ABSTRACT

BALAR, NRUP LALJIBHAI. Blade-coating and Characterizing Organic Photovoltaic Devices for Roll-to-Roll Production. (Under the direction of Dr. Brendan O’Connor).

Organic solar cells have potential to reduce the manufacturing cost of solar cells and ultimately the cost of solar power. Currently, high efficiency organic photovoltaic (OPV) active layers are processed in the laboratory using spin casting, which is not suitable for scalable roll-to-roll production. Here, we explore the use of the scalable processing approach of blade coating, which is a prototype technique for roll-to-roll production. In blade coating, the solution concentration, substrate temperature, blade position and speed are all parameters that will influence the resulting film thickness and morphology, and have a direct impact on solar cell performance. We systematically vary these parameters for polymers exhibiting high aggregation characteristics to achieve high efficiency solar cells. Performance of OPV devices are highly dependent on the morphology of polymer films which is generally studied using optical as well as X-ray based measurement techniques. We demonstrated capability to carry out non-destructive characterization of OPV films using spectroscopic ellipsometry on ex-situ basis. We also used the blade-coater and the Variable Angle Spectroscopy Ellipsometer (VASE) system to study in-situ growth of polymers and understand the kinetics of drying of the films. Capability to study mechanical properties of OPV films was developed using a delamination based test system. Adhesion energy of a polystyrene (PS) film with a silicon (Si) substrate was measured and compared with available experimental results to understand the testing system and the methods.
Blade-coating and Characterizing Organic Photovoltaic Devices for Roll-to-Roll Production

by

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1. Organic Solar Cells

1.1. Photovoltaic Effect

The photovoltaic effect was observed by a French physicist Edmund Becquerel in 1839. He found that certain materials produced small amount of current when exposed to light. Einstein explained photoelectric effect, in 1905, which established the fundamental understanding of photovoltaic effect. When photons from light are illuminated on metal, electrons get energized and leave the surface of metal. The energy received by an electron is dependent upon the energy of the photon, which is dependent upon the frequency of the light rather than intensity. Electrons in the excited state quickly relax to the ground state. It is necessary to collect the excited electrons and holes left into ground state, at electrodes, to create a functional PV device.

When light shines on a semiconductor, electron in a valance band absorbs photon and gets excited. If the energy of the photon is equal to or more than the band gap the excited electron jumps to the conduction band. The electron in the conduction band can be collected at the electrode. Today, silicon is the most commonly used material to make solar cells. Silicon doped with Boron (electron deficient) and phosphorus (electron surplus) act as p-type and n-type conductors, respectively. Majority charge carriers in case of p-type conductors are holes while electrons in case of n-type.

1.2. Bulk Heterojunction OPV Cells

OPV cells consist of a donor that is functionally similar to p-type semiconductor and an acceptor that is functionally similar to n-type semiconductor. Energy conversion process in an OPV device can be divided into four steps: (1) Absorption of light and generation of excitons (hole-electron pair), (2) diffusion of excitons to the donor-acceptor interface, (3) dissociation of excitons into electrons and holes and (4) charge collection of electrons and holes at cathode and anode respectively. Generally, exciton diffusion length is of the order of 10 nm [1][2][3][4][5][6][7]. Hence it is necessary to have optimum acceptor-donor interface for efficient exciton dissociation [1][8][9]. Ideally, the most optimal structure would be a bi-
continuous blend structure with interpenetrating network of acceptor and donor domains sandwiched between electrodes [10]. However complex patterning would be required to create such structures which would eventually make OPV cells commercially unviable as OPV devices are looked upon as cheap solution printed devices. The most prevalent way is Bulk Heterojunction (BHJ) OPV devices.

**Figure 1** Kinetic representation and simplified energy level diagram of energy conversion in organic solar cells [11] (i) Light absorption by the donor forming an exciton, (ii) diffusion of exciton to the heterojunction, (iii) dissociation of the exciton at the donor-acceptor interface, (iv) separation of the exciton, and (v) charge transport to electrodes

It becomes very difficult to control the morphology of a solution processed film which is conducive to improved performance, as the morphology of a film can be affected by the rate of evaporation of solvent, coating forces acting on the material (such as centrifugal forces during spin coating). Researchers have also explored different options such as solvent vapor annealing [12], thermal annealing [12][13], use of binary and ternary solvent systems [15][16] to achieve optimum morphology. However, most of the literature tunes processing parameters with respect to spin coating, and there is very limited information about parameters for blade-coating.
2. Blade Coating OPV Films

2.1. Introduction to Coating Processes

Spin coating is the most prominent method to coat OPV films at laboratory scales. This is chosen for its simplicity and well-controlled final film thickness and uniformity. The thickness of a spin coated film is primarily dependent upon the spin speed, concentration of the solution, boiling point of the solvent, surface energy of the substrate and molecular weight of the polymer [17][18][20]. Final film formation takes place in two steps: (1) initially solution is ejected out under the effect of centrifugal force acting on the material and (2) once a very thin film of solution is left on the substrate, remaining solvent evaporates out of the film. It is observed that a very fine morphology of small phase domains is observed when spin coated at high speed [21] while spin coating at low speeds slows down evaporation of solvents and gives enough time for the polymer to aggregate and hence larger phase domains. Highest efficiency of OPV devices achieved so far is 11.3 % [22]. However, spin coating is plagued by excessive waste of material and is a batch process, which hinders transitioning the process to industrial scale.

Slot-die coating is looked upon as the most promising roll to roll production technique for OPV’s. One of the advantages slot die coating has is that high concentration solution can be processed using this process. The final film thickness is primarily dependent upon the coating width of the web, flow rate of the solution, web speed and height of the
feeder from the web [19]. Final film morphology is achieved by deciding the rate of drying. Hence it is evident that parameters affecting the final film are different in case of spin-coating and slot-die coating.

![Slot-die coating schematic](image)

**Figure 3** Schematic of slot-die coating

Slot-die coating needs complex die/head to dispense the solution which needs to be designed based upon the application. Hence, it can be really expensive to identify parameters to optimize films and study the morphology. This mandates the need to establish a process that can closely mimic the film formation of slot-die coating and is less expensive to make prototypes.

![Blade coating schematic](image)

**Figure 4** Schematic of blade coating

**Blade coating** is an inexpensive prototyping tool for slot-die coating and can be used for piece coating. Films can be prepared on substrates as small as 15 mm x 15 mm. It is a
self-metered coating technique, meaning that the thickness of a film is independent of the volume of solution dispensed on a substrate. This is distinguished from a pre-metered coating method such as slot-die coating, where the thickness of a film will be determined by the amount of solution dispensed on a substrate in addition to other variables such as web speed, concentration of solution etc. In blade coating, film coating takes place from the competition between (1) capillary forces holding the polymer solution between the stationary blade edge and the substrate, and (2) frictional drag exerted on the same solution as the blade is pulled across the substrate [23].

2.2. Experimental Setup and Procedure

Experimental Setup

Figure 5 (a) Blade coater setup attached to the ellipsometer (b) Components of the blade coater setup: (1) Translation stage, (2) Stepper motor, (3) XY Travel stage, (4) Translation stage, (5) Tip-Tilt and rotation stage

The experimental setup was based upon the design reported by Stafford et al [23]. Our experimental setup was attached to an ellipsometer (M2000, J A Woollam Co) as shown in the figure 5 (a). The entire blade coater setup is mounted on an optical table (Thor Labs). The blade coater mainly consists of a translation stage (404XR-150, Parker Automation, (1) in figure 5(b)) which converts the rotational motion of a computer controlled stepper motor (DMX UMD 23, Arcus Technology; (2) in figure 5(b)) which controls the motion of the
blade. The XY translation stage ((3) in figure 5(b)) is mounted on top of the linear actuator to adjust the position of the blade in the horizontal plane. A translation stage ((4) in figure 5(b)) is used to adjust the blade gap controlling the vertical translation. A tip-tilt-rotation stage ((5) in figure 5(b)) is used to ensure that the blade edge is horizontal and well aligned with the edges of the substrate. The substrate is placed on the heating stage module, which was supplied with the ellipsometer, so that the temperature of the substrate can also be controlled which eventually enables us to control the rate of evaporation of solvent. The substrate is held stationary with vacuum.

