

Bulk Heterojunctions in Photovoltaic Devices

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To my wife, who has faithfully supported me through this endeavor, who's contribution to this accomplishment matches, if not exceeds, my own, who has endured and patiently listened to each practice presentation, and who continually makes my lab mates jealous with the home-cooked meals I eat in front of them.

Abstract

Current solar cells, on the market today, have little room for improved efficiency or cost reduction. Part of this is due to the costly manufacture of high purity silicon and the current fabrication methods for solar cells. Solution processable solar cells would mark a great stride forward to cost reduction. If such cells can be demonstrated to be efficient enough and stable enough it would be a turning point in history. However, solution processable devices still need much work before they can compete in the market. This text addresses characterization problems in the TEM, covers a study dealing with optimization strategies for organic bulk heterojunction devices, and introduces a strikingly high efficiency perovskite device that has a bulk heterojunction like structure.

This text is arranged in four major portions; chapters 1 and 2, chapters 3 and 4, chapter 5, and chapter 6. The first two chapters give an introduction to some of the materials and microscopy techniques referred to throughout the text. Chapters 3 and 4 introduce a new sample thickness or density measurement technique (chapter 3), and illustrate how such a technique can be quite useful in studying organic photovoltaic materials by facilitating quantitative material fraction measurements (chapter 4). Next, chapter 5 details a study of organic photovoltaic systems highlighting optimization strategies. Specifically, chapter 5 describes the effect of various solvents and solvent annealing times on the P3HT/PCBM system. Finally, chapter 7 introduces a state-of-the-art, high efficiency perovskite device that

exhibits large, single crystal domains as well as increased hole transport contact area through a bulk heterojunction like structure.

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Chapter 1

Background

1.1 Abstract

Organic photovoltaic (OPV) materials are a promising candidate for future clean, renewable energy generation [Dang et al. \(2011\)](#); [Chen et al. \(2012a\)](#); [Darling and You \(2013\)](#). The technology is yet in its nascent stages and requires deeper understanding of material properties and interactions before devices of sufficient efficiency can be fabricated at low cost.

One of the challenges of characterizing OPV device structures is that the feature length scales are on the order of a few tens of nanometers (below the wavelength of light) [Chen et al. \(2012a\)](#). This prevents their examination with optical microscopy. Transmission electron microscopy (TEM) solves the problem of spatial resolution but presents a new one. Contrast is quite low in the TEM due to the similarity between the materials. They are both carbon-based polymers with similar densities. In order to distinguish the materials from each other contrast must be enhanced.

There are two popular techniques for overcoming this problem in the TEM. The first is to defocus the beam which induces wide oscillations in the contrast transfer function [Chen et al. \(2012a\)](#); [DeLongchamp et al. \(2012\)](#). This, in turn, enhances density contrast but introduces aberrations in the image which raises concerns about

the interpretation and reliability of the images. The second, perhaps more reliable method, is to introduce an energy window in the energy dispersion plane and center it on a feature of interest in the electron energy loss (EEL) spectrum characteristic of one of the phases [Nicholson and Castro \(2010\)](#); [Herzing et al. \(2010\)](#); [Drummy et al. \(2011\)](#); [Pfanmöller et al. \(2011\)](#); [Schindler et al. \(2012\)](#); [Kozub et al. \(2011\)](#); [Huang et al. \(2014\)](#); [Brady et al. \(2011\)](#). These energy-filtered TEM (EFTEM) images will show intensity variations corresponding to material phase. EFTEM images are visually appealing yet only qualitative because they do not give a measure of the purity of each phase (i.e. phase ratio). A third, less common, technique involves the combination of one of the previous two with tomography. This technique produces 3D information about sample morphology but relies on one of the previously outlined contrast enhancement methods and so is subject to the same pitfalls.

It is important that researchers have a variety of characterization tools to make independent measurements of the same quantities. This establishes the validity and accuracy of experimental results. OPV characterization in the TEM, therefore, needs new techniques for independent verification and quantification of established techniques. Herein we propose several new characterization techniques for use in a transmission electron microscope, namely quantitative phase ratio mapping, quantitative elemental areal density mapping, average thickness measurements and quantitative plasmon peak position mapping.

1.2 OPV materials

1.2.1 A brief history

The study of organic photoactive materials dates back to the beginning of the 20th century [Spanggaard and Krebs \(2004\)](#) but efficiencies remained low and solid state devices outperformed the organic devices right from their initial discovery at Bell Labs in 1954 [Chapin et al. \(1954\)](#). It wasn't until 1986 that organic devices made a

huge break-through. Tang demonstrated that a donor and acceptor polymer could induce excitation separation at their interface, thereby increasing charge collection [Tang \(1986\)](#). Tang’s cell finally broke the 1% mark for organic devices. In the mid 1990s the 2% mark was achieved [Nelson \(2002\)](#). More recently, single junction cells in the range of 8%-9% have been demonstrated [You et al. \(2013a\)](#) and in 2013 Jingbi You demonstrated a tandem cell with efficiencies exceeding 10% [You et al. \(2013b\)](#).

1.2.2 The advantages of OPV materials

While these results are very impressive, OPV devices still exhibit much lower conversion efficiencies than their solid state counterparts and even solid state devices have failed to capture more than half a percent of the energy generation market. In order to reach grid parity, the cost must decrease and the efficiencies must increase. Silicon devices, which represent 99% of the installed PV, have already been optimized and are approaching the thermodynamic efficiency limit ($\sim 30\%$) [Darling \(2009\)](#). It is also unlikely that the cost of manufacturing silicon will dramatically decrease. Organic devices, on the other hand, have significant room for improvement and have the potential for radically reduced manufacturing costs through the use of solution processing and roll-to-roll techniques [Kim et al. \(2007\)](#).

In addition to low cost manufacturing OPV materials have several other unique benefits. Because they are polymers, they are intrinsically lighter weight than solid state materials, are flexible, can be dyed any color for applications where aesthetics are significant, and are highly absorbing in the right portions of the solar spectrum. This makes OPV materials exciting potential alternatives to silicon based solar cells.

1.2.3 Not Just OPV Materials

While the thrust of this paper will be directed at organic photovoltaic materials, the same or similar materials are also being investigated for various other applications.

The Organic and Printed Electronics Association (OE-A) has organized the organic materials applications into five key areas of promise;

- Organic LED (OLED) lighting,
- Printable organic photovoltaics (OPV),
- Flexible displays,
- Electronics and components, (printed memory and batteries, active components and passive components), and
- Integrated smart systems (ISS, including smart objects (also RFID), sensors and smart textiles).

One of the major challenges OE-A have identified that must be overcome to further the technological development in these areas is characterization of the materials. Characterization solutions that are implemented for one of these areas will have a direct impact on the other areas as well.

1.3 Device Operation

In this study we will focus on bulk heterojunction materials, specifically π conjugated polymer chains that form an electron donor and light absorbing matrix such as poly(3-hexylthiophene) (P3HT), and electron accepting materials such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). Figure 1.1 shows the chemical structure of these two molecules.

In a working device, the acceptor molecule absorbs a photon and becomes excited. The excited state is called an exciton and can be thought of as a loosely bound electron-hole pair (EHP). An exciton can easily move along the carbon chain by transferring between the conjugated π orbitals Hoppea and Sariciftci (2004). The diffusion distance of an exciton is typically on the order of 10 nm Nicholson and Castro (2010). If the exciton does not dissociate into an electron-hole pair (EHP) it will recombine and the possibility for charge extraction will be lost.

When brought together in a working device, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the donor material are both higher than the HOMO and LUMO of the acceptor material [Spanggaard and Krebs \(2004\)](#); [Hoppea and Sariciftci \(2004\)](#). This encourages electrons to transfer from the donor to the acceptor molecule and provides the added energy needed to dissociate the exciton, usually around 0.1 to 1 eV [Hoppea and Sariciftci \(2004\)](#). Once separated, the electrons and holes can travel through the acceptor and donor molecules to the contacts and be extracted as useful current.

Two important and conflicting pathways should be noted. In order to encourage exciton dissociation, the path length from any point within the donor material to the acceptor material should be smaller than the exciton diffusion distance. This promotes exciton dissociation at the material interface and is achieved by having an interpenetrating network of donor and acceptor domains. Smaller domain sizes produce better charge separation. In order for separated charges to be extracted from the matrix, well-defined, continuous pathways to the electrodes for electrical conduction must be present. This is accomplished by having large interconnected domains. These two conflicting requirements present a design challenge that has yet to be optimized. Characterizing the junction morphology is clearly central to this task.

1.4 Current state-of-the-art OPV characterization techniques in the TEM

The transmission electron microscope (TEM) is an ideal tool for imaging OPV materials. Its resolution capabilities are adequate to resolve the nanometer sized phase separation within the active materials. The entire active region is often less than 100 nm thick and a fully functional device may be imaged. Because the TEM beam penetrates through the sample, information about the entire volume of the

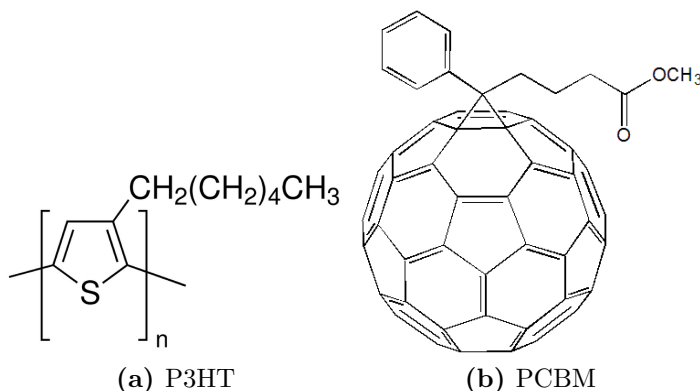


Figure 1.1: Chemical structures of P3HT and PCBM. PCBM acts as the electron acceptor in the junction. P3HT acts as the primary light absorber and electron donor. Excitons, generated by the incident light, travel along the π conjugated polymer backbone to reach the PCBM molecule. At the interface the exciton can dissociate into an oppositely flowing electron and hole.

sample is present rather than just surface information. Other techniques, such as atomic force microscopy (AFM), are limited to surface studies exclusively. Scanning electron microscopy (SEM) is quick and easy but lacks the resolution to clearly resolve nanometer sized phase changes. In this section we seek to highlight the main techniques used in the TEM for studying OPV devices.

1.4.1 Energy filtered TEM (EFTEM)

The major challenge to be overcome when studying OPV materials in the TEM is contrast. Both materials are carbon-based polymers of similar densities and so exhibit very similar contrast in the TEM. Two distinct, adjacent phases will look identical. The challenge is to produce contrast between them. One way this is done is by using an energy filter.

Energy filtered TEM (EFTEM) takes advantage of feature changes in the electron energy loss (EEL) spectrum to produce contrast [Nicholson and Castro \(2010\)](#); [Herzing et al. \(2010\)](#); [Drummy et al. \(2011\)](#); [Pfannmöller et al. \(2011\)](#); [Schindler et al. \(2012\)](#); [Kozub et al. \(2011\)](#); [Chen et al. \(2012a\)](#). Figure 1.2 shows an example spectrum

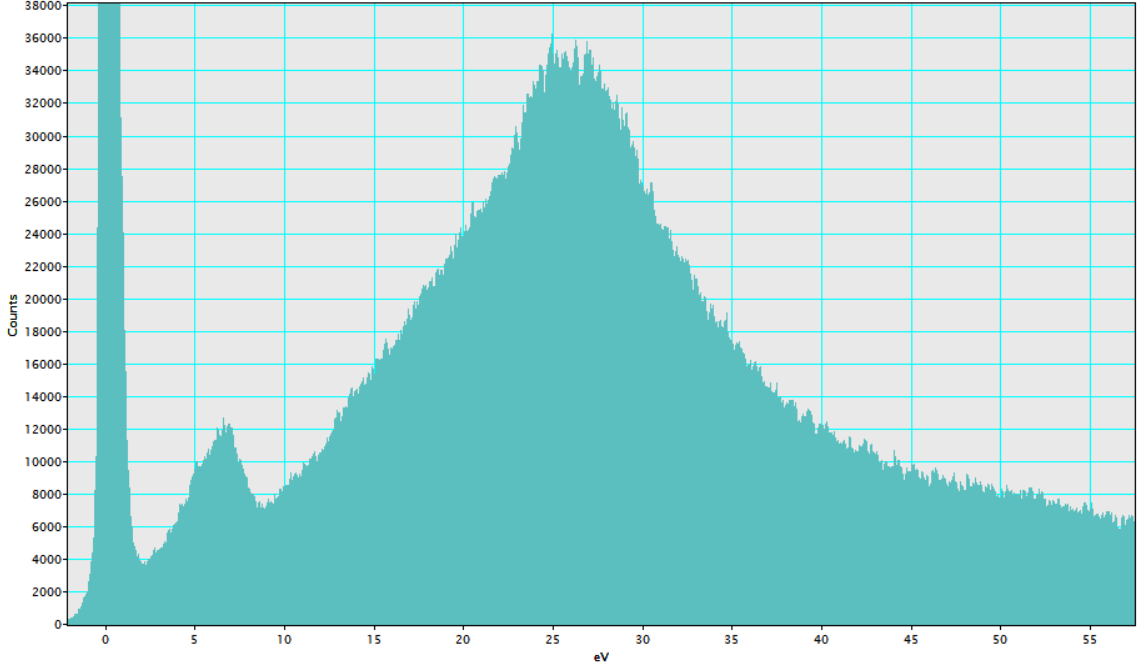


Figure 1.2: Example low-loss EEL spectrum of a pure PCBM film showing a bulk and surface plasmon signal.

taken from a pure PCBM film. The large peak at 26 eV is the bulk plasmon peak. This peak is produced as the incident electrons excite valence oscillations within the sample. The energy at which this peak occurs is dependent on how strongly the electrons are bound. The plasmon peak for P3HT is slightly lower, at about 21 eV, shown in figure 1.3.

In order to filter the images, a slit is introduced into the energy dispersive plane of the TEM and used to block all electrons that fall outside of a specific energy range. Using a slit width of 8 eV centered at 19 eV will preferentially allow electrons that have interacted with P3HT form the image [Drummy et al. \(2011\)](#). This makes the P3HT rich regions appear brighter than the rest. Centering the energy window at 30 eV enhances the intensity of PCBM. The composite image formed by superimposing these two signals produces excellent contrast as can be seen in figure 1.4. Additionally, it is advisable to take a zero filtered image, which highlights thickness variations, to demonstrate that the signals generated by the other images are not correlated with

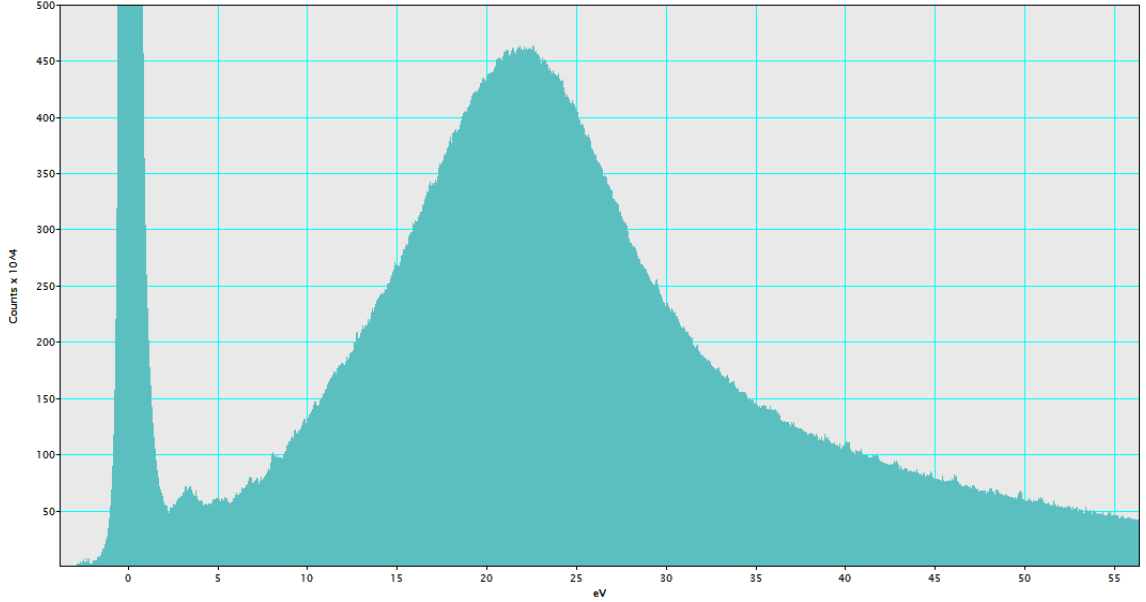


Figure 1.3: Example low-loss EEL spectrum of a pure P3HT film. The bulk plasmon peak is shifted relative to that of PCBM (figure 1.2).

thickness (i.e. that they are indeed due to material composition). For additional discourse see for example Pfannmüller et al. (2011); Drummy et al. (2011); Herzing et al. (2010); Chen et al. (2012a).

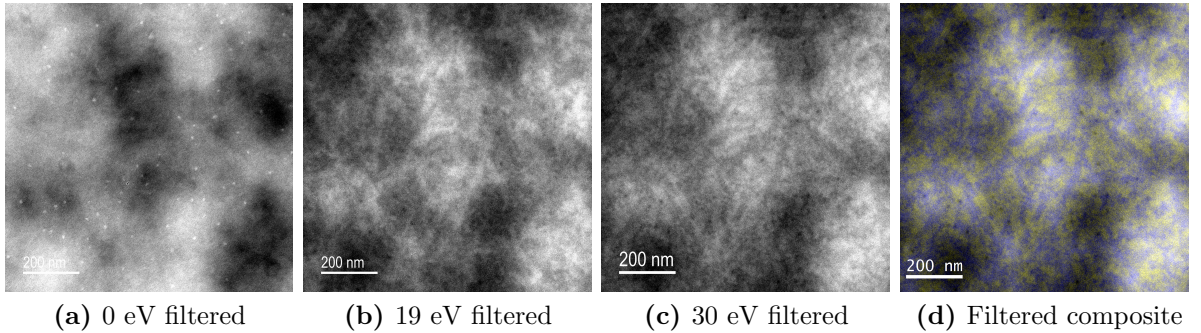


Figure 1.4: Example EFTEM data. a) shows the zero filtered image capturing sample thickness variations, b) shows intensities correlated with P3HT concentration, c) shows intensities correlated with PCBM concentrations, and d) shows the artificially colored composite image where blue corresponds to P3HT from b) and yellow corresponds to PCBM from c).

While this method produces visually stunning results it remains completely qualitative. We can see clear phase separation and can compare images of different

samples side-by-side but it tells us little about the purity of each phase or the sharpness of the transition from one phase to the other. Also, any phase separation that occurs perpendicular to the beam will carry signals from both P3HT and PCBM obscuring the interpretation. Nevertheless, this technique is widely used to demonstrate phase separation and give a rough domain size estimate.

1.4.2 EFTEM tomography

An extension of EFTEM imaging is the combination with tomography. Tomography is a technique whereby a series of images are acquired at various angles. A computer program tracks feature positions in the sample and then constructs a model of intensity positions in 3D [Midgley and Weyland \(2003\)](#); [Bavel et al. \(2009a\)](#). This technique allows a much more detailed view of the internal structure of a bulk heterojunction than a simple projection can give. Specifically, a projection fails to distinguish between overlapping domains and a blended phase. A major drawback to EFTEM tomography is that it requires many exposures to the beam and is technically difficult.

1.5 Why new techniques are needed

The major drawback in using a TEM for OPV characterization is that BHJ materials are very similar; they are both formed of carbon chains of similar density. This presents a problem when imaging in the TEM. TEM images are grayscale so all the information contained therein is due to contrast. There are a variety of contrast sources, such as material density fluctuations, thickness changes, strain fields, diffraction, defects, and Z number, but most of these sources fail to differentiate between BHJ materials. The notable exception is density fluctuations. Typical imaging cannot detect the density fluctuations between OPV materials, but defocussing the electron beam causes the contrast transfer function to oscillate widely,

which, in turn, causes slight density fluctuations to be greatly enhanced [Handlin and Thomas \(1983, 1984\)](#); [Moon et al. \(2009\)](#). While this method has been used successfully, proper interpretation of the images remains unclear since the image contrast will change with defocus value and it is not obvious what defocus value produces contrast representative of phase location. Furthermore, defocussing the electron beam introduces aberrations and delocalization of the beam which decreases image quality and makes measurement values questionable [DeLongchamp et al. \(2012\)](#). Such imaging certainly can be used effectively, but enhanced techniques are clearly needed.

EFTEM imaging does not suffer from defocussing the electron beam and has become a routine method for obtaining a qualitative view of the microscopic structure within a BHJ [Pffannmüller et al. \(2011\)](#); [Chen et al. \(2015\)](#); [Schindler et al. \(2012\)](#); [Herzing et al. \(2013\)](#); [Nicholson and Castro \(2010\)](#); [Drummy et al. \(2011\)](#). This technique, described in more detail in section 1.4.1, enhances contrast between donor and acceptor phases based on their differing plasmonic responses. EFTEM images are visually appealing but still lack quantitative information. Pure domains that overlap cannot be distinguished from a mixed phase so that, even though a clear general picture of the junction may be produced, precise interpretation and quantitative measurements are elusive.

EFTEM tomography solves the problem of overlapping domain ambiguity found in regular EFTEM. This technique produces a 3D reconstruction of the material which allows a surface rendering of the domain microstructure. The stunning results demonstrated to date (see, for example [Bavel et al. \(2009a\)](#)) give a much clearer picture of the structure in a BHJ. This enables a more quantitative analysis of concentration gradients, interconnectivity, and domain structure with nanometer resolution. The drawbacks are that this technique is challenging, time consuming, and requires many exposures to the electron beam. The information gleaned also does not provide a quantitative measure of the purity of the phases.

Microscopic techniques must be developed to answer questions about, for example, phase purity, crystallinity, crystallographic orientation, HOMO-LUMO gap, electronic properties of the material interfaces, and optical responses. These properties must be analyzed on a nanometer length scale within a working device to properly understand the principles of operation and material considerations that will allow future devices to be purposefully designed for optimum efficiency, stability, and cost.

Chapter 2

Methods

2.1 Energy filtered TEM

Energy filtered TEM (EFTEM) was used to provide a baseline comparison for the rest of the studies. All samples were imaged with a slit width of 8 eV centered at 0, 19 and 30 eV as discussed in section 1.4.1. This allows a direct comparison between the new techniques (discussed later) and current state-of-the-art investigation practices.

