplets with long-range lateral order. We propose design guidelines for templating ordered arrays of these unusual droplet shapes. These guidelines consider commensurability between the dimensions

of the patterned surface and the dominant instability wavelengths at each stage in the dewetting process.

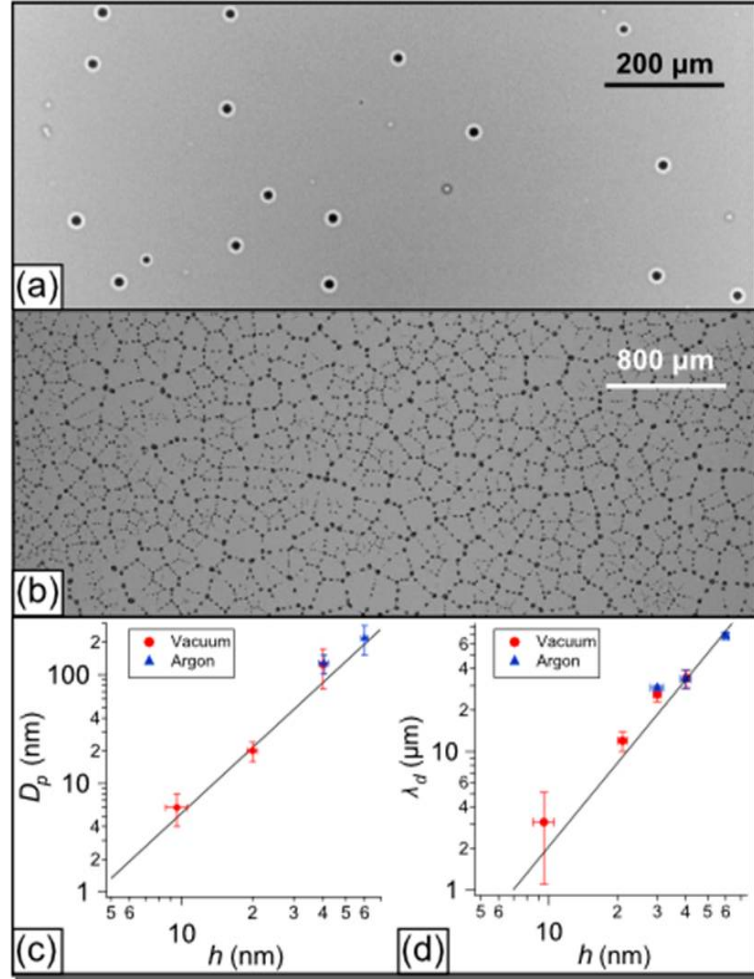


Figure 8.1: (a,b) Optical micrographs of PS dewetting on SiO₂ surfaces annealed for (a) 16 hrs and (b) 1 day at 160°C. (c) Polygon size D_p as a function of h . (d) Correlation length of dewetted droplets λ_d as a function of h .

8.2 Experimental Methods

Micropatterned surfaces are prepared with photolithography and wet chemical etching. Substrates are (100) silicon coated with 200 nm of silicon dioxide (SiO₂)

grown by thermal oxidation. The photomask is patterned with arrays of hexagonal windows. The hexagons range in width from $L = 5$ to $95\text{ }\mu\text{m}$ and are separated by spaces of $L = 3.6$ to $7\text{ }\mu\text{m}$ (see Figure 8.2).

The lithographic process is fairly standard: Substrates are cleaned with ultraviolet light/ozone, coated with approximately $1\text{ }\mu\text{m}$ of S-1813 positive-tone photoresist (Diazonaphthoquinone/novolac, MicroChem), and then baked at 115°C for 60 seconds to drive off residual solvent. The lithography was completed with a contact aligner (broadband ultraviolet light) at a dose of 90 mJ/cm^2 . Relief images were developed in MF-319 (aqueous tetramethyl ammonium hydroxide, MicroChem) for 30 seconds, rinsed with deionized water, and dried with nitrogen.