Coating Procedure

Figure 6 (a) Position of a blade with respect to the substrate, (b) dispensing solution and formation of meniscus

A substrate is placed on the heating stage and vacuum is turned on to hold the substrate in its place. The heating stage is ensured to be horizontal using a bubble gauge. Microscopic glass slides are used as the blades that are disposable which make blade coating inexpensive however silicon or metal strips can also be used as blades. A blade is placed between two plates of blade holders. The top plate of the blade holder is grooved to ensure proper placement of the blade. The blade angle is maintained at ~ 4.75° (Figure 6(a)). The blade edge is brought to be horizontal using a tip-tilt-rotation stage to ensure that there is no gradient of thickness in the coated film. The blade is later brought into contact with the
substrate using vertical translation stage. Then the blade gap is adjusted using the adjustment knob. Desired amount of solution is dispensed, using a micropipette, between the blade and the substrate forming a continuous meniscus across the width of the substrate (Figure 6(b)). After dispensing the solution, the blade is immediately set into motion at desired speed.

2.3. Optimizing Parameters

Variables

Efforts have been made by researchers to theoretically predict the thickness of blade coated films however it is very difficult due to the complex nature of fluid mechanics [23]. The thickness of a blade coated film, as mentioned earlier, depends upon blade gap, blade velocity, concentration of solution and hence the viscosity of the solution and rate of evaporation of solvent. Polymers can widely be considered as non-Newtonian fluids and hence their effective viscosities will be dependent on the shear rate, which is associated with the blade velocity in our case. Le Berre et al. performed deposition of multilayered phospholipid films using blade coating and established a correlation between the thickness of the dry film and the blade speed [24]. The thickness of the resultant films will significantly be determined by the rate of evaporation and the speed with which the solution is sheared as shown in the figure 6. At low speeds where the solvent evaporates at a rate higher than the rate of coating the film, the polymer molecules are concentrated near the contact line and the film is deposited behind the meniscus while at high speed the solution is drawn out by the viscous force and the film dries later [23][25].
This fundamental understanding of the formation of a dry film can help estimate the relations of other parameters with the film thickness.

**Blade Gap**

Thickness of the film is directly proportional to the blade gap [23]. It can be associated with the increased amount of solution in the meniscus in the blade gap and hence increased thickness. It is interesting that changing the blade gap does not affect the evaporation or the Landau-Levich regime and hence the thickness of the dry film just increases or decreases with increase or decrease in the blade gap respectively. As shown in the figure 7, reducing the blade gap reduces the thickness of the film at a constant rate of evaporation (from red line to green line) [25]. Doctor blading, which is similar to blade coating in terms of film formation, also exhibits linear relationship of the film thickness with blade gap [19].
Concentration

Increase in concentration should shift the evaporation regime to the right on the thickness vs blade velocity graph. It can be argued that relatively lower amount of solvent in the solution quickens the evaporation and hence the evaporation regime is approached at higher speeds. Increasing the concentration of the solution increases the thickness of the film [23], along with aggregation of the polymer [26].
Figure 9 Variation of thickness with concentration of solution [23]

Substrate Temperatures

Substrate temperature affects the rate of evaporation of solvent and effectively shifts the evaporation and Landau-Levich regime. It can be safely estimated that the increase in temperature will shift the evaporation regime to the higher speeds. Hence it can be predicted that the film processed at higher temperature will have lower thickness than the film processed lower temperature at the same blade velocity.
Figure 10 Patterns produced due to instabilities while coating C8-BTBT:PS blend films, scale bar reads 100 µm

It becomes important to combine all parameters together to process a uniform film of desired thickness. For an example, a film processed at a low concentration, a low speed and high substrate temperature (i.e. in evaporation regime) will result in a non-uniform film with stripes parallel to the contact lines which can be attributed to unstable meniscus [25][27][28][29].

Casting Conditions on Polymer Morphology

We have established general relations and sets of experiments one needs to perform to identify the variables to achieve optimum thickness of blade coated films. However the motivation of the blade-coating setup here is to be able to process high efficiency solar cells. It is necessary to process a sufficiently thick film to maximize the absorption of light, which results in higher charge generation, as well as optimized aggregation of a polymer and phase separation of the donor and acceptor to maximize the efficiency of an OPV device.

Researchers have documented effects of blade velocity on formation of crystals of small molecule semiconductors [30][31][32][33]. Low blade velocity results in ribbon like structures, which assists in achieving better charge transport in blade-coated Organic Field Effect Transistor films, while high blade velocity results in spherulite formation [30]. Diao et al reported that blade coating at high speed and high temperature helps kinetic trapping of metastable forms [34][31].
Quite a few reports exist that discuss the effect of blade coating parameters on the morphology of OPV films of blended donor and acceptor systems[35]. Reinspach et al. reported that blade coating at higher speed results in better aggregation, hence improved absorption and higher crystallinity [35]. They also reported that use of low boiling point solvent resulted in smaller aggregates and less crystalline films compared to films processed using high boiling point solvents. Effect of higher speed can be attributed to the fact that the film is coated primarily because of viscous forces and takes a while for the solvent to evaporate. Remnant traces of solvents in the film allow the polymer to aggregate further and hence better aggregation and crystallinity. Going by the same theory, high boiling point solvent remains in the film and improves aggregation and crystallinity of the film compared to low boiling point solvent.

**Experimental Procedure**

The donor polymer that was used to study optimization of blade coating parameters was PffBT4T-2OD (purchased from Solarmer and Cal-os), which is one of the best performing solution processed single junction solar cells[22]. PffBT4T-2OD is highly crystalline and hence the blend film with fullerene acceptor results in highly pure but sufficiently small domains which result in high fill factor (FF) and efficiency [36]. It has been reported that high efficiency devices can be obtained for a film thickness of 300 nm. It exhibits very high temperature dependent aggregation characteristics as it quickly aggregates at temperatures below 55 °C. Hence the films have to be processed above 55 °C. Blade-coating has the advantage that the temperature of substrates can be controlled isothermally.

ITO coated glass substrates were cleaned by sonicating in deionized water, acetone and iso-propanol for 10 minutes each. Later they were UV-ozone treated for 10 minutes. PEDOT:PSS (CLEVIOS™ P VP AI 4083A) was spin coated on the substrates at 5000 RPM for 60 seconds. PEDOT:PSS is filtered twice using 0.45 µm filters (GE Whatman filter) prior to spin-coating on the substrates. PffBT4t-2OD:[C70]PCBM solution was prepared in a blend of chlorobenzene and 1,2-dichlorobenzene at different concentrations. Glass slides used as blades for blade-coating were cleaned by rinsing with IPA prior to coating. The
blade-coating process was followed as discussed in the previous section. The time delay between dispensing of solution and coating was kept as little as possible as it was observed that further delay resulted in excess evaporation of solvents and quick aggregation of the polymer. This caused non-functioning or poorly performing devices. 25 nm of Ca and 900 nm of Al were thermally evaporated as an interlayer and cathode respectively.

