ANALYZING NOVEL FABRICATION AND DOPING METHODS OF ORGANIC PHOTOVOLTAIC DEVICES THROUGH A LUMPED CIRCUIT MODEL

by

Roy Murray

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

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ABSTRACT

The field of organic photovoltaics (OPV) has progressed rapidly. With new materials and methods being briskly developed, the characterization of OPV also needs to be updated. A simple, quantitative analysis that can be shared between labs would help the field achieve uniformity and increase the pace of research. Current-voltage (JV) measurements yield valuable insight into the internal physics of OPV devices. A simple lumped circuit model, previously used to analyze various inorganic thin film PV and more recently applied to OPV, has been used to quantify the electrical behavior of a device. To investigate how the lumped circuit model parameters vary with device treatment, we carried out an annealing study of P3HT:PCBM blend OPV devices. In addition to this study, we also studied the effect of various inorganic materials, such as plasmonic nanoparticles or novel inorganic electrodes on the parameters of the model. We characterized and quantified the effect of these changes (novel materials, thermal annealing, plasmonic nanoparticles, and inorganic electrodes) by studying how the model parameters changed. While studying the resistances in unannealed and annealed devices, a barrier was found around the flat band voltage. This barrier disappeared upon annealing, indicating that it was due to material characteristics related to the crystallinity or the phase separation. In addition to the JV investigations, we investigated where the current in an OPV device originates. Using high resolution microscopy images, we were able to image the

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workings of a device to greater understand how light is absorbed and where electrons originate. All data was used to better characterize effects of materials on OPV devices and create a framework for future studies to be benchmarked against.

Chapter 1

MOTIVATIONS

1.1 Introduction

With the world's growing energy needs, humanity has a responsibility to pursue every energy source possible. 7 billion people will not be able to reach their full potential with the rolling blackouts, load shedding, and in some cases total lack of electrification seen in parts of the world. Social justice and security necessitate a better distribution and availability of energy to all people of the world. While no one technology exists to solve this crisis, solar energy is one of the most promising.

The surface of the earth receives on average over 100 PW (1 x 10¹⁷ W) of solar power. In 2008 the world used 144 PWhrs of energy, meaning that the capturing the earth's sunlight for just 90 minutes would be enough to provide every person on earth with enough power for a year. Nearly all power (nuclear, tidal and geothermal excepted) comes indirectly from the sun. Photosynthesis grows plants, which are then either burned directly or allowed to turn into coal or oil and later burned. This extremely inefficient process is only still used because of its low cost. With the energy needs of the human population expected to continue to grow, the sun is the only energy source large enough to fulfill our needs indefinitely. Cheap and efficient use of the sun will be needed to carry all humans into the modern era. Photovoltaics (PV), which directly convert solar energy into electricity, are the most efficient way to produce electricity. Solar energy is not only important in the long run to provide power to every person on the planet; it is important in the short run to stave off disaster. The Intergovernmental Panel on Climate Change (IPCC) predicts that rising amounts of CO2 in the atmosphere will lead to the planet warming. This warming will likely result in wide spread change over the planet, with natural disasters such as droughts and hurricanes increasing in probability and extremity. Some of these predictions have already started to come to fruition. To prevent more problems, mankind must shift energy production from carbon dense energy sources such as coal and oil to carbon free energy sources, such as wind, nuclear, and solar. Since solar is the most plentiful and least likely to enrage various groups, it is the obvious choice to pursue.

PV also has an additional benefit: scalability. While typical fossil fuel power plants cost \$100's of millions, PV panels can be purchased for under \$100. Small solar powered lanterns with built in cell phone chargers have already started to replace kerosene lamps and diesel generators. These lanterns are available free of charge through donations, or can be purchased by families in remote parts of the world for under \$30. While still not enabling remote, poverty stricken areas to obtain a western standard of living, it does benefit the people living in these regions. Kerosene lamps are smoky, linked to asthma, expensive to run, and are a major fire hazard. The solar lantern allows children to study at night, and provides a way for families to keep phones charged, enabling communication.

While solar lanterns are a major enabling energy source for families in remote areas, they are still not enough to fully boost a family out of poverty, nor do they come close to enabling communities to commercialize through manufacturing and industry. In general, a country's GDP is directly proportional to its energy use (Figure 1.1).

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While there are certainly some outliers, in general for a country to increase its GDP and thereby the standards of living of its citizens, it must increase its energy supply. Solar energy has the lowest startup cost, reduces the needs for transmission lines, and has the lowest future environmental impact.



Figure 1.1: Plot of GDP vs energy use for a range of countries

1.2 Organic Photovoltaics

90% of the photovoltaic modules sold are silicon. As module prices have dropped dramatically from \$4 per watt to around \$0.56 per watt, justifying novel photovoltaic materials has become more difficult. Silicon is relatively efficient at around 25% record lab efficiency, low cost, and the supply chain is well developed. However, silicon is still not an ideal material and would have never have reached this status without the boost of high purity silicon from the semiconductor industry. With more research, other materials are sure to appear which can topple silicon's throne. Organic photovoltaics may be that material.

Few areas of energy research have progressed as quickly as organic photovoltaics. With efficiencies jumping from 5% in 2005 [1], [2] to 12% in 2014 (NREL Efficiency Chart), organic photovoltaics are poised to become a major player in the solar industry. Future efficiencies of up to 22% are theoretically possible [3] and will be necessary to compete with silicon PV. However, if efficiencies this high can be achieved, production costs of a roll to roll device promise to be much lower than the batch processing that silicon requires [4].

Organic photovoltaics possess other desirable qualities for a PV material. One of the major ones is their flexibility. Modules can be printed on plastic substrates, making them a very flexible technology [4], [5]. This enables many different end uses, such as a roll out roofing material, solar tents, backpacks, and clothing. OPV also can be color tuned, with colors available from blue to red to clear. This control over the final color is unique to OPV and enables unprecedented decorative options for building integrated PV. It also enables solar windows [6], which take advantage of the already existent window installation costs to cut down on some balance of systems costs.

These unique applications include placing solar in places that are not typically accessible by PV, whether due to the high costs, rigidity, or the look. The navy is currently looking into using OPV for underwater remote power supplies. OPV performs better in low light than most other PV, making it desirable due to its low cost and higher power output than other PV. OPV can also be used for purses and backpacks. In the fashion world, a lifetime of 3-5 years is typical. Remote power is

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desirable in an urban setting. Purses with a plug to charge a phone, or a backpack that can charge a computer pose an advantage compared to competitors.

Unfortunately (or fortunately for a PhD student) there are many problems with OPV. One of the major problems is device lifetime [7], [8]. While silicon modules can last for 40+ years in the field, OPV suffers from high reactivity with oxygen and some light induced degradation. This can be addressed through proper encapsulation with highly impermeable barrier materials, but these materials greatly increase the cost of a device. Chemists are attempting to design less reactive OPV materials, but to this date high efficiency has not been accompanied by stability.

1.2.1 Basic Physics of Organic Photovoltaics

OPV works by absorbing a photon and exciting an electron to a higher energy level. All materials behave in this way, but for any material to provide a viable PV mechanism there must be a gap between the highest filled electron energy level and the lowest unfilled level. In typical inorganic materials, these energy levels are know as energy bands, with the highest occupied energy level known as the valence band and the lowest unoccupied energy level known as the conduction band. These are similar to the energy levels in OPV. However, for an energy "band" to form, the material must exhibit some large scale crystallinity with a periodic atomic structure.

While organic materials do exhibit crystallinity, their electron levels are due to the molecular structure of the materials. OPV uses semiconducting polymers, which contain a large gap (on the order of several eV) between their highest occupied molecular orbital (HOMO) and their lowest unoccupied molecular orbital (LUMO) electron levels. In many of the devices shown in this dissertation, poly(3hexylthiophene-2,5 diyl) (P3HT) was used as the light absorber and thus the major

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creator of excited electrons. When an electron is excited from the HOMO to the LUMO level, the resulting tightly bound electron/hole pair is known as an exciton.

These excitons will recombine if they cannot be quickly split into a free electron and hole. To split them, we use an electron acceptor material in close contact with the P3HT. These two materials create an electric field between them capable of splitting the exciton. This process is illustrated in Figure 1.2, where [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is the electron acceptor material. Even though a strong electric field exists between the P3HT and PCBM, the exciton must form close to the interface between the two materials. This is because the excitons have a relative short diffusion length of ~10 nm [9]–[11], making it imperative to fill the device with interfaces to split these excitons.

To best maximize interfaces, a bulk heterojunction (BHJ) structure is utilized. To obtain a BHJ structure, we mix P3HT and PCBM in solution and then apply them to the substrate. The two materials slightly phase separate, creating regions of P3HT and regions of PCBM in intimate contact. The size of these phases will be explored thoroughly in Chapters 3 and 6. A cartoon illustrating an approximation of a BHJ structure is seen in Figure 1.2b, where blue and red symbolize the electron acceptor (PCBM) and electron donor (P3HT) regions.



Figure 1.2: a) Graph of HOMO and LUMO levels for a typical OPV device b) Example of a bulk heterojunction structure and two sketches of the materials used in these devices

Nearly all modern OPV devices utilize the BHJ structure. It enables higher efficiencies even when diffusion lengths remain short by minimizing the distance from an exciton generation site to an interface where the exciton will be separated. Perhaps a material with a higher diffusion length will soon be fabricated, but until then the electron donor and acceptor must remain intimately mixed.

Chapter 2

TECHNIQUES

2.1 Introduction

In this dissertation, two types of organic photovoltaic devices were explored. Both use a polymer blended with a fullerene and utilize the same structure and nearly the same fabrication techniques. These techniques are standard in the research community and reliably produce well-functioning devices. Unfortunately the methods used are not applicable to large scale devices and would not be practical in an industrial process, but they are very simple and repeatable for bench scale research.

2.2 Fabrication

All devices in this study were fabricated on indium tin oxide (ITO) coated polished float glass substrates (8-12 ohm, Delta Technologies). The ITO substrates were cleaned sequentially in a bath sonicator in detergent, purified water, acetone, 2propanol (IPA), and then again in water. After drying with nitrogen, the substrates were spin coated with 20 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Clevios PVP, Heraeus). This layer acts as an interface layer between the ITO and the polymer to promote adhesion and help create better film morphology. It also increases the conductivity of the ITO and slightly modifies the work function. The PEDOT:PSS layer was annealed at 130°C for 10 minutes in a nitrogen filled glove box . The active layer was composed of 1:0.7 weight ratio of P3HT:PCBM (P3HT: Highly regioregular poly(3-hexylthiophene-2,5 diyl) P200 from Rieke Metals, PCBM: [6,6]-phenyl-C61-butyric acid methyl ester from Nano-C). The P3HT and PCBM were mixed in a solution of di-chlorobenzene (99.8% anhydrous, Sigma Aldrich) for 12-24 hours at 50°C. They were mixed together and spin coated onto the PEDOT:PSS layer to form an approximately 150 nm thick layer.

Upon deposition of the active layer, the P3HT devices were annealed at 150° C for 15 minutes. This annealing is one of the most crucial steps in the fabrication process and will be explored further in the next several chapters. After annealing, 0.3 nm of LiF followed by 100 nm of Al was thermally evaporated onto the devices at a pressure below $9x10^{-6}$ mbar. The area of the Al and therefore the device is 0.4 cm². Once all layers have been deposited, the device structure appears as shown in Figure 2.1. Aside from testing and the PEDOT:PSS deposition, all steps were carried out in the glove box.

Where noted, other devices were investigated using a 1:0.8 blend of Poly({4,8bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl} {3-fluoro-2-[(2ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) to [6,6]-phenyl-C71-butyric acid methyl ester (PC70BM). PC70BM shares the same base structure of PCBM, ie a fullerene with a butyl group attached to increase the solubility. However, PC70BM utilizes a larger fullerene with 70 carbon atoms. We use PC70BM due to its higher absorption in the uv region than PCBM, which complements the absorption spectra of PTB7 (high in the 550 to 750 nm region, dropping off quickly elsewhere). PTB7:PC70BM devices follow the same procedure as P3HT:PCBM, except for the annealing temperature of the active layer. We only anneal the PTB7:PC70BM at 80° C for 10 minutes.

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Figure 2.1: Device structure (left) and picture of device used in this study, with Al contacts appearing shiny

2.3 JV Curve Analysis

We test all solar cells by applying a fixed voltage to the device and measuring the current output. In our case we sweep the applied current from about -1 V to 1 V and measure current outputs, typically in the range of -20 to 20 mA/cm². Due to the semiconductor nature of the materials, in the dark, these measurements resemble a diode, where the diode equation closely defines the behavior:

Equation 2.1
$$I = I_0 (e^{\frac{qV}{nkT}} - 1)$$

- I is the current
- I₀ is the dark saturation current, typically measured empirically (dependent on the purity of the material, the doping conditions, and the temperature)
- q is the charge of an electron
- V is the voltage
- n is the diode ideality factor

- k is Boltzmann's Constant
- T is the temperature

While Equation 2.1 does closely model the behavior of a solar cell in the dark, it does not match the light behavior. When light is applied to a solar cell, carriers are excited from the valence band (or, in the case of molecules, the highest occupied molecular orbital HOMO level) into the conduction band (lowest unoccupied molecular orbital LUMO level). This creates a current source in parallel with the diode. Every real diode will also have some non-ideal conditions, such as shunts and series resistances. To fully model a solar cell and include these non-idealities, we can use a simple 'one diode' equivalent circuit model, seen in Figure 2.2:



Figure 2.2: Equivalent one diode circuit model of a solar cell

This model takes into account most of the non-idealities in a typical solar cell, with any additional defects being accounted for by the diode ideality constant (n in Equation 2.1). We will discuss the equation to represent this model more in Chapter 3. When plotted as J (current density) vs V, the circuit pictured in Figure 2.2 gives a plot similar to the one seen in Figure 2.3. Figure 2.3 is a plot of actual data from a P3HT:PCBM solar cell.