2.2 Focused Ion Beam (FIB) Sample Preparation

This section was adapted from a portion of the author’s contribution to *Organic Solar Cells: Materials, Devices, Interfaces, and Modeling* in chapter 9 Nanophase Separation in Organic Solar Cells* [Chen et al. \(2015\)](#).

A well-established technique for preparing cross-section TEM/STEM samples employs the use of a focused ion beam (FIB). The instrument used in these studies was a Zeiss Auriga dual beam FIB SEM which is equipped with a scanned electron

*Wei Chen, Feng Liu, Ondrej E. Dyck, Gerd Duscher, Huipeng Chen, Mark D. Dadmun, Wei You, Qiquan Qiao, Zhengguo Xiao, Jinsong Huang, Wei Ma, Harald Ade, Jong K. Keum, Adam J. Rondinone, Karren L. More, and Jihua Chen

probe as well as the ion beam which allows a dual function as a scanning electron microscope (SEM). The FIB source was a Ga+.

Using a FIB for OPV sample preparation has several advantages over other techniques. The FIB technique allows precise selection of the location for sample extraction on the bulk sample. It also produces a very uniform thickness sample, which is important for proper interpretation of TEM/STEM generated data, particularly so with low contrast materials where thickness induced contrast can distort the images. Soft materials are often prepared using an ultramicrotome to slice thin sections from a bulk sample. When used for OPV applications the material must be transferred from the original substrate, often silicon or glass, to a softer material to facilitate slicing. This can contaminate the sample. Also the slicing procedure will shear and possibly tear the sample which can induce structural changes from the pristine film [White et al. \(2001\)](#); [Bassim et al. \(2012\)](#). For these reasons, the FIB technique was used for preparing cross-section samples.

The main caveat with the FIB technique is that milling the material necessarily destroys it. It is important to take measures to limit beam damage to the final sample brought on by heating, knock-on damage, and radiolysis [Bassim et al. \(2012\)](#). Precautions were taken to address this issue. First, the area of interest was covered through deposition of a protective platinum layer before milling. This limits direct exposure to the beam. To address sample heating during the final thinning, a frame of native material was left around the thinned area to reinforce the mechanical strength of the sample and provide a heat sink. Additionally, beam current and energy were reduced to 10 kV and 20 pA during final thinning. The ion beam heating is given by, [Bassim et al. \(2012\)](#)

$$\Delta T = \frac{JV}{2k}r_0 \quad (2.1)$$

where ΔT is the change in temperature, J is the beam current density, V is the accelerating voltage, k is the thermal conductivity, and r_0 is the beam radius. The

current density can be found by $J = \frac{I}{\pi r_0^2}$ where I is the beam current. Therefore, a final polish with beam currents ≤ 50 pA and accelerating voltages ≤ 10 kV should ensure limited beam induced heating.

2.3 Electron Energy Loss Spectroscopy (EELS)

2.3.1 Introduction to EELS

The electron energy loss (EEL) spectrum is produced by dispersing the electron beam according to energy after interaction with the sample. The primary feature in the spectrum is the zero loss peak (ZLP). These electrons have passed through the sample without depositing (losing) any energy. The full width half maximum (FWHM) of the ZLP represents the energy resolution of the spectrum.

After the ZLP, the next portion of the spectrum is termed the low loss region. It is loosely defined as extending from the ZLP to around 60-100 eV. Signals from this region include bulk and surface plasmon losses, band gap onsets, and interband transitions. Optical properties of the material can be gleaned from this portion of the spectrum as well.

The core loss region of the spectrum follows the low loss region. In this portion of the spectrum we find characteristic elemental edges that allow determination of the chemical composition of the sample. Information regarding bonding and electronic structure can be obtained from this region.

2.3.2 Low loss electron energy loss spectroscopy

In the low loss region we are particularly interested in the bulk plasmon position. As mentioned in section 1.4.1 the bulk plasmon occurs at a characteristic energy for different OPV materials (figures 1.1b and 1.1a). In order to quantify the plasmon peak positions Gaussian peaks were fit to the data. A multiplication of two lorentzian functions was used to approximate the ZLP and a summation of the rest of the

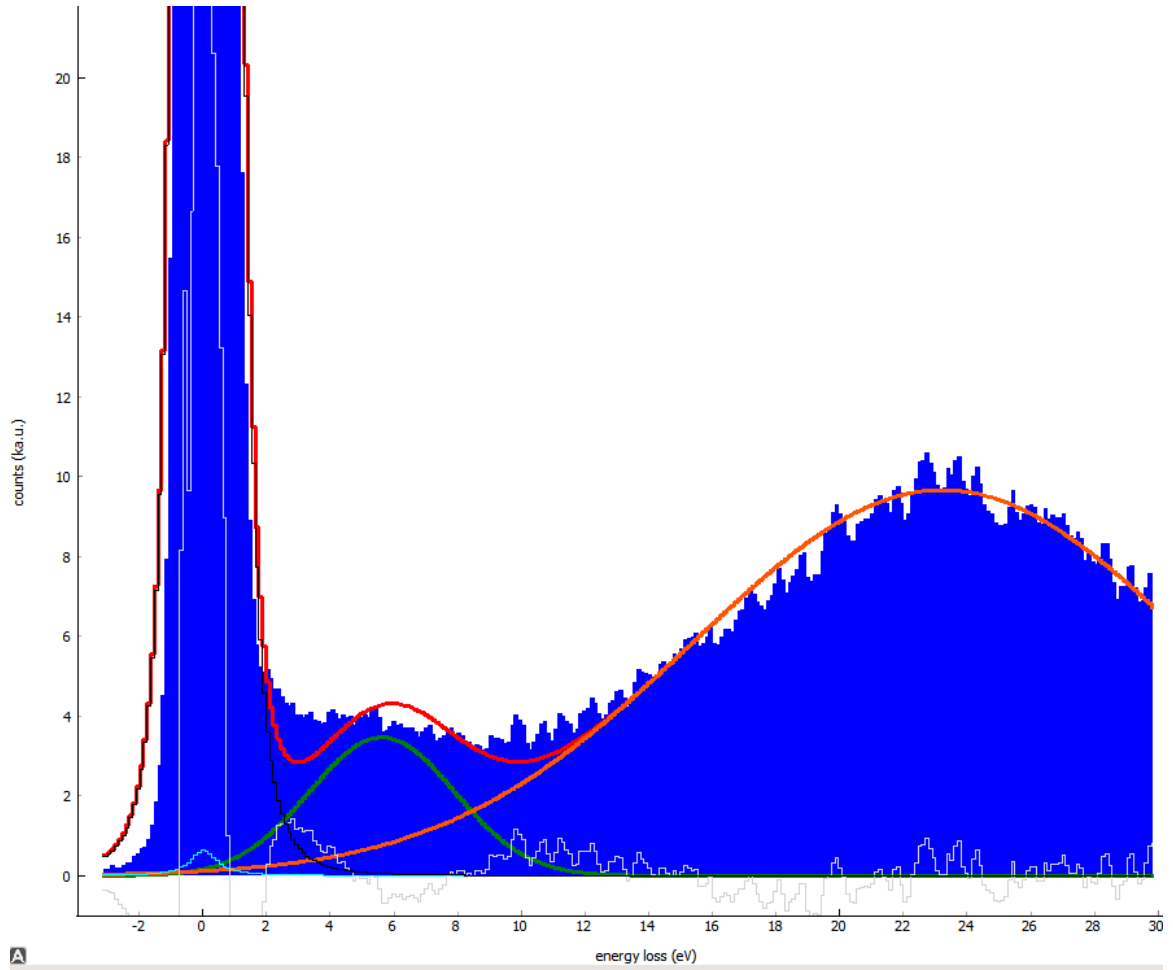


Figure 2.1: Example fit of two Gaussian peaks into a low loss spectrum. The model (red) fits poorly below 15 eV but accurately captures the bulk plasmon peak which is represented by the orange curve.

Gaussian peaks to produce noise free model of the low loss spectra. When the model satisfactorily fits the data, the peak positions are noted. Figure 2.1 shows this process being done. The orange peak accurately captures the bulk plasmon signal. Moreover, once a model is properly fit to a spectrum, an entire spectrum image may be fit starting from the initial peak parameters.

2.3.3 Core loss electron energy loss spectroscopy

The core loss EELS signal, beyond about 60 eV, contains valuable information from the sample. This is where we find the elemental edges that give a distinct fingerprint for each element. The structure and intensity of the edges give information about bonding, electronic density of states, and atomic concentration (among other things) [Egerton \(2011a\)](#). In this text we are primarily concerned with atomic concentration. In the following chapter we detail a new method for obtaining sample thickness or density from the atomic concentration.

Chapter 3

Thickness or density measurements with EELS*

3.1 Abstract

We demonstrate the ability to measure the thickness or density of a sample on a nanometer length scale. Absolute sample thickness measurements in a TEM are often inaccurate or impossible on some specimens due to the requisite knowledge of the electron mean free path. For the technique introduced here, the thickness may be measured if the density of the material is known. Since density is much more readily measured or calculated from crystal structure this method facilitates a thickness measurement in cases where other methods may fail. Alternatively, if the thickness can be reliably measured through some other technique, the technique described herein may provide a density measurement instead.

This method can be used to map, for example, the density of dopant materials or ion implantation gradients, the thickness of a single component material in a composite, or used to verify the number of layers in 2D materials.

*O. Dyck, M. Tian, G. Duscher, Manuscript in progress

Core-loss electron energy loss spectra (EELS) are fit with a quantitative model to extract atomic areal density. Areal density is the material volume density multiplied by the thickness of the sample. Knowledge of one of the parameters (volume density or sample thickness) allows a measurement of the other. The technique is demonstrated on a single layer tungsten sulfide sheet where the thickness (one layer) is known, as well as the structure of the material, from which the atomic density can be easily calculated. Further demonstration on a spherical nanoparticle is possible assuming the diameter is equal to the thickness. Finally, the density of argon gas in spherical cavities is measured, allowing a temperature vs. pressure curve to be obtained, illustrating the unique capability of this technique.

From these results we also conclude that a carefully modeled EELS core-loss edge gives a partial scattering cross-section with errors less than 10% and in well-behaved cases less than 5%.

3.2 Introduction

Obtaining a reliable sample thickness measurement in the transmission electron microscope (TEM) is not a trivial task. The log ratio method [Malis et al. \(1988a\)](#) is one option that relies on low-loss electron energy-loss spectra (EELS) but requires knowledge of the electron mean free path (λ) for which reliable data is absent for most materials. There are estimation schemes for λ but such approximations can themselves be problematic. For further discussion on this method see Egerton (2011) [Egerton \(2011a\)](#). Another, more reliable [Allen and Hall \(1982\)](#), method for determining sample thickness in the TEM is by using the thickness fringes apparent in a convergent beam electron diffraction (CBED) pattern [Kelly et al. \(1975\)](#); [Allen \(1981\)](#). This technique involves tilting the specimen into two beam condition, measuring the distance between the oscillating thickness fringe intensities, and fitting them to a model. This technique works well for thicker samples but requires that the material be crystalline since it relies on the diffraction pattern. For very thin, or

amorphous samples, this technique cannot be used. For a more detailed discussion see Carter and Williams (2009) [Carter and Williams \(2009\)](#).

Likewise, reliable measurements for the density of nanoscale materials (thin films, nanowires, and nanoparticles) is also absent for most materials. There may also be cases where the material being studied varies in density on a short length scale which cannot be measured through traditional bulk density measurements. In these situations a method is needed for measuring density at very precise positions on the sample.

The object of this paper is to present a technique for measuring the thickness or density of a specimen using core-loss electron energy-loss spectroscopy (EELS). Measuring the thickness requires that one know the density; measuring the density requires that one know the thickness.

3.3 Equipment

The microscope used in these experiments was a Zeiss Libra 200 MC transmission electron microscope (TEM) equipped with a monochromator and Schottky field emission gun. The TEM was operated at an accelerating voltage of 200 kV. It is worth noting that, although this microscope is equipped with a high energy resolution monochromated spectrometer, high energy resolution is not necessary for the techniques introduced here. It is only necessary that the elemental edges are clearly resolved.

3.4 Procedure

We will address the necessary components in three steps: 1) converting spectrometer “counts” to scattering probability, 2) fitting the spectra with a hydrogenic model, and 3) relation of areal density to volume density and sample thickness.

3.4.1 Converting spectrometer “counts” to scattering probability

The first requirement for this technique is that the spectrometer “counts” be converted to scattering probability. This requires that the spectrometer CCD be calibrated such that the intensity value (counts) can be interpreted as number of electrons. To measure this conversion factor we illuminated the CCD with the beam throughout a range of currents and directly compared the CCD count output to the number of electrons incident upon it. With the count-to-electron conversion factor, each pixel in a spectrum was converted to current by dividing the charge of the collected electrons in each pixel by the exposure time. A beam current measurement was acquired just prior to acquiring the spectrum (i.e. under the same operating conditions) and the ratio of incident beam current to scattered beam current gives scattering probability:

$$p = \frac{I}{I_0} \quad (3.1)$$

Here, I_0 is the incident beam current, I is the beam current in a pixel from the spectrum, and p is the resulting scattering probability.

A calibrated CCD is not strictly necessary if the beam current, I_0 , is measured in counts on the spectrometer so that it is in the same units as I . This can be easily done by positioning the beam in vacuum and taking an image of the defocused zero-loss peak with the spectrometer CCD.

CCD Calibration

This section details our calibration experiments. While the Zeiss Libra 200MC is equipped with a faraday cup built into the phosphor screen (which is connected to a picoampere meter), the lowest measurable current is around 15 pA. Many experiments have beam currents far below this value. In order to measure the beam current in these situations we chose to use the CCD camera. The CCD is coupled to a scintillator

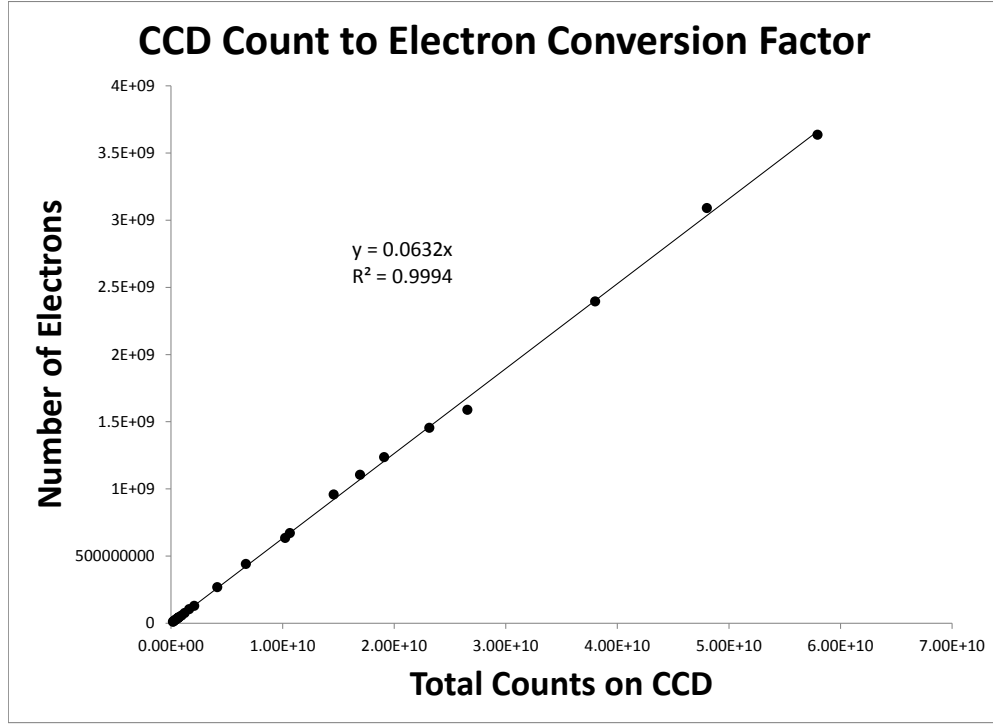


Figure 3.1: Relationship between beam current (number of electrons) to the measured counts on the CCD. A conversion factor of 0.0632 electrons per count is obtained.

and is quite sensitive to very low doses of the beam. We used the picoampere meter to determine the beam current at various intensities and used the CCD to image the beam under similar conditions. The data gathered indicates a linear relationship between beam current and counts on the CCD. This is not surprising since CCDs tend to be nicely linear. In fact, any deviation from linearity in the measurements is likely due to the picoampere meter fluctuations rather than CCD nonlinearities. Figure 3.1 shows the data acquired with a linear fit to the data. This gives a conversion factor of 0.0632 electrons per count with an R^2 value of 0.9994.

With this information we can easily measure the number of electrons involved in any experiment.

3.4.2 Fitting the spectra with a hydrogenic model

First, the background of the edge must be modeled and subtracted to ensure accurate fitting. A background model of the form $E^{-r} + aE^2 + bE + c$ was used [Su and Zeitler \(1993\)](#); [Egerton and Malac \(2002\)](#). This represents a power law background fit modified by a second order polynomial. The constant, c , enables the background to be moved vertically, bE allows for an alteration in the slope, and aE^2 allows for a change in the curvature. These alterations adjust the perfect power law decay to allow a better fit to the background and a more accurate representation of the true core loss edge. Figure [4.2](#) shows the background model for a sulfur L₃ edge and the resulting background subtracted signal.

For fitting the core-loss edge a model of the form

$$I = C\sigma I_0 \tag{3.2}$$

was used, where I is the integrated intensity of the background subtracted core-loss signal, C is a fitting parameter (discussed next), σ is the scattering cross-section of the ionization edge in units of barns, and I_0 is the total beam current measured in vacuum. The probability of scattering may be written as

$$p = N\sigma \tag{3.3}$$

where N is the atomic areal density of the element under examination within the sample (i.e. atoms/nm²). Substituting equations [3.1](#) and [3.2](#) into equation [3.3](#) gives

$$N\sigma = \frac{I}{I_0} = \frac{C\sigma I_0}{I_0} \tag{3.4}$$

$$\Rightarrow N = C. \tag{3.5}$$

We see that the fitting parameter C is the atomic areal density of the element under consideration within the sample, which, after fitting the spectrum, is calculated

through the following equation.

$$N = \frac{I}{I_0\sigma} \quad (3.6)$$

In order to obtain σ , a hydrogenic approximation for the generalized oscillator strength (GOS) per atom may be used as outlined by Egerton (2011) [Egerton \(2011b\)](#). This technique relies on the analytical solution of the Schrödinger equation for hydrogen. The nuclear charge is modified to account for the number of protons and screening is addressed. Because the model remains “hydrogen like”, standard procedures may be used to solve for the wavefunction and GOS. Computer code that performs the fitting of the hydrogenic model to the data was adapted from Egerton (2011). Because the hydrogenic model does not take into account the fine structure signal, the model edge is fit to the smooth decay tail (see figure 3.2). Therefore, the fine structure need not be resolved, and high energy resolution is not required for this technique. For more accurate fitting, a low-loss spectrum (taken from the same position) may be convolved with the hydrogenic model to account for experimental factors such as the instrument resolution and plural scattering effects. This avoids the noise amplification problem when attempting to deconvolve the low-loss signal from the core-loss signal. An alternative edge profile that may also be used instead of the hydrogenic model is the Hartree-Slater method. This relies on iterative solutions to the Schrödinger equation that have been tabulated for each atom. This can be more reliable, however, far from the edge onset a power law is used to extrapolate the edge to higher energies and, thus, may not always be the best choice. The choice of model must be determined on a case by case basis. Once a model is chosen and fit to the data, N is obtained.

Of paramount importance in properly fitting the model to the spectrum is the background slope and the edge decay slope shown in figure 3.2. These must very closely match the data for the result to be accurate [Bertoni and Verbeeck \(2008\)](#). A background model that is too steep (decays too quickly) overestimates the edge but may not, to the untrained eye, look like a particularly poor fit. Likewise, looking at

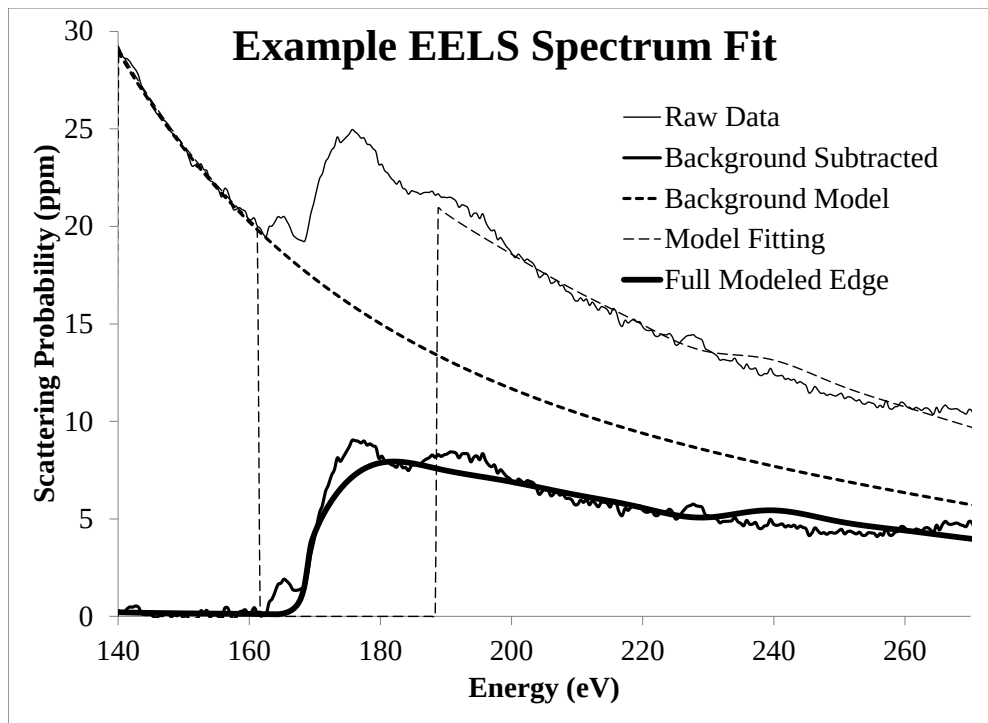


Figure 3.2: Sulfur L3 edge analysis. A background was first modeled using the pre-edge signal and subtracted from the raw data to give the background subtracted edge. The edge onset for the hydrogenic model was chosen such that it coincides with the data. The hydrogenic edge was then convolved with a low loss spectrum to more accurately mimic the shape of a real edge, and fit to the smooth tail above 190 eV. The “full modeled edge” represents the edge that best fits the data on top of the background model. We see it closely matches the background subtracted edge. Because we do not model the fine structure, high energy resolution is not necessary.

the model fitting at 190 eV, one may question its accuracy, however we see that the *slope* is quite accurate (in the 200-240 eV range) and the full modeled edge captures the background subtracted data acceptably well. Without data points around 190 eV included in the fitting area, the full modeled edge no longer lies on top of the background subtracted data because of a slight change in the slope.