**Optimization Process**

Parameters that need to be optimized to achieve high efficiency are weight ratio of acceptor to donor, system of solvents, blade coating parameters i.e. substrate temperature, blade gap and blade velocity, and post-processing drying or annealing of films before depositing electrodes. High concentration solution can be processed with blade coating [19] and is sometimes necessary to control uniformity of the coated film as low concentration and imbalanced evaporation can cause meniscus instabilities, as discussed above. In the process of optimization for the thesis the concentration of solution was varied from 44 mg/ml to 48 mg/ml. The performance of solar cell devices made with low concentration demonstrated low efficiency with low short circuit current densities which can be attributed to low film thickness and hence low absorption of light. The short circuit current density increased substantially when the concentration of solution was increased and hence high efficiency of 6.36% was achieved from 2.58%. The performance is summarized in the table 1 in Appendix A.
Figure 11 Variation in Efficiency of devices with Thickness of films for PffBT4T-2OD: [C\textsubscript{70}]PCBM blend; Error bars exhibit standard deviation around average values measured for 4 devices per film

[C\textsubscript{70}]PCBM (purchased from nano-c) was used as the acceptor and the donor to acceptor ratio was fixed at 1:1.4 based on the optimization conducted by Solarmer. Mixture of different solvents is used to control aggregation of donor and acceptor and thus achieve sufficiently small domains. Binary and ternary systems of solvents have been proposed by researchers to achieve high efficiency OPV devices [16][37][15]. For the purpose of the thesis, ternary system of 50:50 volume ratio of chlorobenzene (low boiling point solvent, BP – 131 \(^{0}\)C) and 1,2-dichlorobenzene (medium boiling point solvent, BP – 180.5 \(^{0}\)C) and 3\% volume fraction of 1,8-diiodooctane (high boiling point solvent, BP – 363 \(^{0}\)C). The ratio was chosen based upon the work of Liu et al [38][26] and was not changed.

The substrate temperature was maintained at 90 \(^{0}\)C to ensure that the polymer does not aggregate while coating. Attempts were made to blade coat films at temperatures at 70 \(^{0}\)C
and 80 °C but the processed films were very non-uniform. It is thought that the reason was quick aggregation of polymer due to cooling effect of suction draft created by a nearby solvent exhaust vent, even though the solution was maintained at temperatures above aggregation temperature. Films were not coat at temperatures higher than 90 °C as higher temperature would quicken evaporation of solvents and hinder aggregation of polymers.

Blade speeds were varied from 40 mm/s to 80 mm/s, however most optimum devices were formed at blade speed of 40 mm/s. At speeds lower than 40 mm/s films again showed excess aggregation of the polymer which resulted in non-functioning devices, while at higher speeds non-uniform films were formed. The reason for non-uniformity could be attributed to the drying fronts that form as the films are coated so quickly that the resultant film is essentially wet and eventually dries as the solvent evaporates from the edge of the films to the inner part.

Blade gap was varied from 150 µm to 300 µm. The films prepared with blade gap of 150 µm resulted in very thin films which resulted in low short circuit current density. The blade gap was increased to 300 µm to increase the thickness which eventually resulted in increased short circuit current.

2.4. Results

Performance curves and AFM topographical images of the best performing devices are as shown in the figure 11. It is interesting to observe that the topography of both blade-coated and spin-coated films exhibit different roughness which suggests that the morphologies of the resultant films are different but comparable performance is achieved. The figure 11 (a) shows average performance of films summarized in table 1. It is fairly apparent that the performance of the devices was consistent which indirectly assures the uniformity of the coated films.
Figure 12 (a) Performance curves, AFM topographical images of (b) blade-coated and (c) spin-coated films (*Spin coated devices were processed by Masoud Ghasemi, Physics Department, NCSU)
Figure 13 Variation in Efficiency of devices with Thickness of films for PDPP3T: [C$_{70}$]PCBM blend; Error bars exhibit standard deviation around average values measured for 4 devices per film

Similar optimization technique was used for another system of donor and acceptor PDPP3T and [C$_{70}$]PCBM and performance of blade-coated films comparable to spin-coated films was achieved. PDPP3T exhibits similar aggregation characteristics however weaker than PffBT4T-2OD. The solution of PDPP3T:[C$_{70}$]PCBM in the mass ratio of 1:1.5 was prepared with concentration of 12.5 mg/ml in DCB with 5% V/V of DIO. The solution was prepared and electrodes were evaporated by Masoud Ghasemi, Physics Department, NCSU.
Figure 14 (a) Performance curves, AFM topographical images of (b) blade-coated and (c) spin-coated films (*Spin coated devices were processed by Masoud Ghasemi, Physics Department, NCSU)
2.5. Conclusion and Future Work

Optimization of processing parameters for blade-coating was demonstrated for making high efficiency devices. It was concluded by comparing the AFM topographical images of the best performing spin-coated and blade-coated devices that the resultant morphologies were different. The similar work can be used for other polymer systems and these parameters can be used to extrapolate for roll-to-roll production techniques (essentially slot-die coating).

It would be interesting to understand the fluid flow caused during the blade-coating process and its effect on morphology of the resultant films. Also, study of mechanical properties of blade-coated films can reveal properties such as Crack Onset Strain (COS), Elastic Modulus and cohesive energy of the blend film which can help us estimate reliability of roll-to-roll produced films and devices.
3. Characterization of Polymer Films using Ellipsometry

Ellipsometry is an optical measurement technique to measure dielectric constants (real and complex refractive indices) of thin films. The measurement technique can be used to characterize composition, thickness, roughness, crystalline nature and other material properties. Spectroscopic ellipsometry [39] has been gaining lot of attention as a non-invasive technique to analyze properties of multi-layered thin films of OPVs. The technique can be used to study in-situ and real time dynamics of growth of polymer films. In this section of the thesis, the basis of Variable Angle Spectroscopy Ellipsometry (VASE) will be introduced and then techniques employed to derive an optical model of a thin film and to conduct in-situ analysis of the growth of an OPV film.

3.1. Introduction to Ellipsometry

Polarization State of light

Light is a transverse electromagnetic wave whose state of polarization can be defined by the direction of oscillation of electric field. Light is called polarized if there is any preferential direction of oscillation of the electric field. Light from any point source for an example the sun is un-polarized which means there is no preferential direction of oscillation of the electric field. Existence of preferential directions of the action that the electric field in the wave exerts on electric charges in matter is the reason for the importance of polarization [54].
The most general polarization of a monochromatic light is elliptic as depicted in figure 14. The time evolution can be denoted by superimposition of harmonic vibrations along two perpendicular axes. The amplitudes of the electric field in the x and y directions are denoted by $X$ and $Y$. Assuming the direction of propagation of light in the z direction of the right-handed cartesian coordinate system $x$-$y$-$z$, the time dependence vector $\vec{E}(t)$ in plane $z = 0$ can be written in a complex form,

$$\vec{E}(t) = \begin{bmatrix} E_x(t) \\ E_y(t) \end{bmatrix} = \text{Re}\left\{ \begin{bmatrix} X e^{i\Delta} \\ Y \end{bmatrix} e^{i\omega(t-t_0)} \right\}. $$

As shown in the figure 14 at time $t = t_0$, the y component is at its maximum and reaches maximum of the x component after $t = \Delta/\omega$, where $\omega$ is defined as the angular frequency of the oscillation of electric field and $\Delta$ can be defined as the relative phase of the vibrations along x and y directions. Another parameter that is required to define the elliptic polarization is the ratio of $X$ and $Y$ which is defined as the relative amplitude. It can be defined with the help of angle $\psi$. From the figure 14, $\tan \psi = X/Y$. Thus, multiplying $X$ and $Y$ with a common factor will merely change the intensity. Thus, the elliptic polarization can be represented by Jones Vector
Linear and circular polarization can be expressed as special cases of elliptic polarization. Linear polarization is achieved when $\Delta = 0^0$ for any value of $\psi$. On the other hand the polarization is circular when $\Delta = 90^0$.