Figure 2.3: JV curve of a P3HT:PCBM solar cell with important values labeled

Figure 2.3 shows the important values typically extracted from a JV plot. In literature, most groups report the V_{OC} , J_{SC} , fill factor (FF), and the power conversion efficiency (Pmax/Pin). These values, as well as values from the one diode model shown in Figure 2.2 and discussed further in Chapter 3, will be reported for all devices included in this dissertation.

2.4 X-Ray Diffraction

In most organic photovoltaics, the morphology of the bulk heterojunction is of utmost importance in the final performance of the device. Bulk morphology of \sim 100 nm thick films can be difficult to probe, but x-ray diffraction (XRD) is a powerful tool for this job. It gives information on the degree of crystallinity, the crystalline orientation, and on the size of the crystallites.

An x-ray diffractometer utilizes single wavelength x-rays to probe matter. To generate these single wavelength x-rays, high energy electrons are generated from a heated tungsten coil. Electrons accelerate into a copper target due to a high voltage field between the target and the tungsten coil. These high energy electrons knock core electrons out of the 1s copper atomic orbitals. Once core electrons are knocked off, valence electrons (from the 2p orbitals in the case of Cu K α) fall into the core to satisfy the unbalanced electric charge of the nucleus. To conserve energy, this process must release a photon. The Cu K α transition releases photons with energies of around 8 keV (8.028 keV for the 2p1/2 and 8.048 keV for the 2p3/2 orbital) [12]. This splitting due to electron spin can produce shoulder peaks in the XRD spectrum, so some sort of filtering is advantageous.

Our Rigaku D-Max B system utilizes a crystal that diffracts each photon wavelength at a different angle, thereby only measuring the stronger K α 1 line (2p3/2 – 1s transition). This K α 1 line has a wavelength of about 1.54 Å, putting it well into the x-ray regime, and also allowing it to investigate feature sizes similar to the wavelength.

When the Cu K α x-rays impinge on a sample, they have a chance to diffract off the top layer of atoms, mostly diffracting off the electron cloud. Some electrons diffract off the top layer of atoms, but some continue past the top surface and diffract

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off the second layer of atoms. The x-rays continue this pattern of diffracting or transmitting as they travel into the material, typically penetrating \sim 3 µm into a normal sample.

Due to the nature of waves interfering with one another, the x-rays diffracted from the second layer of atoms will interfere with the x-rays from the top layer of atoms either constructively, destructively, or somewhere in between. This interference is stated simply by Bragg's Law:

Equation 2.2 $n\lambda = 2dsin(\theta)$

- n is an integer
- λ is the wavelength
- d is the spacing between parallel lattice planes
- θ is the angle between the incident x-rays and the lattice plane being measured

In order to properly detect the constructive interference, and thus measure the d spacing between lattice planes, a detector must be placed to properly detect the diffracted x-rays. Proper placement according to Bragg-Brentano geometry states that the should be placed so the angle between the incident beam and the detector is 2x the angle between the incident beam and the sample, or 2θ . When x-rays are scanned through every angle, a "diffraction pattern" is created, with a peak occuring at every value of 2θ as determined by Equation 2.2. These patterns look something like Figure 2.4:



Figure 2.4: XRD pattern of sucrose, with selected peaks labeled to their corresponding lattice planes

XRD patterns provide useful data about the lattice spacing of a material, which helps identify the crystalline phase of the material. This provides useful in sample identification and phase identification. XRD patterns provide other useful data, such as the strain in the material. Any strains will result in a peak shift due to the lattice spacing (d) changing. The other major piece of interesting data available from XRD patterns is the crystallite size, provided the crystallites are small enough (<100 nm). Scherrer's method [13] relates the broadening of peaks to the crystallite size using the equation

Equation 2.3
$$\tau = \frac{\kappa\lambda}{\beta \cos\theta}$$

• τ is the lower limit on the crystallite size

- K is the shape factor, which varies between 0 and 1 but is typically approximated as 0.9
- β is the peak full width half maximum line broadening, with the machine broadening subtracted out

The Scherrer formula provides a lower limit and a fairly close approximation of the crystallite size for nanoparticles. While crystallite size does not necessarily correspond to particle size, at the nm scale most particles are made of a single crystallite.

XRD gives an excellent insight into a material's crystallinity and particle size. It is a bulk technique, giving good statistics based on an area of $\sim 10-100 \text{ mm}^2$ and a depth of $\sim 2 \mu \text{m}$. Unfortunately XRD cannot give information about the stoichiometry of a material and cannot probe non-crystalline materials. To investigate stoichiometry and chemical bonds in non-crystalline materials, we must use x-rays in a different manner.

2.5 X-Ray Photoelectron Spectroscopy

To investigate chemical bonds in a material, we again turn to x-rays, but this time we use x-rays to investigate electron binding energies using x-ray photoelectron spectroscopy (XPS). XPS uses Al K α radiation impingent on a material being studied. The x-rays are generated in the same way as the Cu in XRD. However, in this case we study the electrons being knocked off by the x-rays. Al K α waves have an energy of 1486.7 eV, which is high enough to strip a nucleus of most electrons. When these electrons are stripped off the nucleus, they go flying off in all directions. Due to the conservation of energy, each electron will have a kinetic energy of the incoming x-ray minus its binding energy:

Equation 2.4
$$KE = 1486.7 - BE$$

- KE is the kinetic energy of the ejected electrons measured in eV
- BE is the binding energy of the electrons orbiting the nucleus, also measured in eV

As the exact value of the binding energy is very important in probing the sample properties, the electrons cannot lose any energy on their path to the detector. For this reason, the experiment must be carried out in ultra high vacuum ($<1 \times 10^{-7}$ Torr, or $\sim 10^{-10}$ times atmospheric pressure). In order to remove any low energy electrons ejected from natural processes, the machine maintains some bias field to filter out electrons. This bias makes the electrons lose some energy, and the detector also causes some loss in energy, which together are known as the work function. These corrections are summed up in the machine work function. When applying this to Equation 2.4, we find:

Equation 2.5
$$BE = 1486.7 - (KE + \phi)$$

• ϕ is the work function of the instrument

Since any electrons emitted from within the bulk of the sample are likely to lose some energy to the lattice before reaching the sample surface, only electrons emitted close to the surface will create a true BE peak. For this reason, XPS is truly a surface technique, only probing the first few nm of a sample (1-10 nm depending on the density and elemental makeup).

This can be a useful property, allowing very thin samples to be investigated independent of any substrate they are on. However, it can also cause problems. The surface of a sample does not always represent the bulk, and surface contamination issues are exasperated. Sputtering off the top layer with Ar ions can alleviate this, but no samples in this dissertation were sputtered due to instrument limitations. The binding energy of an electron is dependent on several things, including the orbit of the electron, the spin, and what element the host nucleus is bound to. For instance, Titanium (element 22) is typically probed using its 2p orbital. The 2p orbital splits into the 2p1/2 and 2p3/2 due to the electron being spin up or down. This creates a split in binding energies, with the 2p1/2 peak appearing at 460.2 eV and 2p3/2 at 453.8 eV for elemental Ti. When in the compound TiO₂, the peaks shift to 464.3 and 458.6 for 2p1/2 and 2p3/2 respectively. While the peak shift is very large in TiO₂, most materials have some peak shift depending on the binding element, making XPS a powerful technique to understand bonds in an element.

2.6 Microscopy

Using X-rays to probe the structure of materials reveals large amounts of information, but sometimes being able to visualize the structure of materials is the best way to understand structural (or in the case of Chapter 5, electrical) properties. To better investigate the morphology of the OPV devices, we used several different types of microscopy: atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). All techniques will be discussed further below:

2.6.1 Atomic Force Microscopy

To better understand the surface morphology of OPV devices, we utilized AFM. AFM scans the surface of a sample using a very sharp silicon tip. This tip interacts with the surface via van der Waals forces (amongst many others), causing it to deflect based on the topography of the surface. All AFM images in this manuscript use tapping mode. In the tapping mode, the AFM tip is driven to oscillate at the
resonant frequency of the tips (~300 kHz). Interactions with the surface cause the tip to change its phase and amplitude of oscillation. The tip's oscillation is measured via a laser hitting the back of the tip. Any movements cause a movement in the reflection of the laser. The equipment translates these changes in the reflection to generate a topographic profile of the sample, with the height mapped out. The phase shift can also be mapped out, with the shift corresponding to the hardness of the material.

AFM can theoretically have a resolution of around 1 Å, though the instrument used in all studies featured here has a resolution closer to 3 nm. In this dissertation, all data was taken with a Nanoscope V AFM using 300 kHz Si tips from budgetsensors.com.

2.6.2 Scanning Electron Microscopy

A scanning electron microscope is also used for scanning the surface of materials, but scans in a different way. The instrument focuses high energy electrons (0.1 - 20 keV) onto the surface of the sample. Since the scattering of electrons would ruin the resolution of the instrument, the measurements are carried out under high vacuum (~ 10^{-4} Torr). Once the electrons have been focused onto the sample surface using electromagnetic lenses, they excite and emit secondary electrons from the sample surface. The intensity of the scattered electrons depends on the material, its charge state, and the angle the primary electron beam meets the sample. A detector collects the secondary electrons, creating an image based on the intensity of the secondary beam.

Other detectors can be installed in the instrument to provide useful information. This study will use a few images from an energy dispersive x-ray (EDX) detector. This essentially works in reverse from an XPS machine. The high energy primary electron beam knocks electrons out of the inner orbitals of the sample atoms. Electrons drop from the outer orbitals to satisfy charge conservation, releasing x-rays to conserve energy. These x-rays have an energy characteristic of the element they came from. The EDX detector identifies the x-ray energy, using it to identify the elements in the sample. Since the primary electron beam has high energy, it will penetrate deep into the sample (~ 30μ m), providing composition information from a relatively bulk area. While this can be desirable to improve statistics, it can be detrimental when trying to map elements in a small area. To improve the EDX resolution, a lamella sample (typically < 100 nm thick) can be used to reduce the interaction area of the primary electron beam.

The resolution of the instrument is based on the focusing capabilities of the lenses, but is typically ~ 1 nm. This high resolution allows for the imaging of nanoparticles and other small sample features. The extreme zoom capabilities of an SEM (30x - 1,000,000 x) allow the user to easily locate and investigate any interesting features on the sample. This makes SEM great for looking at cross section images, where a thin film sample is cleaved and placed in the machine vertically. Cross section images allow measurement of the film thickness and investigation of any internal morphology. If cross sections cannot be prepared by simply cleaving a sample, the focused ion beam attachment can prove useful.

2.6.3 Focused Ion Beam

To prepare very smooth highly intact cross sections (in addition to many other techniques), we can use a focused ion beam (FIB). In the SEM, the FIB attachment accelerates Ga ions towards the sample, focusing them using electromagnetic lenses. These lenses focus the ion beam to a diameter of a few nm, with a sputtering rate of a

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few nm per second dependent on beam energy. The FIB can mill out very small structures, or in the case of this study, be used to remove small slices of material, as seen in the 50 nm thick slice in Figure 2.5.



Figure 2.5: a) SEM image of a thin cross sectional slice of an OPV device, b) representation of each layer in the device (Image from [14])

Many pages can be written about the preparation of lamella samples using the FIB SEM. It is a very time consuming and intricate process, with a high chance of failure. All FIB preparation seen in this dissertation was performed by Dr. Nopporn Rujisamphan. Thus, the preparation will not be discussed in detail here. For more details on the preparation of TEM samples using the FIB SEM, please see other works [15], [16].

2.6.4 Transmission Electron Microscopy

The final microscopy technique used in this manuscript is the transmission electron microscope (TEM). A TEM uses a focused electron beam in much the same way as an SEM, but detects the electrons very differently. While an SEM detects secondary electrons emitted from the same side of the sample as the primary electron beam, a TEM detects transmitted electrons that pass through the sample. Because electrons need to pass through the sample, only very thin samples or small particles can be imaged, with thickness <100 nm necessary. TEMs are capable of extremely high resolution, with the capability of resolving features <0.5 nm. With this high of a resolution, lattice planes can be observed, allowing one to measure the lattice d spacing to support XRD images.

Crystallinity and d spacing can also be measured using the diffraction of electrons through the sample. Much in the same way that an XRD measures how electrons diffract and then interfere with each other, a TEM can use selected area electron diffraction (SAED) to measure crystallinity. The TEM can also be fitted with a detector to measure the electron energy loss when passing through a sample. While a TEM usually detects contrast between various materials in a sample by a difference in electron density, this is not always possible. When imaging P3HT:PCBM blends, a traditional TEM image just shows a poorly contrasted blend of the two materials. However, we can use electron energy loss spectroscopy (EELS) to measure the energy loss in a material (Figure 2.6). Once we know the amount of energy an electron loses in a given material, we can filter out all other electrons to selectively enhance a given material.