Photoresist residue in the hexagons was removed by short exposure to oxygen plasma. Hexagonal wells are made by etching in aqueous hydrofluoric acid (7 wt%) to a depth of $(120 \pm 20)\text{ nm}$. The photoresist is removed by soaking in *N*-methylpyrrolidinone for 2 minutes. The oxide patterns are cleaned with Piranha solution (4 parts sulfuric acid, 1 part 30 wt% aqueous hydrogen peroxide), which destroys any organic contamination and makes the oxide surface very hydrophilic. Clean patterned surfaces are immediately spin-coated with $(40 \pm 2)\text{ nm}$ of polystyrene (PS) film (molecular weight = 10.3 kg/mol , polydispersity index = 1.03). All samples are annealed in either a low vacuum oven (10 mTorr) or an Argon-purged heat cell that has a viewing window for optical microscopy. Annealing temperatures were 140°C or 160°C for all samples. We note that dewetting kinetics are often different for the two environments, with shorter time scales for annealing under Argon compared with vacuum. The reasons for this discrepancy are uncertain, but it is possible that oxide surfaces are slowly contaminated by oil vapors or other residues, and the type/rate of contamination will vary among different environments. It is also possible that SiO_2

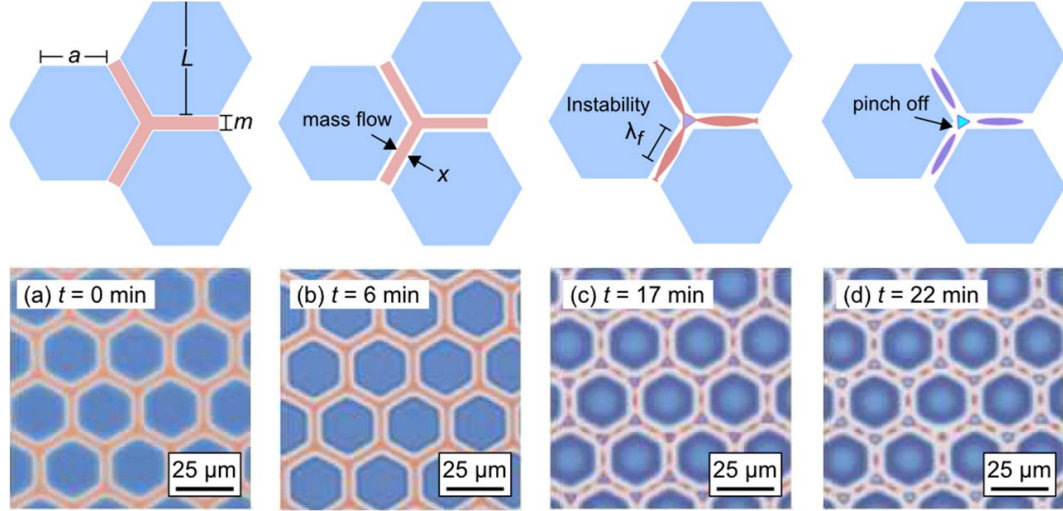


Figure 8.2: Dewetting of a 40 nm PS film on a micropatterned surface at 140°C under Argon.

surfaces are dehydrated under low vacuum, which changes the types of interactions at the polymer-substrate interface. Similar findings have been reported by others [131]. Despite differences in the kinetics, the dewetting mechanisms and outcomes are the same. The dimensions of the PS structures are characterized with both bright-field optical microscopy (Nikon LV100) and tapping-mode atomic force microscopy (Veeco Dimension 3000). The sizes and locations of holes or droplets are calculated from each micrograph with a particle detection algorithm in IGOR Pro (WaveMetrics) or ImageJ, and then the average separation between holes or droplets is determined by Delaunay triangulation in MatlabTM.