### Configuration of an Ellipsometer

![Figure 16 Schematic of an ellipsometer [54]](image)

A schematic explaining the basic configuration of an ellipsometer is shown in the figure 15. In most commercial ellipsometers the light source is a deuterium or halogen based bulbs or both depending upon the range of wavelengths the system is equipped with. A linear polarizer acts as a Polarization State Generator (PSG) which generates a known state of polarization of the source light. The incident light reflects from the surface of the substrate and loses its well defined state of polarization. The Polarization State Detector (PSD) detects the polarization state of the reflected light. Either the PSG or the PSD will have a rotating polarizer element depending upon the design of the system, which eventually measures the intensity of detected light in terms of $\psi$ and $\Delta$. Figure 17 shows the data that are generally collected through a scan. The data does not translate to thickness, optical and other material properties directly. Regression based modeling techniques need to be followed to convert gathered data to desired information.
3.2. Method of modeling

Fundamentals of Reflection

Ellipsometric data is essentially collected through the light reflected off the substrate. Thus the data collection and analysis is driven by the laws of reflection. The Fresnel reflection coefficients are defined as

\[ r_{pp} = \frac{n_1 \cos \phi_0 - n_0 \cos \phi_1}{n_1 \cos \phi_0 + n_0 \cos \phi_1} \]

\[ r_{ss} = \frac{n_0 \cos \phi_0 - n_1 \cos \phi_1}{n_0 \cos \phi_0 + n_1 \cos \phi_1} \]

Here \( n \) is the complex refractive index which is defined as \( n = n - ik \), where \( n \) is refractive index of the material and \( k \), the complex part, is extinction coefficient which can be used to calculate the absorption coefficient \( \alpha = \frac{4\pi k}{\lambda} \). In case of a beam of light reflected through a single layer of film, total reflection is

\[ r_{pp,ss} = r_{1,pp,ss} + r_{2,pp,ss} \exp(-2ib) \]

\[ 1 + r_{1,pp,ss} r_{2,pp,ss} \exp(-2ib) \]

Where \( b \) is phase change from top to bottom of the film, \( b = 2\pi \frac{d_f}{\lambda} n_f \cos \phi_f \). Here \( d_f \) is the thickness of the film.

Data Interpretation

Referring the figure 15, assuming that the light is monochromatic and \( p \) and \( s \) polarized lights are parallel and perpendicular to the plane of incidence. Four reflection coefficients are required to describe reflection from an ideal surface which is easily described by Jones matrix

\[ J = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} = \begin{pmatrix} E_p^o / E_p^i & E_s^o / E_p^i \\ E_p^o / E_s^i & E_s^o / E_s^i \end{pmatrix} \]

Where \( E_p^o \) and \( E_p^o \) are complex quantities that define the reflected beam and \( E_p^i \) and \( E_s^i \) define the incident beam. Fresnel reflection coefficients \( r_{pp}, r_{ss}, r_{ps} \) and \( r_{sp} \) are related to \( \psi \) and \( \Delta \) by defining a complex ratio, \( \rho = \frac{r_{pp}}{r_{ss}} = \tan(\psi) e^{i\Delta} \).

The Jones matrix can be normalized to
\[ \mathbf{J} = r_{ss} \begin{pmatrix} \rho & \rho_{ps} \\ \rho_{sp} & 1 \end{pmatrix} = \begin{pmatrix} \tan(\psi) e^{i\Delta} & \tan(\psi_{ps}) e^{i\Delta_{ps}} \\ \tan(\psi_{sp}) e^{i\Delta_{sp}} & 1 \end{pmatrix}. \]

The off-diagonal elements become zero for isotropic, homogenous systems while they become important for analysis when depolarizing effects are prominent. The Jones matrix can be used to estimate the beam at the detector which can be formulated using transfer matrix model as follows:

\[ \mathbf{E}_D = [\text{Analyzer matrix}] [\text{Sample matrix}] [\text{Polarizer matrix}] [\text{Input beam}]. \]

However it is important to note that the detector detects the intensity of the beam not the electric field. The measured detector intensity is proportional to the magnitude of the electric field i.e. \( I_D = |\mathbf{E}_D|^2 \). The detected intensity can be measured as a function of time as the angular frequency of the rotating polarizer or the rotating analyzer is known.

**Optical Modeling of a P3HT film**

As stated earlier, regression based modeling technique needs to be followed to achieve the thickness and optical constants of the film under observation. Figure 16 depicts the basic algorithm of creating a model for a thin film. The basic steps can be summarized as:

1. Measure SE data on the sample.
2. Build a layered optical model which represents the number of structure on the sample. The model is built to match the measured SE data.
3. Model fit parameters are identified and then automatically fitted by the software to improve the fit between the measured SE data and the model.
4. The results of the fit data are evaluated. If the results are not accepted the fit parameters are modified and the step 3 is repeated.
Measurement of Data

A thin film of poly(3-hexylthiophene) (P3HT) was cast on a silicon substrate with 200 nm thick thermal oxide layer. The P3HT solution was prepared in 1,2-dichlorobenzene (DCB) at concentration of 20 mg/ml. The film was spin coated at 600 RPM. The spectroscopic ellipsometry data of the resultant film was collected in the range of wavelength from 191 nm to 1690 nm at three different angles 55°, 65° and 75° using the VASE system model M2000 from J. A. Woollam Co. The measured data is as shown in the figure 17. CompleteEASE software which was provided with the VASE system was used to model parameters of the P3HT film.
Figure 18 Modeled and collected VASE data for a P3HT film at angles 55°, 65° and 75°

Build a Layered Optical Model

The SE data analysis process begins with creating a layered optical model which corresponds to the sequence of the layers formed on a substrate. Each layer is parameterized with thickness and optical constants, thus each layer describes how light interacts with and propagates through each layer.

Figure 19 Layered optical model for a uniaxial P3HT film

The optical layer created to model P3HT film is as shown in the figure 18. As the substrate was silicon with 200 nm thick thermally grown SiO₂ on it the thickness of 200.40 nm was the
thickness defined for the layer. The model of Si substrate with thermal oxide was used from the library of the software which is defined as 1 in the figure 18. It is important to notice that the film of SiO₂ is transparent and hence does not affect the overall absorbance of the beam of light. The thickness of the SiO₂ was verified by analyzing uncoated clean substrate. Another unidentified layer was created on top of the substrate which corresponds to the film of P3HT. Complete modeling of optical constants was done using three different models in different steps:

**Cauchy dispersion model** was first used to estimate the thickness of the film. The Cauchy dispersion equation is \( n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \). The said model works in the transparent region of the film and hence the model is used in the wavelength range from 800 nm to 1690 nm which is beyond the band edge of P3HT.

**B-spline model** was used to mimic the measured data into the absorbance region of P3HT after estimating the thickness of the film. B-spline model essentially matches the measured values of psi and delta and improves the fit. However, the optical constants achieved using B-spline model may be unrealistic (i.e. negative or very large extinction coefficient) but may roughly mimic the variation of characteristic optical constants with wavelengths.

**General Oscillator model** was finally used to achieve realistic optical model and final thickness over the entire range of wavelength. Different Laurentzian and Gaussian oscillators are available in the software package CompleteEASE. Gaussian oscillators were used for peak to peak fitting of the estimated optical constants achieved using B-spline model. Uniaxial General Oscillator model was used to improve the fit which implies towards existing anisotropy in the direction out of the plane of the film.