Figure 2.6: EELS spectra of a typical OPV device

While the P3HT and PCBM peak seem to overlap in Figure 2.6, they actually have slightly different energies. P3HT has an EELS peak of 19 eV, while PCBM has an EELS peak of 25 eV [14], [17]. By applying an energy filter to only permit electrons of either of these energies (in practice a 30 eV window is used for PCBM to avoid the P3HT peak) we can brighten the desired material. This fact will prove useful in Chapter 5.

This chapter has provided a very brief overview of the techniques used in this manuscript. It is by no means a thorough or complete look into any technique and most knowledge herein is based on a working familiarity with the instruments.

Chapter 3

CURRENT VOLTAGE ANALYSIS OF OPV DEVICES

3.1 Introduction

OPV devices are typically ranked by one figure of merit: power conversion efficiency (PCE), with higher values appearing regularly [18]. While PCE is a very important value for eventual commercialization, a standard method to analyze electrical properties of solar cells is lacking. Literature in inorganic PV benefits from a standard, straightforward analysis of current-voltage (JV) curves that provide easy comparing of values from different labs [19]–[21]. The use of a lumped circuit model, described in the next section, with one or two diodes in parallel with resistance losses makes extraction and sharing of the solar parameters standardized and straightforward. This model has been applied to OPV and similar systems [22]–[24], and our findings on annealing improving OPV devices has been reported in the past. The focus of this chapter is on the values of the model parameters, the changes of these parameters as a result of device treatment, and the meanings of these changes. Some work has been done on the theoretical influence of the parameters of the lumped circuit model on OPV devices [25] but prior to this research an in-depth experimental investigation of the change in lumped circuit model parameters was lacking.

The classic P3HT:PCBM device was chosen for the bulk of this study. At the end of this chapter some values for the PTB7:PC70BM system will be presented, but those will be specifically noted. P3HT:PCBM bulk heterojunctions (BHJ) have been thoroughly studied [1], [2], [26]. While newer material blends with PCE of over 10%

[27] have been developed and world records are being broken every year, we chose P3HT:PCBM devices for our study because devices based on these materials can now be routinely synthesized with reproducible qualities. The information found by applying this model and method to analyzing JV curves of traditional devices will be useful in creating a metric for analyzing new blends.

One of the key methods of post-production device treatments is thermal annealing. Much work has been carried out on optimizing the annealing protocol of P3HT:PCBM OPV devices. Ma et al. showed that by thermally annealing P3HT:PCBM BHJ devices at 150°C for 15 minutes, the efficiency, J_{SC}, and crystallinity were all increased [2]. Other researchers have shown that the annealing of P3HT:PCBM blends leads to an increase in the crystallinity, causing a shift in the absorption edge [28] and an improvement in carrier mobility [1], [29]. Another benefit of annealing seems to be the increase in phase separation [28], [30],[15]. While the BHJ architecture has a high contact area between P3HT and PCBM, which is necessary to split excitons, there are many "islands" of material with no path for charges to flow to the appropriate electrode for collection. Kiel et al. showed that annealing helps to cause phase separation of the P3HT and PCBM and leads to an increase in paths for charges to be collected [30].

3.2 Results and Discussion

3.2.1 Circuit Model

We use a simple lumped circuit model with only a single diode to describe the behavior of the P3HT:PCBM BHJ system. While other papers [22], [23] have used a more complex circuit model involving multiple diodes to describe the non-ideal

behavior of most OPV devices, we found that the behavior of our P3HT:PCBM devices is close enough to the single diode model to justify not going to more complicated models to deal with some loss mechanisms. In Chapter 2 we mentioned that Figure 2.2 was applied with some corrections to the one-diode equation (Equation 2.1). These corrections manifest themselves in Equation 3.1

The current in a solar cell can be characterized by the series resistance corrected diode equation plus the solar current, with the voltage adjusted for the losses from the series and shunt resistances (**Error! Reference source not found.2**.2):

Equation 3.1 $J(V)=J_0\{\exp(q(V-R_SJ)/(nk_BT))-1\}+GV-J_L(V)$

- J is the externally measured current density
- J₀ is the saturation current density
- R is the series resistance
- G (equal to 1/shunt resistance R_{SH}) is the shunt conductance
- J_L is the photocurrent

In all analysis except for the carrier collection efficiency we only analyze the dark curves, meaning we set $J_L(V)$ equal to 0. This is due to non-ideal behavior of the light generated current in OPV. This is not typical in crystalline silicon, where superposition of the dark and light curves applies. In fact, by analyzing many of these devices we found that the voltage dependent collection is the dominant term in the light curve. We then use this equation to find G and R by taking the derivatives dJ/dV and dV/dJ. Taking the first derivative of this equation around V=0 in the dark leads to:

Equation 3.2
$$dJ/dV = G+qJ_0/(nk_BT)*exp(qV/nk_BT)$$

Plotting Equation 3.2 as dJ/dV vs V gives the shunt conductance, G. The shunt conductance is the intercept when V=0 and when J=J_{SC}. The shunt conductance is a measure of the ohmic conducting pathways through the active layer of the device. For the scope of this study, only the dark shunt conductance was studied. The dark shunt conductance is a measure of the device and the heterojunction, while the shunt conductance in the light, includes effects from the J_L(V) term. In this study, a dark shunt conductance below 1mS/cm² (corresponding to R_{SH} > 1000 Ω /cm²) was required for the device to be considered non-shunted. All devices fabricated passed this criteria though a noticeable upward trend in the shunt resistance was observed upon annealing. Looking at the dark curve, inverting the derivative and solving the equation for dV/dJ gives:

Equation 3.3
$$dV/dJ = R_S + nk_BT/qJ$$

By plotting dV/dJ vs J^{-1} we can find the series resistance R_S and the diode parameter n. Generally, the shunt conductance is extracted from the data around 0Vbias while series resistance is extracted at large forward bias near Voc. A more careful examination of the finding of these parameters from plots can be found in Ali et al. [24]. Once J_L (the current measured in the light) and J_d (dark current) have been corrected for series and shunt losses, G and R_S , the voltage dependent collection function, which describes the probability of collecting a carrier at the electrode, can be found using:

Equation 3.4
$$\eta(V) = (J_L(V)-J_d(V))/J_{SC}$$

This collection efficiency represents the probability of carriers to be collected at the electrodes. It is a measure of trap density and recombination. Crandall developed an equation to fit the voltage dependent collection efficiency [31]. In his model, Crandall assumed an intrinsic region with a uniform electric field where free charge carriers may flow freely. While this model neglects excitons, it still accurately describes the BHJ region between the two electrodes. This equation has only two fitting parameters, which increases the confidence of the fit and the simplicity of interpretation:

Equation 3.5 $\eta(V) = L_c/D (1-V/V_{FB}) \{1-\exp(-D/L_c(1-V/V_{FB})^{-1})\}$

- L_C is the collection length
- D is the device thickness
- V_{FB} is the flatband potential

The applicability of this equation to solar devices other than p-i-n amorphous silicon has been found to be acceptable for general thin film solar cells [20] and more specifically for OPV [24].

Equation 3.6
$$L_c/D = \mu \tau V_{FB}/D^2 = \tau_R/\tau_d$$

Solving for $\mu\tau$ leads to the limiting carrier lifetime-mobility product. As the P3HT:PCBM blend has been shown to have a higher hole mobility than electron mobility (hole mobility of about $3x10^{-4}$ cm²/Vs [32], [33] vs an electron mobility of 8.24x10⁻⁷ cm²/Vs [34]), we assume that electrons are the limiting carrier. Some studies have shown the opposite, with hole mobilities of 10^{-8} upon annealing, compared to electron mobilities of 10^{-7} [35]. Fortunately, the analysis does not depend on the type of limiting carrier and merely gives the lifetime-mobility product of the limiting carrier, whatever it may be. It should be mentioned that this method of finding $\mu\tau$ provides a much simpler analysis than traditional methods of finding lifetime or mobility. The usefulness of data found using more complex measurements such as time of flight and impedance spectroscopy measurements [36], charge extraction by

linearly increasing voltage (CELIV) [37] or in situ measurements such as field-effect transistors [29] can be unclear. Finding the $\mu\tau$ product from actual devices under standard AM1.5 illumination using simple curve fitting of the data that is already typically measured on every cell has tremendous value. Data such as the $\mu\tau$ product, the series and shunt resistances, and recombination parameter give insight into any barriers and problems in a device and can lead to methods to fix these problems.

3.2.2 Annealing Effects

As found by others, annealing P3HT:PCBM BHJ devices improves efficiency [2], and the devices studied here also performed better after heat treatment. This increase in device performance, primarily due to improved J_{SC} and FF, is usually attributed to better phase separation and increased crystallinity of the P3HT and PCBM, apparent in Figure 3.1. As seen in Figures 3.2 and 3.3, the J_{SC} increased significantly upon annealing above 100°C. This increase in J_{SC} corresponds nicely with the increase in the P3HT crystallite size, as seen in Figure 3.1b. The decreasing width of the π - π stacking peak at 5° indicates an increase in the crystallite size. The slight increase of the intensity of the peak at 11° shows an increase in the organization of the film. The powder XRD used in this study specifically shows in plane crystal spacing. The peaks in Figure 3.1a show both the increase in the quantity of crystallization (intensity) and in the size of the crystallites (peak width). The size of the crystallites was calculated using the Scherrer Formula [13].



Figure 3.1: a) The XRD patterns of devices annealed from 30°C (bottom) to 180° C (top). Note the increase of intensity and decrease of peak width upon annealing. b) The increase in crystallite size amongst multiple samples, each annealed at an individual temperature, indicates that the annealing increases the crystallinity

Previous studies have shown that the crystallization of P3HT leads to an increase in its mobility by up to an order of magnitude [29], [33]. The J_{SC} increase is attributed to the increased crystallinity and mobility of P3HT and phase separation of

the P3HT and PCBM. This increase is shown directly by the increase in J_{SC} , which corresponds to an increase in the PCE of the devices.



Figure 3.2: a) The JV curves of an as prepared device tested in the dark and light. b) The JV curves of a device after annealing at 180° C for 20 minutes



Figure 3.3: The V_{OC} , J_{SC} and efficiency of one set of devices fabricated in this study. The efficiency increase is mainly due to the J_{SC} increase. FF was relatively unrelated to annealing, remaining between 40 and 55%

3.2.3 Circuit Model Parameters

While the increases in efficiency and J_{SC} due to annealing are well characterized, the more fundamental parameters of the proposed model are not. Here, we analyze the P3HT:PCBM BHJ solar cells according to previous work [20], [24]. We fabricated and annealed a large number of devices at different temperatures to investigate the change in the model parameters. The parameters investigated in this study are the series resistance R_s, the diode ideality factor n, the dark saturation current J₀, the lifetime mobility product $\mu\tau$, and the shunt resistance R_{SH} at V=0. While the data was noisy, a general trend was observed of the shunt resistance increasing, sometimes by an order of magnitude, upon annealing. Due to the minimal effect of shunt resistance on the device PCE once it is greater than the imposed minimum R_{SH} of 1000 Ω , the data was not included. Upon extracting all these parameters from the data, they can be put back into Equation 1 and plotted with the data. The model can be seen to fit well with the data in Figure 3.4. At lower annealing temperatures the devices are non-ideal and only marginally match the one diode model (not shown here). However, upon annealing, the devices quickly approach the one diode model and are easily fit. Figure 3.4b shows a device measured in the dark. Ambient room light caused the V_{OC} of this device to shift from 0 to 350 mV. This required an addition of a small light current to the dark model to achieve proper fitting, but this correction factor does not change any parameters discussed earlier.



Figure 3.4: The fit (green stars) can be seen to match up well with both and dark (a) and light (b) data from a device annealed at 180°C before contact deposition

Looking at the plot of dJ/dV vs V in Figure 3.5, from which R_{SH} is found at the intercept at V=0, we see a noticeable hump in the unannealed device (Figure 3.5a). This hump is indicative of a strong inflection in the JV curve of the device and can, in conjunction with the second derivative d^2J/dV^2 , reveal slight deviations from the normal JV diode curve. These derivatives from the JV curves in Figure 3.2 are shown in Figure 3.5a and 3.5b before and after annealing at 180°C for 20 minutes, respectively. The hump disappears after annealing. In fact, the hump is found to disappear after annealing beyond 120°C. The hump begins to occur where the exponential in the diode equation (Equation 3.2) increases. The dJ/dV value under illumination in Figure 3.5a spikes between 600 and 800 mV due to some doping effect. This spike indicates an increase in the conductivity of the device, likely due to a doping effect from an increase in minority carriers. The effect happens around the flat band voltage, when the external applied field cancels the internal field of the device. This causes an increase in carriers, building up and doping the device. This doping has been overcome in Figure 3.5b, with the light curve behaving more ideally. Upon annealing it seems that some barrier at the electron collection interface has been overcome, allowing the charges to be collected even without an internal electric field. This will be discussed further near Figure 3.11. While the peak of the increase in the shunt conductance usually appears within 100 mV of V_{OC} , no trend with V_{OC} was observed.