8.3 Results and Discussion

The stability of thin PS films on SiO₂ surfaces has been studied extensively through experiments, theoretical models, and simulations [107,131–134]. Stability can be predicted as a function of initial film thickness (h) using a model for the effective PS/SiO₂ interface potential that incorporates short- and long-range interactions,

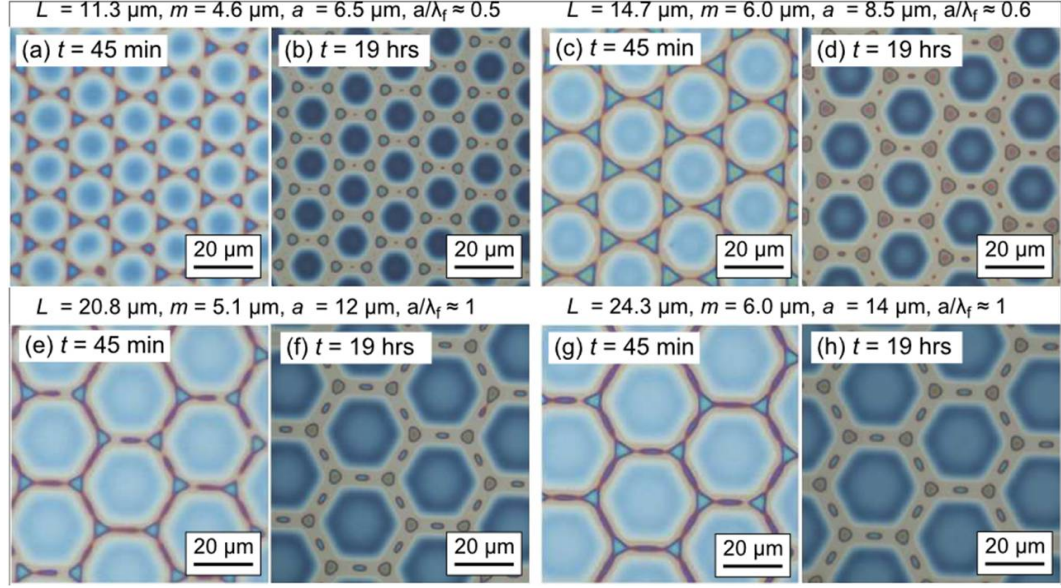


Figure 8.3: Dewetting of a 40 nm PS film on patterned SiO₂ surfaces with varying dimensions. Samples were annealed at 160°C under low vacuum for 45 minutes or 19 hours.

$$\phi(h) = c/h^8 - A_{SiO_2}/12\pi h^2, \quad (8.1)$$

where c is a short-range interaction strength and A_{SiO_2} is the Hamaker constant of PS on SiO₂. Interactions with the underlying bulk silicon are neglected in the model for $\phi(h)$ because we are using a thick SiO₂ layer [133]. The PS film is unstable when the second derivative of the interface potential is negative, i.e., $\phi''(h) < 0$, meaning capillary waves at the PS surface are amplified and the film will spontaneously dewett. This process is commonly referred to as “spinodal dewetting.” The wavelength of the dominant instability mode is calculated from the interface potential,

$$\lambda_s(h) = [-8\pi^2\sigma/\phi''(h)]^{1/2}, \quad (8.2)$$

where σ is the melt surface tension of PS. We annealed all samples at temperatures in the range of 140-160°C, where others have reported the parameters $c \simeq 6 \times 10^{-76}$ Jm⁶, $A_{SiO_2} \simeq 2 \times 10^{-20}$ J, and $\sigma \simeq 30$ mN/m [133]. Under these conditions, ultra-thin PS films are unstable ($\phi''(h) < 0$) and can rupture through spinodal dewetting. The predicted instability wavelength λ_s for a 40 nm PS film on 200 nm of SiO₂ is approximately 40 μ m.

The spinodal mechanism can be confirmed by examining the dewetting patterns of PS films on flat SiO₂ surfaces as a function of annealing time [107, 118, 131]. At short annealing times, the spinodal instabilities will generate correlated holes, meaning holes that are uniform in size with a characteristic separation length λ_h . This separation length is several times larger than λ_s , because only some of the modulations produced by surface instabilities will lead to hole formation [118, 131]. At long annealing times, the film will break up into correlated droplets with a length scale λ_d .