**Modelling Fit Parameters**

Parameters chosen for the fit are always related to thickness or optical constants. As stated earlier, the fit is carried out by the software in such a way that the model exhibits the closest possible match with the measured data. The closeness of the match or the goodness of
the fit is defined by the parameter Mean Squared Error (MSE). The MSE, in the software, is defined as

$$\text{MSE} = \frac{1}{3n-m} \sum_{i=1}^{n} \left[ i^{N_{E_i} - N_{G_i}} \right]^2 + \left( i^{C_{E_i} - C_{G_i}} \right)^2 + \left( i^{S_{E_i} - S_{G_i}} \right)^2.$$ 

Here, $n$ is the number of wavelengths, $m$ is the number of fit parameters, and $N = \cos(2\psi)$, $C = \sin(2\psi)\cos(\Delta)$, $S = \sin(2\psi)\sin(\Delta)$. The optimum MSE to consider whether the fit is good or acceptable or not is dependent upon parameters such as the complexity of the absorption spectrum of the material, thickness, number and accuracy of models of the films considered in the stacked layers. Hence the high or low value of MSE does not necessarily guarantee accurate and realistic models.

Introducing more number of fit parameters in the model sometimes helps improve the MSE. In the case of the Cauchy dispersion model if the MSE using the fit parameters using thickness and constant $A$ is not very good then other constants $B$ and $C$ can also be added to achieve a better fit. However, this can result in unrealistic models as introducing other parameters may result in non-transparent model which goes against the basic assumption of Cauchy dispersion equation. Similarly, the resolution of B-spline can be increased i.e. the number of points the model uses to map the measured data but it can result in correlation of the fit parameters as the number of data points measured may be less than the fit parameters and eventually affect the uniqueness of the model. Kramers-Kronig consistent B-spline model can also be used to reduce the correlation [[40]]. In the case of General Oscillator, more number of oscillations can be used to map optical constants but this can result in absence of characteristic features of the material (i.e. transition peaks etc.).

It is often considered that the simplest model is the best. A way to identify unique fit parameters is to study the uniqueness of the parameters to affect the MSE. CompleteEASE software is equipped with a program to check uniqueness of an identified parameter for a model (Figure 19). A uniqueness of a parameter can also be identified by the error bar of the value of the parameter i.e. smaller the error bar more unique the parameter to the model. In other words sharper the minima of MSE vs Parameter means more unique parameter. The appendix B shows the list of fit parameters used in the modeling of P3HT and the values
calculated and the error bars. The parameters with very large error bars are shaded yellow. It was verified that removing those parameters from the fit did not affect the MSE of the model. Researchers of also suggested of using multi sample analysis i.e. analyzing films coated with different processing parameters simultaneously which helps reduce the correlation of different fit parameters.

The optical constants of the model are as in the figure 20. The optical constants exhibit similar shape and characteristic features pertaining to absorbance spectra of P3HT films which suggest that the model is accurate (Figure 21).

![Parameter Uniqueness Fit](image)

**Figure 20** Parameter uniqueness fit for the thickness of a P3HT film
**Figure 21** Modeled optical constants of a P3HT film

**Figure 22** (a) Absorption coefficient of a P3HT film based upon a VASE model, (b) absorbance of a P3HT film (Data courtesy: Tianlei Sun)
3.3. In-situ analysis of P3HT:PCBM film

The VASE modeling of a thin OPV film discussed in the previous section was done on a dry film which helps us understand the characteristics of the processed films. However, dynamics of growth of the film gives insight into aggregation characteristics with evaporation of solvents and eventually helps us select right solvents and processing parameters for optimum morphology and performance [41][42]. Attaching the blade coating setup with the ellispometer, as explained in the section on blade coating, helps us collect real time in-situ data. The same modeling techniques, explained in the previous section, can be used to create the optical model of the coated film which eventually provides the data on the growth of the thickness of the film and aggregation with time.

Solution of P3HT:PCBM with weight ratio of 1:1 was prepared in DCB with concentration of 36 mg/ml. The substrate temperature was set at 30 °C, the blade gap was 300 µm and the blade speed was set at 50 mm/s. Silicon with 200 nm thick thermally grown SiO₂ was used the substrate. The procedure discussed in the section on blade coating was used to coat the film. In-situ data collection mode was used to measure the data with time while the film was coated. There was a delay of a few seconds between coating of the film and beginning of data collection. Data was collected at an interval of 2.5 s for 10 minutes (i.e. 599.4 s). Psi and delta data were collected at just one angle of 75° for real time measurement and note the change in data with drying of the film.

Modeling Technique

The growth of the film from the solution stage to dry film can be divided into three stages (1) wet film, (2) transition stage of the film i.e. part of the film starts drying and (3) completely dry film after all solvent has evaporated. The model is required to estimate the variation of thickness of the film and aggregation of the polymer with time through all three stages. It was observed that a single model cannot predict thicknesses at all three stages (the MSE explodes to large values for stages other than the stage for which the model was
developed) and hence separate models were developed for each stage and plotted together. Each model will be discussed below:

In the **Wet Film** region loss of intensity of beam light was observed, which is essentially a result of depolarization of light, which is evident from the Signal Intensity vs Time graph (figure 22) as the intensity of signal received by the spectrometer increases after 300 s. Cauchy dispersion model, as discussed in the previous section, was used from 1200 nm to 1690 nm wavelengths. Depolarization effects were compensated for by including thickness non-uniformity and bandwidth as fit parameters. The model explodes to high MSE values in the time range from 282 s to 330 s which resulted in unrealistic thicknesses. Multi Sample Analysis model was employed in that time range where parameters at every recorded time slice were fitted with recorded $\psi$ and $\Delta$ values, however fitting the same parameters used in the liquid regime from 0 s to 280 s. The layered model and recorded values at each time slice are as in Appendix C. The same model, as stated earlier, does not work in the case of the transition stage (330 s – 390 s) either.

![Parameters vs. Time](image)

**Figure 23** Change in signal intensity received by the detector of the ellipsometer with time
The modeling technique (wavelength range 1000 nm to 1690 nm), exactly similar to the one explained in the previous section, was utilized to measure the thickness of the dry film (time range 391 s to 599s) i.e. no depolarization effect was considered. It was understood that the film had completely dried which is evident from the figure 23 that the thickness was constant with time and the refractive index in the transparent regime also became constant. It was also noted that the MSE improved if depolarization effect was included due to thickness non-uniformity which may indicate presence of the solvent; however the change was very small and hence the growth of the film was considered to be complete.

Graded layer approximation was utilized in conjunction with depolarization effects to model the film in the transition stage. In-homogeneity was used as a fit parameter to incorporate grading of the film. Presence of any gradient essentially means that the refractive index at the bottom layer of the film (i.e. at the substrate) and that at the top layer are different. The model exhibited negative values of % inhomogeneity which indicates that the refractive index at the top of the film is lower than that at the bottom. The change in % inhomogeneity is reported in the figure 35 in appendix D. The grading indicates reduction in the percentage of the liquid film at the top indicating drying of the film. The reduction in the thickness of the film is as exhibited in the figure 22 and the trend matches those reported in literature [42][41].
Figure 24 Modeled thickness variation with time for the blade-coated P3HT:PCBM film

The same effects of depolarization or grading were considered and the Cauchy dispersion model was parameterized to Kramers-Kronig consistent B-spline model with resolution of 0.1 eV over the wavelength range from 400 nm to 1690 nm. The aggregation of the polymer was deduced through the growth of the 0-0 transition peak at the wavelength ~595 nm. It should be noted that the 0-0 transition peak for P3HT typically lies near 605 nm, which doesn’t match with the current model. It was also observed that the 0-1 transition peak and the 0-2 transition peak were at ~540 nm and ~490 nm which should have be ~550 nm and ~500 nm respectively. It was, through further investigation, noticed that the measured data in psi and delta exhibited a kink (discontinuity) between 1000 nm and 1010 nm. This discontinuity seems to have resulted in the shift in the measured data and hence the model. The M2000 ellipsometer is equipped with two detectors i.e. Si based detector for measurement from 191 nm to 1000 nm and InGaAs based detector for measurement beyond
1000 nm. The measured data may have a kink if both the detectors do not “see” the specimen at the same angle. If the specimen is not aligned horizontal, coated liquid film may have resulted into a flood back due to gravity. The measured data marking the kink is shown in the figure 36 in Appendix E. Change in the value of k at 595 nm wavelength was plotted against time in figure 24 (b). It was observed that the value of k increases starting from the time slice ~250 s until the time slice ~400 s and later stays constant. This indicates that the growth of polymer can also be associated with the drying of the film and can be concluded that aggregation of the polymer is complete when the solvent has evaporated from the film. The similar has been reported in literature, too [41].