Figure 3.5: dJ/dV in the dark and light . The intercept at V=0 gives the shunt conductivity G. a) A non annealed device. The large hump indicates a barrier causing a build up of electrons, increasing conductivity around V=0.5V. b) A device annealed at 180°C for 20 minutes pre-contact deposition shows much more ideal behavior with no humps

As stated earlier, prevailing knowldege points to crystallization and phase separation as major reasons for the increase in PCE upon annealing. This should be most aparent in the decrease in series resistance. The expected decrease in series resistance was observed by plotting Equation 3.3. Figure 3.6 shows a decrease in the series resistance upon annealing. It should be noted that in Figures 3.7,3.8,3.10 and 3.11 the three lines represent three different sets of devices, each uniquely annealed at the specified temperature for 20 minutes. Each line contains one data point per specified temperature and no averaging was done. In a larger data set taken from cells made in our lab, devices started from an average value of $R_S = 82 \ \Omega/cm^2$ in the unannealed state which reduced to an average value of $20 \ \Omega/cm^2$ after annealing. We attribute the decrease in the series resistance observed in Figure 3.6 to the crystallization of the P3HT and PCBM, which helps in the conduction of charges. An increase in the uniformity of the devices is also found upon annealing, indicating that annealing helps to reduce local defects created in the devices upon production.



Figure 3.6: Device series resistance as a function of annealing temperature. The decreases in series resistance are significant, in some cases a factor of 8. Each line is a series of devices, annealed after (post), before (pre), and 10 minutes before and 10 minutes after (pre/post) the evaporation of the Al contact

The decrease in series resistance results in a higher voltage available at the junction, or V-RJ. Unfortunately, due to the very low current found in typical OPV devices, the gain from a decrease in series resistance is also rather small. We define an efficiency corrected for series resistance:

Equation 3.7 $\eta = (V_{max}-R_S I_{max})I_{max}/(A*100 \text{mW/cm}^2)$

- V_{max} and I_{max} are the voltage and current, respectively, at the maximum power point
- A is the device area
- 100 mW/cm^2 is the illumination power

Looking at the series resistance decrease from 82 Ω unannealed to 20 Ω after annealing, the change in efficiency due to this decrease in series resistance is only

0.4%. Thus, the significant increase in device efficiency (0.5% to 2.5%) observed upon annealing must be due to more than just the elimination of series resistance. This decrease in the series resistance could be either due to a decrease in the resistance of the material or a decrease in the resistance of the contact. To separate the two effects, multiple annealing studies were performed.

Three experiments were performed to separate the annealing of the contact from the annealing of the bulk. All devices were annealed at the specified temperature for 20 minutes. However, by annealing some devices before depositing the Al contact and others after the Al deposition, we were able to investigate effect of bulk and contact annealing separately. The bulk annealing increases the crystallinity and phase separation of the active layer, which we discuss as the major cause of an increase in efficiency upon annealing. The annealing of the device after depositing the contact layer should help form a better bond between the aluminum electrode and the P3HT:PCBM active layer. We found that annealing devices after depositing the A1 electrode resulted in a higher PCE than annealing the device before depositing Al. Annealing after Al deposition resulted in up to 33% higher efficiency than annealing before depositing the Al. This corresponds to other results using solely Al cathodes [2], as opposed to the commonly used LiF/Al. Contrary to our pure Al contacts, LiF/Al P3HT:PCBM devices have been shown to respond better to annealing before depositing the electrode [38]. While our data agrees with other studies using Al electron contacts, what is unique here is our separating the effect of annealing the bulk from the contact as opposed to annealing the bulk with the contact. Shown below, there was no significant difference in the series or shunt resistances, the

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recombination, or the charge carrier collection efficiency between either annealing approach. This means that annealing primarily improves the bulk properties.

Equation 3.3 also contains the diode ideality factor n. By plotting dV/dJ vs J^{-1} , the slope of the straight line gives n. The ideality factor is a lumped parameter, which can be broadly related to the recombination mechanism. n has a significant downward trend upon annealing, as seen in Figure 3.7. This downward trend can be linked to a change in the recombination. In traditional thin film devices, a diode ideality factor exceeding 2 is linked to excessively high recombination and non-standard defect kinetics such as recombination through band tails with high trapping density, or very localized defects [39]. In fact, a diode ideality factor greater than 2 is generally linked to donor-acceptor pair recombination via deep levels in crystalline silicon [40]. Donor-acceptor pair recombination method, so these findings suggest that a high n corresponds to a high exciton recombination. An n of 2 corresponds to majority limited carrier recombination. Once n decreases to 1, the minority carrier limits the recombination [41].

While all of the data points in Figure 3.7 are variable, the range is seen to converge upon annealing. The downward trend converges to a small range from 1-4, indicating the devices become more uniform with annealing. This suggests that annealing helps to remove defects in the device that may have been present from the processing.

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Figure 3.7: The diode ideality factor, n, which corresponds to recombination, as a function of annealing temperature

The decrease of the diode ideality factor signifies a decrease in not only the recombination magnitude but also a change in the mechanism. The high diode parameter in unannealed devices suggests mostly exciton recombination. Upon annealing the primary recombination mechanism changes to free carriers, with the best devices having a minority carrier limited recombination. This change is most likely due to the increased lifetime mobility in the device due to the crystallization of the materials. This increase in the lifetime mobility can be found by plotting Equation 3.4 and then fitting the $\eta(V)$ plot with Equation 3.5. One of the major benefits of Equation 3.5 is the simplicity of only two fitting parameters, the collection length L_e/D and the flat band voltage V_{fb} . Comparing the flat band voltage to the experimentally derived value serves as a check that the model is working properly.

In Figure 3.8, the flat band voltage is the point where the carrier collection efficiency goes to 0. The flat band voltage is the point where the applied voltage is equal to the internal voltage in the device. This is larger than V_{OC} due to resistances in the device. Without any internal voltage across the device, the charges cannot be collected. Figure 3.8a has a steep slope with response to increasing voltage, indicating high recombination, which means a low lifetime mobility product. Figure 3.8b shows a standard response of the charge collection efficiency to applied voltage.



Figure 3.8: The carrier collection efficiency, normalized to η =1 at V-RJ=-1. a) As cast device with a curve indicative of high recombination. b) Annealing at 180°C leads to a curve indicating low recombination

Our values of $\mu\tau$ found by fitting Equation 3.5 to Figure 3.8 are comparable to other reported values in literature. Yang et al. reported electron mobility values as low as $6.5 \times 10^{-8} \text{ cm}^2/\text{V}$ -s from SCLC measurements [42]. Coupling these values with electron lifetime measurements as low as 1×10^{-6} s from Garcia-Belmonte et al. [43], we find that the literature supports electron lifetime-mobility products in the range of $10^{-14} - 10^{-10} \text{ cm}^2/\text{V}$. We found $\mu\tau$ to have an average value of $6.7 \times 10^{-14} + 10^{-15} \text{ cm}^2/\text{V}$ in unannealed devices, which increased to an average value of $2 \times 10^{-13} + 1 \times 10^{-13} \text{ cm}^2/\text{V}$ after annealing. While our values are smaller than many values found in literature, they are values measured from actual P3HT:PCBM solar cells while they are operating under illumination.



Figure 3.9: The lifetime mobility product, as found from Equation 4, increases upon annealing due to increases in carrier mobility and crystallinity

The dark saturation current J_0 can be found from Equation 3.1 by plotting log(J-GV) vs (V-R_sJ). In some cases a non-ideality in the JV curves due to space charge limited current required an additional fitting of Equation 1 to the original data, but this was performed on very few data sets. J_0 signifies how much current flows at reverse bias through the diode due to diffusion of the minority carriers from neutral regions to depletion regions [44]. It is related to the diode ideality factor n, and is inversely proportional to the device performance. As J_0 decreases, V_{OC} and FF both increase [41]. As we can see from Figure 3.10, the dark saturation current overall tends to decrease with higher annealing temperature. In all devices that were annealed after evaporating the contacts, which were our most efficient devices, the average J_0 taken from 3 data sets (not shown here) decreased only slightly, from $3.6x10^{-4}$ A to $1.1x10^{-4}$ A. This small change in J_0 with annealing is consistent with the small change in V_{OC} .



Figure 3.10: The dark saturation current J_0 is quite noisy, though the average values lead to a decrease

Applying the analysis procedure described above, as embodied in Equations 3.1-3.7, allows for detailed insight into the internal operation of the device and can reveal other associated problems. For example, in Figure 3.11 the voltage dependence of the conductance (Equation 3.2) is plotted for several annealing temperatures for devices annealed before (Figure 3.11a) and after (Figure 3.11b) contacting. The peak in the shunt conductance near V_{OC} is apparent in both cases. This indicates that this sudden increase and decrease in the conductivity has no relation to the electron contact. In both cases in Figure 3.11 (a and b), the unannealed devices reach the diode "turn on" voltage at the same point as the devices annealed at 180°C. However, in the unannealed and partially annealed devices, there is a reduction in conductivity at higher voltages due to some barrier. Near 1V the conductivity begins to increase again as expected for a normal diode under forward bias. This is possibly due to tunneling of the carriers through the barrier or due to the barrier being lowered at the higher voltage. The annealing progressively reduces some barrier either at a contact or between regions of P3HT and PCBM. This barrier could be due to the smaller crystallite size, supporting the theory that the barrier is at the interface between regions of P3HT and PCBM. Upon annealing above 100°C, the reduction in the conductivity due to the barrier decreases and dJ/dV turns into a smooth monotonic curve with a steeper slope, as expected for a higher quality diode. This transition could allow determining the minimum annealing time and temperature for OPV devices.



Figure 3.11: dJ/dV vs V as a function of annealing temperatures in devices a) annealed after Al evaporation and b) annealed before Al evaporation

3.2.4 Comparison to PTB7:PC70BM System

All device results shown thus far have been from P3HT:PCBM devices. This is the most characterized OPV material system due to its availability, relative low cost, and the fact that it was the highest efficiency system from 2005-2010, a period of intense research in OPV. The bulk of this dissertation covers P3HT:PCBM devices, but as a side note, I will present the results of analyzing a PTB7:PC70BM device. PTB7:PC70BM devices were first fabricated and characterized in 2010, making ripples in the community as the highest efficiency OPV devices yet made [45]. The system was first found to produce 7.4% efficient devices, but was eventually optimized at 9.2% when using an inverted structure (electrons flow towards ITO) [46]. Devices in our studies reached a maximum efficiency of 4.84% utilizing a traditional structure (ITO anode). To provide an idea to the readers of how these PTB7 devices compare to the P3HT:PCBM system, we compare the values in Table 3.1. Most values are close, with the only major exception being in the dark saturation current J₀. This parameter is dependent on the material or junction properties, with parameters like recombination and minority carrier diffusion changing. Again, a smaller value results

| | P3HT:PCBM | PTB7:PC70BM |
|---|-----------|-------------|
| PCE (%) | 2.85 | 4.84 |
| Voc (mV) | 631 | 750 |
| $Jsc (mA/cm^2)$ | 10.1 | 12.1 |
| FF | 44.9 | 53.2 |
| $\operatorname{Rs}(\Omega)$ | 13.9 | 48.8 |
| $\operatorname{Rsh}\left(\Omega\right)$ | 2.57E+06 | 1.46E+06 |
| n | 1.45 | 1.17 |
| Jo (mA/cm^2) | 1.55E-04 | 3.63E-05 |
| $\mu\tau$ (cm ² /V) | 2.16E-13 | 3.17E-13 |

in a better device with a better V_{OC} .

Table 3.1:Device parameters measured from a well functioning P3HT:PCBM
device and a well functioning PTB7:PC70BM device

We did not perform a study on the effects of annealing on PTB7 devices. PTB7 has been found to crystallize quickly, forming phase segregated regions much larger than the exciton diffusion length [47]. Annealing exacerbates this problem. To keep phase size to a minimum, we use the solvent additive 1,8-diiodooctane (DIO). DIO dissolves PC70BM, allowing it to remain in solvent longer and segregate into the PTB7 regions. The device shown in Table 3.1 contains 1.5 vol% DIO added to the CB solvent.

3.3 Conclusions

Careful analysis of OPV devices, looking at both the light and dark curves, leads to a more in depth knowledge of their internal losses. By analyzing P3HT:PCBM solar cells using the well characterized simple lumped circuit model combined with a carrier drift model for finding the lifetime mobility product, we were able to better quantify annealing effects. While the benefit of annealing has long been known, our analysis revealed the abrupt decrease in series resistance, which indicated the annealing temperature where the material becomes more conductive. The analysis of the shunt resistance and dark saturation current does not show the material developing any shunts during annealing, which demonstrates that P3HT is an efficient OPV material.

The decrease in the series resistance upon annealing was shown to be due to the crystallization of the material and not due to the change in contact resistance upon annealing. The fact that all parameters behaved the same in devices annealed before, after, or before and after Al contact evaporation indicates that annealing is a primarily bulk effect. This is a unique issue to OPV due to low processing temperatures and indicates that most contact crystallinity and diffusion occurs upon evaporation.

The ability to obtain the lifetime mobility product $\mu\tau$ from only the light and dark JV curves of standard solar cell structures is extremely valuable. Our values are comparable to in situ measurements on partially completed P3HT:PCBM blends, confirming the applicability of this model. This ex situ measurement may prove useful in analyzing new materials and comparing them to well characterized OPV materials such as P3HT and PCBM.

A thorough current voltage analysis also reveals other interesting information about these devices. Figures 3.5 and 3.11 both reveal some barrier causing an increase in the conductivity of unannealed devices due to a buildup of carriers. The fact that this barrier is present in both Figures 3.11a and 3.11b indicates that it is not due to the aluminum electron contact. Annealing seems to overcome this barrier, suggesting that the barrier is due to one of the parameters investigated in this paper. Since all parameters, including R_s , the $\mu\tau$ parameter, the crystallinity and crystallite size, and the diode ideality factor respond favorably to annealing, it is difficult to determine the origin of this barrier. However, this method can be applied to other materials for the investigation and reduction of barriers through device treatment or to investigate alternative materials such as the replacement of ITO with tungsten oxide.