We use optical microscopy to study hole formation and film rupture, where the experimental variables are annealing time and film thickness. Annealing temperature is constant at 160°C for all studies (vacuum oven and Argon-purged heat stage), and statistics are calculated from 5-6 micrographs for each sample. After annealing for short times, correlated holes are observed in the film (Figure 8.1a). We find less than 5% variation in the hole dimensions (within each sample), which is consistent with the early stages of spinodal dewetting, and the correlation length λ_h ranges from approximately 100 μ m to 200 μ m as h is increased from 12 to 40 nm. After annealing for long times, the PS films have completely dewetted to form correlated droplets arranged in a polygonal pattern (Figure 8.1b). The circle-equivalent diameter of the polygons, D_p , is controlled by the dominant instability mode λ_s and the average

number of holes that combine to form a polygon N_c : [107]

$$D_p = \sqrt{\frac{\lambda_s^2 N_c^4}{\pi}} \propto h^2. \quad (8.3)$$

Figure 8.1c reports D_p as a function of h , along with the theoretical scaling predicted by Equations 8.1-8.3 with $N_c=3$. We found an excellent agreement between the model and experimental data. The value of $N_c=3$ has been reported by others for dewetting of PS films on solid surfaces, [107, 131] and our in-situ observations of the dewetting process confirm that most polygons are formed through coalescence of three holes. The droplet correlation lengths λ_d are summarized in Figure 8.1d as a function of initial film thickness h . These data follow the scaling $\lambda_d \propto h^2$ (solid line), consistent with other reports, [113] where these patterns are controlled by fingering instabilities during the final stages of dewetting [107, 108, 135].

In addition to spinodal dewetting, thin polymer films can rupture through thermal or heterogeneous nucleation. As discussed elsewhere, thermal nucleation is possible near the sign reversal for $\phi''(h)$ [133]. This criteria corresponds with a PS film thickness near 1 nm, so thermal nucleation should not be observed in our studies. However, heterogeneous nucleation can be induced by chemical or topographical defects [110, 117, 136–139]. With these predictions in mind, we expect that film rupture can be controlled with patterned surfaces through two routes. First, spinodal dewetting can be suppressed by lateral confinement at a dimension less than the critical spinodal wavelength, i.e., $L < \lambda_s/\sqrt{2}$ and $m < \lambda_s/\sqrt{2}$ [117]. Second, rupture can be initiated with high spatial resolution at heterogeneous sites, such as elevated mesas [109]. The geometry of the mesas will then determine the size, shape, and locations of polymer droplets [114, 122, 124].

Figure 8.2 illustrates the kinetics of PS film rupture, dewetting, and droplet

formation on a micropatterned surface at 140°C. The mesas and wells are initially coated with a conformal PS film that is 40 nm thick. The conformality of the PS coating is verified with atomic force microscopy measurements of the sample surface. Film thickness is measured from un-patterned (flat) regions of the sample using spectroscopic ellipsometry. The flat part of the sample is marked by the "star" in Figure 8.4a, which reports an optical micrograph of a patterned surface after coating with 40 nm of PS. One can see that the apparent film color is continuous from the patterned mesas to flat oxide surfaces. It is well-known that small changes in film thickness will produce large changes in the apparent color, so optical microscopy supports our assertion that films are uniform over these surfaces. The color changes near the edges of the wells due to the sidewall slope (continuous change in thickness of the underlying oxide). From atomic force microscopy in Figure 8.4b-c, we see that the film on top of the mesas is flat (no "beading").

As soon as the annealing temperature exceeds the glass transition temperature (ca. 100°C), the film begins to recede from the edges of the mesas and wells. This directional mass flow is observed because the film curvature is a maximum at the edges, which produces a local excess chemical potential that drives PS diffusion towards the flat regions of the substrate [114,140]. The PS film is then thinner at the edges of the mesa compared with the center (Figure 8.2a). With further annealing, different dewetting mechanisms govern pattern formation on the mesas and in the wells. These mechanisms are discussed in the following paragraphs.