![Figure 25](image)

**Figure 25** (a) Evolution of extinction coefficient with time from the in-situ SE experiment, (b) onset of aggregation at 595 nm with time

### 3.4. Conclusion and Future Work

Techniques to model different polymer films to estimate thickness and optical constants were discussed. The understanding of the modeling techniques was utilized to estimate variation of thickness with time from right after coating to the dry film. Also the technique to create models to estimate aggregation characteristics was also demonstrated. The same techniques can be utilized estimate variations in thickness with time with usage of different solvents and solvent additives and aggregation characteristics with thickness variations as discussed previously.
4. Mechanical Testing

4.1. Introduction

As stated in the introduction of the thesis, the OPV devices exhibit possibilities in production of flexible devices. However robust interconnects and device structures are necessary for manufacture for functioning flexible devices [43]. Thus, adhesion energy of a BHJ film with its neighboring layers and the cohesion energy of the film are important parameters to judge mechanical stability of OPV devices. Failure of a film at any front will result in non-functioning OPV devices. Various research groups have carried out studies of adhesion energy of various thin films with different substrates [43][44] and intermediate layers [46][47] as well as cohesion energy of photovoltaic materials [48][49]. The parameter associated with the mechanical stability of OPV device structures is fracture energy (Gc), which is defined as the strain energy dissipated during fracture per unit of newly created fracture surface area. A method used to study adhesion of thin films to substrates is indentation method which relies on the formation of dilated plastic zone in the film to cause the film to blister [46]. The value of Gc may get affected by volume of indentation and resultant debonding. This requires calibration and assumptions of complex compression fields around indentation. Other techniques have been developed in which films are pulled from the substrates to measure adhesion energy such as peel test [51], four point bending (FPB) and double cantilever beam (DCB)[46] etc. FPB and DCB testing methods are used to measure cohesion energy of films as well. Here, FPB and DCB testing methods were used to develop the capabilities to measure adhesion and cohesion energies of OPV devices.

Basic Delamination Testing Principles

**Four Point Bending (FPB)**

FPB testing method essentially involves the principle that the compliance (ratio of strain and stress) of a beam increases as the crack propagates [52].
A polymer film is sandwiched between two silicon substrates and is bent as shown in the figure 25. Initially the substrate under tension (the top substrate in the figure 25) cracks first as the bending moment increases gradually and the crack propagates vertically into the interface. The crack propagates into the interface if the interface is weak but it can also propagate into the film causing cohesive failure if the adhesion energy is higher. When the crack tip is sufficiently far away from the vertical precrack ($a>2h$ [52]), the strain energy release rate becomes independent of the crack length which is characteristic of steady-state crack growth. Applying the beam theory, the strain energy release rate is defined as,

$$G = \frac{21}{4E} \frac{(1-\nu^2)M^2}{b^2h^3}.$$  

Here the bending moment $M = PL/2$, where $P$ is the applied load, $L$ is the spacing between the inner and the outer pins, $b$ is the width of the beam, $h$ is the thickness of the wafer, $E$ and $\nu$ are the elastic modulus and the Poisson’s ratio of the substrate, respectively.

**Double Cantilever Beam (DCB)**

DCB testing method works on the same principle as the FPB testing method. Vertical force is applied to a sandwiched test specimen as shown in the figure 26. Unlike in the case of FPB test method, the strain energy dissipated during the fracture is dependent on the crack length. A crack forms as the polymer film delaminates at the weak region and eventually the crack propagation takes place. Similar to the case of the FPB method, the crack propagates
into the interface or the polymer film depending upon which of the cohesion energy or the adhesion energy is higher. The strain energy release rate is given by

\[ G = \frac{12(1-\nu^2)P_c^2a_c^2}{Eb^2h^3}. \]

**Figure 27** Schematic of a DCB specimen [55]

Here \( P_c \) is the critical load that is the maximum load till which the deformation is elastic i.e. the material takes load. \( b \) and \( h \) are the width and the half of the total thickness of the test specimen respectively. \( E \) and \( \nu \) are the elastic modulus and the Poisson’s ratio of the material of the beams respectively. \( a_c \) is the crack length which is derived from the compliance (inverse of the slope of Load vs Displacement curve) of the stack,

\[ C = \frac{\delta}{P} = \frac{2a_c^3}{3EJ}. \]

Here \( \delta \) is the displacement of the beam in the direction of the load which is observed from the displacement of the actuator. \( P \) is the applied load on the test specimen. In the case where the elastic modulus is much larger than that of the film, the area moment of inertia \( I \) can be calculated from \( I = bh^3/12 \).

**Specimen Preparation**

Adhesion energy of Polystyrene (PS) with Silicon substrate was studied for the work of the thesis. Silicon substrate of size 40 mm x 40 mm was cleaved from a silicon wafer. 20 mm wide strip of 20 nm thick film was thermally evaporated on a clean Si substrate which acts as a weak region. The spots along which the gold layer is evaporated on FPB and DCB
specimens are depicted in the figure 27. 240 nm thick PS film was prepared by spin coating the solution on the silicon substrate at 4000 RPM for 30 s. 10 mg/ml solution of PS was prepared in Toluene. The thickness of the film was measured using ellipsometry. Cauchy dispersion model was used from 350 nm to 1690 nm, to measure the thickness. 15 nm thick layer of Ti and then 200 nm thick layer of Al were thermally evaporated on top of the PS film. The stack of the films was sandwiched by another silicon substrate of the same size as that of the bottom substrate.

![DCB Specimen](image1) ![FPB Specimen](image2)

**Figure 28** Multilayered stacks of DCB and FPB specimens

Epoxy (EPO-TEK 353) was used to paste the top substrate onto the stack of films. It is important to note here that the layers of Ti and Al were deposited to ensure that the epoxy does not flow to PS as it may result in plastic deformation of epoxy which would eventually overestimate the adhesion energy. Epoxy was cured at 80 °C for 5 hours. The sandwich of the film was then diced using high speed diamond saw in strips of size 40 mm long and 3.7 mm wide test specimens. A notch 0.3 mm wide and 0.3 mm deep was created on the substrate to the PS side for the FPB specimens. It was ensured that the notch was created on the weak region where gold was deposited. The notch creates a weak region which causes the precrack to form quickly at a low bending force.

![FPB Test Specimen](image3) ![DCB Test Specimen](image4)

**Figure 29** (a) FPB test specimen, (b) DCB test specimen [55]
For the DCB test specimens, two custom manufactured loading tabs were attached to the substrates using the epoxy. It was ensured that the loading tabs are attached on the same side where the weak region was created. As little as possible amount of epoxy was used to attach the loading tabs so that epoxy does not flow onto the edges of the test specimens. Excess epoxy that flowed to the edges of the test specimens was scraped using a blade. Epoxy was cured at 80 °C for 5 hours in the air. Care was taken to align the loading tabs along the same line so that the load applied on a test specimen acts along a straight vertical line.