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Chapter 4

INDIUM FREE TRANSPARENT ELECTRODES WITH A TUNGSTEN OXIDE HOLE TRANSPORT LAYER FOR OPV DEVICES

4.1 Introduction

In this chapter, we explore the fabrication of OPV devices on alternative substrates. We cover the fabrication of these devices and the characterization, utilizing the JV diode model discussed in Chapter 3. We explore the results of JV characterization and modeling and extract data from the JV curves. This data helps explain some physics of the OPV devices and how they interact with the substrates.

While research on organic materials for photovoltaics is progressing rapidly, devices are still being fabricated on the same substrate material, namely ITO. Work has been done on ITO replacements [4], [48], but thus far no replacement has been found due to ITO's superior transparency (>80%) and low resistivity (<12 Ω/\Box). Most donor materials also have HOMO levels that align well with ITO, making it a useful anode material in conjunction with an Al cathode. However, one of the downsides of ITO is its high cost, making it one of the most expensive materials in a OPV device [48], [49]. Other problems with ITO include the relative scarcity of indium and the need to be sputtered onto a high temperature substrate to achieve low resistivity. This makes ITO incompatible with most flexible plastic substrates.

To address these issues, we investigated the use of a thin silver film encased by two metal oxides. Similar work has been done in the past [50], [51] using various oxides for their different conductivities, transparencies, and work functions. Work has also been done using silver nanowires and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) [51], [52] or silver nanoparticles [53] to form a transparent electrode. While these electrodes require no sputtering and thus can be fabricated at atmospheric pressure, they have lower transparency and conductivity than ITO. The use of a thin silver conducting film allows transparency and conductivity close to those of ITO with lower costs [54]. We encapsulated the silver films between two oxide layers for both protection and to achieve a tunable work function at the active layer interface. The ability to choose oxides with various work functions to place between the silver and active layer negates the need for the PEDOT:PSS layer that is required in ITO devices. We used Al-ZnO as our glass interface and WOx as our active layer interface. To test the electrodes, we made devices from various materials and compared the performance of WOx electrode based devices to standard ITO devices.

4.2 Experimental

Due to some of the specialized fabrication and characterization techniques relevant only to this section, we will briefly discuss the fabrication of these devices. This work was performed during an internship at the Fraunhofer Institute for Solar Energy Systems in Freiburg, Germany. We performed some work on analyzing the JV curves at lowered temperatures using a cryostat at the institute. Measurements were semi-automated using Labview.

4.2.1 Electrode Preparation

For the fabrication of the electrodes cleaned float glass substrates were coated by DC magnetron sputtering at $3x10^{-6}$ Torr. The sputtering process deposited a stack of Al-ZnO (40 nm), silver (9 nm), very thin W as a sacrificial layer (~1 nm) and WOx (10 nm to 100 nm). For the deposition of Al-ZnO a ceramic target was used containing 2% aluminum. Al-ZnO was deposited at a power density of 2.5 W/cm² in an argon atmosphere with 9% O_2 . A metallic silver target was used for the deposition of the thin silver layer at a power density of 0.7 W/cm² in a pure argon atmosphere. Since sputtering the WOx layer required the use of O_2 gas, we deposited a layer of pure W in a pure Ar environment to protect the Ag layer from any oxidation. To deposit the sacrificial layer and the WOx layer we used a metallic tungsten target. The sacrificial layer was deposited at a power density of 0.3 W/cm² in a pure argon atmosphere. The WOx layer was deposited at a power density of 2.6 W/cm² in an argon atmosphere with 37% O_2 . The substrates were structured with shadow masks. This structure can be viewed in a diagram in Figure 4.1 or the cross sectional TEM image in Figure 4.3.



Figure 4.1: a) Diagram of ITO free electrodes used in this study b) Work function of the WOx vs the thickness of the WOx layer

The sheet resistance of the electrodes was determined to be 12 Ω/\Box by a fourpoint measurement. Transmittance and reflection were measured with a fourier spectrometer. Transmittance and reflection were weighted by the P3HT:PCBM absorption spectrum. As seen in Figure 4.2, the transmittance of the electrode with a 10 nm WOx layer was determined to be 71%, the reflection to be 12%. The transmittance of the electrode with a 100 nm WOx layer was 58%, the reflection 24%. All optical properties were measured with light perpendicular to the film, but no significant angular changes were noticed. This is likely due to the 8 nm Ag film, which is much smaller than the wavelength of incident light.



Figure 4.2: a) Optical data for an electrode with the specified Al-ZnO/Ag/10 nm WOx layer and for b) Al-ZnO/Ag/100 nm WOx

4.2.2 Device Fabrication

All devices were made on WOx electrodes that had been cleaned using a UV-Ozone treatment for 20 minutes. Most devices in this chapter were fabricated using the method outlined in Chapter 2. To better explore a change in the HOMO and LUMO levels of the electron donor material, we used the polymer poly[[9-(1-octylnonyl)-9Hcarbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5thiophenediyl] (PCDTBT) as an electron donor in addition to the devices made with P3HT. PCDTBT has a HOMO level of -5.3 eV, slightly different from the HOMO level for P3HT (-5.1 eV). Our finished device layers consisted of glass/Al-ZnO/Ag/WOx/electron donor:PCBM/LiF/Al with the respective thickness of each layer being 1.1 mm/40 nm/9 nm/10-100 nm/200 nm/0.3 nm/100 nm. As a control, we used devices with a PEDOT:PSS coated ITO electrode. These devices consisted of glass/ITO/PEDOT:PSS/electron donor:PCBM/LiF/Al with respective layer thicknesses of 1.1 mm/120 nm/40 nm/200 nm/0.3 nm/100 nm.

4.2.3 Electrical Measurements

JV curves were generated using a class C solar simulator at 100 mW cm⁻², corrected for spectral mismatch, inside a nitrogen filled glove box with a Keithley 2400 SourceMeter. Devices fabricated at UD were measured outside the glovebox in air. The devices can suffer a slight degradation, but it is typically not a concern on the timescales necessary to measure a device. However, at Fraunhofer the measurement
system was in a glovebox, and thus these JV measurements were carried out in nitrogen.

4.2.4 Temperature Measurements

To better reveal any barriers to electron flow, we investigated the JV curves at low temperature. Barriers exist in the device, but are difficult to quantify at room temperature. When the thermal energy of electrons is on the order of the barrier height, electrons have a high probability of flowing through these barriers. However, when the thermal energy in the system decreases, the probability of electron flow decreases and the barriers become more apparent and easy to quantify. Temperature measurements were taken in a chamber with a base pressure of 1×10^{-5} Torr, with temperature controlled by liquid nitrogen and a heater. JV curves were measured using a halogen lamp to illuminate the devices and a Keithley 2400 SourceMeter, with all measurements and temperatures being controlled by a Labview program.

4.3 **Results and Discussion**

4.3.1 Electrode Morphology

In order to confirm that the sputtering process produced well-organized films, we investigated the device cross section using TEM. Figure 4.3 shows compact films with sharp interfaces in the Al-ZnO/Ag/WOx layer. The interface between the WOx and the active layer is well formed, indicating that the WOx layer does not degrade or interact with other layers after device fabrication and treatment. This is typical for oxides, but not for metals. Our group has done research into the diffusion of Al into polymers at the cathode interface of OPV devices [15]. This shows a mixed diffusion layer of ~5 nm, which typically increases conductivity at the interface. However, here

we do not see any inter diffusion, indicating the WOx layer has a high cohesive



Figure 4.3: TEM crosssection of a device with 10nm WOx. a) The entire device, with Pt protective layer on top b) The sputtered electrode area, with sharp interfaces between all layers

The sputtered electrode's work function was measured using a Kelvin Probe technique in ambient atmosphere with a gold reference. We found the work function of the WOx to vary with the thickness, from -5 eV at 10 nm WOx to a saturation of - 5.4 eV at 40 nm, after which the work function became independent of thickness and remained constant up to WOx thickness of 100 nm (Figure 4.1b). Figure 4.4 shows this range in relation to the highest occupied molecular orbital (HOMO) level of a polymer used in this study. This suggests that the WOx layer becomes doped with electrons from the thin silver film underneath. The carriers from the silver migrate into the WOx, raising its work function closer to that of silver (-4.26 eV for amorphous material [55]). This phenomenon has been investigated in the past, and is attributed to

metal induced gap states (MIGS) for metal/semiconductor interfaces [56], [57]. Although the WOx used in this study is amorphous, we believe the work function varies due to gap states being introduced near the Fermi level by the metal. This variable work function could be used to tune the transparent electrode to better work with different materials (P3HT's HOMO level is -5 eV, while PCDTBT has a HOMO level closer to -5.3 eV).



Figure 4.4: The WOx work function can vary, resulting in different alignments relative to the donor acceptor level

We first tested the WOx electrode using the standard P3HT:PCBM system and measured the JV curves, as seen in Figure 4.5a and 4.5b. We found the power conversion efficiency (PCE) of the best WOx electrodes to be less than the ITO/PEDOT:PSS electrodes (1.9% vs 3.0%). These values can be found in Table 4.1. The value of 1.9% PCE occurred with a WOx layer thickness of 10 nm, corresponding to a work function of -5eV. The lower PCE with respect to the ITO may be due to the interface between the active layer and the electrode. The PEDOT:PSS layer both smoothens any surface roughness of the ITO and provides a polymer/inorganic interface material. Another reason for the lower PCE is the lower transparency of the WOx electrodes. The 10% lower transparency could account for the drop in J_{SC} between the two electrodes. The average J_{SC} of the ITO devices was 7.85 +/- 0.22 mA/cm², while the average J_{SC} of the WOx devices was 7.11 +/- 0.06 mA/cm². This 9.4% drop in J_{SC} lines up very closely with the drop in transparency.

| Device Structure | V _{OC} (mV) | J_{SC} (mA/cm ²) | FF (%) | PCE (%) |
|----------------------|----------------------|--------------------------------|---------------|---------------|
| ITO/P3HT:PCBM | 628.7 +/- 2.2 | 7.85 +/- 0.22 | 62.1 +/- 2.0 | 3.06 +/- 0.17 |
| 10 nm WOx/P3HT:PCBM | 573.5 +/- 10.9 | 7.11 +/- 0.06 | 46.7 +/- 0.02 | 1.91 +/- 0.09 |
| 100 nm WOx/P3HT:PCBM | 535.8 +/- 15.9 | 6.55 +/- 0.07 | 48.3 +/- 0.00 | 1.70 +/- 0.04 |
| ITO/PCDTBT:PC71BM | 794.5 +/- 6.3 | 8.94 +/- 0.16 | 44.2 +/- 0.01 | 3.14 +/- 0.07 |
| 10 nm | 297.5 +/- 47.0 | 7.74 +/- 0.23 | 28.4 +/- 0.01 | 0.66 +/- 0.12 |
| WOx/PCDTBT:PC71BM | | | | |
| 100 nm | 531.7 +/- 4.8 | 6.42 +/- 0.15 | 44.0 +/- 0.00 | 1.50 +/- 0.05 |
| WOx/PCDTBT:PC71BM | | | | |

 Table 4.1:
 Device parameters of the WOx and ITO electrodes used in this study

To investigate the changing work function, we made devices with another electron donor material. We chose PCDTBT due to its lower HOMO level with respect to P3HT. While the HOMO level may have shifted due to the differing substrates, the HOMO level of PCDTBT has been found to be -5.3 eV on PEDOT:PSS [58] while P3HT's HOMO level is closer to -5.0 eV on PEDOT:PSS [59]. These values can shift on different substrates, but it was beyond the scope of this study to measure that change on the WOx electrodes. This means that the energy level of P3HT is more closely aligned with the work function of the 10 nm WOx (work function of 5eV), while the PCDTBT is more closely aligned with the 100 nm WOx (work function of 5.4 eV). Indeed, as seen in Table 4.1 and Figure 4.5c and 4.5d, the 100 nm WOx electrode has a higher Voc than the 10 nm device. This is in contrast to the P3HT device in Figures 4.5a and 4.5b, which has a higher Voc for the 10 nm WOx layer. The 10 nm WOx curve in Figures 4.5c and 4.5d is shunted (Rshunt = 51 Ω) due to a hole in the active layer. While this does change the result, the V_{oc} will not change significantly from a shunt of 51 Ω . We calculate the shift to be around 2%, or a 15 mV drop. The work function for 10 nm WOx of -5eV corresponds more closely to the HOMO level of the P3HT (-5 eV), showing that closely aligned energy levels are important for a good device.

Literature shows that the work function of the electrodes can vary the V_{OC} by small amounts in the same active layer material [60]. However, when the electrode work function is drastically different than the HOMO level of the donor, the change increases due to non-Ohmic contacts being formed [61]. The difference of only 100-300 meV between the anode work function and the donor HOMO level should remain Ohmic and only have a slight effect on the V_{OC} .