8.3.1 Dewetting on mesas

The PS film dewetts on the mesas and forms cylindrical rims at short annealing times (Figure 8.2b). This dewetting process is initiated at the mesa edges where the PS film is thinnest [114,141]. When the width of each rim reaches a critical value on

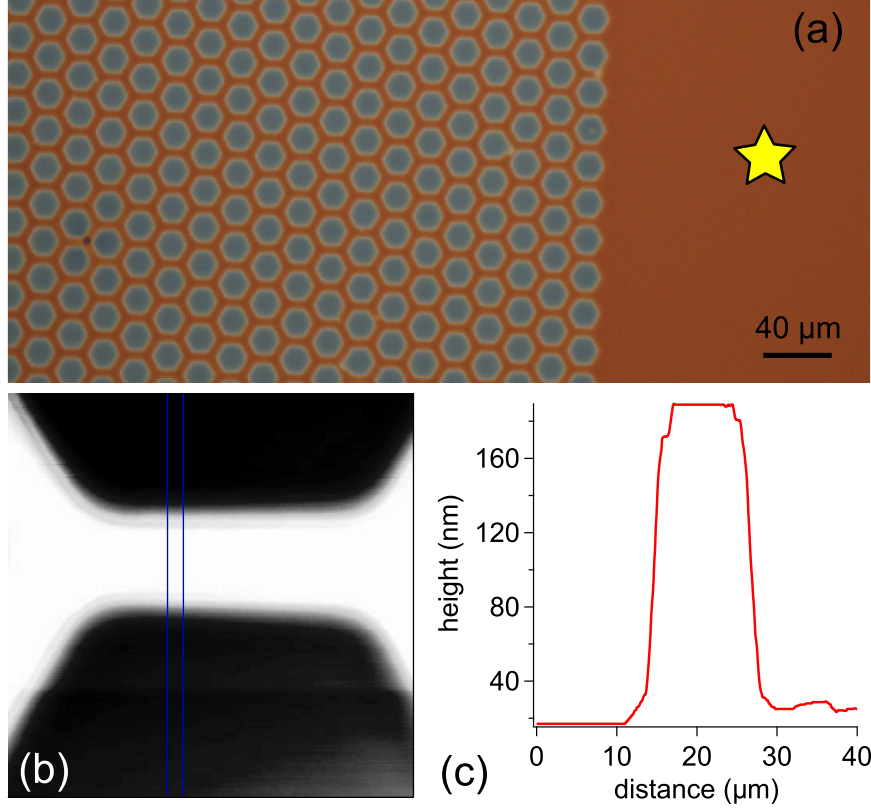


Figure 8.4: Data for patterned surfaces coated with 40 nm of PS film. (a) AFM measurement of the coated patterns. (b) Line cut from measurements in (a) that illustrates the flat mesa surface. (c) Optical micrograph of a coated surface.

the order of 1 μm , we observe the onset of a capillary instability that drives the rims to break apart into discrete patterned domains (Figure 8.2c) [120, 125, 135, 142, 143]. Further annealing primarily affects the pattern shapes, where geometries with high-curvature corners are transformed into circular shapes to reduce the line tension (Figure 8.2d).

The size, shape, number density, and placement of PS droplets are controlled by the mesa geometry and spreading dynamics [130]. The three-fold symmetry at each vertex of the hexagons will generate droplets with triangular shapes at short