One may notice the gradual rise above 260 eV. This is caused by diffuse pre-peaks at the carbon K edge onset and care must be taken that this does not affect the slope of the model fitting since this is not part of the sulfur signal. The spectrum shown in figure 3.2 actually includes the carbon edge. This edge was modeled concurrently to ensure an accurate fit of the entire spectrum, but is omitted here for the sake of simplicity.

3.4.3 Relation of Areal Density to Volume Density and Sample Thickness

N is the atomic areal density. This is dependent on the thickness of the sample. If the sample is thicker, there will be more atoms per square nanometer under the beam. If we can determine the elemental density of the material (for example the amount of S per volume in WS_2) then we can determine the thickness of the sample through the relation:

$$N = \rho t \tag{3.7}$$

where N is our measured atomic areal density, ρ is the elemental density of the material, and t is the thickness of the sample. We use the term “elemental” to highlight the fact that ρ should not be mistaken for the density as it is traditionally defined (i.e. g/cm^3). Here ρ is the number of atoms *of a particular element* per volume (i.e. S atoms/ nm^3). Alternatively, if the sample thickness is measured through some other technique, the density of the material can be measured on a nanometer length

scale which may prove to be quite useful in some situations. We discuss one such situation in section 3.7.

Preliminary experimentation on measuring thickness

Let t be the sample thickness in nm, and ρ be the carbon density in atoms/nm³ then $t\rho$ is the carbon areal density in atoms/nm² that we would measure in the microscope (for example in figure 4.3b). If we know the carbon density of a material we can then calculate the thickness based off of the measured carbon areal density.

Measuring an amorphous sample thickness is typically accomplished by obtaining a low loss spectrum and applying the log-ratio method to obtain the thickness as a fraction of electron inelastic mean free path. The expression is,

$$\frac{t}{\lambda} = \ln \left(\frac{I_t}{I_0} \right) \quad (3.8)$$

where I_t is the total integrated intensity from the spectrum, and I_0 is the integrated intensity under the ZLP. For more details on this method see *Electron Energy-Loss Spectroscopy in the Electron Microscope*, R. F. Egerton, (2011). The main drawback for determining absolute thickness is that the inelastic mean free path must (λ) must be known. To our knowledge these values have not been measured for the materials in question so we are left with a relative thickness. Nevertheless, we will make use of this information.

Low loss and core loss spectra were obtained from several films of P3HT:PCBM blends while scanning the electron beam over a large area during EEL spectrum acquisition. The large area (several microns) scanning is important so that variations in phase concentration average out, as well as slight thickness variations. This produces an average signal for the film.

Low loss spectra were used to produce a log-ratio thickness measurement in fraction of inelastic mean free path (i.e. t/λ), and core loss spectra were used to produce absolute thickness measurements (i.e. t). These two methods are clearly

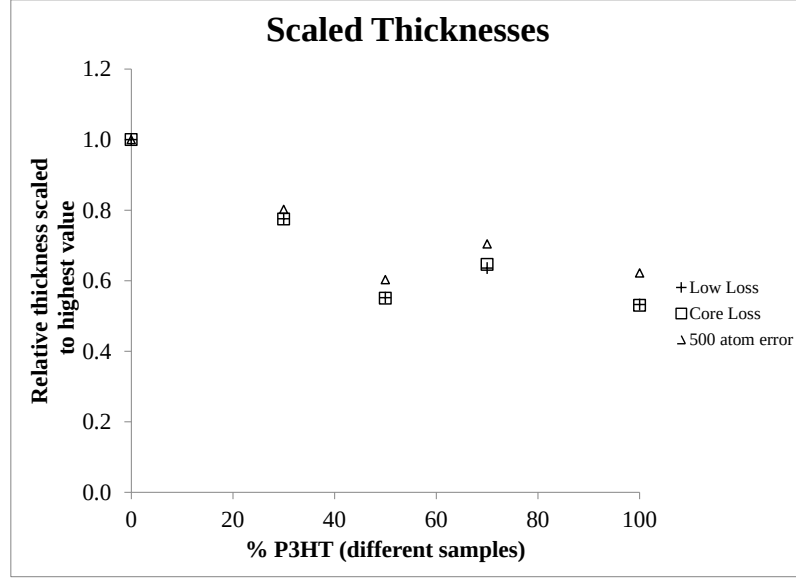


Figure 3.3: Comparison of the relative thickness produced through the log-ratio method (equation 3.8) and the absolute thickness gleaned from the carbon areal density. Introduction of an artificial 500 atom error to the core loss data produces significant deviation between the two measurements. % P3HT simply refers to samples of different compositions.

not directly comparable. For comparison, we divided each measurement by the largest measurement to produce a thickness in fraction of the thickest sample. In this way both measurements are converted to a relative but comparable form. Figure 3.3 shows these results. The close agreement between the two methods seems to indicate that the absolute measurement technique is working. Moreover, intentionally introducing an additive error into the quantitative measurement of just 500 atoms causes a significant deviation between the two methods. The reader should note that this method of comparison forces all measurements for the thickest sample to a value of 1. Agreement at this data point is given.

We have established that relative changes in the carbon areal density thickness measurements agree quite well with the log-ratio thickness measurements. A second test of the validity of this technique is that it be self-consistent. In order to

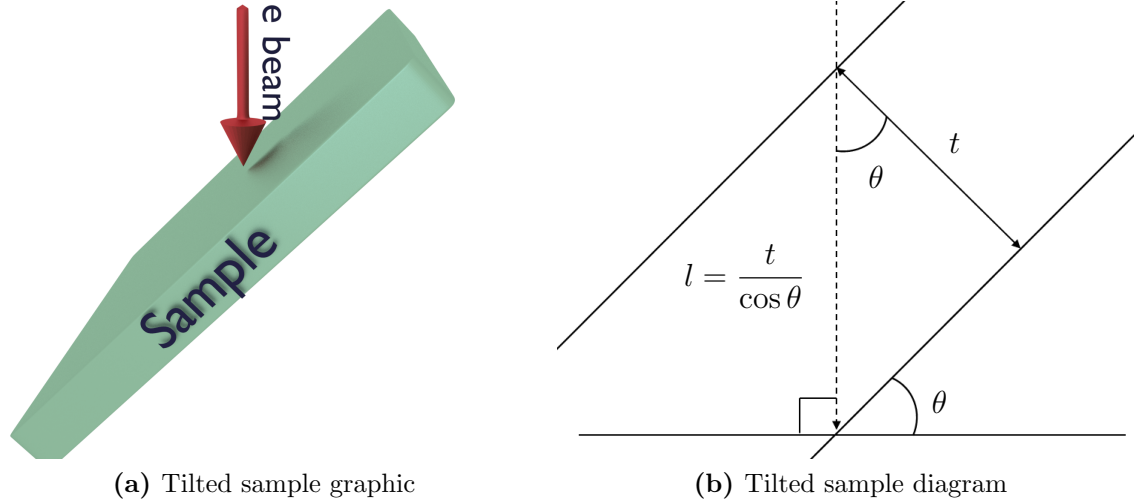


Figure 3.4: a) graphic of the tilted sample and electron beam orientation to aid understanding of the diagram in b). b) Diagram of the tilted sample and corresponding geometry.

demonstrate this we chose one sample and obtained carbon areal density thickness measurements at a series of different tilt angles. By tilting the sample we make the beam pass through more material which produces a predictable thickness measurement change. Figure 3.4 shows the sample orientation and relevant geometry.

When the sample is tilted, the electron beam passes through a length of material $l = \frac{t}{\cos \theta}$ where t is the sample thickness and θ is the tilt angle. Plotting l vs $\frac{1}{\cos \theta}$ will give a linear relationship with a slope equivalent to the thickness, t , and an intercept of zero. Figure 3.5 shows a plot of the data taken during these experiments. The thickness determined by the slope of the line is 32 nm while the thickness determined using the carbon areal density measurement directly resulted in a thickness of 31 nm. The standard error in the slope of the linear fit, 0.14 nm, gives us a quantitative value for the precision.

These are not independent measurements so their agreement does not come as a surprise. However, this serves to illustrate that, as the sample thickness changes, the measured thickness values change precisely as expected (i.e. the change in sample thickness does not somehow invalidate the method). To serve as further proof of

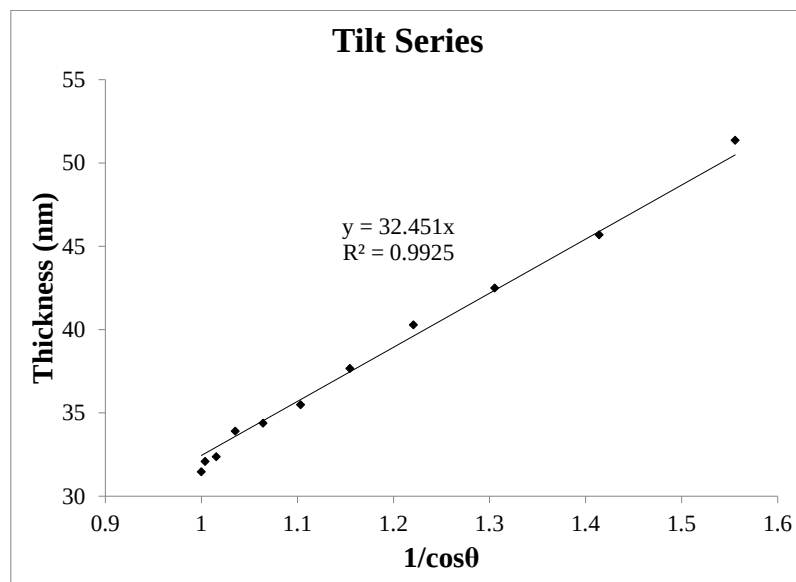


Figure 3.5: Plot of the tilt series data. The slope corresponds to the sample thickness of 32 nm, which is in close agreement with the direct carbon areal density thickness determination of 31 nm. The standard error in the fit is 0.14 nm indicating a high level of precision.

this thickness measurement technique two experiments were performed on samples of known thickness to check that the method worked properly.

3.5 Counting atoms in tungsten sulfide

Single layer tungsten sulfide provides an attractive test bed for this method. Single layer tungsten sulfide has a lattice parameter ($a=b$) of 3.18 Å. Coupled with the knowledge of hexagonal symmetry, we calculate 2 sulfur atoms in every 8.757 Å² or 22.8 sulfur atoms per nm².

A section of sample was found where the single layer had folded upon itself and an EELS spectrum image was acquired extending from vacuum, across the folded layer, and onto the single layer. The sulfur signal was fit with a theoretical model as described in section 3.4.2. Figure 3.6 shows the areal density mapping of the sulfur signal. The color represents sulfur areal density; x and y axes, position. The average value of the light blue region is 22.3 atoms/nm² (within 2.2% of the calculated value) with a standard deviation of 2.7 atoms/nm². The average value of the red region is 65.7 atoms/nm² with a standard deviation of 2.9 atoms/nm². This is within 4% of the value we would expect from a triple layer. We also notice the signal in each region is quite uniform which means our fitting routine is consistent. Variations within the data are likely due to noise in the spectra or slight variations from stoichiometry (i.e. vacancies) in the film.

3.6 Thick, silver nanoparticle

A problem arises for thicker samples due to electron scattering to high angles. In this case, electrons that would have contributed to the core-loss signal are not accounted for and the measured edge will produce anomalously low values. This problem can be rectified by using a reduced beam current value that represents the scattering lost to high angles. To determine what the reduction in beam current should be, we recorded

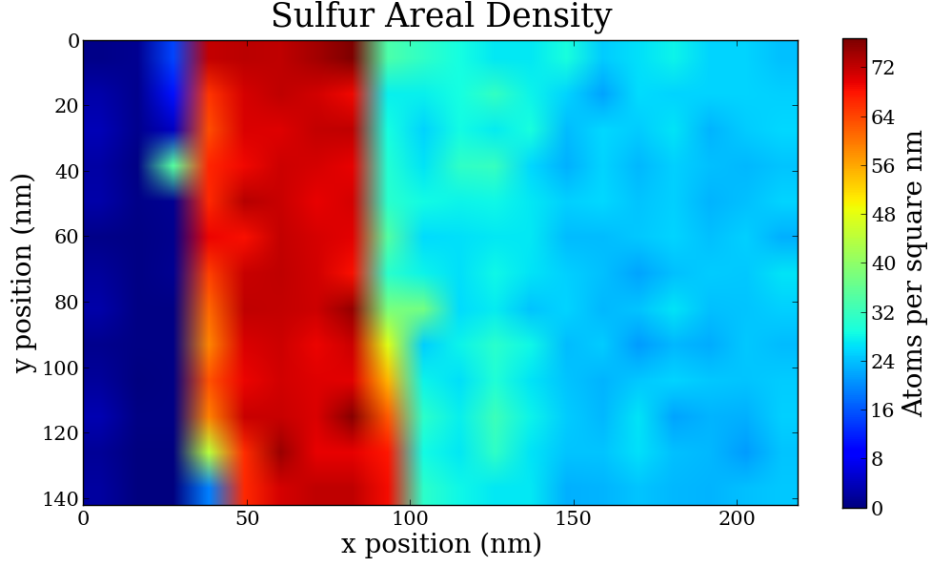


Figure 3.6: Measured sulfur areal density as a function of position on the sample. Color represents areal density, x and y , position. Single-layer tungsten sulfide has 22.8 sulfur atoms/nm² and a triple layer has 68.4 sulfur atoms/nm². Here we average 23.3 atoms/nm² over the single layer area and 65.7 atoms/nm² over the triple layer area, within 2.2% and 4.0% of the true values.

the zero-loss peak in vacuum and through the center of a silver nanoparticle shown in figure 3.7. The ratio of the two integrated spectra gives a conversion factor for how much of the beam is lost due to scattering (or absorption). We can then reduce the beam current measurement by this factor. This alters equation 3.6 as follows:

$$N = \frac{I}{I_0 \sigma_0} \frac{I_v}{I_s} \quad (3.9)$$

where I_v is the beam current as approximated by the vacuum low-loss spectrum, and I_s is the beam current as approximated by the low-loss spectrum through the sample. Ideally one could simply measure I_s and use this value instead of I_0 in equation 3.6 however, the focused zero-loss peak signal, from which I_s is obtained, displays a systematic error when compared to the true beam current measurement. One would expect $I_v = I_0$ however, we find that $I_v < I_0$. This is either due to the CCD being operated close to saturation or errors in exposure time due to such short exposures.

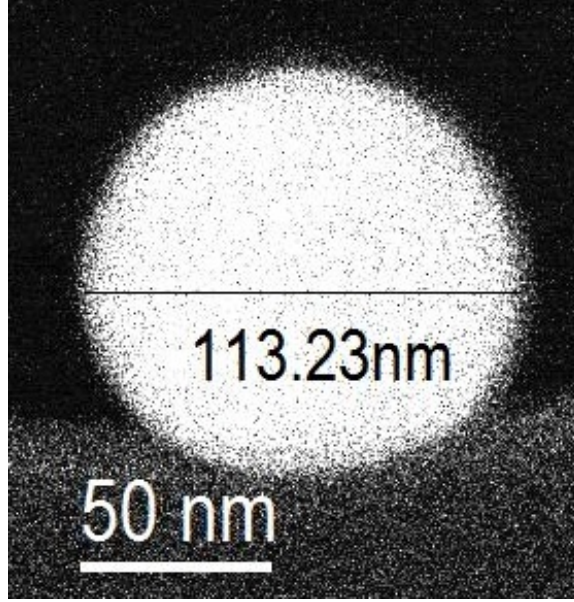


Figure 3.7: Z-contrast image of a spherical Ag nanoparticle with a diameter of 113 nm. An initial thickness of 25 nm is measured at the center of the particle. After the high-angle scattering correction is applied the measured value is 114 nm. The average thickness produced from a range of fitting parameters is 110 nm $\pm 7\%$. This indicates that thicker samples may also be reliably measured if high-angle scattering is taken into account.

To account for this discrepancy the ratio I_v/I_s is used. The discrepancy in I_v cancels with the same discrepancy in I_s and reduces the accurate measurement (I_0) by the appropriate amount. In this case we found the beam current reduces by a factor of 4.56. Fitting the silver $M_{4,5}$ edge produced thickness values of around 25 nm when we used an atomic density of 59 atoms/nm³. This is clearly not true as we can see in figure 3.7, the particle is 113 nm. However, when we multiply by 4.56 to account for scattering loss, we obtain a value of 114 nm (less than 1% error). We conclude that, even thicker samples that scatter a large portion of the beam to high angles can be examined with this method if an appropriate reduction in beam current is used.

Here we must also mention the variability in fitting results. After the background is fit acceptably well, the second most important fitting parameter under our control is the selection of the fit starting point after the edge onset. In the case of this Ag nanoparticle excluding a range of values (185 eV to 240 eV) all produced “acceptable”

results. This corresponds to a range of thickness measurements from 107 to 117 nm. A strategy that may be employed is to calculate the thicknesses for every 5 eV interval within this range and obtain an average. Here we obtained an average of 110 nm. So on an edge where a best fit is ambiguous we see a variation in values of $\pm 7\%$ while the average value is within 3% of the measured diameter. In actuality the initial parameters that we determined simply by examining by eye were more accurate than this averaging technique, however, there was no definitive reason for our particular choice of parameters except that it “looked” best. Often there is not so much ambiguity in the proper fit. For example, when fitting multiple peaks, the ratio of the elements may be used as a guide for determining the proper fit. Also, the energy range between peaks may limit the available choices for fitting. At times changing the fitting parameters makes very little difference in the fit. In these cases the spread in values is reduced providing a higher confidence in the measurement. Nevertheless, averaging over a range of values in an ambiguous case seems to be a fairly accurate way of determining the proper fit despite a spread of values of $\pm 7\%$.

3.7 Measuring density to obtain pressure

In this experiment we examined several spherical cavities in a zirconium copper alloy which had been irradiated with an argon ion beam. EELS spectra of the argon L edge confirmed the presence of argon within the cavities. The diameter of the cavities was measured and this was taken to be the thickness of the cavity. Given a known thickness we used equation 3 to calculate the density of the material (in this case argon). Figure 3.8 shows a Z contrast image of the cavities.

The EELS spectra were acquired at the center of each cavity and each spectrum was analyzed according to section 3.4 to obtain an areal density. The areal density was then divided by the thickness to obtain volume density. The volume densities were 20.6, 20.0, 20.7, 20.0, and 20.1 atoms/nm³ for cavities 1-5 respectively. The average is 20.3 atoms/nm³ with a standard deviation of 0.35 atoms/nm³. Since each

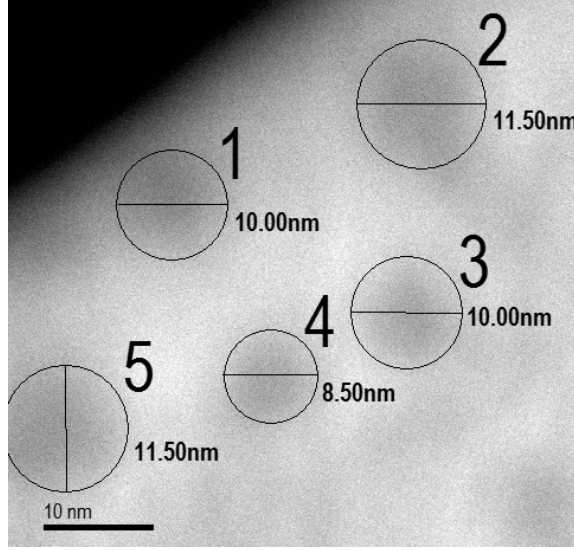


Figure 3.8: Spherical cavities in a zirconium copper alloy contain argon, as confirmed through EELS. The diameter of each cavity gives a close estimate of the thickness of the cavity. Given the thickness we use the EELS data to calculate the density of the argon and thus, obtain a pressure/temperature relation.

cavity was formed under the same conditions and they all have similar dimensions we expect the density within each one to be fairly consistent and this is indeed the case. To our knowledge, no one has previously performed an experiment to measure the Ar density in such an alloy. However, C. A. Walsh et al used EELS to measure the He density in irradiated PE16 alloy and found a density of $5-28.6 \text{ atoms/nm}^3$ [Walsh et al. \(2000\)](#) (they found the density to vary with diameter of cavities in their experiment). While this does not directly translate to the present experiment, the density values are quite similar.

In order to approximate the argon pressure within the cavities we used the ideal gas law. However, at such high densities, it is likely that the ideal gas law is no longer valid so we also used the virial expansion to approximate the argon pressure. The ideal gas law gives a temperature/pressure relation as follows.

$$PV = Nk_B T \quad (3.10)$$

$$\Rightarrow P = \frac{Nk_B}{V} T \quad (3.11)$$

Here, P is pressure, V is volume, N is number of atoms, k_B is Boltzmann's constant, and T is temperature. Thus, multiplying the volume density by Boltzmann's constant gives the slope of the temperature/pressure relation which allows for an easy calculation of the pressure of the argon for any given temperature. From the data we find a slope of $2.80 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2} \text{ K}^{-1}$ which gives a room temperature (300 K) pressure of 83.9 MPa.

The virial expansion:

$$P = k_B T \rho (1 + B\rho + C\rho^2) \quad (3.12)$$

where ρ is the density (N/V), and B and C are the temperature dependent second and third virial coefficients for argon [Stewart and Jacobsen \(1989\)](#).

Figure 3.9 shows both relations plotted over a range of temperatures and pressures. It is not surprising that the ideal gas law gives a pressure much lower than the virial expansion since the models diverge as the density of the gas increases [Walsh et al. \(2000\)](#). At room temperature (300 K) the virial expansion gives a value of 146 MPa. An in depth discussion on the various models for temperature/pressure relations is beyond the scope of this work. We simply demonstrate that such a measurement is possible on a nanometer length scale through EELS core-loss analysis.

3.8 Conclusion

We have demonstrated a unique technique for measuring either the thickness of a sample or the density using a core-loss EELS spectrum. The spectrum is fit with a model to obtain the atomic areal density which is the density times the thickness of the sample. Knowledge of either of these parameters gives the other.

The validity of the technique was tested on single and triple layer tungsten sulfide and a spherical nanoparticle where, in each case, the thickness of the material was known. The technique produced thickness measurements within 4% of the known values.