4.2. Test Procedure and Data Analysis

The Delaminator Adhesion Test System, purchased from DTS Company, Menlo Park, CA, was used to conduct both the tests discussed above. The test system is equipped with a high precision linear actuator which is capable of providing linear motion of 50 mm. The test system also has a LabView based program which controls the motion of the actuator and collects the load data. It is also capable of display of the real-time Load vs Displacement graph and of calculating crack length and fracture energy. The load cell was calibrated before conducting the tests and was zeroed after fixing the grips or the loading tabs and before engaging the specimen.

Four Point Bending

The method followed to prepare the test specimen has been discussed previously. Sets of fixed and adjustable grips are supplied with the test system. An FPB test specimen was placed between the grips. It was ensured that the notched side of the test specimen was kept towards the wider grips and the notch was adjusted to be in the center. Adjustment screws provided on the grips were used to ensure that the line of contact between the test specimen and the pin was perpendicular to the vertical plane. The distance between the inner pins was kept at 27 mm and that between the outer pins at 35 mm. The displacement rate was set at 0.2 µm and compression load was begun to be applied. The measured Load vs Displacement
graph is as shown in the figure 29. The curve can be divided into 4 regions. The linear region marked as “1” indicates that the specimen starts taking load. The load suddenly drops as the pre-crack in the Si beam propagates to the interface. The load plateaus as the crack tip propagates along the interface which is shown in the inset in the figure 29. The plateaued region (shaded yellow in the inset) was very small in the case of the current experiment. It could be because of the large amount of energy required to form the pre-crack in the Si slab which results in the strain energy, which is more than the adhesion energy, to be released into the crack [53].

![Graph showing Load vs Displacement plot of a FPB specimen.](image)

**Figure 30** Load vs Displacement plot of a FPB specimen

The calculation is elaborated in the Appendix F. The region “4” indicates that the crack has propagated all the way to the inner pins and eventually the inner pins have started
taking the load which is indicated by the linear increase in the load with displacement. The adhesion energy of the Si-PS interface was calculated to be 0.26 J/m$^2$. It is important to note that only 1 out of 6 tested specimens demonstrated the plateau which points to serious issue with the reproducibility of the results. The same can be avoided by making the Si slab even weaker by creating a deeper notch or using a thicker notched substrate and thinner substrate on the top [53].

**Double Cantilever Beam**

The test specimen was fixed into quick adjustment grips supplied with the test system using pins. The rate of displacement was set at 0.5 µm/s and tensile load was begun to be applied. The recorded Load vs Displacement graph is as shown in figure 30. The curve can be divided into 4 regions. Region “1” indicates the slack in the system being taken up which results in very small load on the system. Region “2”, which exhibits a sharp linear increase in the load, indicates that the test specimen is starting to take the load. The sudden drop in the load, indicated by region “3”, is a result of the formation of a crack at the interface.
The testing begins in the region “4” which helps us calculate the fracture energy. Cyclic load is applied to the specimen after the crack has propagated. The initial load vs displacement plot is linear as elastic energy is stored via elastic beam bending. The slope of the line is used to calculate the compliance and hence the crack length. The critical load is noted when the curve leaves the linearity which indicates debonding of the film. The compression load is applied after the debond extends by a desired amount. The load curve initially increases and then begins to decline as the debond extends, during every cycle. Sufficient numbers of loading-unloading cycles are conducted and \( a_c, P_c \text{ and } G_c \) are calculated for each cycle. Thus a DCB yields more than one values of \( G_c \) unlike FPB. Average value of critical energy for two DCB specimens was calculated to be 0.54 J/m\(^2\). The calculation of the conducted experiment is explained in Appendix G. Adhesion energy of PS with Si substrate was confirmed to be around 0.6 J/m\(^2\) (Courtesy: Dr. Reinhold Dauskardt, Stanford University).
4.3. Conclusion and Future Work

Experiments were performed to develop the capability to test adhesion energy using 4pt bending method and double cantilever beam method. It was observed that the adhesion energy of PS with Si was measured to be of the same order. Works of other researchers also exhibited the value to be of the same order validating our results. The use of the delaminator system can be extended to study mechanical properties (adhesive energy with substrates and cohesive energy of a film) of OPV devices relating performance, morphology, processing conditions and material systems.

Figure 32 Adhesion energy measured with different test methods
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[52] Ma, Q. A four-point bending technique for studying subcritical crack growth in thin


APPENDICES
Appendix A

**PffBT4T-2OD:[C\textsubscript{70}]PCBM**

<table>
<thead>
<tr>
<th>Blade Gap (µm)</th>
<th>Blade Speed (mm/s)</th>
<th>Substrate Temperature (°C)</th>
<th>Concentration (mg/ml)</th>
<th>Thickness (nm)</th>
<th>Jsc (mA/cm\textsuperscript{2})</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
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**Table 1** Parameters and performances of high efficiency OPV devices from PffBT4T-2OD:[C\textsubscript{70}]PCBM

**DPP3T:[C\textsubscript{70}]PCBM**

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<th>Concentration (mg/ml)</th>
<th>Thickness (nm)</th>
<th>Jsc (mA/cm\textsuperscript{2})</th>
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<td>57</td>
<td>37.5</td>
<td>40</td>
<td>12.5</td>
<td>137.5</td>
<td>11.56</td>
<td>0.60</td>
<td>61.04</td>
<td>4.26</td>
<td>4.61</td>
</tr>
<tr>
<td>1000 RPM for 30 s</td>
<td>12.5</td>
<td>110</td>
<td></td>
<td>12.10</td>
<td>0.66</td>
<td>64.64</td>
<td>5.15</td>
<td>5.26</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** Parameters and performances of high efficiency OPV devices from PDPP3T:[C\textsubscript{70}]PCBM
### Appendix B