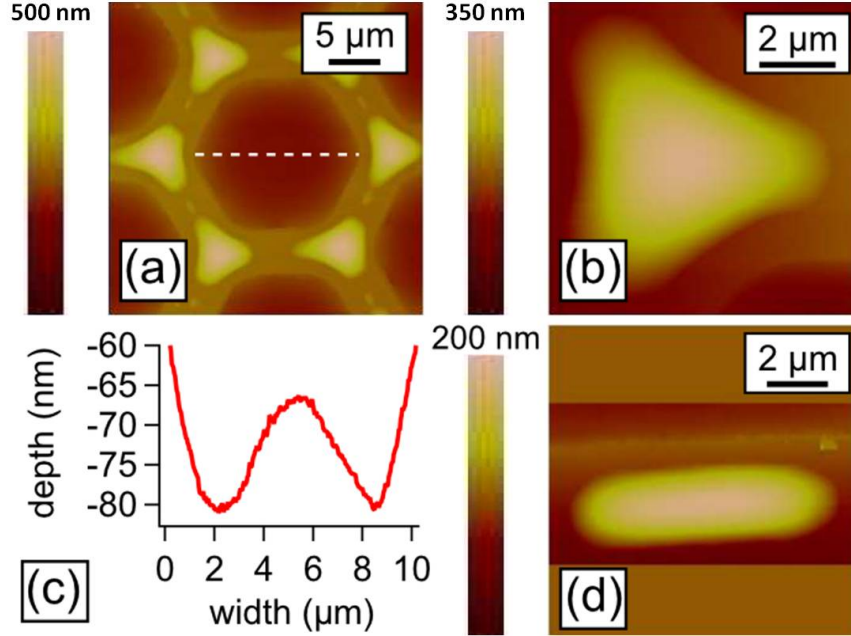


Figure 8.5: (a,b,c) Dewetting of a 40 nm PS film on a micropatterned surface (d) Rod-like droplet formed on larger mesa.

annealing times, and further annealing transforms the triangular patterns into distorted circles. Perfect circles are only observed on the smallest mesas ($a < 7 \mu\text{m}$) that exhibit the fastest dewetting dynamics. Figure 8.3 includes examples of triangular and circular droplets with long-range lateral order. When the length of the mesa a exceeds approximately $10 \mu\text{m}$, a regular pattern of elongated droplets is formed at the midpoint of each mesa. These elongated droplets reflect the two-fold symmetry along the length of the mesas. Figure 8.5 includes high-resolution atomic force microscopy measurements of these unusual droplet shapes. The sizes of all droplets will increase in proportion to mesa length a and width m , because larger mesas hold a larger PS volume. Note that all non-circular droplets are most likely kinetically-trapped.

The mesa lengths a are less than the critical spinodal wavelength, so we explain droplet formation on the mesas using models for rim (Rayleigh) instability. As illustrated in Figure 8.2, the initial stage of PS dewetting involves the formation of a

narrow cylindrical rim. This rim is unstable and will break apart into smaller droplets. The instability wavelength λ_f is proportional to the rim width x [125, 135, 144],

$$\lambda_f \simeq 4x = 4 \frac{\sin(\theta)}{\sqrt{\theta - \sin(\theta)\cos(\theta)}} \sqrt{mh}, \quad (8.4)$$

where $h=40$ nm is the film thickness and $\theta = (9\pm 2)^\circ$ is the equilibrium contact angle. This contact angle was calculated by measuring the droplet height profile with atomic force microscopy, and then fitting those data to a circular cap model. The extracted value of 9° is very consistent with other studies of PS/SiO₂ interfaces [133]. The mesa width m in our experiments varies from $3.6 \mu\text{m}$ up to $7 \mu\text{m}$, so the predicted instability wavelengths range from approximately $10 \mu\text{m}$ to $15 \mu\text{m}$. We find that the ratio a/λ_f controls the number of droplets per mesa, which is illustrated by the transient and equilibrium patterns in Figure 8.3. When the mesa length is commensurate with the instability wavelength, i.e., a/λ_f , the unstable rim on each mesa will pinch-off at two points near the hexagon vertices. This mechanism generates two droplets per mesa that are located at the vertex and midpoint. In cases where $0.4 < a/\lambda_f \leq 1$, the rim thins near the midpoint of the mesa and the polymer flows towards the vertices. This process generates very thin polymer strands that are sometimes drawn toward the vertices with the primary drops, but these strands are often unstable and can break off into very small drops at the middle of the mesas. These two cases are illustrated by Figure 8.3a/c and Figure 8.3b/d, respectively. We do not observe unstable strands when $a/\lambda_f \leq 4$. Figure 8.6 includes data for very long mesas for a 40 nm PS film annealed at 160°C for 85 minutes (vacuum), i.e., $a/\lambda_f > 1$. In these cases, the rim pinches off from the vertices and then breaks apart into multiple smaller droplets. It is possible that both spinodal instabilities and rim instabilities are driving droplet formation on these long surfaces (because a is similar to a/λ_s).