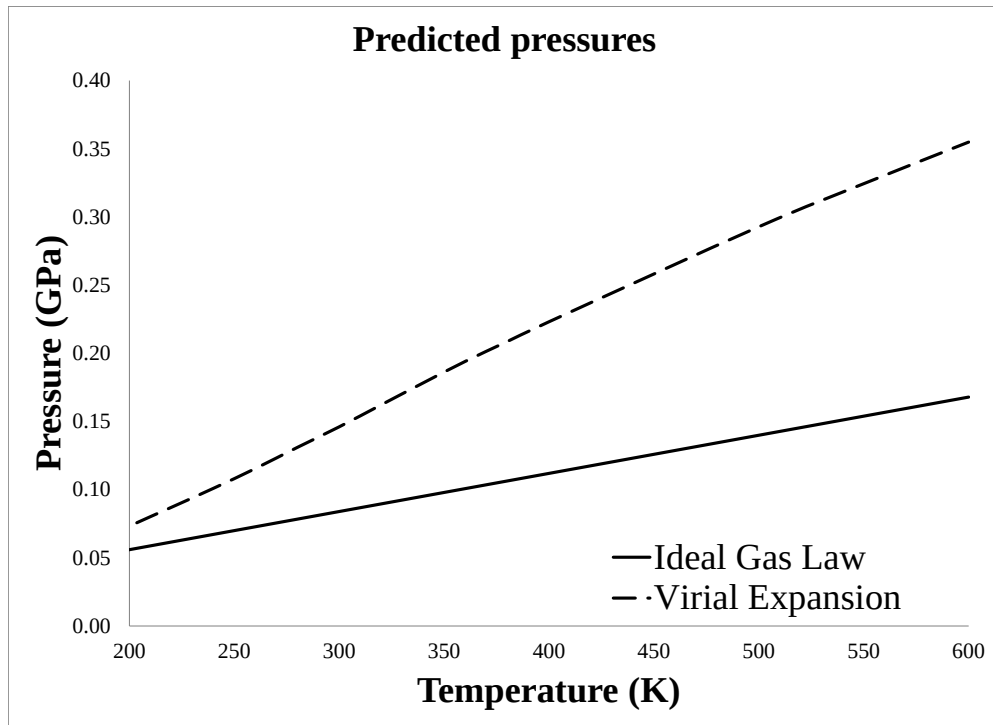


Figure 3.9: The temperature/pressure relation given from the ideal gas law and the virial expansion plotted over a range of temperatures for argon at a density of 20.3 atoms/nm³

We then used the technique to measure the density of argon in spherical voids. Once the density was known, the pressure as a function of temperature was calculated. We found the density of the argon to be 20.3 atoms/nm³ which corresponds to a pressure of (at 300 K) 83.9 MPa using the ideal gas law and 146 MPa using the virial expansion.

Furthermore, these results indicate that a carefully modeled EELS core-loss edge gives a partial scattering cross section with errors less than 10% and in a well-behaved case, where the proper fit is clear, errors less than 5% can be obtained.

Chapter 4

Quantitative Phase Mapping for OPV Materials*

4.1 Introduction

In the previous chapter we established a technique whereby a sample's density or thickness may be measured on a nanometer length scale. While sample thickness measurements may have limited applications, the intimate link to the material density enables some valuable measurement capabilities. In the previous chapter we demonstrated a density measurement on spherical argon gas pockets which allowed for a calculation of the pressure/temperature relation. In this chapter we show how the density differences between two organic materials blended to form a bulk heterojunction (BHJ) can be used to determine phase location and purity on a nanometer length scale

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4.2 Data Analysis

Data analysis of core-loss EELS spectra was carried out as described in chapter 3. Low loss data was fit with Gaussian peaks by a least squares routine. The zero loss peak (ZLP) was approximated by the multiplication of two Lorentzian functions.

4.3 Introduction

Recent years have seen an increasing interest in organic photovoltaics (OPV) [Dang et al. \(2011\)](#); [Chen et al. \(2012a\)](#); [Darling and You \(2013\)](#). As a result there is a high scientific demand for microstructural characterization of the various fabricated devices [Chen et al. \(2012a\)](#). Here we introduce several techniques for examining OPV materials in a (scanning) transmission electron microscope ((S)TEM) instrument capable of electron energy-loss spectroscopy (EELS). The materials under investigation here are P3HT, PTB7 and PCBM. These materials offer a good test system for demonstrating carbon density phase detection due to their different carbon densities (71 carbon atoms/nm³ for PCBM, 38 carbon atoms/nm³ for PTB7, and 42 carbon atoms/nm³ for P3HT, discussed later). Although this study is material specific, the techniques discussed here can certainly lend themselves to other material systems given that either the densities of an element are different between the two materials or a unique identifying element exists in one of the materials.

Organic materials exhibit poor contrast in the TEM due to their low Z number and fairly uniform densities [Chen et al. \(2012a\)](#). Energy filtered TEM (EFTEM) is an increasingly common method for enhancing contrast in organic materials. This is accomplished by introducing a post-specimen energy window that only allows electrons having a specific range of energies form the image [Nicholson and Castro \(2010\)](#); [Herzing et al. \(2010\)](#); [Drummy et al. \(2011\)](#); [Pfanmöller et al. \(2011\)](#); [Schindler et al. \(2012\)](#); [Kozub et al. \(2011\)](#); [Huang et al. \(2014\)](#); [Brady et al. \(2011\)](#). The motivation behind the use of this technique is that the different materials within

the bulk heterojunction (BHJ) have plasmon losses at different energies. For example, in the P3HT/PCBM system, positioning the energy window at 19 eV will cause the P3HT to brighten and the PCBM to darken. Positioning an energy window at 30 eV will cause the PCBM to brighten and the P3HT to darken [Drummy et al. \(2011\)](#). Hence, an artificially colored composite of these two images gives clear contrast between the materials.

One of the drawbacks of this method is that it is a projection. A second drawback is that it is a qualitative measurement. Together, these can distort one’s perception of the actual structures in the material. Intensities are linked to a predominance of one material or another but this says nothing about purity. For example, if one were to examine a sample and find areas of high PCBM concentration the natural interpretation would be to assume these are PCBM aggregations in a network of donor polymers. However, this same picture can be explained as an interconnected donor polymer web in a PCBM matrix. Without knowing purity (or the volume fraction) of each constituent polymer these two cases become indistinguishable. EFTEM tomography alleviates the problem of projection and is thereby able to distinguish between these two cases but still lacks quantitative information about purity. This technique is also technically challenging and has seen limited use in the investigation of OPV material systems.

In this study we explore an alternative material detection mechanism that allows for a quantitative measurement of the fraction of each material. In the first part of the paper we show how this can be accomplished, given a few assumptions, with a spectrum image that captures the carbon K edge. Using this technique we find evidence for a mixed phase in a P3HT/PCBM system. We then outline a further refinement of the technique that relies on both the carbon K edge and the sulfur L_{23} edge. With an additional measurement, fewer assumptions are required and a comparison of several calculations allows an error bar of $\pm 20\%$ to be assigned to the technique. Here we illustrate the detection of a PTB7 web in a PCBM matrix rather than what initially appears to be PCBM aggregates in a PTB7 matrix.

4.4 Experimental

4.4.1 Materials and Device Fabrication

Two material systems were investigated in this study: P3HT/PCBM and PTB7/PCBM.

For the P3HT/PCBM system: Regio-regular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) (99.5%) were purchased from Rieke Metals Inc., and Nano-C Inc., respectively.

The substrates used were silicon wafers first cleaned in hot piranha (1:3 H₂SO₄:H₂O₂) for 30 min, then washed in deionized (DI) water and dried under nitrogen gas. P3HT:PCBM (in a weight ratio of 1:0.8) was then dissolved in *o*-dichlorobenzene (ODCB) to achieve a solution with P3HT and PCBM concentrations of 10 mg/ml and 8 mg/ml, respectively. Spin coating this solution on the substrate produced 70 nm thick films. Subsequent solvent vapor annealing in Toluene was performed for 1 hour at 90% of the solvent vapor pressure to enhance phase separation.

For the PTB7/PCBM system: Poly (4,8-bis [(2-ethylhexyl) oxy] benzo [1,2-b:4,5-b'] dithiophene-2,6-diyl 3-fluoro-2- [(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl) (PTB7) and PC₇₁BM were purchased from 1-Material and Nano-C, respectively, and used as received. The PTB7:PC₇₁BM blend solution was prepared by dissolving PTB7 and PC₇₁BM (with 1:1.5 ratio and 25 mg/ml total concentration) in dichlorobenzene and heating at 70 °C for several hours.

Indium tin oxide (ITO) substrates were first cleaned by detergent and subsequently sonicated in DI water, acetone, and isopropyl alcohol (IPA) followed by baking at 80 °C for one hour. The PFN solution was prepared by dissolving PFN in methanol (2 mg/ml) with the presence of a small amount of acetic acid, and spun cast onto the UV-treated ITO substrates at 3000 rpm. The active layer was spun cast at 1000 rpm for 90s followed by drying for 30 minutes in inert environment. Finally, devices were completed by thermally depositing 8 nm of MoO₃ and 100 nm of Ag.

4.4.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) studies were performed using a Zeiss Libra 200MC TEM. This TEM is equipped with an energy filter and monochromator and was operated at an accelerating voltage of 200 kV.

Cross-section samples were prepared using a Zeiss Auriga Crossbeam focused ion beam (FIB) microscope. A final polish at a beam current of 10 pA and accelerating voltage of 10 kV was used to limit beam damage.

Energy filtered TEM (EFTEM) images have previously shown successful determination of phase separation in similar bulk heterojunctions [Nicholson and Castro \(2010\)](#); [Drummy et al. \(2011\)](#); [Herzing et al. \(2010\)](#); [Pfannmöller et al. \(2011\)](#); [Chen et al. \(2012a\)](#). Following the techniques described in earlier studies, EFTEM images were taken with a slit width of 8 eV centered at 19 and 30 eV. Artificial coloring was added and the EFTEM images were overlaid to enhance visualization of the phases.

EELS imaging was performed with an energy resolution of 0.56 eV (full width half maximum (FWHM) of the zero loss peak (ZLP) in vacuum).

4.4.3 Data Analysis

Data analysis was carried out as described in the previous chapter. Low loss data was fit with Gaussian peaks by a least squares routine. The zero loss peak (ZLP) was approximated by the multiplication of two Lorentzian functions.

The core loss data was fit with a background subtraction routine of the form $E^{-r} + aE^2 + bE + c$. Additionally a representative low loss spectrum of the same area was convolved with the carbon hydrogenic scattering cross section to more accurately fit the edge.

In order to obtain quantitative elemental measurements the scattering probability must be calculated. Once the background is subtracted from a core loss edge, the area under the edge represents the total scattering probability for that element. Scattering probabilities for single atoms are well known [Tougaard \(1997\)](#) and dividing

the measured scattering probability by the known scattering probability produces the number of atoms (of that element) under the beam.

$$N_{atoms} = \frac{N_{tot}/N_s}{P_s} \quad (4.1)$$

Here N_{atoms} is the number of atoms under the beam, N_{tot} is the number of incident electrons, N_s is the number of scattered electrons (area under the EELS edge), and P_s is the probability of scattering from a single atom.

4.5 P3HT/PCBM System: Results and Discussion

4.5.1 EFTEM Imaging

In order to give a baseline comparison for the EELS imaging results, EFTEM imaging was performed to distinguish between P3HT and PCBM. Figure 4.1 represents a typical EFTEM image from the sample. We can clearly distinguish between the P3HT and PCBM rich areas. The PCBM rich area in this sample aggregates near the Si substrate.

One of the caveats for using the bulk plasmon for this type of imaging is that many materials have bulk plasmons in similar ranges. For example silicon has a sharp bulk plasmon peak at ~ 19 eV which falls precisely in the energy range usually used to detect P3HT. In Figure 4.1 we can see that this causes the silicon to exhibit a strong “P3HT” signal. This is not a problem in this case because we are well aware of the silicon plasmon location before any EFTEM image is taken; however the introduction of contaminant materials [Nikiforov et al. \(2013\)](#) or unexpected variations in the bulk plasmon could easily distort EFTEM images. For this reason, recorded spectra should accompany EFTEM imaging. Ideally an EELS image should be used so that precise analysis of spectral variations with sample position can be examined post-acquisition.

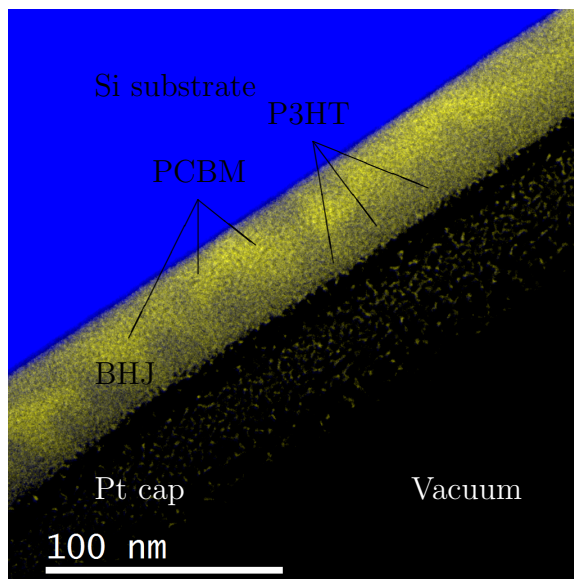


Figure 4.1: EFTEM image in cross-section reveals the phase separation between P3HT and PCBM. The Si substrate appears blue due to the large bulk plasmon peak of Si near the 19 eV energy window.

4.5.2 EELS Imaging

EELS images were also taken of the cross-section samples. With this technique the electron beam is slowly rastered across the sample and an EELS spectrum is recorded at each position. Figure 4.2 shows one such spectrum from a spectrum image fitted with two Gaussian peaks to capture the position of the bulk plasmon peak.

The movement of the bulk plasmon peak labeled “Peak 2” is responsible for the intensity variations highlighted in the EFTEM images (Figure 5.7e). This peak position can be seen to shift by about 1 eV depending upon which material the beam is incident, Figure 4.3a. The color in Figure 4.3a shows the energy position of peak 2 while the x and y dimensions represent physical position on the sample. It should be noted that peak 1 was merely used so that the fitting algorithm did not attempt to use peak 2 to represent data below about 15 eV. Additional peaks do improve the fit in the low energy range but are unnecessary for accurate fitting of the bulk plasmon. Peak 2 does indeed capture the bulk plasmon peak quite well so the position measurements for this peak are well represented. It is not surprising that

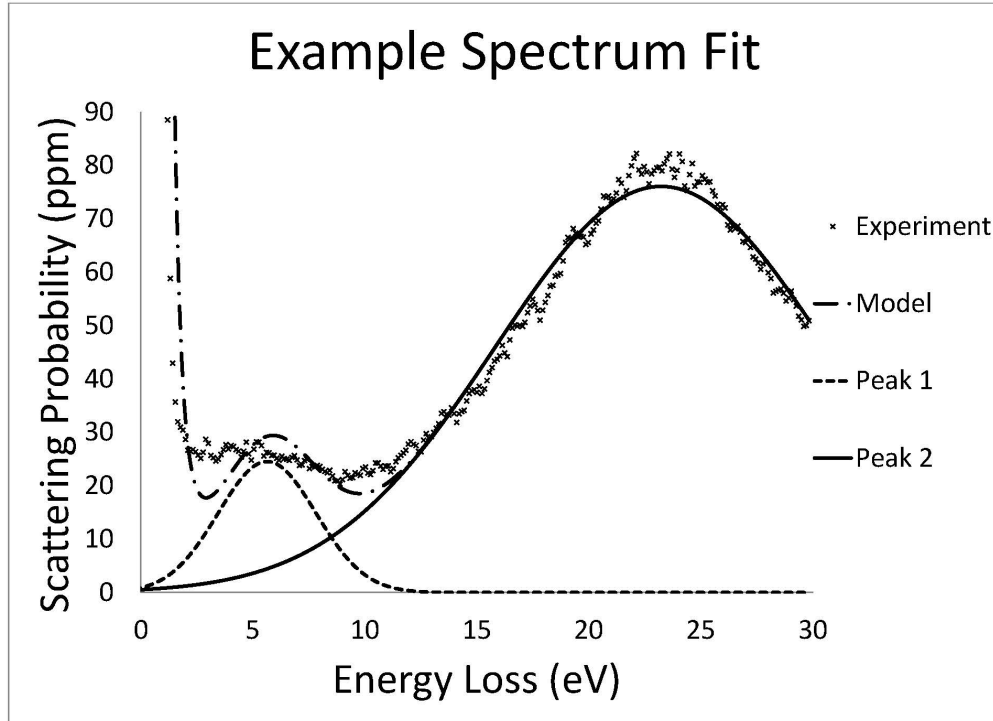
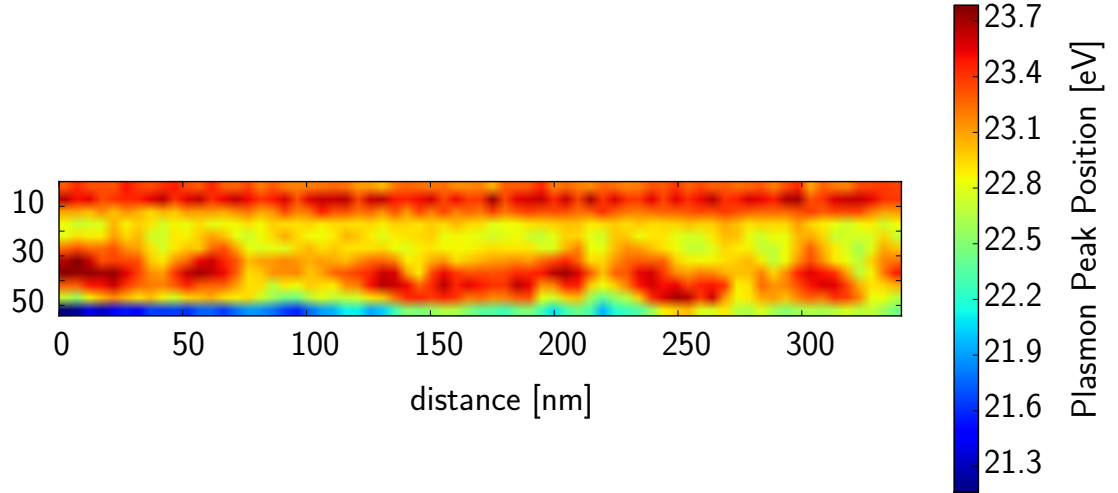


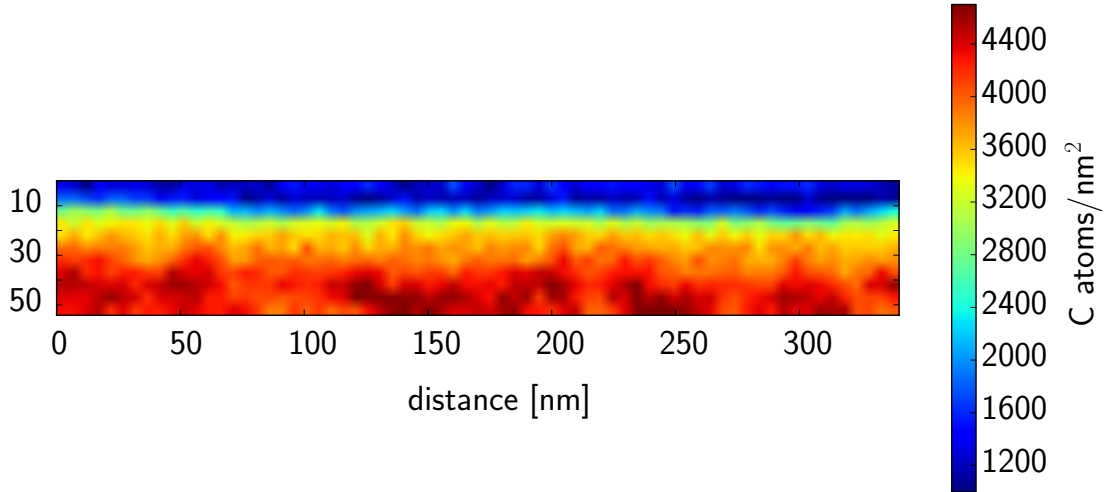
Figure 4.2: Example fit of a single spectrum from the EELS spectrum image. Peak 2 captures the bulk plasmon peak position which is mapped across the sample in figure 4.3a.

this produces similar results to the EFTEM image since they both rely on the same spectral feature changes.

The EELS plasmon map is not a completely independent measurement technique from EFTEM imaging as it also relies upon the movement of the plasmon peak to differentiate the component materials. Specifically, this measurement seems to indicate a PCBM-rich layer at the surface of the sample as seen in Figure 4.3a. We know that there is also a layer of platinum somewhere in this region so it is unclear whether this signal is truly from PCBM. A second method is needed to confirm this observation.



(a) Quantitative view of the plasmon peak shift between the PCBM rich and P3HT rich phases. The Si substrate is at the bottom of the image. The PCBM rich area is found where the plasmon peak shifts to higher values near the substrate. The top layer that generates a signal similar to that of PCBM has a very low carbon concentration (see Figure 4.3b) and is attributed to the platinum protective layer deposited during sample preparation.



(b) Carbon areal density measured across the same area as in Figure 4.3a (a small vertical drift is present). The higher carbon density areas closely match with the plasmon peak position shift in Figure 4.3a demonstrating the viability of this technique.

Figure 4.3: The agreement between Figures 4.3a and 4.3b gives credence to the techniques. The plasmon signal at the top in Figure 4.3a highlights the possible misinterpretation of the plasmon variations which make this area appear as a high PCBM concentration area, yet Figure 4.3b shows it to be devoid of carbon.

In order to obtain a completely independent measurement we noted that the carbon density in P3HT is about half that of the carbon density in PCBM. We calculated carbon density by multiplying the carbon weight percent, obtained from the linear formulas, by the density of each material and converting to appropriate units. For P3HT we used a the linear formula $C_{10}H_{14}S$, and density of 1.15 g/ml, as specified by the supplier, to predict a carbon concentration of 42 atoms/nm³. This density value, presumably determined from a bulk specimen, is, nevertheless, well within the range of experimentally determined densities for P3HT films in the literature [Ro et al. \(2012\)](#); [Prosa et al. \(1992\)](#); [Kiel et al. \(2010\)](#); [Tada et al. \(2011\)](#).

For PCBM we used the liner formula, $C_{72}H_{14}O_2$, and a density of 1.6 g/ml [Ro et al. \(2012\)](#); [Tada et al. \(2011\)](#) to calculate a carbon concentration of 71 atoms/nm³.

It is important to note that these density values are rather rough estimates taken from measured literature values. Table 4.1 shows a few of these values and we see there is a significant spread, particularly in the density of PCBM. It seems likely that processing parameters play a significant role in the final density and that one may even find a range of densities within the same sample due to (for example) degree of crystallinity. Future refinements of this technique may heighten the precision such that these small density fluctuations become apparent (and their detection would be quite revealing). Indeed, as outlined previously, precision density measurements on a nanometer scale should be possible on a specimen of known thickness (on a single, uniform material). In this case, however, the thickness is unknown, therefore we must rely on literature values for the material densities which is one source of error in the resulting measurements.