Figure 4.5: P3HT:PCBM devices on ITO, Al-ZnO/Ag/10 nm WOx and Al-ZnO/Ag/100 nm WOx electrodes a) in the dark and b) under illumination. Notice the changes in Voc based on the thickness of the WOx layer. c) Devices made of PCDTBT:PC70BM in the dark and d) in the light

Misaligned work functions can lead to the formation of a barrier for charge flow. This barrier from the poorly aligned anode work function/donor HOMO level may result in lower V_{OC} , a low fill factor, or any number of problems. To better explore any barriers that might arise from the WOx layer, we cooled our devices while measuring the JV curves. This has been done in the past to explore barriers in PV [19], [24]. By cooling the device, the charge carrier thermal energy drops. With lower thermal energy, the carriers do not have the energy to overcome barriers. This manifests itself in a kinked solar cell at low temperatures (Figure 4.6a). To quantify this kink, we applied the basic diode model of a solar cell to our curves, as discussed in Chapters 2 and 3. As a brief reminder, the equation used for this is:

Equation 4.1
$$J(V)=J_0\{\exp(q(V-R_sJ)/(nk_BT))-1\}+GV-J_L(V)$$

By taking the derivative of this equation and assuming a large shunt resistance (Rshunt>3 k Ω) [62], we were able to find a measure of the conductivity:

Equation 4.2
$$dV/dJ = R_S + nk_BT/q(J+Jsc)$$

Where dV/dJ will have the units of Ω -cm². By plotting dV/dJ vs 1/(J+J_{SC}), a kink will appear as a peak in the resistance (Figure 4.6b). Following the methods of Hegedus and Ali [19], [24], and assuming that the resistivity returns to that of a typical cell at high values of 1/(J+J_{SC}), we can fit a straight line to large values of 1/(J+J_{SC}). We make this assumption based on the fact that series resistance is negligible around J_{SC} except for very large values of R_S.



Figure 4.6: a) JV curves of P3HT:PCBM devices on Al-ZnO/Ag/10 nm WOx electrodes measured at various temperatures from 180K to 310K. b) The derivatives of the curves from a)

Taking the curves seen in Figure 4.6b and linearly extrapolating the values of R_s at high values of $1/(J+J_{sc})$ to lower values, we can find the barrier height. To do this we subtract each peak height from the expected value of resistance were there no peak. Taking these values at different temperatures gives us a range of barrier resistance at different temperature. To better analyze the barrier resistance, we assumed the devices behavior closely followed an Arrhenius relationship :

Equation 4.3
$$Rb = Ae^{E_a/kT}$$

- Rb is the barrier resistance
- E_a is the activation energy

Plotting the ln(Rb) vs 1/T and taking the slope, as seen in Figure 4.7, gives us the activation energy E_a , which we can relate to the barrier energy in the device.



Figure 4.7: The Arrhenius plot of the resistance from Figure 4.6b, where the red line is the fit using the Arrhenius equation

The linear fit on the graph (exponential fit of the data due to the logarithmic y axis) suggests that our analysis is correct and the carriers do overcome the barriers through thermal energy. Looking at the slope of the line, we can find E_a . For the 10 nm WOx electrode thickness with P3HT:PCBM, we found the barrier energy to be 100 meV. This is lower than the 140 meV barrier found for 100 nm WOx electrodes with P3HT:PCBM. The higher barrier of 140 meV for 100 nm WOx could be due to the lower work function of the 100 nm WOx (-5.4 eV) as compared to the 10 nm WOx (-5eV).

4.4 Conclusion

We have found that combining a thin metal film with a semiconductor creates an efficient anode for OPV devices. The use of WOx is especially desirable due to its close alignment of the work function relative to commonly used OPV materials. By varying the thickness of the WOx we were able to vary the work function at the surface, which helped to facilitate charge transfer. This was visible mostly in the changing V_{OC} of the devices. By cooling these devices down, we found a barrier to manifest itself as a kink in the JV curve. Analyzing this kink led to the appearance of a barrier, which we were able to quantify to be around 100 meV. This barrier increased directly proportional to the thickness of the WOx layer. This increase is most likely due to the work function of the WOx dropping to below the HOMO level of the electron donor material.

While these electrodes did not result in an increase in device efficiency, they did provide a simple mechanism to change the work function of the anode. This gave us a tool to investigate the effect of a work function mismatch at the interface between the anode and the electron donor material. We found that a larger mistmatch created a lower V_{OC} and a higher barrier energy as found by the Arrhenius plot. Should new materials be created and require characterization, WOx electrodes provide a method to investigate how well they work on different work function electrodes.

Chapter 5

PREDICTING CURRENT FROM CROSSECTIONAL IMAGES OF OPV DEVICES

5.1 Introduction

In previous chapters, we discussed the necessity for the BHJ structure. Most discussions of the BHJ structure contain some crude approximate cartoon like the one in Figure 1.2. The difference between actual structure and the approximation will not affect the JV diode model used throughout this dissertation, but it could prove useful in controlling the way OPV active layers are formed. To further the field, we need a better understanding of the morphology of these devices and how it affects their performance [17], [28], [63]. Novel characterization techniques are required to better probe the morphology of these devices.

Much work has been done on the interaction between light and the organic materials of the active layer in order to optimize OPV devices. Absorption modeling was done in the past to increase the device efficiency [64]. These studies find the optimal thickness of a device with respect to maximizing both light absorption and carrier collection. Other absorption models were used to find the interaction between light and the active layer. Moule et al. used a Fresnel matrix to predict J_{SC} and found it to closely match their experimental values [65]. Shaw et al. used a transfer matrix to model the absorption and find the diffusion length in P3HT:PCBM devices [9]. Work has also been carried out to compare the absorption of P3HT and PCBM and concluded that the low absorption of PCBM needs to be offset by P3HT to form an

efficient device. This study was able to make an estimate of the exciton collection from various phases of P3HT:PCBM devices, as we propose to do in this chapter [66]. Interesting predictions of the device morphology combined with Monte Carlo simulations can also provide accurate estimates of the charge collection, but this data lacks detailed information about the bulk morphology [67].

In order to better understand the BHJ structure, many groups have investigated the bulk morphology of OPV devices. 2-D surface morphology mapping has been done using precise optical techniques, revealing morphology and photo collection at the surface [68]. This method provides interesting details about surface morphology, but cannot probe the bulk of the layer. Atomic force microscopy (AFM) studies also provide rich details of surface morphology, but cannot reveal details important to device operation, such as phase separation and donor/acceptor distribution. Neutron studies have proven useful for determining material distribution and have helped resolve the debate about material distribution in OPV [69]. In a previous report from our group Transmission Electron Microscopy (TEM) studies combined with energy filtering and analytical techniques [70] have also been used to study bulk morphology. This technique provides the most detailed information about the inner workings of the device. More references and information on morphology characterization can be found in the recent review by Pfanmöller [71].

Energy filtered TEM (EFTEM) is a powerful characterization technique and can be used to reveal contrast between the materials used for a device. More information regarding EFTEM can be found in Chapter 2 or in our previous work [14], [15]. While EFTEM is a very powerful technique and can resolve OPV morphology from a convoluted blend of nano-scale phase separation to clear images, it has some

limits. Sample preparation is both costly and time consuming, taking up to 20 hours per sample including TEM imaging. The images also only provide a 2-D glimpse of a 3-D structure, leaving questions as to the true state of island phases. Keeping these limits in mind, EFTEM cross sections still offer accurate glimpses into the morphology and phase separation of OPV devices.

5.2 Experimental

5.2.1 FIB Sample Prep

With the help of Dr. Nopporn Rujisamphan, samples were prepared for EFTEM using a focused ion beam (FIB) system (Auriga FIB 60). Samples were milled using a gallium ion beam to create cross section lamella of functional solar cells that were approximately 50 nm thick. Further information regarding this sample preparation can be found in our previous work [14], [15]. Once the lamella samples were prepared, they were placed onto a copper TEM grid and transferred to the TEM (LIBRA 120° PLUS, Zeiss with an accelerating voltage of 120kV).

5.3 **Results and Discussion**

5.3.1 EFTEM Images

Both P3HT and PCBM exhibit broad plasmon loss peaks which can be measured using electron loss spectroscopy (EELS). As shown in Figure 2.6, work by Herzing et al. has shown P3HT to have a resonance peak at 22.2 eV and PCBM to have a resonance peak at 25.5 eV [72]. By analyzing the sample using an energy loss filter, we can selectively remove most of the P3HT or PCBM signature from the signal. All EFTEM images shown here were taken with a 30 eV energy loss filter with

a 7 eV window width applied, effectively darkening the P3HT signal and leaving the PCBM rich regions bright. We performed EFTEM on two samples annealed for different times (Figure 5.1).



Figure 5.1: EFTEM images with a 30 eV energy loss filter applied showing the cross section of a) a cross section image of a device annealed for 20 min at 160°C, b) the active layer shown with a digital filter applied, and c) a digitally filtered image of a cross sectional sample from a device annealed for 10 hours at 160°C

The 30 eV filter applied to the EELS signal creates a contrast in the active layer that is not visible using traditional TEM techniques. Groups in the past have attempted to use defocused TEM [73] to image the difference between donor and acceptor materials. Unfortunately, defocused TEM has been shown to provide unsatisfactory results [69]. EFTEM creates a superior contrast and has been confirmed to work on P3HT:PCBM systems [17], [72] as well as many other materials systems

[74], [75]. Combining EFTEM with the FIB cross section preparation technique, cross sections made from functioning devices give us the ability to see phase separation and charge collection pathways in actual devices.

Sample preparation with an FIB produces 50 nm thick lamella samples. Due to the thickness being larger than the observed phase size, some stacking of P3HT and PCBM regions is expected. Thus, the maps shown here provide the dominant material in each region. While this study is only looking at a 2D cross section, the region is fairly large and can provide some estimate of the morphology of the total device. A difference can be observed between the 20 minute and 10 hour annealed devices (Figure 5.1b and 5.1c). Larger areas and more contrast are apparent in the 10 hour device due to increased phase separation.

Even with an energy loss filter applied, the raw images produced by EFTEM (Figure 5.1a) need additional contrast. After rotating and cropping the image to contain only the active layer with the ITO side on the top of the image, we filtered the image. By applying a threshold filter to the image (Figure 5.1b and 5.1c) we were able to obtain an image that has high contrast. To achieve the binary image in Figure 5.2, we applied an averaging filter to the image using Matlab. To reduce noise and increase contrast, we binned the original image pixels into regions of 2.5 nm. We then applied a cutoff, making every pixel darker than average black and lighter than average white. The average in each region was determined by averaging the regions surrounding it. This was to smooth any non-uniformity in the image due to different thicknesses in the lamella.

After obtaining a rough black and white image, we then smoothed the image, removing isolated pixels. These isolated pixels may be due to noise. Unfortunately,

this also removes mixed regions from the device, creating a 2-phase image and ignoring all mixed regions. While this may be a problem, exciton separation occurs at P3HT:PCBM interfaces, which will predominantly occur at the interface between P3HT rich and PCBM rich regions. Using this binary image (Figure 5.2), we were able to create a Matlab program to analyze the absorption and exciton collection in the device.

5.3.2 Phase Separation

By creating a map of P3HT and PCBM rich regions, as seen in Figure 5.2, we were able to explore the vertical phase separation in the device. Summation of the PCBM pixels in each row led to the plot of PCBM concentration in the device (Figure 5.3). A high PCBM concentration at the PEDOT:PSS interface is very apparent, which causes a decrease in charge transfer. A buildup of PCBM also exists near the Al interface, though a layer of P3HT rich material exists at the interface, aiding charge flow. This data corresponds well with other studies, such as the neutron study of vertical phase separation in P3HT:PCBM systems by Kiel et al. [69].



Figure 5.2: The filtered and cropped image of a device annealed for 20 min at 160°C converted to a 2-phase system



Figure 5.3: Relative PCBM content as a function of layer thickness, as measured from the digitized image Figure 5.2

To convert the phase separated images (Figure 5.2), we wrote a simple Matlab program to model light absorption and exciton diffusion. The program used a simple absorption and exponential exciton collection model to predict the short circuit current of the finished device. We started by taking the AM1.5G spectrum and binning it by wavelength into 100 meV bins. We applied a non-wavelength dependent 10% reflection to the incident spectrum to take into account any reflection at the air-glass interface (~8%) and the glass-PEDOT interface (~2%) [76]. Any remaining light was then taken to be incident on the binary image (Figure 5.2).

5.3.3 Absorption Modelling

While standard absorption coefficients are typically used for scales greater than the wavelength of the incident radiation, here we successfully applied them to the interior of these OPV devices. This model is based on ray optics, which while commonly used in OPV, is a rough approximation to the actual absorption that occurs in devices. It does not account for any interference, which is certainly a contributing factor owing to the low thicknesses of the films. A transfer matrix [9], [76] is another approximation which takes into account interference in these devices. Unfortunately, it assumes a uniformly blended active layer and does not take into account the morphology of the films and the different absorption coefficients of P3HT and PCBM. For these reasons, we chose to use ray optics and the Beer-Lambert law.