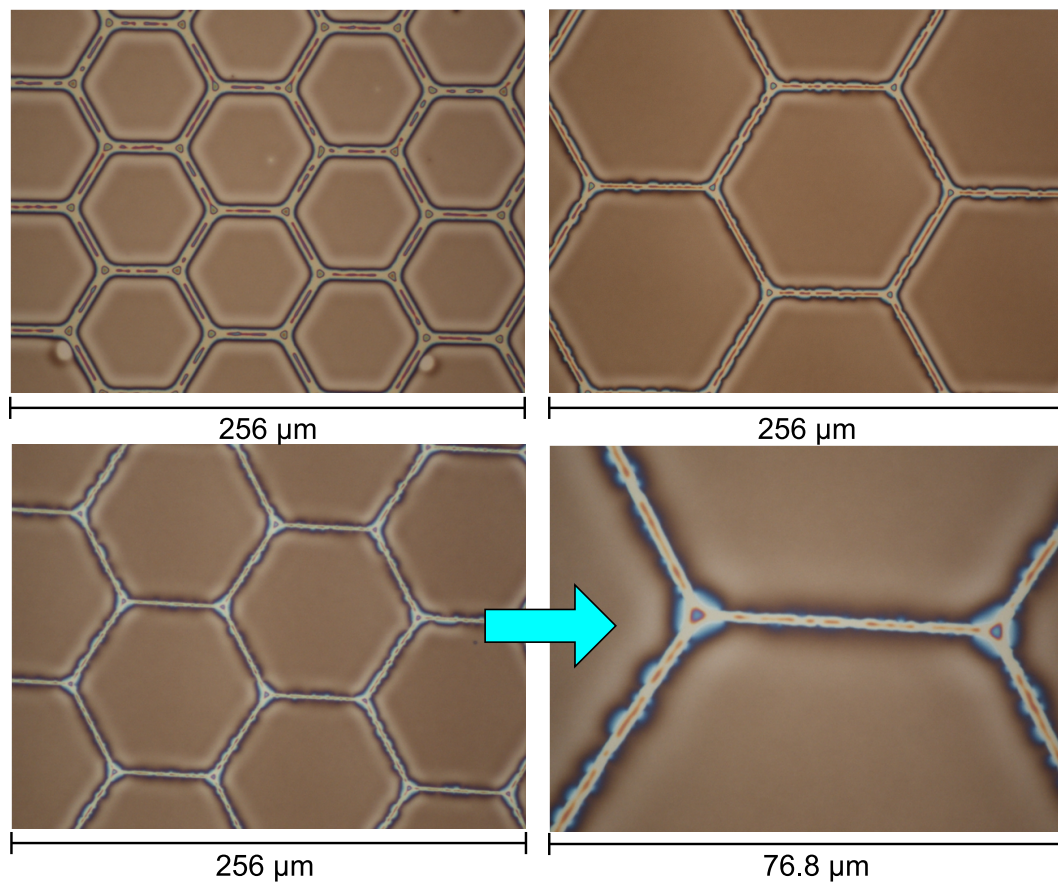


Figure 8.6: Break-up of cylindrical PS rim on long mesas.