In order to measure this difference, another EELS image was obtained in the same area and the carbon core loss edge was recorded. For each spectrum, the background was subtracted and the carbon areal density was calculated based on scattering probability as outlined in the Data Analysis section. The resulting image is shown in Figure 4.3b where the x and y coordinates are the position on the sample and the color represents carbon areal density.

Table 4.1: Summary of densities for the various materials studied. All values are in g/cm³.

PCBM	P3HT
1.64 ^{a,b}	1.16 ^a
1.50 ^{c,d,e}	1.15 ^f
1.33 ^f	1.12 ^g
1.25 ^f	1.10 ^{e,g}
References:	<i>d</i> Bulle-Lieuwma et al. (2003)
<i>a</i> Ro et al. (2012)	<i>e</i> Geens et al. (2004)
<i>b</i> Tada et al. (2011)	<i>f</i> Kiel et al. (2010)
<i>c</i> Sun et al. (2013)	<i>g</i> Prosa et al. (1992)

The similarity between Figures 4.3a and 4.3b is clear. There is a higher carbon density in the same locations where the plasmon peak shifts to higher energy. The only area in which they disagree is in the surface layer. The carbon density map shows low carbon density indicating little PCBM while the plasmon peak position map shows a PCBM-like shift. This layer is indeed the protective platinum layer deposited during the FIB sample preparation and is a good illustration of the importance of verifying measurements through multiple independent techniques. Another advantage to using carbon density for distinguishing composition is that it is relatively insensitive to beam damage. Even if the polymers are damaged (bonds are broken and the sample chemically altered) during the data acquisition, the amount of carbon present in the sample will not change. However, one of the challenges of this technique is carbon contamination during data acquisition, i.e. the buildup of additional carbon on the surface of the sample will mask the carbon variations. Hence, extreme care must be taken to ensure a contamination free experimental environment.

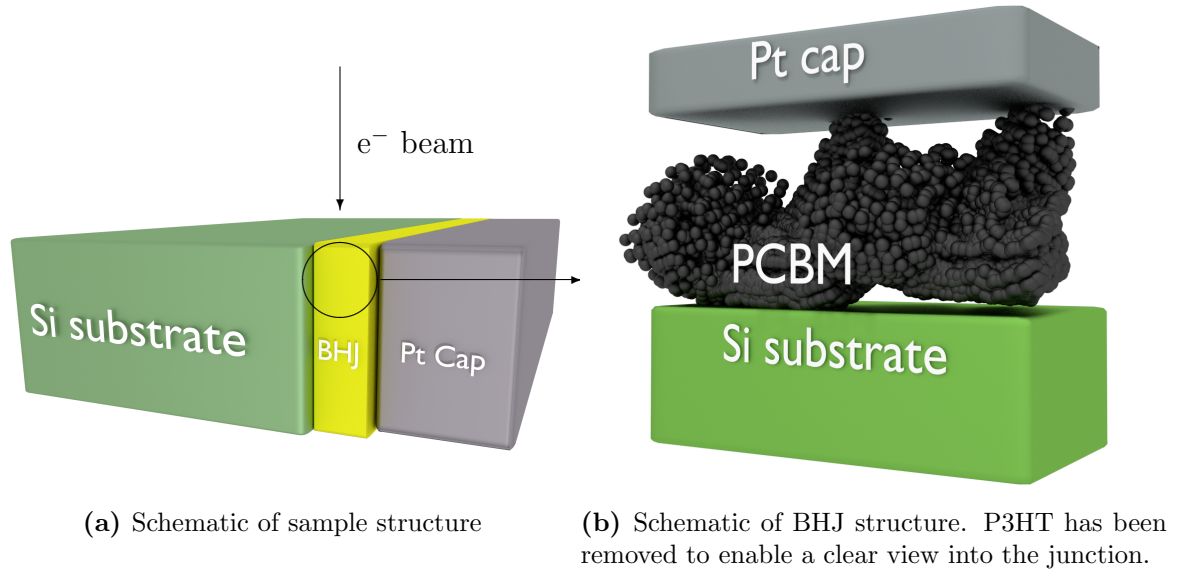


Figure 4.4: Conceptual diagram to aid understanding of the equations. The left-hand diagram is oriented perpendicular to the beam which traverses the sample vertically. We assume P3HT occupies some thickness within the BHJ (t_{P3HT}) and that the rest of the BHJ is occupied by PCBM (t_{PCBM}). In general, the total thickness of the sample is $t_{tot} = t_{P3HT} + t_{PCBM}$. In certain areas of the BHJ, however, the beam will go through either all P3HT (near the Pt cap) or all PCBM (near the Si substrate). In these cases the total sample thickness becomes $t_{tot} = t_{P3HT}$ and $t_{tot} = t_{PCBM}$ respectively.

4.6 Phase Ratio Mapping

With a carbon density map a further quantification becomes possible, namely the ratio of the component materials under the beam. In order to obtain this information we must know the thickness of the sample. If we know the thickness and we know the carbon density of the materials involved we can calculate the fraction of each component present through a linear combination of the predicted carbon density.

Let ρ_{P3HT} and t_{P3HT} be the carbon density and thickness of the P3HT, and ρ_{PCBM} and t_{PCBM} be the carbon density and thickness of the PCBM. $\rho_x t_x$ is then the carbon areal density we would measure for material x . In general, our measurement, M , is comprised of two parts:

$$\chi\rho_{P3HT}t + (1 - \chi)\rho_{PCBM}t = M \quad (4.2)$$

Here, χ represents the volume fraction of P3HT and is precisely what we would like to determine at every point on the sample. The only other unknown in this equation is t , the thickness of the sample.

In order to get a measurement of t we must meet three criteria.

- The area of interest over which the spectrum image is acquired must be of uniform thickness.

In order to ensure this criterion is met as close as possible, the sample was prepared in a FIB with the specific intention of making the front and back faces coplanar, the width of the junction under examination is only about 100 nm, and Zero filtered imaging shows little thickness variation. With the addition of the sulfur signal this criterion can be removed as discussed later.

- There are some areas of pure material.

This criterion is rather restrictive. It requires that the feature sizes within the junction (i.e. the phase separated domain sizes) are at least as large as the thickness of the sample. This requires large domain sizes which do not represent the ideal OPV structure. Many samples investigated did not meet this criterion and could not be analyzed with this first method. With the addition of the sulfur signal this assumption can be removed as discussed later.

- The sample is contamination free.

Naturally, any contamination build-up during data acquisition will alter the carbon signal. We acquired images before and after the EELS acquisition to verify that contamination was not present.

If these three criterion are met, then in the areas of highest and lowest carbon concentration, equation 4.2 simplifies since χ is either 0 or 1 (making use of the

presence of pure material). The areas with the highest carbon density are pure PCBM while the areas with the lowest carbon density are pure P3HT. This is expressed as:

$$\rho_{P3HT}t_{P3HT} = M_{P3HT} \quad (4.3)$$

and,

$$\rho_{PCBM}t_{PCBM} = M_{PCBM} \quad (4.4)$$

where M_{P3HT} and M_{PCBM} are the measured areal densities of the highest and lowest value pixels within the junction (i.e. taken from the data in figure 4.3b in locations where the beam is actually within the junction not on the Pt cap). We can then use the literature densities and our measurements to obtain the sample thickness. If the three criterion are indeed met, $t_{P3HT} = t_{PCBM} = t$. The values obtained are summarized in table 4.2. Their close agreement indicates that the criterion were met acceptably well.

As an independent check on the validity of the thickness measurement, low-loss spectra were collected on the Si substrate and analyzed using the log-ratio method to determine a thickness [Malis et al. \(1988b\)](#) of 62 and 67 nm depending on the method used to determine the electron inelastic mean free path (IMFP or λ) see the following section for details. This solidifies the veracity of the thickness measurement and indicates that our model and assumptions are reasonably accurate.

Taking the thickness of the sample to be 65 nm the carbon density map can be re-interpreted as a phase ratio map by solving equation 4.2 for χ :

$$\chi = \frac{M - \rho_{PCBM}t}{\rho_{P3HT}t - \rho_{PCBM}t} \quad (4.5)$$

Figure 4.5 shows the carbon densities re-interpreted as a fraction of P3HT. What we immediately see from this picture is that we have a large amount of mixed material that is always present between the pure phases. There are three possibilities that may account for this. The first possibility is that the transition region from one material to

Table 4.2: Summary of different thickness measurements.

	Thickness	Δ Average	Equation
t_{PCBM}	65 nm	0.0%	Eqn 4.3
t_{P3HT}	66 nm	1.5%	Eqn 4.4
Log-ratio power-law	62 nm	-4.6%	See sup. materials
Log-ratio linear	67 nm	3.0%	See sup. materials
Avg	65 nm	0%	Average

the other is not perpendicular to the electron beam which will make a sharp transition appear much smoother. This option, although possible, seems unlikely since we do not see a sharp transition anywhere. If the mixed material was simply due to overlapping domains we would expect to get a sharp transition somewhere. Alternatively, fractal-like structure with well defined (sharp) boundaries yet decreasing in feature size could also produce a similar component profile. The third possibility, which may not actually be much different from the second except in how it is expressed, is that there is a mixed phase composed of both P3HT and PCBM. There is mounting evidence that such a mixed phase exists Pfannmüller et al. (2011); Zhang et al. (2012); Tvingstedt et al. (2010); Treat et al. (2011a). Treat et al. (2011a) observed quick diffusion of PCBM into the amorphous areas of P3HT, suggesting that, though crystalline P3HT is immiscible with PCBM, amorphous P3HT readily mixes upon heating. Pfannmüller et al. (2011) observed such a mixed phase employing EFTEM imaging and a nonlinear multivariate statistical analysis. They found that the mixed phase decreases device performance due to a decrease in charge separation. Tvingstedt et al. (2010) and Zhang et al. (2012) also uncovered evidence for the presence and detriment of a mixed phase through the use of photoluminescent spectroscopy and near-infrared femtosecond transient absorption spectroscopy. Therefore it seems most likely that what we are observing in figure 4.5 is a mixed phase between the pure domains of P3HT and PCBM.

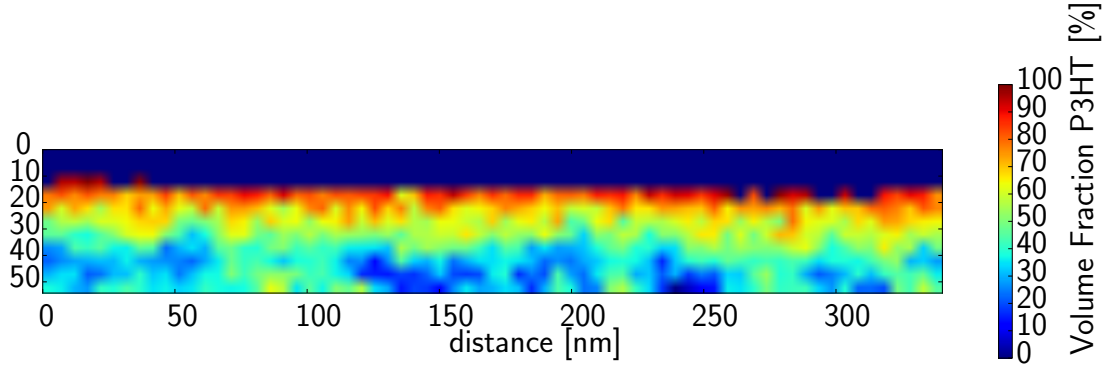


Figure 4.5: Data from figure 4.3b re-interpreted as a fraction of P3HT. In some areas equation 4.5 produces false values (above 100%) due to the low carbon concentration in the Pt cap toward the top. In these cases it is not a physical result. These values have been set to zero.

4.6.1 Log-ratio thickness measurements

A well-established technique for determining sample thickness is the log-ratio method outlined by Malis et al. (1988) [Malis et al. \(1988b\)](#). This technique depends on knowledge of the electron inelastic mean free path (IMFP or λ) within the material. Accurate measurements are often lacking since the IMFP varies according to beam energy as well as collection angle. Approximation schemes are accurate only to 10-20% [Mitchell \(2006\)](#); [Lee et al. \(2002\)](#) so we chose to rely on interpolation between values in a previously measured dataset [Mitchell \(2006\)](#). Figure 4.6 shows experimental values for IMFP (λ) at 200 kV for various collection angles (β). Similar findings were also presented by [Lee et al. \(2002\)](#). The data was fit with a power-law curve (equation of best fit superimposed) which seemed to represent the trend in the data most accurately. The power-law equation was then used to find a λ value of 187 nm based on the collection angle of 5.1 mrad used in our experiments. Since the power-law fails to capture the precise trend of the data (i.e. underestimates at the lowest value and overestimates on the following three), this value can only be taken as a guess. Based on the closeness of $\beta = 5.1$ to the lowest value, it's likely an underestimate. A linear interpolation of the first two data points results in a λ value

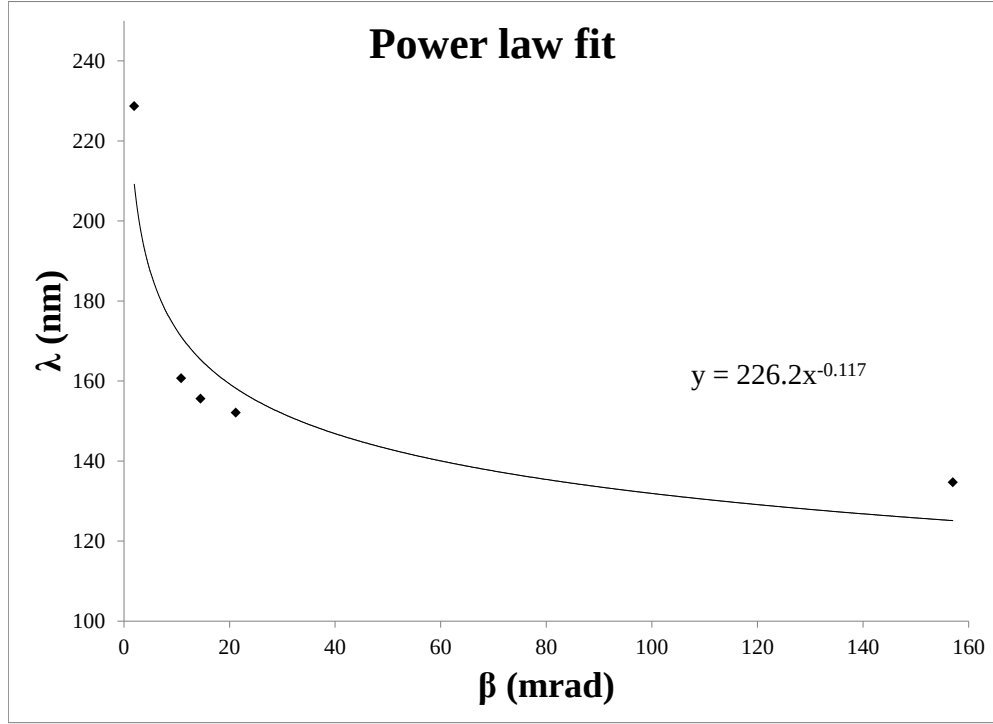


Figure 4.6: Power law fit to experimental data from [Mitchell \(2006\)](#). From the equation of best fit (superimposed) a λ value of 187 nm is determined from the β angle of 5.1 mrad used in our experiments.

of 204 nm, which, based on the general curve of the data, we assume to be a slight overestimate. Therefore, 187-204 nm is the best guess for λ .

Low-loss spectra taken from the Si substrate just below the spectrum image acquisition site give a relative thickness of $0.33\lambda = 62 - 67$ nm using $\lambda = 187$ nm and $\lambda = 204$ nm. These thicknesses are in close agreement with the other thickness measurements discussed in section 4.6.

4.7 PTB7/PCBM System: Results and Discussion

4.7.1 Density measurement

We found no previously reported literature value for the density of PTB7. The density of PTB7 was obtained by measuring neutron scattering length density (nSLD) of spun-cast PTB7 film using neutron reflectivity. In nSLD, β is defined as,

$$\beta = N_a \rho_m \sum_{k=1}^n \frac{b_k}{m_{a,k}} \quad (4.6)$$

where N_a and ρ_m are Avogadro's number (mol^{-1}) and the mass density of the material (g/cm^3), b_k and $m_{a,k}$ are the coherent neutron scattering length (fm) [Sears \(1992\)](#) and atomic mass (g/mol) of the k^{th} atom in a molecule with total n atoms. The obtained mass density of PTB7 was found to be $1.17 \text{ g}/\text{cm}^3$.

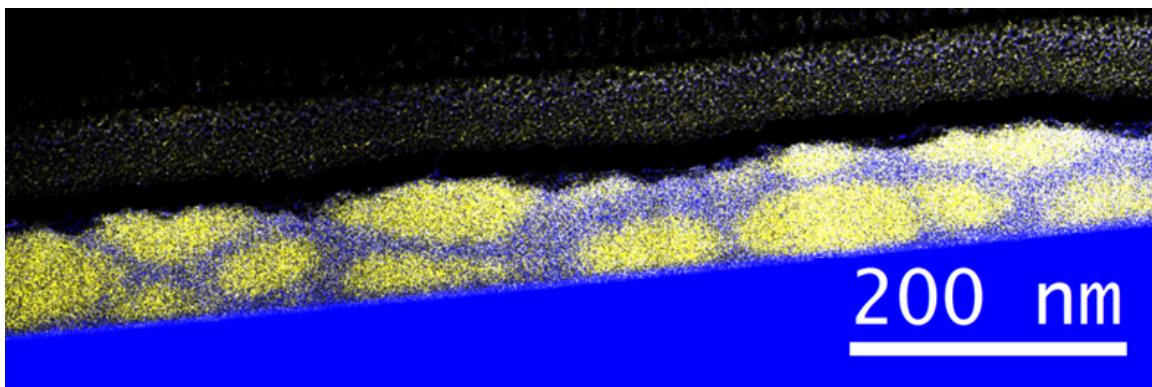
4.7.2 Quantitative elemental mapping

An EELS image was obtained from a PTB7/PCBM phase separated cross section sample and the carbon K edge and sulfur L_{23} edge were recorded. For each spectrum, the background was subtracted and the carbon areal density was calculated based on scattering probability as outlined in the Data Analysis section. The resulting images are shown in [Figure 4.7](#).

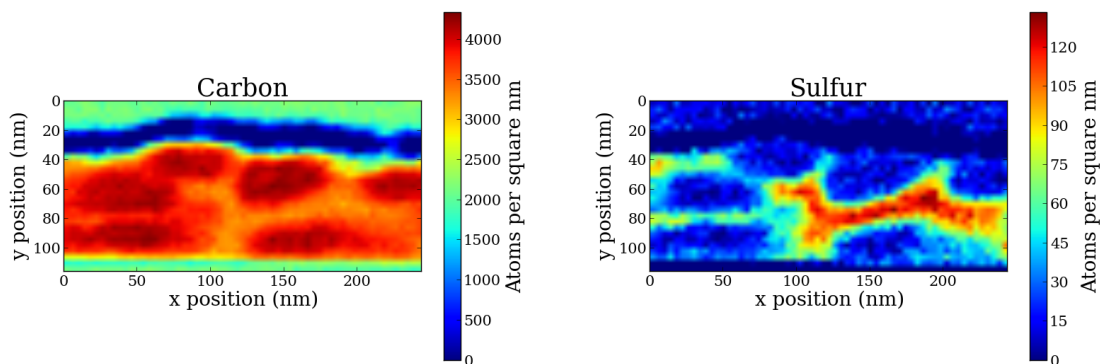
[Figures 4.7b](#) and [4.7c](#) are clearly complementary. The sulfur signal denotes the PTB7 while the high carbon density denotes the PCBM.

4.7.3 Mathematical description

Further refinement of this technique is possible with the additional information provided by the sulfur signal present in many of the donor polymers used in OVPs such as PTB7, which has a sulfur density of $3.72 \text{ atoms}/\text{nm}^3$. Specifically, two additional ways to calculate the volume fraction of the component materials become available.



(a) EFTEM imaging provides a baseline comparison. Here we see PCBM in yellow and PTB7 in blue.



(b) Carbon areal density in atoms/nm². The features shown in the EFTEM image are clearly visible in the carbon density variations. The layer with no carbon content is a gold layer.

(c) Sulfur areal density in atoms/nm². Sulfur is only found in PTB7. This agrees nicely with the EFTEM image and the carbon areal density map.

Figure 4.7: We clearly have qualitative agreement between the sulfur and carbon areal density maps which show features similar to the EFTEM image.

The first is to use the thickness obtained from equations 4.3 or 4.4 and calculate what the sulfur signal should be in a pure PTB7 area. For example, if the sample was 100 nm thick, given a sulfur density of 3.72 atoms/nm³, we would expect an atomic areal density of 372 atoms/nm². We can then divide our actual measurement by this value to obtain a fraction of the predicted total. We express this as

$$\chi = \frac{M_S}{M_{S_{tot}}} \quad (4.7)$$

where M_S is our measured sulfur areal density, and $M_{S_{tot}}$ is the total predicted sulfur areal density for a pure PTB7 region. This is not much better than the previous method for calculating volume fraction since it still works under the criteria that the sample must be of uniform thickness and there must be a pure area to measure the sample thickness. This is not surprising since here we are simply using the sulfur signal instead of the carbon signal.

The third way to calculate volume fraction is by making use of both the carbon and sulfur signal together. In general, the carbon signal is composed of two parts, the PCBM part and the PTB7 part. The sulfur signal, however comes only from the PTB7. We can, therefore, use the sulfur signal to predict how much of the carbon signal is from PTB7. The sulfur signal can be written

$$M_S = \rho_S t_{PTB7} \quad (4.8)$$

where M_S is the measured sulfur areal density, ρ_S is the density of sulfur in PTB7, and t_{PTB7} is the thickness of the PTB7 (not the total thickness). We can then solve for t_{PTB7} and use it in the relation

$$M_{PTB7} = \rho_{PTB7} t_{PTB7} \quad (4.9)$$

where M_{PTB7} is the unknown component of the carbon signal due to PTB7 and ρ_{PTB7} is the carbon density of PTB7. The ratio of M_{PTB7} to the total carbon signal measured gives the fraction of PTB7 in the film.

$$\chi = \frac{M_{PTB7}}{M} = \frac{\rho_{PTB7}t_{PTB7}}{M} = \frac{\rho_{PTB7}M_S}{\rho_S M} \quad (4.10)$$

In this equation we no longer require any area of pure material, and we also do not require that the sample be of uniform thickness. In fact, once the ratio of the component materials is determined we may calculate a thickness for every pixel in our spectrum image based on the carbon areal density with the following equation.

$$t = \frac{M\chi}{\rho_{PTB7}} + \frac{M(1-\chi)}{\rho_{PCBM}} \quad (4.11)$$

This measurement becomes handy because equations 4.5 and 4.7 both need a thickness input that is acquired by assuming pure material somewhere on the sample and also assuming uniform thickness. By using equation 4.11 for the thickness we eliminate both requirements for equations 4.5 and 4.7. In fact, equations 4.5 and 4.7 actually become identical when equation 4.11 is used for the thickness.