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
<th>ERROR BAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>14.863</td>
<td></td>
</tr>
<tr>
<td>Thickness #3 (nm)</td>
<td>232.62</td>
<td>0.178</td>
</tr>
<tr>
<td>Einf</td>
<td>0.78</td>
<td>0.228</td>
</tr>
<tr>
<td>UV Pole Amp.</td>
<td>142.6804</td>
<td>51.91034</td>
</tr>
<tr>
<td>UV Pole En.</td>
<td>12.369</td>
<td>1.2878</td>
</tr>
<tr>
<td>Amp1</td>
<td>1.228504</td>
<td>0.240298</td>
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<tr>
<td>Br1</td>
<td>7.6534</td>
<td>0.35623</td>
</tr>
<tr>
<td>En1</td>
<td>10.938</td>
<td>0.632</td>
</tr>
<tr>
<td>Amp2</td>
<td>0.091138</td>
<td>0.001854</td>
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<tr>
<td>Br2</td>
<td>0.5346</td>
<td>0.01398</td>
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<tr>
<td>En2</td>
<td>4.505</td>
<td>0.004687</td>
</tr>
<tr>
<td>Amp3</td>
<td>0.242844</td>
<td>0.018094</td>
</tr>
<tr>
<td>Br3</td>
<td>0.9068</td>
<td>0.05018</td>
</tr>
<tr>
<td>En3</td>
<td>3.148</td>
<td>0.0507</td>
</tr>
<tr>
<td>Amp4</td>
<td>0.784842</td>
<td>0.157315</td>
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<tr>
<td>Br4</td>
<td>0.5509</td>
<td>0.06376</td>
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<td>En4</td>
<td>2.636</td>
<td>0.0573</td>
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<td>Amp5</td>
<td>1.830405</td>
<td>0.466016</td>
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<td>Br5</td>
<td>0.2124</td>
<td>0.02221</td>
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<tr>
<td>En5</td>
<td>2.196</td>
<td>0.006171</td>
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<td>Amp6</td>
<td>1.770953</td>
<td>0.414745</td>
</tr>
<tr>
<td>Br6</td>
<td>0.3315</td>
<td>0.05173</td>
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<tr>
<td>En6</td>
<td>2.374</td>
<td>0.0299</td>
</tr>
<tr>
<td>Amp7</td>
<td>0.879918</td>
<td>0.070774</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
<th>ERROR BAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br7</td>
<td>0.101</td>
<td>0.00475</td>
</tr>
<tr>
<td>En7</td>
<td>2.024</td>
<td>0.002665</td>
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<tr>
<td>Einf</td>
<td>1.979</td>
<td>2.233</td>
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<tr>
<td>UV Pole Amp.</td>
<td>19.3567</td>
<td>698.8918</td>
</tr>
<tr>
<td>UV Pole En.</td>
<td>12.919</td>
<td>117.5604</td>
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<tr>
<td>Amp1</td>
<td>1.397689</td>
<td>0.802715</td>
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<tr>
<td>Br1</td>
<td>1.5819</td>
<td>0.52625</td>
</tr>
<tr>
<td>En1</td>
<td>7.473</td>
<td>0.5223</td>
</tr>
<tr>
<td>Amp2</td>
<td>0.32858</td>
<td>0.051696</td>
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<tr>
<td>Br2</td>
<td>2.8112</td>
<td>0.35151</td>
</tr>
<tr>
<td>En2</td>
<td>5.878</td>
<td>0.337</td>
</tr>
<tr>
<td>Amp3</td>
<td>659.5328</td>
<td>9.40E-07</td>
</tr>
<tr>
<td>Br3</td>
<td>0</td>
<td>0.09214</td>
</tr>
<tr>
<td>En3</td>
<td>1.00E-08</td>
<td>0.0921</td>
</tr>
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<td>Amp4</td>
<td>-100</td>
<td>0.155372</td>
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<tr>
<td>Br4</td>
<td>0.008628</td>
<td>823.7571</td>
</tr>
<tr>
<td>En4</td>
<td>0.00863</td>
<td>823.6716</td>
</tr>
<tr>
<td>Amp5</td>
<td>0.248063</td>
<td>0.021023</td>
</tr>
<tr>
<td>Br5</td>
<td>0.8631</td>
<td>0.09699</td>
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<tr>
<td>En5</td>
<td>2.785</td>
<td>0.0734</td>
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<td>Amp6</td>
<td>0.700289</td>
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</tr>
<tr>
<td>Br6</td>
<td>0.4518</td>
<td>0.02553</td>
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<tr>
<td>En6</td>
<td>2.315</td>
<td>0.009891</td>
</tr>
<tr>
<td>Total Thickness (nm)</td>
<td>434.02</td>
<td>0.178</td>
</tr>
</tbody>
</table>

**Table 3** Fit parameters for the P3HT film
Appendix C

Figure 33 Multi Sample Analysis at different time slices

Figure 34 Snapshot of the parameters MSA of the multilayered optical model
Appendix D

Figure 35 Multilayered model at 388.9 s

Figure 36 Percent Inhomogeneity with time
Appendix E

Figure 37 Psi data measured at 75° and the time slice 587.3 s showing the discontinuity between 1000 nm and 1010 nm
Appendix F

Figure 38 Load vs Displacement plot under analysis for the FPB test specimen

Origin 8.5 software was used to analyze the plot. Plateau was analyzed in the displacement from 85 µm to 86.36 µm. The slope of the plateau was found to be 0.00142 N/µm using the software. Average load in the said range was found to be 0.33 N.

Plateau Load, \( P = 0.33 \) N

Distance between inner and outer pins, \( L = (35 \text{ mm} - 7 \text{ mm}) = 28 \text{ mm} \)

Half height of the specimen, \( h = 1.1 \text{ mm}/2 = 0.55 \text{ mm} \)

Elastic modulus of Si, \( E = 1.69 \) GPa

Poisson’s ratio of Si, \( \nu = 0.27 \)

Width of the test specimen, \( b = 3.7 \text{ mm} \)

Critical fracture energy, \( G_c = \frac{21(1-\nu^2)(P_cL)^2}{16Eb^2h^3} = 0.26 \text{ J/m}^2 \)
Appendix G

Specimen# 1

![Load vs Displacement plot](image)

**Figure 39** Load vs Displacement plot under analysis for the DCB test specimen# 1

The loading-unloading cycle was run from 400 µm to 550 µm and bonding-debonding curves were analyzed to calculate critical energy for each cycle. Slope of each bonding cycle was calculated using Microsoft Excel. Measured data are tabulated below and were used to calculate $G_c$ for each cycle.

Compliance, $C = 1/$slope

Elastic modulus of Si, $E = 1.69$ GPa

Poisson’s ratio of Si, $\nu = 0.27$

Plain strain modulus, $E' = \frac{E}{1-\nu^2} = 1.82$ GPa

Width of the substrate, $b = 4.9$ mm

Half height of the test specimen, $h = 0.53$ mm
Crack length was calculated from the equation, \( C = \frac{\delta}{P} = \frac{2a_c^3}{3EI} \)

Moment of inertia, \( I = \frac{bh^3}{12} = 6.09\times10^{-14} \text{ m}^4 \)

<table>
<thead>
<tr>
<th>Slope (N/m)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compliance (m/N)</td>
<td>0.00023</td>
<td>0.00031</td>
<td>0.00059</td>
<td>0.00056</td>
</tr>
<tr>
<td>( P_c ) (N)</td>
<td>0.41</td>
<td>0.30</td>
<td>0.34</td>
<td>0.24</td>
</tr>
<tr>
<td>( a_c ) (m)</td>
<td>0.015</td>
<td>0.017</td>
<td>0.021</td>
<td>0.020</td>
</tr>
<tr>
<td>( G_c ) (J/m(^2))</td>
<td>0.71</td>
<td>0.47</td>
<td>0.93</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**Table 4** Calculated values of adhesion energy for the specimen# 1

Average value of \( G_c \) was calculated to be 0.64 J/m\(^2\).

**Specimen# 2**

![Load vs Displacement plot under analysis for the DCB test specimen# 2](image)

**Figure 40** Load vs Displacement plot under analysis for the DCB test specimen# 2
The loading cycle was run from 335 µm to 360 µm and bonding-debonding plots were analyzed the same way as explained in the case of Specimen# 1. Mechanical properties of Si beam were considered to be the same.

Width of the substrate, \( b = 3.7 \) mm

Half height of the test specimen, \( h = 0.55 \) mm

Moment of inertia, \( I = 5.13 \times 10^{-14} \) m\(^4\)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slope (N/m)</strong></td>
<td>92300</td>
<td>40500</td>
<td>15500</td>
<td>3700</td>
</tr>
<tr>
<td><strong>Compliance (m/N)</strong></td>
<td>0.000011</td>
<td>0.000025</td>
<td>0.000065</td>
<td>0.00027</td>
</tr>
<tr>
<td><strong>( P_c ) (N)</strong></td>
<td>0.88</td>
<td>0.74</td>
<td>0.37</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>( a_c ) (m)</strong></td>
<td>0.0053</td>
<td>0.0069</td>
<td>0.0094</td>
<td>0.015</td>
</tr>
<tr>
<td><strong>( G_c ) (J/m²)</strong></td>
<td>0.6</td>
<td>0.75</td>
<td>0.36</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**Table 5** Calculated values of adhesion energies for the specimen# 2

Average value of \( G_c \) was calculated to be 0.44 J/m\(^2\).