Using experimentally measured absorption coefficients in addition to those taken from literature [77], we analyzed how much light was absorbed at each pixel by applying the P3HT coefficient for P3HT regions and the PCBM coefficient for PCBM regions. We assumed the light was incident perpendicular to the surface and would propagate directly through the device. Due to the closely matched indices of refraction

of P3HT and PCBM (n=1.9 [78] and n=2.0 [79], respectively), we assume no bending of the light at any P3HT/PCBM interface. We then applied the Beer-Lambert law to each layer in the device. The Beer-Lambert law is generally written as:

Equation 5.1 $I = I_0 \exp(-\alpha x)$

- I and I₀ are the transmitted and incident light intensities, respectively
- α is the absorption coefficient
- x is the thickness of the layer in cm (where 1 layer = 1 row of pixels = 2.7 Å)

By taking I₀-I, we find the amount of light absorbed by the layer. For this study, we assumed all absorbed light results in electrons being excited. If every absorbed photon creates one exciton, we then know the number of excitons generated in each pixel. The transmitted light intensity I is then passed to the next layer down, where it becomes I₀ and the process is repeated. We assumed a 90% reflection at the polymer-Al interface on the back layer, and then repeated the absorption as the light is reflected up the device. This created the map of absorption shown in Figure 5.4. White represents the areas of highest absorption, which correspond to P3HT rich regions. P3HT has a much higher absorption coefficient in the visible range, $1.7x10^5$, as compared to $2.7x10^4$ for PCBM. Shading in the lower areas is observed as the P3HT above absorbs a significant amount of light.



Figure 5.4: An absorption map of the device annealed for 20 min at 160°C where white corresponds to high absorption and dark to low absorption of incident light

5.3.4 Exciton Diffusion and Collection

To find the probability that an exciton will be collected, we assumed an exponential collection probability. If any exciton formed far from the interface, its chance of recombination was high. The diffusion length was taken to be 10 nm, as commonly cited in the literature [9]–[11]. To find the collection probability, we used the diffusion equation

Equation 5.2

$$CP = \exp\left(-\frac{x}{L}\right)$$

- CP is the collection probability
- L is the diffusion length

We used Matlab to create a map of the device cross section to estimate the collection probability at any point in the device (Figure 5.5a). We assumed a radius of annihilation (R_A) of 2 nm [9], which means that any excitons forming within 2 nm of

an interface were given a 100% chance of collection, visible as the bright white lines in Figure 5.5a. It can be seen in Figure 5.5a that there are dark areas with a low collection probability due to a long distance from an interface. We ran one simulation considering island interfaces, and a separate one not including them as collection sites due to the lack of a charge collection pathway. Due to the use of a 2D image to represent a 3D structure, it is impossible to say which island regions are in fact islands and which connect through the z axis. For this reason, we ran both simulations and compared the results. Figure 6 is shown including island interfaces as collection regions.



Figure 5.5: a) Exciton collection probability based on the distance from an interface, where white is 100% collection, black is 0%. b) Combination of exciton collection probability with exciton formation information to map where charges are generated in the device By combining the information on exciton generation from the absorption modeling with the exciton collection probability (Figure 5.5b), we can find an estimate of the short circuit current J_{SC} . For the 20 minute annealed device shown in Figure 5.1-5.5, the predicted J_{SC} is 9.7 mA/cm² when island regions are considered. This contrasts with a predicted J_{SC} of 7.8 mA/cm² for a device annealed for 10 hours at 160°C. The higher J_{SC} is to be expected, as 20 minutes is a much more optimal annealing time than 10 hours [2], [80].

We next compare the predictions from the absorption/exciton diffusion model to the experimental JV results. The device annealed at 160°C for 20 minutes was more efficient than the 10 hour device, with an experimental power conversion efficiency (PCE) of 2.0%, V_{OC} of 612 mV, J_{SC} of 7.3 mA/cm² and a fill factor (FF) of 45.6%. The device annealed at 160°C for 10 hours had a PCE of 0.9%, V_{OC} of 591 mV, J_{SC} of 3.8 mA/cm², and a FF of 39.6%. We compare these experimental values to the predicted values in Table 5.1. The ratios of current from island areas to current from non-island areas are similar in both devices. This contribution from the islanded areas suggests that hopping is an important contributing factor to the charge collection of the device and the J_{SC} .

| Device | Predicted | Predicted Current | Experimental | % Current |
|------------------|-------------|-------------------|--------------|-----------|
| | Current | Without Islands | Current | from |
| | Considering | (mA/cm^2) | (mA/cm^2) | Islands |
| | Islands | | | |
| | (mA/cm^2) | | | |
| 20 Minutes 160°C | 9.7 | 6.0 | 7.3 | 36% |
| Anneal | | | | |
| 10 Hours | 7.8 | 3.1 | 3.8 | 15% |
| 160°C Anneal | | | | |

Table 5.1:Predicted current compared to experimental data from the devices,
showing how much current must come from island areas

5.4 Conclusions

EFTEM images allow the field to move away from the commonly seen schematic drawings of the cross-sections of OPV devices and give an insight into actual device morphology. This also gives us the ability to quantify the impact of the morphology on device performance. Using a simple absorption and exciton diffusion model, we were able to closely predict the J_{SC} in a device. We found that island regions likely contribute to the J_{SC} , suggesting that hopping is an important charge collection mechanism. EFTEM has already proven useful in determining morphology of materials other than P3HT [74]. This technique only requires EFTEM images and some knowledge of the absorption and charge collection in the material to carefully study the carrier collection in the device.

Sample preparation using a FIB is costly and time consuming, making large scale studies difficult. Samples are small and typically only give a narrow view into the morphology of the device, making erroneous results possible. Additionally, this model assumes a pure phase separation between materials, which is a crude approximation. While there are P3HT and PCBM rich areas, a BHJ structure will most likely contain amorphous blend regions in addition to pure crystalline phases. However, even with these short comings the J_{SC} of functional devices was predicted and compared to experimental data, showing a correlation in charge collection when island areas are taken into account. This connection between morphology of the device and the electrical characteristics can be used to predict ideal annealing parameters and their effect on device output. This work may prove useful in the study of new

materials, providing a method to correlate the device morphology with the current output and giving insight into the hopping of electrons through island areas.

Chapter 6

CURRENT VOLTAGE ANALYSIS OF SILVER NANOPARTICLE DOPED OPV DEVICES

6.1 Introduction

Due to their short exciton diffusion lengths [9], [10], OPV devices are confined to thin film BHJ structures. They have a high absorption coefficient [77] and thus are successful at converting light to electricity with a film thickness of ~200 nm. However, if similar absorption could be achieved with a much thinner film, excitons could be collected more efficiently. New organic materials have increased absorption coefficients and the exciton collection efficiency [45], [58], but still fall behind inorganic materials. One way to address this mismatch is to create OPV devices mixed with inorganic materials.

The most common organic/inorganic hybrid devices use materials such as TiO₂ or ZnO to create solar cells that can be more efficient than OPV devices. TiO₂ is often used to either increase the absorption and energy collected from high energy photons or as a hole blocking layer. Some devices, namely PCDTBT:PC₇₁BM, use TiO₂ as an optical spacer [81]. This layer helps increase the effective thickness of OPV devices when the materials suffer from both a low absorption and low mobility, requiring thin devices to transport charge but also thick devices to capture photons.

Another method of increasing photon capture involves using metallic nanoparticles to increase the effective absorption of a material [81], [82]. These nanoparticles, typically gold or silver, use the surface plasmon resonance (SPR) effect to capture photons, which can then be transferred to the PV material. Incoming light activates a resonance mode of the free electrons in the nanoparticles, trapping the energy in the nanoparticle. The size and shape of the nanoparticle help define the resonant mode and thus the wavelength of light trapped. Many different methods of incorporating SPR nanoparticles have been attempted with very different results. The most common method involves synthesizing nanoparticles via a chemical reaction and doping them into the active layer of a BHJ device. This method works well in most studies, but the nature of a chemical preparation leaves behind some surfactant from the creation of the nanoparticles. This surfactant can inhibit charge transfer and lower the effectiveness of the nanoparticle's light trapping capabilities.

To overcome the presence of these surfactants, we created surfactant free silver and gold nanoparticles. We prepared these nanoparticles via thermal evaporation, where a thin layer of metal is evaporated and then stopped before the film can become continuous. This thin layer forms islands, which clump together to form "nanoparticle" type islands, as can be seen in Figure 6.1.

The growth of these islands follows the Volmer-Weber (VW) growth mechanism. VW growth is characterized by island formation as a film is grown atomically. This is different from Frank-van der Merwe (FM) growth, where a film grows monolayer by monolayer. The type of growth is determined by the atomic chemical potential of each additional atom, with the change in the chemical potential determinging the film growth type (Equations 6.1 and 6.2):

VW growth:
$$\frac{d\mu}{dn} < 0$$
Equation 6.1FM growth: $\frac{d\mu}{dn} > 0$ Equation 6.2

a..

This can be simplified by analyzing the atomic attraction between the additional atoms (adatoms) and the surface and the adatoms and themselves. If the surface adhesive force is greater than the additional atom's cohesive force, FM growth will occur and no islands will form. If the opposite is true, and the additional atoms are more attracted to each other than the film, islands will form. As seen here, VW growth is typical for Ag and Au on non-metals. If the films were grown on a metallic substrate, FM growth would take place, but as all of the surfaces involved in an OPV device are non-metallic (not counting the capping Al layer), we can count on VW growth and islands to form.



Figure 6.1: Left: AFM height image of 20 nm average Au nanoparticles evaporated on silicon. Right: SEM image of Ag nanoparticles evaporated on ITO coated glass

There are several benefits of using thermal evaporation to create a film of nanoparticles. As seen in Figure 6.1, thermal evaporation creates uniform particle distribution when the VW growth mechanism is dominant. These two images are of Au on silicon (Figure 6.1a) and Ag on ITO (Indium Tin Oxide) coated glass (Figure 6.1b), showing that VW growth is easily accessible with a range of materials and substrates and produces well structured uniform islands. Thermal evaporation is a very easily controllable, low cost process. Typical surfactant free nanoparticles tend to agglomerate, but thermal evaporation with VW growth keeps them spread out in a thin layer. It also eliminates the use of any dangerous chemicals used in the preparation of nanoparticles, of which there are many. Another benefit of thermally evaporated nanoparticles is the ability to deposit them on most non-metallic surfaces, provided the surface can be exposed to vacuum.

The only disadvantage to using thermally evaporated surfactant free nanoparticles is the inability to dissolve them in solution. Nearly all OPV devices are fabricated using a solvent based method utilizing either spin coating [2] or screen printing for roll to roll large scale fabrication [5]. One method to investigate the solubility of these surfactant free nanoparticles involves evaporating them onto the active layer of a solar cell, dissolving the active layer in solvent, then re-spin coating it to distribute the nanoparticles in the new active layer. We attempted this with some favorable results, but the large variability in processing made it unfeasible and the results will not be included here.

6.2 Experimental

This study utilized both P3HT:PCBM and PTB7:PC71BM devices in the traditional architecture discussed in Chapter 2. In some devices, in order to embed the Ag nanoparticles inside the active layer, we first spin coated a layer of organic material, then deposited the Ag layer, then spin coated another layer of organic material. By varying the spin coating speeds, we were able to control the thickness of

these layers. A typical device uses an ~150 nm layer of organic material, referred to here as "Thick". We also utilized thin layers of ~70 nm, referred to as "Thin". Thus, a device labeled "Thick/Ag/Thin" consists of a 150 nm layer of organic material, a thin layer of Ag nanoparticles, then a 70 nm layer of organic material. For devices not using the sandwich structure, Ag nanoparticles were evaporated into the device at different stages in fabrication, using a traditional resistively heated tungsten boat to evaporate materials at a pressure of $<1 \times 10^{-5}$ mbar. For all nanoparticles, an equivalent layer of 2 nm was deposited, as measured by a quartz crystal thin film monitor. The device labeled Ag/LiF/Al involved evaporated on top of the Ag nanoparticles.

6.3 Results

6.3.1 Absorption Measurements

Thermally evaporated nanoparticles have a characteristic plasmon resonance peak around 475 nm for 20 nm Ag nanoparticles. This peak, as seen in Figure 6.2b and d (most apparent in the ITO/Ag curve), is due to light of a certain wavelength resonating with the electron cloud of a nanoparticle, creating a sharp absorption peak. The broadness and location of this peak is determined by the shape and size distribution of the nanoparticles. The location of the peak can also be shifted based on the dielectric coefficient of the material surrounding the nanoparticle. Our nanoparticles have a large size distribution as seen in Figure 6.1, causing the absorption peak to be wider than normal.

Figure 6.2 shows absorption measurements from devices with Ag nanoparticles embedded between different layers of the device. While Figures 6.2a

and c do not show a significant change in the overall absorption, when the standard device (Glass/ITO/organic layer/LiF/Al) absorption curve is subtracted from the data of devices with Ag embedded, broad peaks are left behind (Figures 6.2b and d). This helps reveal the true absorption of the Ag nanoparticles and shows which part of the spectrum the nanoparticles will absorb.



Figure 6.2: PTB7 (a) and P3HT (c) devices with Ag nanoparticles evaporated between different layers or dissolved in the active layer, as noted in the legend. PTB7 (b) and P3HT (d) absorption spectra of devices with Ag nanoparticles with standard device subtracted out. Ag nanoparticle surface plasmon resonance peaks become clearly visible We can see that the peak shifts when the Ag nanoparticles are embedded in different layers of the device. Peak shifts are due to the change in the dielectric constant of the material surrounding the nanoparticles. Jensen et al. investigated peak shifts in Ag nanoparticle films, finding the peak absorption wavelength to increase with the dielectric constant of the medium [83]. Even with the shift, all samples have a very recognizable surface plasmon resonance peak. This indicates that the Ag layer is acting as desired, trapping light of a certain wavelength for transfer to the active layer of the device.

It is also worth noting that the devices labeled Thin/Ag/Thin have a higher relative absorption than the standard device. This is surprising, considering the total thickness of the device is only 140 nm, more than 10 nm lower than the control. The difference is made up by the Ag nanoparticles, illustrating the benefit of using Ag to achieve thinner devices with higher absorption.