4.7.4 Comparing the models

We used the variable thickness from equation 4.11 to generate a thickness map (figure 4.8a) and then used this map as input into equations 4.5 and 4.7 (which result in the same expression) to form the PTB7 volume fraction map shown in figure 4.8b. Figure 4.8c shows the PTB7 volume fraction map obtained from the combined sulfur and carbon signal from equation 4.10. We note that they both show the same overall structure and agree with each other to about 10-20%. One feature that is common is that there is no pure PTB7 anywhere. This is not evident from examining the EFTEM image shown in figure 4.7a. In the EFTEM image it appears as though we have PCBM aggregates in a PTB7 matrix. This would imply that the PTB7 areas

are pure. Instead we see that the maximum PTB7 concentration is between 49% and 64%. This implies that what we are actually seeing is an interconnected network of PTB7 in a matrix of PCBM.

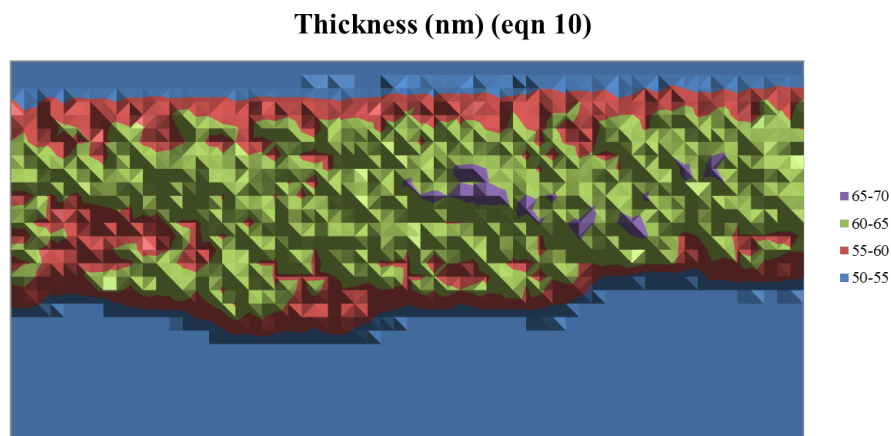
4.7.5 Sources of Error

Agreement between the equations of only 10-20% is not surprising since we know that we have a few uncertainties in our measurements. One source of error is uncertain material densities mentioned earlier. Variation in reported densities may not just be errors in measurement but rather actual variation in density of the material based on processing parameters. For example, the P3HT density in the mixed phase is not necessarily the same as amorphous (or crystalline) P3HT. None of these variabilities are taken into account. Table 4.1 shows the range of values found in the literature for P3HT and PCBM densities. The density for PTB7 was not found in the literature, which prompted our own measurements.

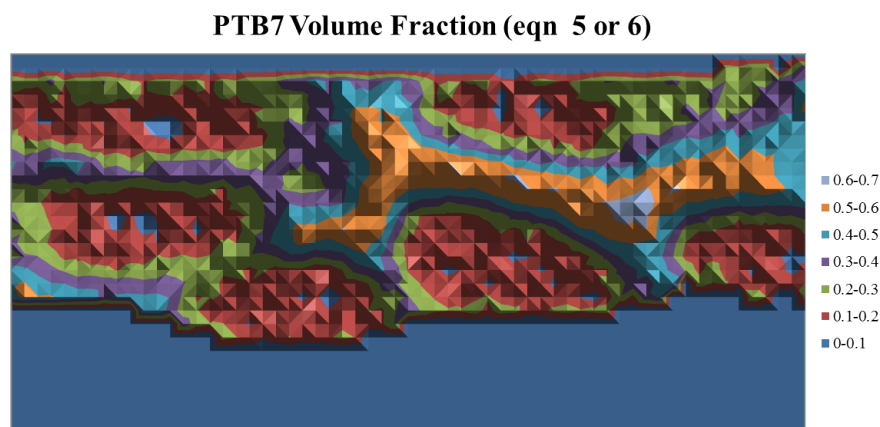
A second source of error is in the fitting of the sulfur signal. The sulfur concentration is fairly low and this results in a small signal on top of a relatively large background. The smaller the signal is, the more uncertain is the measurement. This could lead to inaccurate representations of the PCBM regions (PCBM has no sulfur) and indeed, in the thickness map (figure 4.8a) we see slight structure that follows the PTB7 structure which may be introduced by the sulfur fitting.

A third, less pronounced, source of error is in fitting the carbon signal. This is a strong signal, well above the background. Nevertheless, fitting errors can occur but are generally less than 5% in well-behaved cases.

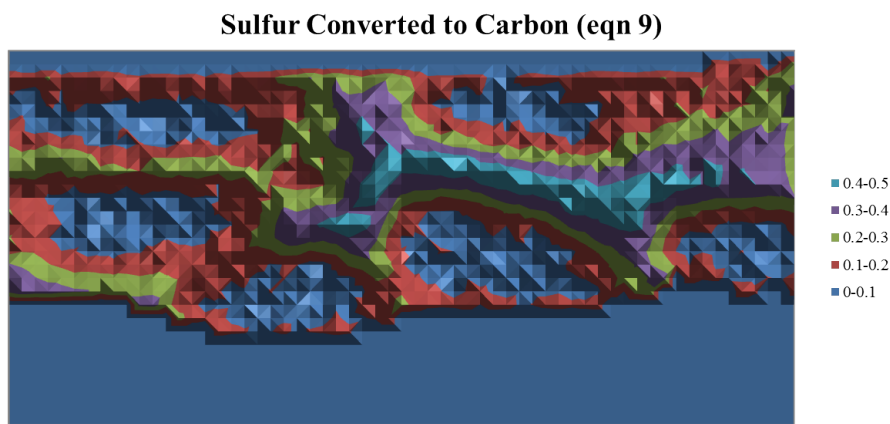
A fourth, possible source of error is that FIB milling may create a thin, dense amorphous carbon layer on the surfaces. This is not taken into account in any of the equations and should have some effect on the calculated volume fractions, how much is, at this point, unknown.



(a) Thickness map based on equation 4.11. Most values lie between 55 and 65 nm.



(b) Volume fraction of PTB7 based on equations 4.5 or 4.7 using the variable thickness (from a)) in lieu of assuming a constant thickness.



(c) Volume fraction of PTB7 based on both the sulfur and carbon signal (equation 4.10).

Figure 4.8: Comparison between the methods for calculating volume fraction of PTB7. We see agreement within about 10-20%.

4.8 Conclusion

We have shown two methods for component material detection in OPV systems, namely EELS imaging for plasmon peak position mapping and EELS imaging for core loss carbon concentration mapping. The plasmon peak position mapping relies on plasmon position shifts that are well established for EFTEM imaging but, to the author’s knowledge, no quantitative position mapping across a sample has been done. Such a map gives slightly more detailed information about the sample because each spectrum can be analyzed independently post-acquisition for possible artifacts.

EELS image analysis for quantitative carbon concentration mapping demonstrated component detection capabilities due to the carbon density differences between P3HT and PCBM. We further demonstrated that carbon and sulfur areal density maps may be transformed into a component ratio map which offers a much more useful quantification of the data. This requires that the sample thickness be known, which we demonstrated can be obtained from the carbon areal density map, with a few assumptions, or from the sulfur and carbon areal densities together without assumptions. The component ratio map may be employed to determine the sharpness of the component separation as well as the purity of the separated phases which will have significant impact on device performance.

The ability to interpret core loss EELS images in terms of absolute atomic density has much farther-reaching applications than just OPV characterization. It could be used in studies on block copolymers, ionomers, or other biological samples. It could be used to determine impurity concentrations, atomic ratios, or ratios of composite materials. Moreover, once the data is converted to atomic density, rather than counts, different experiments under different conditions in different microscopes may be reliably compared to each other.

4.9 Acknowledgment

This research has been made possible through funding by Sustainable Energy and Education Research Center (SEERC), Tennessee Solar Conversion and Storage using Outreach, Research and Education (TN-SCORE), the Department of Energy, Basic Energy Sciences (DOE-BES).

Chapter 5

Phase structure evolution with solvent annealing in OPV devices*

This chapter was adapted from the author’s publication “The Impact of Selective Solvents on the Structure and Function Evolution in Solvent Annealed Organic Photovoltaics” [Hu et al. \(2014\)](#).

5.1 Abstract

This study examines a photovoltaic thin film comprised of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). In order to link performance of these organic solar cells to their mechanical properties and fabrication techniques, the effects of four solvents used to promote phase separation between P3HT and PCBM during solvent vapor annealing (SVA) were examined. Evolution of P3HT crystallinity as well as the growth of PCBM aggregates in the solvent annealed thin films was observed by Grazing Incidence Wide Angle X-ray Scattering (GIWAXS), and Energy Filtered Transmission Electron Microscopy (EFTEM).

For the solvents that have a finite P3HT solubility, P3HT crystallinity increases initially then decreases with time. PCBM aggregates grow continuously with SVA,

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modulated by the PCBM solubility. High P3HT crystallinity and moderate PCBM phase separation correlates to improved power conversion efficiency (PCE). Relative P3HT/PCBM solubility plays the crucial role in choosing the best SVA time of different annealing solvents. For the samples annealed using solvents that prefer P3HT, PCE benefits from further SVA after P3HT crystallinity peak time, which is ascribed to the additional PCBM phase separation; whereas the PCBM preferred solvents induce excess PCBM phase separation at further SVA times, which limits exciton dissociation hence PCE. EFTEM cross section images indicate that PCBM is distributed toward the bottom, whereas SVA with high PCBM solubility may induce PCBM to move towards the surface, which benefits charge transport processes by preventing electron-hole recombination.

5.2 Introduction

Organic photovoltaic (OPV) solar cells are a promising technology to provide clean and renewable energy, primarily because they are lightweight, low cost, and flexible [Krebs \(2009\)](#); [Chen et al. \(2009a\)](#); [Peet et al. \(2009\)](#). The archetypal bulk heterojunction (BHJ) cell consists of a mixture of regio-regular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), which serve as electron donor and acceptor respectively [Bavel et al. \(2009b\)](#); [Savenije et al. \(2005\)](#); [Ma et al. \(2005\)](#). The power conversion efficiency (PCE) of this type of solar cell, i.e., exciton dissociation and charge transport, is a very intricate function of the morphology of the active layer [Dennler et al. \(2009\)](#); [Li et al. \(2005\)](#).

In BHJ solar cells, excitons dissociate at the interface between donor and acceptor, where the separate holes and electrons must then travel to each electrode respectively [Nalwa \(1997\)](#). Thus, the ideal morphology of the BHJ active layer has often been depicted as a nanoscale phase separated structure with domains that are less than the exciton diffusion length (around 10-20 nm), thus enabling bi-continuous percolation paths for charge transport [Yu et al. \(1995\)](#); [Halls et al. \(1995\)](#); [Gadisa et al. \(2007\)](#);

Chen et al. (2009b). Recently, a 3-phase model for the BHJ domain has also been proposed, namely, a system that contains a P3HT crystalline phase, a PCBM rich phase and a miscible amorphous phase of P3HT and PCBM, where the miscibility and interdiffusion of P3HT and PCBM plays a pivotal role in determining the nanoscale morphology Yin and Dadmun (2011); Chen et al. (2012b). However, in most common fabrication processes, fast solvent evaporation occurs during spin coating, which kinetically blocks the evolution of the structure, initially forming a thin film with minimal crystallization and phase separation of the two components: a morphology that results in poor photovoltaic performance. In addition, it has been found that the electron acceptor material PCBM forms a PCBM-rich layer in the bottom of the thin film, which is attached to the PEDOT:PSS layer as well as the anode ITO glass in a conventional solar cell; while a P3HT-rich layer, which serves as the electron donor, prefers to occupy the top of the thin film, connecting to the cathode. Such a vertical structure due to the different component surface energies γ ($\gamma = 26.9 \text{ mNm}^{-2}$ for P3HT and $\gamma = 26.9 \text{ mNm}^{-2}$ for PCBM) Germack et al. (2010) will result in a longer path-length for both electron and hole transportation to each electrode, which in turn dramatically increase the probability of exciton recombination Yip and Jen (2012). As a result, a number of groups have adopted thermal annealing (TA) of the sample immediately after spin coating to allow the system to evolve towards equilibrium. This thermal annealing induces in-plane $\pi - \pi$ stacking of P3HT chains where charges can easily transport from one grain to another, improving the photovoltaic performance of the active layer Lloyd et al. (2007); Kim et al. (2006); Honda et al. (2009). However, the undesirable vertical structure can only be slightly modified by TA method, while the conjugated polymer may also suffer degradation or large-scale phase separation during TA at an elevated temperature which detrimentally affects the photovoltaic cell performance Woo et al. (2008).

As an alternative protocol, solvent vapor annealing (SVA) has been used to impart molecule mobility of the BHJ components, allowing accurate control of P3HT crystallinity Li et al. (2005, 2007); Lu et al. (2008). During SVA, the OPV thin films

are exposed to a specific solvent vapor environment, where the solvent molecules diffuse into the deposited layer, which induces a change in the nanoscale morphology. The thermodynamic driving forces that lead to these morphological changes are still not well understood. Several parameters such as treatment time, solubility of both polymer and fullerene in the solvent, and solvent vapor pressure, can dramatically impact the structural changes that occur during solvent annealing [Tang et al. \(2010\)](#). It has been reported that solvents with high P3HT solubility can induce excess phase separation creating domains that exceed the exciton diffusion length limiting exciton dissociation [Jou et al. \(2007\)](#); [Park et al. \(2009\)](#). By adjusting the component solubility of the annealing solvent, vertical distribution of P3HT and PCBM phase can potentially be tuned, thus substantially reduce the exciton recombination rate. Therefore, there is a critical need to fundamentally understand how these factors can be readily manipulated to impact the morphological evolution and optimize the solvent annealing process of BHJs.

To this end, a comprehensive experimental study has been conducted to ascertain the effect of SVA on the morphology and OPV performance of P3HT:PCBM active layers, using a series of organic solvents with different component solubility. The solubility of P3HT or PCBM in the examined solvents is measured by UV-Vis. The crystalline structure and the phase separation behavior of the BHJ are first examined using Grazing Incidence Wide Angle X-ray Scattering (GIWAXS). The power conversion efficiency of the resultant active layers was then measured to correlate the structure of the resultant P3HT:PCBM film to OPV function. In addition, Energy Filtered Transmission Electron Microscopy (EFTEM) was used to examine the extent of both horizontal and vertical phase separation.

5.3 Experimental

5.3.1 Materials

All solvents were purchased from Aldrich and used as received. Regioregular P3HT (Mn=37k, PDI=2.0, RR=90-93%) and PCBM (99.5%) were purchased from Reike Metals Inc., and Nano-C Inc., respectively.

Silicon wafers were used as substrates and were first cleaned in hot piranha (1:3 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$) for 30 min followed by washing in abundant deionized (DI) water and dried using a stream of nitrogen gas. P3HT:PCBM (1:0.8, w/w) was then dissolved in *o*-dichlorobenzene (ODCB) to achieve a solution with P3HT and PCBM concentrations of 10 mg/ml and 8 mg/ml, respectively. By spin coating the solution on the silicon wafers, thin films with thickness of around 70 nm were obtained.

5.3.2 Solvent Annealing

Four solvents with different P3HT and PCBM solubility and vapor pressure were used as the solvent in the solvent annealing process; Bromobenzene (BB), Chlorobenzene (CB), Toluene (TL), 2-Chlorophenol (2-CP). A schematic of the solvent annealing apparatus is shown in Figure 5.1, where the total length of the vapor gradient L_0 , i.e., the distance from column opening to solvent surface is 100 cm. The solvent vapor pressure gradient is allowed to reach equilibrium after solvent is added into the column.

For all solvent annealing procedures, the P3HT:PCBM mixture is positioned at $L/L_0=0.9$. This results in the vapor pressure of the solvent during annealing being 90% of the pure solvent vapor pressure. Table 5.1 lists the saturated vapor pressure of the four solvents used in this study at 20, as well as the vapor pressure of the solvent at the surface of the annealed sample (surface vapor pressure).

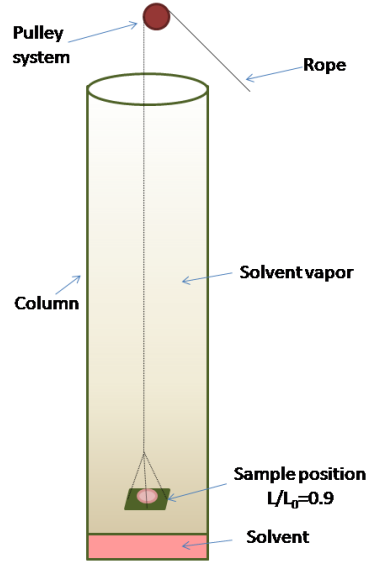


Figure 5.1: Schematic of the solvent vapor annealing apparatus: Variation in solvent vapor pressure during annealing is achieved by changing the position of wafer surface with respect to the solvent surface. $L/L_0 = 0.90$ is used in our experiment.

Table 5.1: Measured solubility of P3HT and PCBM in solvents for SVA and saturated and surface vapor pressure of each solvent.

Solvent	Vapor Pressure 20 (mmHg)		Measured Solubility (mg/ml)	
	Saturated VP	Surface VP	P3HT	PCBM
Bromobenzene (BB)	3.3	2.97	107.9	33.4
Chlorobenzene (CB)	8.8	7.92	33.8	39.4
Toluene (TL)	22	19.8	1.4	16.3
2-Chlorophenol (2-CP)	2.2	1.98	0.1	128.3

5.3.3 Solubility Measurements

The solubility of P3HT and PCBM in the solvents of interest was determined via UV-Vis spectroscopy using Thermo Scientific Evolution 600 UV-Visible spectrophotometers. In this experiment, the absorbance of solutions with known concentration is monitored at 600 nm. According to the Beer-Lambert Law,

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon \cdot c \cdot L \quad (5.1)$$

where A is the measured absorbance, I_0 is the intensity of the incident light, I is the transmitted intensity, L is the path length (1mm), c is the concentration of the absorbing species, and ϵ is the extinction coefficient. Plotting the absorbance as a function of known concentration provides a measure of the extinction coefficient, ϵ . With knowledge of ϵ , the measured absorbance of a solution with unknown solute concentration provides a method to determine the solute concentration.

This UV-Vis method was used to determine the solubility of P3HT and PCBM in all four solvents, and presented in Table 5.1. These results show that BB has the highest P3HT solubility, followed by CB, TL, and 2-CP; while the PCBM solubility is 2-CP > TL > CB > BB.

5.3.4 Characterization

Grazing Incident Wide Angle X-ray Scattering (GIWAX)

Grazing Incidence Wide Angle X-ray Scattering (GIWAX) was used to monitor the crystallinity of the P3HT in the thin film using a Phillips X'pert-Pro diffractometer in grazing-incidence geometry with 45Kv tube voltage and 40mA tube current. The diffraction was measured using 2θ scanning mode from 2 θ 20 The (100) peak area was analyzed to characterize the amount of crystallinity in the polymer, while Scherrer's

equation was used to calculate the size of the polymer crystals L **B. D. Cullity (2001)**

$$L = \frac{0.9\lambda}{b \cos \theta} \quad (5.2)$$

where b is the full width at half maximum (FWHM) of the (100) peak of the P3HT crystals.

Current-Voltage (J-V) Characterization

The conventional organic solar cells with the architecture of ITO/PEDOT:PSS/P3HT:PC61BM (1:0.8, 9 mg/ml)/Ca/Al were studied in this paper. PEDOT:PSS (40 nm, Baytron P 4083) was spin cast on top of pre-cleaned and UV-treated ITO substrates, then baked at 125 for 15 min. The active layer was spin cast on top of PEDOT:PSS in a glove box at 1000 rpm for 90 s. Thereafter, solvent annealing was carried out per aforementioned protocol. The device preparation was followed by thermal deposition of 40 nm Ca and 80 nm Al under a vacuum of 3×10^{-7} Torr. All the devices are encapsulated before characterization and the non-annealed devices are used as control devices. The photovoltaic parameters were deduced from current density versus voltage (J-V) characterization by using a Keithley 2400 source meter under photo-illumination of AM 1.5G 100 mW/cm² from Thermal Oriel 96000 300 W solar simulator.

Transmission Electron Microscopy (TEM)

For microscopic analysis a Zeiss Libra 200MC energy filtered, monochromated transmission electron microscope (TEM) was used with an accelerating voltage of 200 kV. Sample preparation for cross-section imaging was performed in a Zeiss Auriga Crossbeam focused ion beam (FIB) scanning electron microscope (SEM). A final polish at 10 pA and 10 kV accelerating voltage was used to limit artifacts introduced through beam damage.

Sample preparation for plan view samples was performed using a float-off technique whereby the P3HT:PCBM layer was removed from a silicon substrate by

immersion in deionized water. The water was then drained so that the P3HT:PCBM film came to rest on a 400 mesh copper TEM grid. Each sample was dried in a slide warmer at 60 overnight.

Energy filtered TEM (EFTEM) images have been used with success to determine phase separation in similar heterojunction samples [Drummy et al. \(2011\)](#); [Herzing et al. \(2010\)](#); [Pfanmüller et al. \(2011\)](#). Following the established techniques, images were taken with a slit width of 8 eV centered at 19 and 30 eV. The resulting images are artificially colored blue and yellow, and superimposed. In these composite images a distinct phase separation between the P3HT and PCBM can easily be seen which facilitates a qualitative analysis of structure sizes and interconnectivity.

5.4 Results and Discussion

5.4.1 Grazing Incidence Wide Angle X-ray Scattering (GI-WAX)

The GIWAXS scattering curves of the P3HT/PCBM spin-coated film before and after solvent annealing are presented in Figure 5.2. In this Figure, the (100) crystalline peak of P3HT is found at $2\theta = 5.4$. The d-spacing does not change between the as-cast and solvent annealed thin films, whereas the area under the (100) peak and the full width at half maximum (FWHM) of the peak does change. This indicates that the P3HT crystallinity and crystal size (L) transforms during SVA.