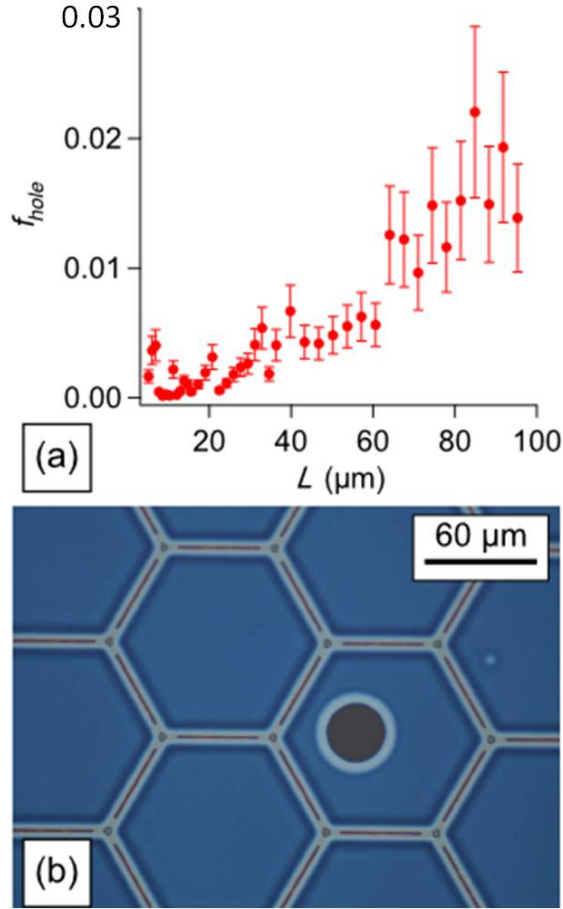


Figure 8.7: (a) Fraction of wells where the PS film has a hole f_{hole} as a function of well width L . (b) Hole formation in 81 μm wide wells.

8.3.2 Dewetting in wells

PS diffuses away from the walls and generates a thicker film at the center of the well. This thickness variation is observed through the changes in color in optical micrographs (such as Figures 8.2-8.3) and confirmed with atomic force microscopy measurements (Figure 8.5c). The PS film in the wells does not rupture, even after prolonged annealing, except in a few isolated locations. The predicted spinodal instabilities are most likely suppressed by the two-dimensional lateral confinement [117,122]. Additionally, the increased film thickness near the center of the well could have a

stabilizing effect. For our studies, the ratio of well width to the spinodal wavelength ranges from approximately $L/\lambda_s \approx 0.1-2$, so the fastest-growing instability modes are completely cut-off in most wells. We observe a slight increase in hole formation as the ratio λ_s approaches 2, but less than 3% of wells contain holes in these cases. This data is summarized in Figure 8.7a. We do not observe the modulations in film thickness that pre-empt spinodal dewetting, [114, 133] so rupture in the few isolated cases is most likely initiated by heterogeneities such as chemical contaminants or dust. The increase in hole occurrence with increasing well size (Figure 8.7b) is explained by the fact that a larger surface area is more likely to contain a randomly-introduced defect site.

8.4 Conclusions

In summary, we demonstrated that topographically-patterned surfaces can direct the dewetting of an overlying polymer film to produce ordered droplets with anisotropic shapes. This approach requires a patterned surface with two-dimensional symmetry, where the pattern dimensions are selected based on the dominant instability length scales at each stage in the dewetting process. We find that lateral confinement at a scale smaller than the critical instability wavelength ($\lambda_s/2$) will suppress spinodal dewetting on the mesas and in the wells. Dewetting is selectively initiated at the edges of mesas where the film curvature is a maximum, and this drives the formation of an unstable rim that breaks into discrete droplets. When the length of the mesa (a) is much smaller than the rim instability wavelength (λ_f), the rim will break apart in the middle and draw the polymer towards the pattern vertices. Under conditions where the mesa can support a full rim instability ($a \approx \lambda_f$), the rim breaks apart near the vertices and forms droplets at the center of each mesa and the pattern vertices. The symmetry of patterned surfaces controls the direction of polymer flow

during dewetting, which in turn sets the shapes and locations of polymer droplets. Our work demonstrates that thermodynamics and kinetics are equally important for pattern-directed dewetting of thin polymer films.

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