6.3.2 JV Results

While the absorption of each device increased, the device performance did not. Figure 6.3 shows the device parameters extracted from the measured JV curves, including the V_{OC} , J_{SC} , FF and PCE. In all of these results, the device without any Ag nanoparticles performed the best. Interestingly, the next best performing device for P3HT:PCBM consisted of the Ag nanoparticles sandwiched between a thick (~150 nm) and a thin (~70 nm) P3HT:PCBM layer. This device would typically suffer from high recombination due to its thickness, resulting in a decrease in the performance. It appears the increase in J_{SC} gave the device a slight advantage when compared to the other Ag nanoparticle devices. Also of interest are the other devices with Ag nanoparticles sandwiched in the active layer (Thick/Ag/Thick, etc). While the absorption was very high for these devices, the J_{SC} was very low. This is perhaps due the nanoparticles changing the morphology of the active layer and reducing pathways for charge collection. P3HT:PCBM and PTB7:PC71BM both have a very low limiting carrier diffusion length [9], which is why the optimum device thickness is typically <200 nm. All other devices showed relatively poor performance, with about half of the PCE of the control device and low FF indicating a high rate of recombination.



Figure 6.3: The cell parameters of devices with Ag nanoparticles embedded throughout the device, showing the a) V_{OC} , b) J_{SC} , c) FF and d) the PCE. Data for cells with P3HT and PTB7 both shown.

Although the absorption results looked promising, the JV analysis showed poor performance in the devices. This is likely due to charge recombination inside the devices, which will be discussed further. However, to decouple charge recombination with the photon collection, we examined the current of the devices under illumination at far reverse bias (-1 V). At -1 V, there is a large external field to aid in charge collection. The current density J at -1 V corresponds to J_L , from Equation 3.1. Investigating J_L will help minimize recombination and give us a better view into the characteristics of the devices. To further investigate how the Ag nanoparticles were aiding in free charge creation, we applied some filters to the incident solar spectrum. The behavior of these filters is visible in Figure 6.4. We utilized a red pass filter, a blue pass filter, and a band pass filter which only passed light around 450 nm.



Figure 6.4: The solar spectrum with the absorption of the devices used in this study and the transmission of the filters used

To best visualize the effect of the Ag nanoparticles on the absorption of the device, we measured J_L for the devices under 1 sun (AM 1.5G), a red filter, a blue filter, and a bandpass filter (all spectra can be found in Figure 6.4). To separate out overall increases in recombination with the effect of the Ag nanoparticles, we plotted the ratio of J_L for each filter to J_L under 1 sun. The J_L filter will be lower, with the 450 nm band pass filter having the lowest photocurrent J_L due to the small spectrum it allows. The actual values of these ratios are not important; what is important is how they compare to the control device.

Figure 6.5 shows these ratios plotted out for each device in the study. In general the devices are all fairly close to the control device. This indicates that while the devices with Ag nanoparticles had a higher absorption, the increase in absorption did not increase the carrier generation. This may be due to photons being absorbed by the Ag nanoparticles not transferring to the active layer. It may also be the case that the Ag nanoparticles are acting as aggressive trap sites, trapping charges even under a -1 V collection field. However, the thinnest device (Thin/Ag/Thin), with two ~70 nm layers of organic material with the nanoparticles sandwiched in-between, had a much higher J_L than any other device. This is likely due to the increased strength of the electric field since the two charged electrodes are closer together in this setup, which reduces the D term in Equation 3.5, effectively increasing the collection efficiency.


Figure 6.5: The ratios of J_L filtered to J_L 1 sun using a red pass, blue pass, and band pass filter

The ratios of J_L filtered to J_L under 1 sun indicate that the nanoparticles neither help nor harm carrier generation. Under a large collection field, the current seems to be constant for the devices. However, the devices with nanoparticles still suffer from poor performance relative to the control. To investigate the reason for this poor device performance with the inclusion of Ag nanoparticles, we did an analysis of the JV curves to extract additional parameters. Following the process of combining a simple lumped circuit analysis with a carrier collection model as outlined in Chapter 3 and performed by Hegedus et al.[21] in the past, and more recently by our group on OPV[24], [80], we were able to look deeper into the JV results.

The most notable results from this analysis were in the values linked to recombination. We were able to extract the dark saturation current from the JV curves by fitting our curves to the standard one-diode model. As in Chapter 3, we found the dark saturation current J_0 by fitting the JV curves. The value of J_0 gives the current flow at reverse bias due to minority carrier diffusion [44]. It is inversely proportional to device performance, most directly influencing Voc, , and was equal to $5.92 \times 10^{-5} \text{ mA/cm}^2$ in the control P3HT:PCBM device. We found J_0 to be higher for all devices with Ag in them. However, the lowest value of J_0 when Ag was present was for the device with Ag at the ITO interface (1.29 x 10^{-4} mA/cm^2). This suggests that the Ag (work function 4.26 for amorphous Ag) blocks electrons flowing in the reverse direction in the ITO case due to the large mismatch in work functions, causing a lower J_0 . However, the Ag acts in the same fashion when at the LiF/Al interface, hindering electron collection and causing higher recombination. We found the lowest (worst) value of J_0 for this arrangement (3.2 x 10^{-2} mA/cm^2).

The other interesting value we found was the diode ideality factor n, as seen in Figure 6.6. This value typically corresponds to the recombination in the bulk, with a value of 1 corresponding to minority carrier limited recombination, a value of 2 indicates recombination in both carriers, and higher values indicate geminate (exciton) recombination[41], [80]. The diode ideality factor shown in Figure 6.6 was found in the dark, indicating majority carrier recombination. All factors shown here are from JV curves in the dark, where majority carriers dominate any recombination effects. The control P3HT:PCBM device had an ideality factor of 1.21, showing mostly minority carrier recombination. When the Ag nanoparticles are sandwiched in the active layer, the n value and the recombination go up. As in the case of J_0 , we found the value of n was low when the Ag nanoparticles were close to the ITO electrode. However, when the Ag nanoparticles are located at the LiF/Al electrode, the value increases significantly. This indicates that the Ag is both creating recombination sites and blocking carriers at the LiF/Al electrode, showing that the nanoparticles must be embedded in the polymer matrix to prevent defect sites at their surface. This may be a result of the nanoparticles not having any surfactant, or it may be a property of nanoparticles in OPV in general.



Figure 6.6: The diode ideality factor (n) for each device

To investigate minority carrier effects (electrons), we looked at the device characteristics in the light. Under illumination, minority carriers are freed and populate the device. To investigate recombination of the minority carriers, we looked at the carrier collection efficiency, as discussed in Chapter 3. Figure 6.7 shows the collection length of the minority carriers, which is a measure of their recombination. As the collection length decreases, the recombination rate increases. This is the collection length under illumination, but it can be seen that it closely matches the trend in Figure 6.6. This indicates that the trap centers affect both electrons and holes in a similar manner.



Figure 6.7: Limiting carrier (electron) collection length under illumination

Using this data, we can see that the ideal location for these nanoparticles is in the active layer, where they can aid in absorption. In the active layer, the nanoparticles have the lowest recombination of any other location, in some cases actually indicating very similar recombination to devices without Ag (n=1.18 for devices with two 70nm layers of P3HT:PCBM, compared to n=1.21 for the standard device). Devices with the best dark saturation current J_0 also had the Ag nanoparticles in the bulk.

6.4 Conclusions

We doped P3HT:PCBM and PTB7:PC71BM solar cells with thin layers of surfactant free Ag nanoparticles using thermal evaporation. We found thermal evaporation to occur with Volmer-Weber growth, creating uniform layers of well dispersed nanoparticles for both Ag and Au, but only carried out this investigation using Ag nanoparticles. Ag nanoparticles had a large absorption peak around 470 nm due to surface plasmon resonance, which they still exhibited when embedded in an OPV device. These nanoparticles helped to increase the absorption of the solar cells, but harmed the recombination. We found the recombination was lowest when the nanoparticles were sandwiched between layers of P3HT:PCBM. The worst recombination occurred when the Ag nanoparticles were located against the LiF/A1 electrode, due to the work function of Ag not lining up well with LiF.

This study was ended due to time constraints, but further work addressing the mechanism of recombination is needed. It appears that the surfactants used in chemical nanoparticle synthesis aid in reducing recombination at the nanoparticle/polymer interface and may help transfer the SPR photon into the active layer for conversion to an exciton. To study this mechanism a series of surfactants

could be applied to the nanoparticles. Their effect on the recombination and J_{light} would reveal their role in charge dynamics

Chapter 7

CONCLUSIONS

Each chapter has its own conclusions on the individual aspect of OPV investigated in the chapter. I will summarize these chapters and their conclusions, and finish with a word on the state of OPV and the future. I will briefly discuss future research possibilities and opportunities for new students looking to join the field.

We began this dissertation with a discussion of solar energy and OPV. I addressed OPV's problems and some solutions to them. While the OPV research field is still a sector of intense research, commercial opportunities have all but disappeared. For OPV to succeed and become a meaningful player in the PV field, its major faults must be addressed: low stability, high costs due to ITO, and low exciton diffusion lengths. To address these issues, this dissertation covered several characterization and fabrication techniques.

To address the problematic stability issues, the field will likely need new materials fabricated by chemists. PV researchers can use these materials to fabricate devices, but in order to better share device properties between research groups, a more robust JV characterization methodology is needed. Chapter 3 presented a different analysis technique and applied this to P3HT:PCBM devices. This technique could be used in future material systems.

To address the issue of high costs due to ITO, Chapter 4 investigated ITO free transparent contacts. While these contacts still utilize sputtering, they use only tungsten and silver, both common metals available at a relatively low cost. They are

also deposited at a low temperature, reducing manufacturing costs and allowing the use of flexible substrates. To investigate these Ag/WOx electrodes, we used some of the techniques presented in Chapter 3. These techniques, in addition to low temp JV measurements, revealed a barrier to electron flow. By fabricating devices on the WOx electrodes using organic materials with two different HOMO levels, we found the barrier height was directly proportional to the difference between the WOx work function and the electron donor HOMO level. This work presented the possibility of using WOx with several different electron donor materials thanks to its tunable work function.

To investigate low exciton diffusion length this thesis took two different approaches. In Chapter 5, to address exciton diffusion length, we imaged how far excitons need to move in order to be collected. Using EFTEM on cross sections of solar cells, we observed the phase separation between P3HT and PCBM. By doing some modeling on these images using Matlab, we found the size of these phases. Annealing was shown to change the phase size, and thus change the distance excitons need to diffuse. This distance was used to estimate J_{SC} , which proved to be similar to experimental results. While this work did not address how to change exciton diffusion length, it did provide a method to visualize exciton diffusion and how it affects the current from a device.

The other method we took to address low exciton diffusion length was to create thinner devices. By imbedding Ag nanoparticles to increase the absorption, we hoped to make thinner devices. Since the exciton diffusion length is ~10 nm, making devices closer to this value will allow a larger percentage of excitons to be collected. Unfortunately, the Ag nanoparticles were found to act as recombination centers,

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increasing recombination and harming the device's overall performance. The techniques outlined in Chapter 3 provided a means to analyze how the Ag nanoparticles harmed the device performance and gave quantitative measures of how the devices react to the Ag nanoparticles.

In conclusion, new materials are required to make OPV a commercially competitive field. This dissertation provided several means to analyze these new materials. From quantifying JV curves to find values indicating recombination to quantifying TEM images to find the J_{SC} , the methods outlined here could prove useful to future researchers in the OPV field.

7.1 Future Work

At the end of Chapter 6 we mentioned the lack of a surfactant possibly harming the Ag nanoparticles. This work needs to be pursued farther. Many devices and papers have been published on the use of Ag and Au nanoparticles to increase the absorption in devices. Most papers show an improvement in the devices, but some show negative effects (such as our study). It is possible that the surfactant choice is a large cause of these changes. Since Ag nanoparticles grown via thermal evaporation require no surfactants to grow, it frees us to use any surfactant to coat the nanoparticles after growth. This allows a study to separate the nanoparticles from the surfactant, which would prove interesting. The surfactant likely moderates the charge transfer from the nanoparticles to the active layer and may be necessary to prevent recombination and pass photons from the nanoparticles to the OPV material.

While research into the reason nanoparticles create recombination in a device would be interesting, there are many other research possibilities in OPV. The OPV field is still a hotbed of research, though it has recently changed. Some researchers are

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still working on developing new OPV materials or fabricating devices in different ways, but the majority of research has shifted to a new class of OPV material: perovskites. Pb halide perovskite solar cells have proven remarkably efficient in a very short time. This efficiency is due to their ideal materials characteristics for solar cells, including intrinsically benign grain boundaries and very high optical absorption coefficients. Unfortunately, Pb halide perovskites are soluble in water and contain Pb, making the path to commercialization difficult. In order to increase the stability and remove the lead, the beneficial properties of Pb halide perovskites need to be reproduced in a more stable material system. Sn halide perovskites are the obvious choice for a first attempt at reproducing the solar cell properties of Pb halides. Some work has been done, finding Sn halides to not produce as high efficiency solar cells as Pb halides. The Pb halide perovskite literature makes it clear that minor differences in processing can produce major differences in film morphology and solar performance. These slight variations need to be explored for Sn halide perovskites to determine if the observed problems are due to processing issues or intrinsic to Sn. This will help identify a path forward to a new material system for stable. Pb free highly efficient perovskite solar cells.

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Appendix A

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