Figure 5.3 shows the change in the area of the (100) P3HT peak with solvent annealing time for the solvents studied. All samples exhibit a crystallinity increase at the initial exposure to each solvent vapor. This is attributed to enhanced P3HT mobility imparted by the presence of solvent vapor, which allows P3HT to crystallize. However, for the three solvents with some P3HT solubility $\sim > 1$ mg/ml, i.e., BB, CB, and TL, the crystallinity decreases dramatically when exposed to solvent vapor for an extended period of time. This loss of crystallinity is attributed to the dissolution

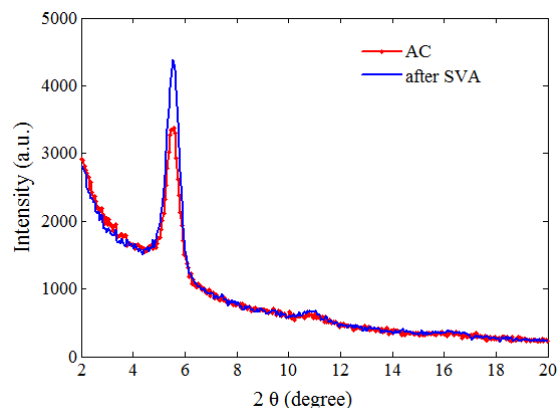


Figure 5.2: Comparison of GIWAX peak of the thin film before and after SVA in CB.

of the P3HT crystals by the absorbed solvent vapor. However, the crystallinity of P3HT in the sample that was vapor annealed in 2-CP does not show this decrease.

2-CP is a non-solvent for P3HT, indicating that polymer solubility is a crucial parameter that controls the ordering of the polymer during solvent annealing. The increase in crystallinity at the onset of SVA in 2-CP is ascribed to the high solubility of PCBM in 2-CP and miscibility of PCBM in amorphous P3HT [Yin and Dadmun \(2011\)](#); [Chen et al. \(2012b\)](#); [Treat et al. \(2011b\)](#); [Chen et al. \(2011\)](#). For all the SVA samples in this study, the time at which the maximum crystallinity is reached is inversely proportional to the P3HT solubility, since higher P3HT solubility increases the amount and rate of absorbed solvent vapor, more quickly allowing the P3HT chains to assemble into the crystalline form.

Figure 5.4 shows the evolution of P3HT crystal size in each solvent annealed thin film as calculated from the 100 peak area. The samples that are solvent annealed in solvents with finite P3HT solubility show a decrease in crystal size at long solvent anneal times, but the crystal size remains relatively constant when annealing in 2-CP. This demonstrates that the dissolution and formation of the P3HT crystals during SVA is mainly influenced by the P3HT solubility in the annealing solvent. In addition, for all the samples annealed in the four different solvents, neither the peak time crystallinity nor the crystal size vary too much from each other.

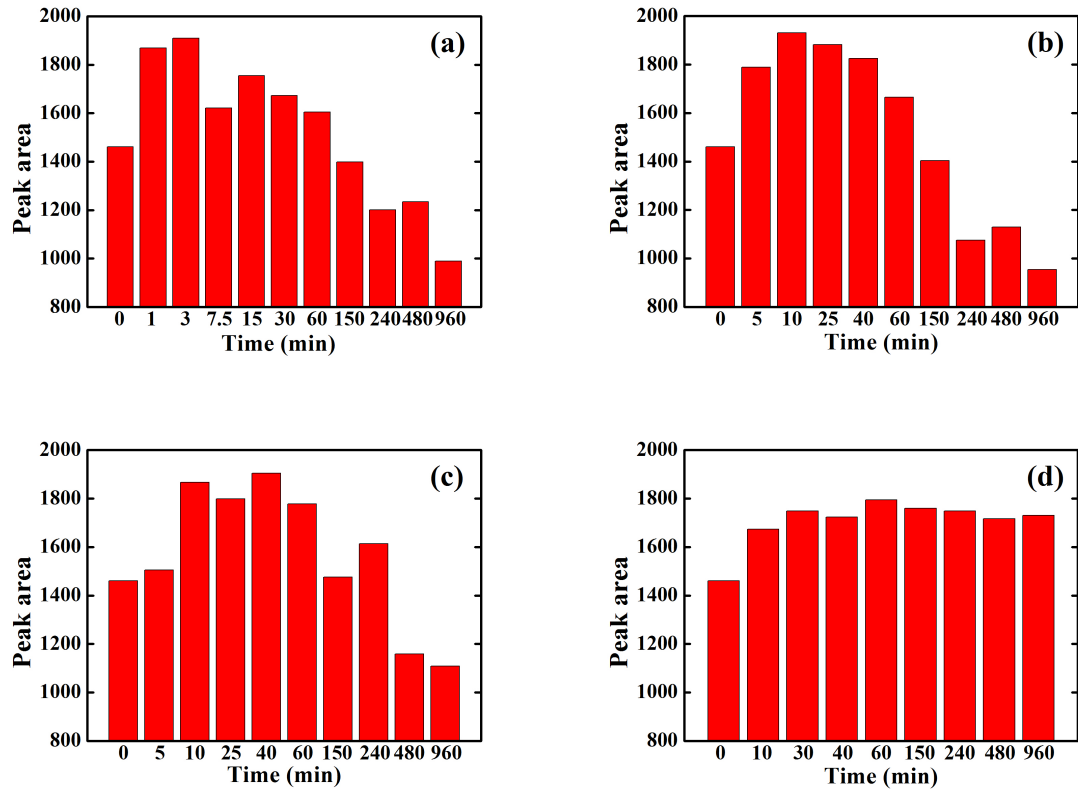


Figure 5.3: Area of the P3HT (100) peak in the various solvent annealed P3HT/PCBM samples: (a) BB; (b) CB; (c) TL; (d) 2-CP.

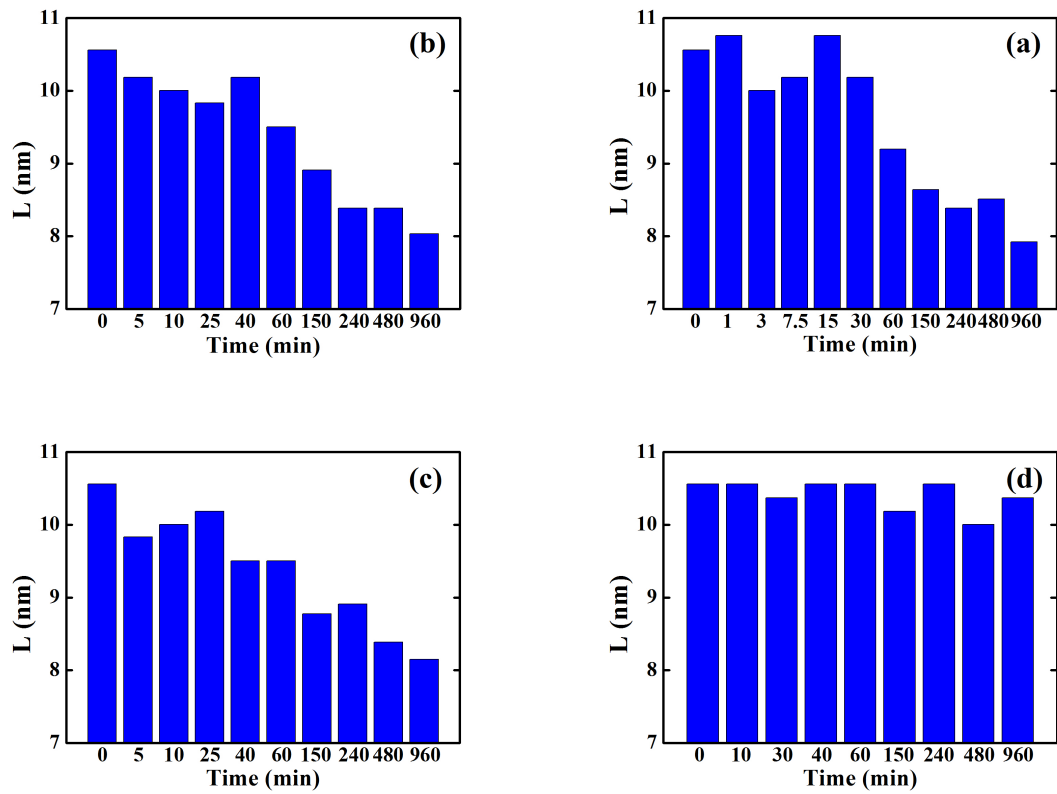


Figure 5.4: P3HT crystal sizes of the P3HT/ PCBM sample annealed in various solvents: (a) BB; (b) CB; (c) TL; (d) 2-CP.

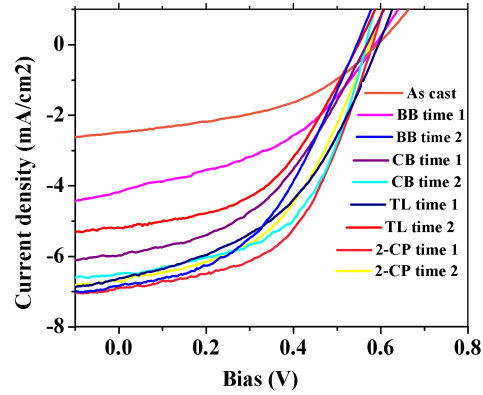


Figure 5.5: J-V curves of solvent annealed P3HT/PCBM composite films.

5.4.2 Solar Cell Performance

To correlate the morphology changes that occur with SVA to the photovoltaic performance of the OPV active layer, nine identical solar cells were fabricated and solvent vapor annealed for the SVA conditions at time1, which is the P3HT crystallinity peak time and time 2, which is approximately double the peak time. The reason of choosing both time is because the time 2 crystallinity for each sample is only slightly lower than peak time crystallinity. Therefore, PCBM phase separation becomes the primary factor that determines efficiencies of the compared samples. The J-V curves and the corresponding PCE data for these samples are presented in Figure 5.5 and Table 5.2. These results show that J_{sc} improves substantially for all solvent annealed samples, and the overall power conversion efficiency (PCE) increases as well. At time 1, where all samples have attained peak P3HT crystallinity, the sample that is annealed in 2-CP exhibits the highest PCE, followed by the samples annealed in TL, CB and BB. At time 2, the samples annealed in BB and CB, which has a higher P3HT solubility than PCBM solubility show an increase in their PCE, while a slight decrease of cell performance at time 2 is found for the other two samples annealed in TL and 2-CP which prefer PCBM than P3HT. This variation is primarily a consequence of the differences in PCBM phase segregation.

Table 5.2: Photovoltaic performance of the solvent annealed active layers

	Sample	Time (min)	(100) area	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE
Time 1	AC	0	1420	2.482	0.591	44.6	0.65
	BB	3	1909	4.183	0.587	42.4	1.04
	CB	10	1931	5.974	0.567	44	1.49
	TL	40	1905	6.618	0.595	44.9	1.77
	2-CP	30	1799	6.888	0.583	52.3	2.1
Time 2	BB	7.5	1621	6.832	0.543	45.8	1.7
	CB	25	1882	6.486	0.567	54.3	2
	TL	60	1778	5.193	0.547	47.8	1.36
	2-CP	60	1794	6.684	0.575	47.7	1.83

Therefore, the development of PCBM phase separation during different solvent annealing was also investigated to account for the aforementioned changes in PCE performances.

5.4.3 TEM Measurements

To establish the relationship between P3HT/PCBM phase separation and solar cell performance, EFTEM images for both horizontal and vertical P3HT/PCBM phase distribution were measured for four typical samples with different PCE performances, i.e., BB time 1, CB time 1, 2-CP time 1 and TL time 2 in Figures 5.6 and 5.7. Energy windows were positioned at 19 eV for P3HT and 30 eV for PCBM, marked as blue and yellow respectively. The dark and light areas are caused by thickness variations as verified in zero energy filtered images (not shown). The horizontal PCBM phase separation in Figure 5.6 indicates that TL time 2 has the largest PCBM domain size, corresponding to the highest PCBM phase separation, followed by 2-CP, CB and BB annealed samples at each P3HT crystallization peak time. When we compare these results with PCE performances, we can conclude that moderate PCBM domain size, i.e., 2-CP time 1, is preferred for obtaining the best OPV performance.

From Figure 5.7 it is evident that PCBM is more prevalent in the bottom of the thin film (closest to the Si substrate), leaving the P3HT phase on top. The obtained distribution of P3HT-rich layer on top and PCBM-rich layer on the bottom is in

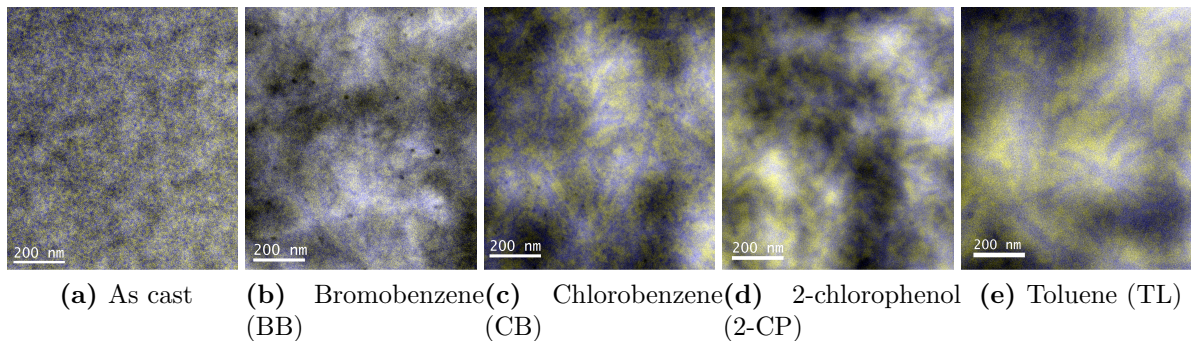


Figure 5.6: EFTEM images showing the solvent chosen for solvent annealing has a clear effect on the promotion of phase separation between P3HT and PCBM. Blue corresponds to an energy window at 19 eV (P3HT), yellow corresponds to an energy window at 30 eV (PCBM). The dark and light areas are caused by thickness variations as verified in zero energy filtered images (not shown).

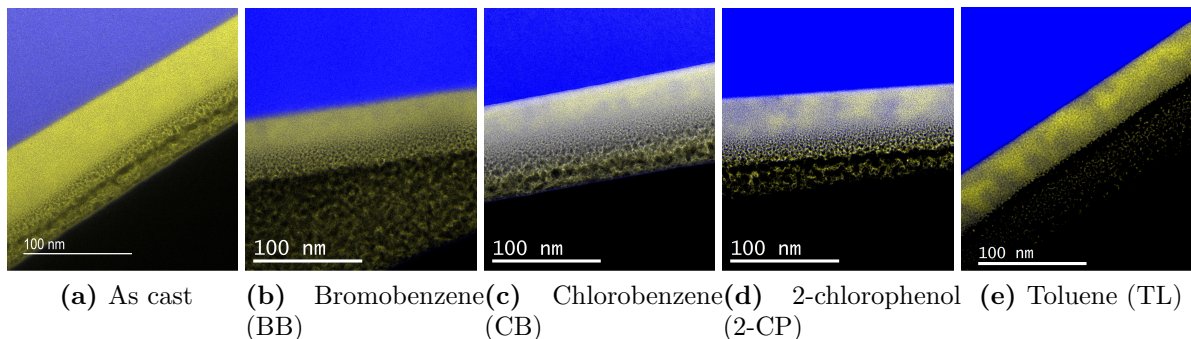


Figure 5.7: EFTEM images in cross-section reveal a higher concentration of PCBM close to the substrate. The Si substrate appears blue due to the large bulk plasmon peak of Si near the 19 eV energy window.

agreement with prior studies, and is primarily due to the difference between P3HT and PCBM surface energy, which induces selective molecule segregation during spin coating [Germack et al. \(2010\)](#); [Yip and Jen \(2012\)](#).

In Figure 5.7 we also see a thin layer of textured material under the platinum cap. This seems to be a result of the ion beam platinum deposition directly onto the polymer material. In most studies the researchers have finished the devices with top contacts that then act as a protective layer under the FIB beam. These samples had

no such layer and the top surface appears altered. The material beneath this region appears undisturbed.

When comparing vertical phase separation in Figure 5.7, BB time 1 shows little contrast between P3HT and PCBM, which means there is little vertical phase separation. The film annealed with CB at time 2 exhibits some vertical phase separation, however, more PCBM is found near the bottom layer, which is not beneficial for the cell performance due to the promotion of exciton recombination. The sample annealed with 2-CP time 1 and TL time 2 both illustrate more elevated PCBM phase distribution along the film thickness, which is driven by the high PCBM solubility of the annealing solvents with the higher vapor concentration at the thin film surface than the bottom. However, excess PCBM aggregation in TL time 2 sample reduces the interface for exciton dissociation and charge transportation, resulting in a decreased PCE when comparing with the sample annealed with 2-CP at time 1.

Comparing with the AFM results, the PCBM domain sizes revealed through EFTEM show the same sequence as their surface PCBM aggregations and RMS roughness, which demonstrate that the surface roughness may be correlated with the PCBM aggregation/phase separation throughout the film, and is driven by both PCBM solubility and SVA time. Also, the rate of P3HT crystal growth is controlled by the solubility of P3HT in the annealing solvents, as indicated previously, therefore the relative solubility, i.e., the ratio of P3HT solubility to PCBM solubility, plays the significant role in choosing the optimal SVA time for different solvents.

Specifically, the samples that are vapor annealed in BB and CB have relatively small PCBM phase separation at the P3HT crystallinity maximum time, which may be ascribed to the fact that P3HT is more soluble in those two solvents than PCBM. This preference for P3HT results in enhanced P3HT molecular mobility, which brings about a faster P3HT crystallization than PCBM aggregation. At the peak P3HT crystallinity time, PCBM has not had sufficient time to aggregate. This limits electron transport in these samples. Further SVA endows more PCBM aggregation, providing more pathways for electron transport and benefiting cell performance.

On the other hand, PCBM has a higher solubility in TL and 2-CP than P3HT. This results in faster PCBM phase separation at the P3HT crystallinity peak time which produces better PCE performance for TL and 2-CP annealed samples at their peak times. Excessive PCBM aggregation is induced at longer annealing times for these two samples, which reduces P3HT/PCBM interfacial area and exciton dissociation, as well as introducing the potential for isolated PCBM domain formations which limit charge transport. Therefore, a reduced PCE is found in these cases.

5.5 Conclusion

The solubility of P3HT and PCBM clearly impacts the development of the morphology of P3HT/PCBM active layers during solvent vapor annealing, which in turn determines the OPV performance of the resultant solar cell. Two distinct phenomena are observed in the morphological progression of the solvent annealed thin films: an evolution of P3HT crystallinity as well as the development of PCBM phase separation.

For the solvents that have a finite P3HT solubility, SVA initially increases P3HT crystallinity until reaching a limiting value. Solvent vapor annealing beyond this optimum lowers crystallinity presumably by dissolving already formed P3HT crystals. The solubility of P3HT in the vapor annealing solvent is pivotal in determining the variation of P3HT crystallinity with solvent annealing. However, the P3HT/PCBM sample that is solvent annealed in 2-Chlorophenol vapor, which has negligible P3HT solubility also favors P3HT crystallinity enhancement by aiding P3HT mobility in the miscible amorphous phase.

A PCBM-rich phase, formed by PCBM aggregation continuously grows with solvent vapor annealing for all solvents studied. The rate of this growth is controlled by the PCBM solubility in the annealing solvent. As might be expected, moderate PCBM aggregation, is preferred, as extended phase segregation reduces interfacial area between P3HT and PCBM, limiting exciton dissociation. Similarly, excess

segregation can lead to isolated domains that limit charge transport to the electrodes; both factors will decrease PCE performance.

Just as the rate of P3HT crystal growth is controlled by the solubility of P3HT in the vapor annealing solvents, the PCBM solubility directs the PCBM aggregation, therefore relative P3HT/PCBM solubility plays the significant role in tuning the right SVA time. Active layers that are annealed in solvent that prefer P3HT (BB and CB in this study) form a P3HT pathway for charge transport before the PCBM domains are able to support efficient electron transport to the electrodes. These samples benefit from further solvent annealing to allow additional PCBM aggregation, but risk the loss of P3HT crystallinity.

P3HT/PCBM thin films that are solvent annealed in solvents that prefer PCBM (TL and 2-CP in this study) show a decrease in active layer performance with excess solvent annealing, which can be ascribed to phase segregation of the PCBM into larger and potentially inaccessible domains that limit exciton dissociation and charge transport pathways to the electrode.

Plan view EFTEM images and AFM surface analysis confirm the relationship between PCE and PCBM aggregation, indicating best PCE corresponds to a moderate PCBM phase separation. Cross sectional P3HT/PCBM phase distribution illustrates an upward movement of PCBM molecules for the samples annealed by solvents which have higher PCBM solubility (2-CP and TL). This benefits the cell performance by providing a more direct path to each electrode.

Chapter 6

High-efficiency $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells*

6.1 Introduction

The recent emergence of organometal halide perovskite solar cell is rising as a promising solar energy harvester with the power conversion efficiency (PCE) rapidly increasing to over 15% in a short time [Burschka et al. \(2013\)](#); [Liu et al. \(2013\)](#). The perovskite material has the form ABX_3 where X is an anion and A and B are cations. In the case of solar cells the perovskite is an organic-inorganic metal halide with the cation A usually being methylammonium (CH_3NH_3^+) [Green et al. \(2014\)](#), the cation B almost always Pb (although success with Sn has recently been reported [Noel et al. \(2014\)](#)), and the anion X I, Br, or Cl [Green et al. \(2014\)](#).

Due to the excellent charge transport property, organometal halide perovskites were initially employed in the semiconductor channel layer to fabricate thin film transistors [Kagan et al. \(1999\)](#). A recent pioneer work found that these hybrid perovskites could also be used as light absorbing dye to make dye sensitized solar cells, which could yield PCE of 3.5% [Kojima et al. \(2009\)](#). After only about five

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years of rapid development, the perovskite photovoltaic cells show a potential for competing with other thin film photovoltaic technologies with the advantages of solution casting capability and excellent optoelectronic properties, including widely tunable direct bandgaps of 1.5-2.2 eV with appropriate structure modification [Eperon et al. \(2014a\)](#); [Edri et al. \(2013\)](#), and large absorption coefficients comparable to those of traditional photovoltaic materials (e.g., silicon, CdTe) [Green et al. \(2014\)](#). A high PCE of over 15% has been demonstrated by using either a mesoporous scaffold structure of titanium oxide (TiO_2) to maximize the interfacial contact area between the perovskite dye and TiO_2 electron transporting layer for efficient charge extraction [Burschka et al. \(2013\)](#), or a simpler planar heterojunction device with a perovskite layer sandwiched between electron transporting layer (e.g., TiO_2 , ZnO) and hole transporting layer (e.g., Spiro-OMeTAD) [Liu et al. \(2013\)](#); [Liu and Kelly \(2013\)](#). Despite this important progress, the perovskite photovoltaic community is focusing research interest on improving material and film processing control [Eperon et al. \(2014b\)](#); [Jeon et al. \(2014\)](#); [Dualet et al. \(2014\)](#); [Tan et al. \(2014\)](#), interfacial engineering [Zhou et al. \(2014\)](#), and advanced optical management [McGehee \(2013\)](#), toward even higher efficiencies of 25% [Green et al. \(2014\)](#); [Service](#). In addition, understanding how to extend the long term stability of these materials and associated photovoltaic devices is another key challenge [Service](#). Both device efficiency and stability in perovskite absorbers (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$) are believed to be significantly affected by the crystal growth, evolution of phase transition and morphology during synthesis and environmental exposure, where fundamental systematic studies are needed.

Fully solution processed, planar devices almost always underperform when compared with the more complicated mesoporous superstructured devices. Most planar, solution processed devices fall in the 9-12% range [Conings et al. \(2014\)](#); [Liu et al. \(2013\)](#); [Eperon et al. \(2014b\)](#). There are a few notable exceptions, however. [Liu et al. \(2013\)](#) demonstrated over 15% efficient planar devices. These were fabricated through the use of vapor deposition rather than solution processing

but it suggests that the planar architecture still holds promise to approach 20% and that a more pristine perovskite layer sharply increases performance. [Liu and Kelly \(2013\)](#) demonstrated over 15% efficiency with fully solution processed planar devices employing a ZnO electron transport layer. ZnO has a much higher electron mobility than TiO₂ and does not require annealing. [Eperon et al. \(2014a\)](#) demonstrated that lowering the band gap of the perovskite material by replacing the methylammonium cation with formamidinium may improve the planar device efficiency to as high as 14% (though the batch average was 10%). This gives hope that simple, solution processed, planar devices may realistically reach 20% efficiency. Indeed, [Liu et al. \(2014\)](#) performed numerical simulations indicating that 20% efficiency should be possible in an optimized planar device provided the defect density was sufficiently low. The first step is to develop fabrication techniques that result in more pristine perovskite crystals that perform as well as those produced by vapor deposition.

In this work, we demonstrate reproducible, high-efficiency, solution-processed, planar perovskite solar cells. The average efficiency was 15.8%, on par with those produced by vapor deposition. The highest efficiency attained was 17.9%. This is rather surprising since (to the author’s knowledge) no other solution processed, planar device, employing a TiO₂ electron transport layer, has achieved over 12%. The reason for this marked improvement, we believe, is twofold: large-scale single crystal domains which lower the defect density in the absorber and formation of a bulk-heterojunction structure which improves charge carrier extraction and increases the active volume. We also investigated the degradation mechanisms of the perovskite materials with the aim of extending the long-term stability of perovskite photovoltaic cells.

15% Loss the anode.

6.2 Device Characterization

We used a source meter (Keithley 2400) to record the J-V curves. The device was illuminated at 100 mWcm⁻², AM 1.5 G solar spectrum. The light intensity of the

lamp was calibrated with Si-reference cell certified by Newport. The device area was defined by the non-reflective mask of 6.5 mm² to rule out the extra-photocurrent generation through sides. The J-V curves were measured in N₂ filled glovebox by sweeping from reverse bias (-0.2 V) to forward bias (1.2 V) and forward bias (1.2 V) to reverse bias (-0.2 V), with the step size of 35 mV, and sweep delay time of 50 ms.

6.3 X-ray diffraction

The X-ray diffraction pattern (2θ scans) were measured from the perovskite films/silicon substrate (100) using an X-ray diffractometer (Panalytical X'Pert Pro), using Cu-K α radiation ($\lambda=1.54050\text{\AA}$).

6.4 Electron Microscopy

The (S)TEMs used in these studies were a Zeiss Libra 200MC operated at 200 kV, and a VG 501HB operated at 100 kV.

TEM samples were prepared via FIB milling in a Zeiss Auriga dual beam SEM FIB. Final polishing was performed at an accelerating voltage of 10 kV or less, with a beam current of 20 pA to limit artifacts from beam damage.

The surface morphological images were taken with scanning electron microscopy (SEM; Zeiss Merlin SEM). The operation voltage was 5 kv. The signal was collected by an in-lens secondary electron (SE) detector.

6.5 Fabrication Methods

The pre-cleaned ITO glass substrates were treated with UV-Ozone for 10 minutes, and then the TiO₂ precursor solution was spin coated onto the ITO substrates. Subsequently, the TiO₂ precursor substrates were fired in furnace at 500 °C for 30 minutes. The PbI₂ solution and CH₃NH₃I solution were sequentially spin-coated on

the TiO₂ substrates. Subsequently, the films were thermally annealed at 100 °C in the N₂-filled glovebox. The spiro-OMeTAD solution was spin coated onto the obtained perovskite films. A top metal contact silver layer with thickness of 100 nm was deposited with thermal evaporation method under vacuum level of 10⁻⁶ mbar. The deposition rate was 1 Å/s.

6.6 Results and discussion

6.6.1 Device Performance

As shown in the XRD pattern in figure 6.1a, the pristine perovskite CH₃NH₃PbI₃ was formed as a result of chemical reaction between PbI₂ and CH₃NH₃I. Two major tetragonal perovskite peaks showed up at 2 theta angle 14.03 and 28.06, which correspond to the (110) and (220) planes in tetragonal phase, respectively. From the SEM image (figure 6.1b), we directly observed layered structure perovskite crystal domains with size of 1 micrometer in the obtained perovskite films, Based on the high quality perovskite films, the fabricated typical photovoltaic device yielded J_{sc} of 21.3 mA/cm², V_{oc} of 1.02 V, FF of 72.7%, and PCE of 15.8%, as shown in figure 6.1c.

6.6.2 Demonstration of Large Scale Single Crystal Domains

The pursuit of large-scale single crystal domains is of great importance in extending the carrier diffusion length and suppressed carrier recombination loss in perovskite solar cells. Growth of large-scale single crystals is still challenging for conventional one-step spin-coating a mixed-solution of lead iodide (PbI₂) and methyl ammonium iodide (CH₃NH₃I). This is due to the formation of a large quantity of stable CH₃NH₃PbI₃ seed clusters during one-step mixed-solution processing [Burschka et al. \(2013\)](#), the nucleation of CH₃NH₃PbI₃ seed clusters preferentially dominates over the crystal-growth during the crystallization process, resulting in substantial difficulty in achieving large-scale single crystals. Since the SEM image showed highly crystalline

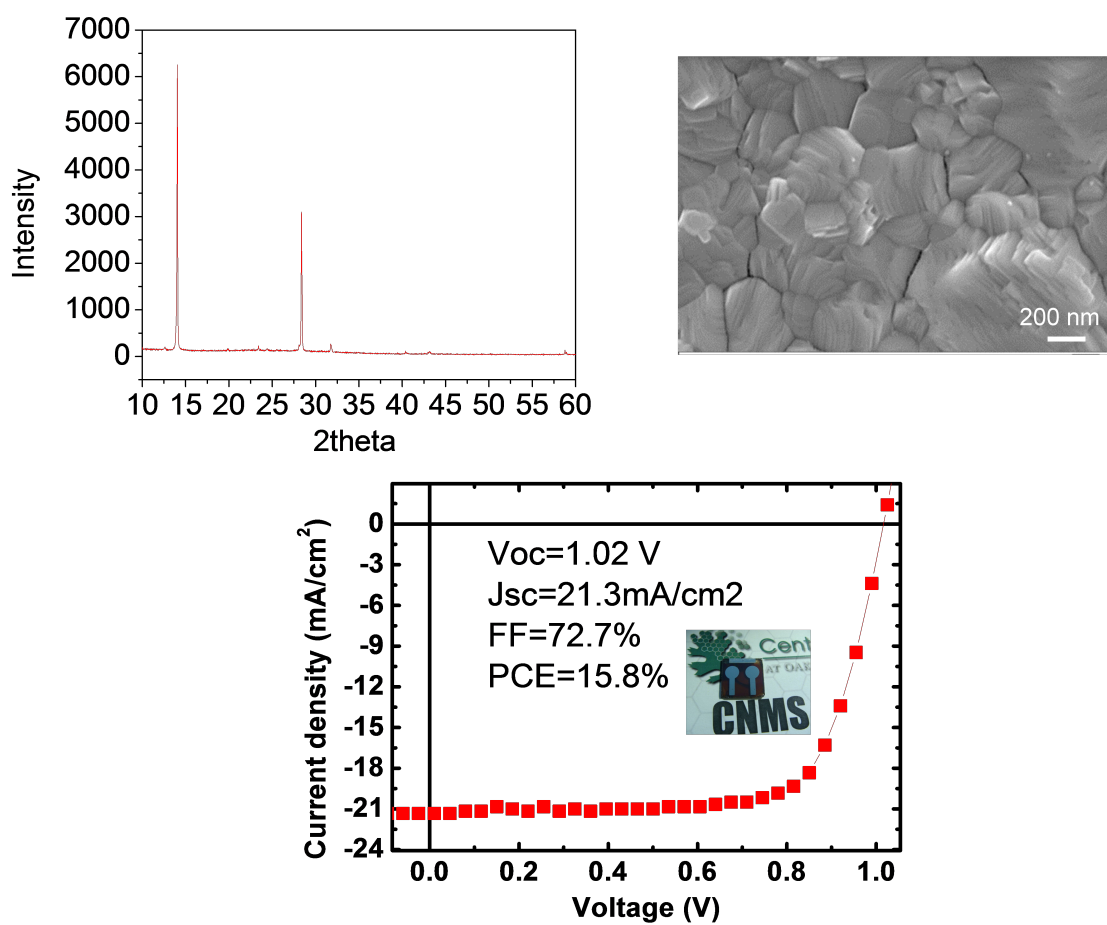


Figure 6.1: XRD pattern (a) and surface morphology (b) of solution spin-coated $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film; the J-V under illumination of 100 mW/cm^2 , G 1.5 AM solar spectrum.

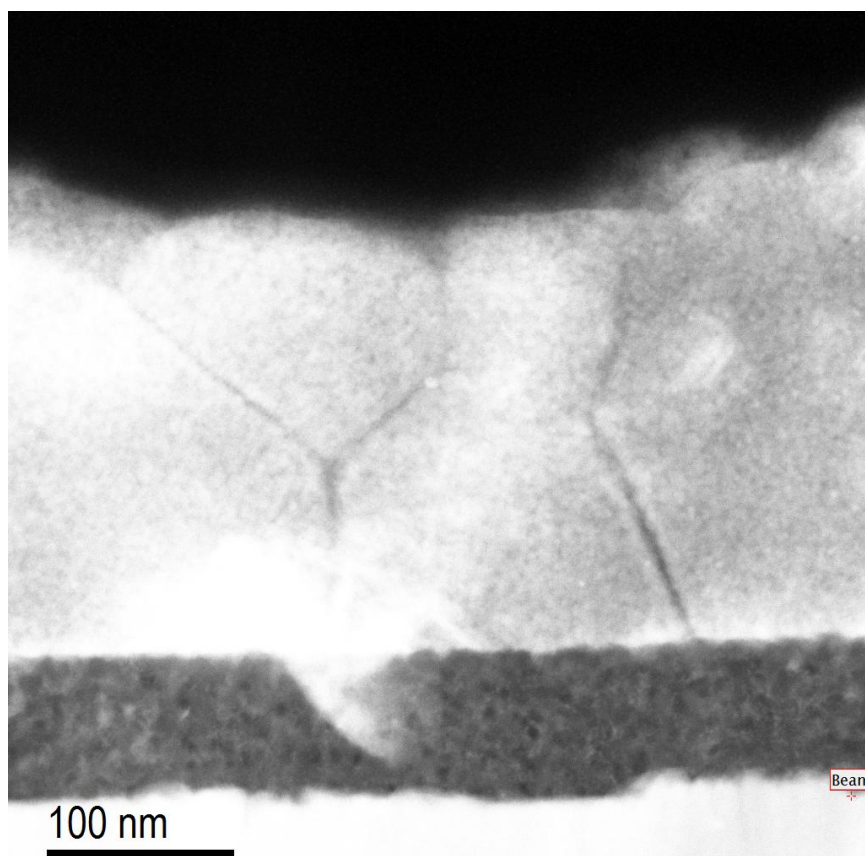


Figure 6.2: Cross section morphology of a typical device clearly showing cracks through the perovskite layer.

layered structure perovskite domains with size of 1 micrometer in the obtained perovskite films, we applied TEM/STEM/SAED to examine the cross-sectional morphology in the perovskite films, and found that the obtained perovskite films have large-scale single crystal domains throughout with dimensions of over 300 nm.

Figure 6.2 is an HAADF image of a typical cross section sample prepared via FIB milling. We can easily see dark cracks running vertically through the perovskite layer. We will discuss these cracks in more detail in the next section. The purpose of this section is to demonstrate primarily single crystalline domains in between the cracks.

To show crystallinity we acquired selected area diffraction (SAD) patterns along the length of the perovskite film shown in figure 6.3. The perovskite film has relatively large, primarily single crystalline domains. What we see is that each pattern

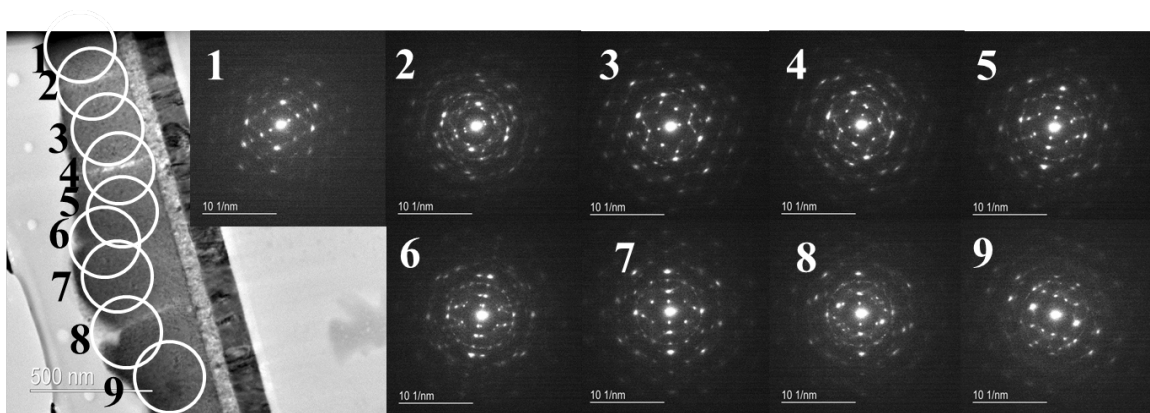


Figure 6.3: Selected area diffraction patterns (1-9) were acquired along the length of the perovskite layer indicated by the numbered circles. All patterns are primarily single crystalline, although most display a weak polycrystalline ring as well. We observe 5 unique crystal orientations in patterns 1, 3, 5, 7, and 9. The other patterns are taken across grain boundaries where we see two crystal orientations superimposed. This spans a distance of 1.6 microns which implies an average crystal size of 320 nm. The aperture size was 300 nm.

displays primarily single crystalline diffraction spots with a small polycrystalline component (i.e. rings). Through the length of the film examined we have 5 distinct crystallographic orientations exhibited in patterns 1,3,5,7, and 9. The patterns in between were acquired across grain boundaries and show the superposition of two single crystal diffraction patterns. The distance examined was 1.6 microns which corresponds to an average grain size of 320 nm. This is consistent with our aperture size of 300 nm which easily illuminates single crystals. If we had estimated an average grain size of 150 nm this would be inconsistent with getting single crystal SAD patterns.

What is more important than the in plane crystal grain size is the vertical crystal grain size. The aperture used in figure 6.3 is just slightly smaller than the thickness of the perovskite film. In order to test this we inserted a smaller SAD aperture (230 nm) and acquired a series of SAD patterns along the vertical direction through the perovskite layer. The results are shown in figure 6.4.

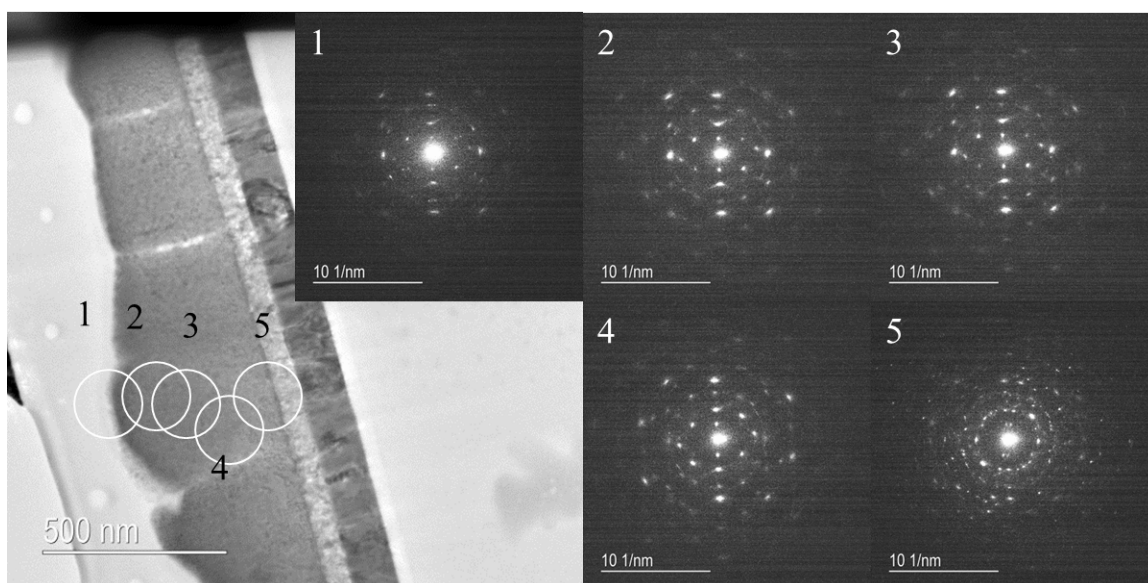


Figure 6.4: Selected area diffraction patterns (1-5) were acquired from the top of the film to the bottom indicated by the numbered circles. We saw very little difference in diffraction patterns 1-4. This indicates that we have primarily one single crystal through the thickness of the perovskite film. In this area the film is 450 nm thick. Note: pattern 5 illuminated the polycrystalline TiO_2 layer which is why we see a polycrystalline pattern here.

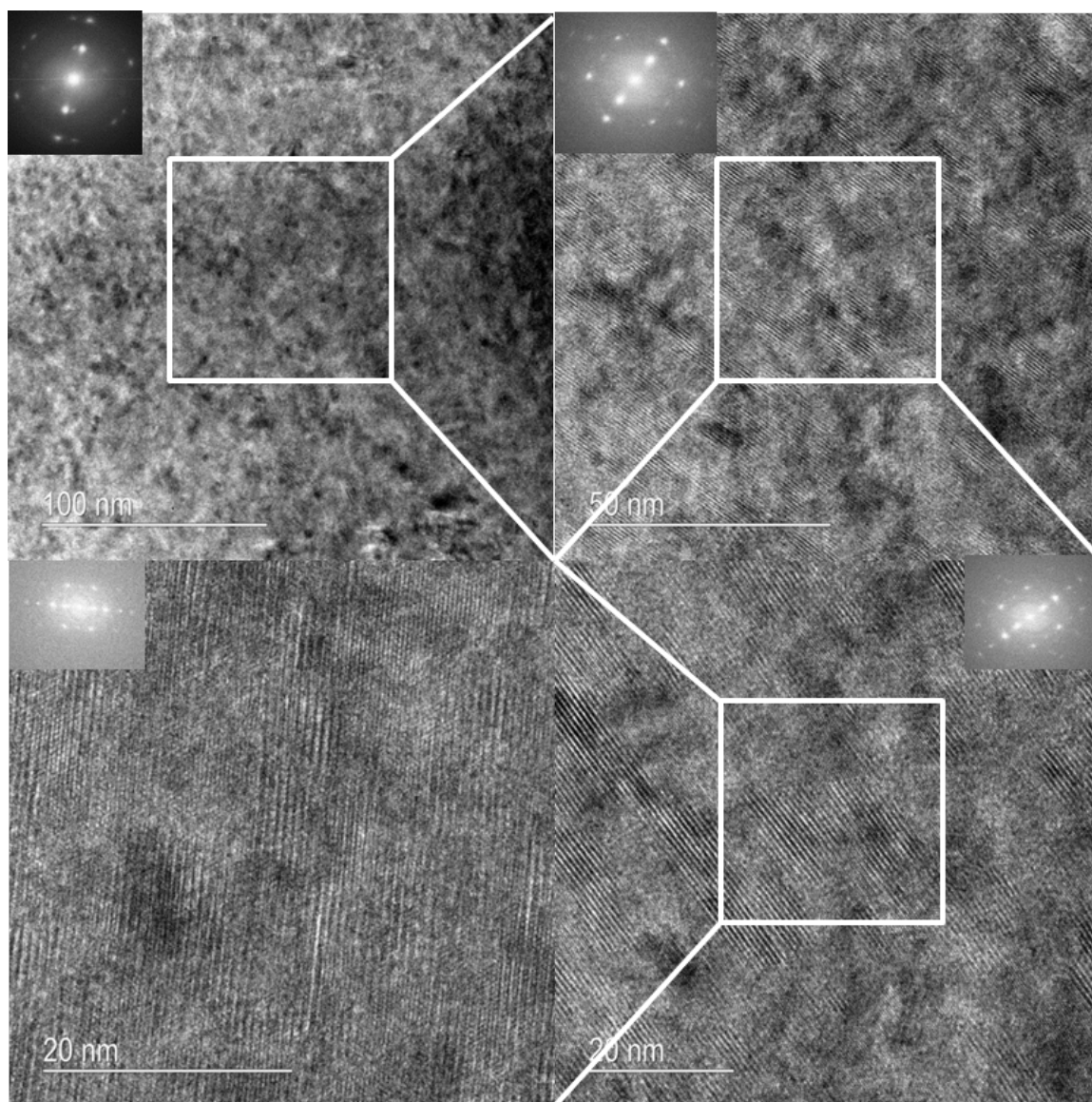


Figure 6.5: High resolution TEM images and their diffractograms (FFTs) also show single crystal perovskite. Despite the apparent polycrystallinity in the upper left image (bright and dark speckles), the FFT shows only two crystals with a low angle grain boundary. As we zoom in we see that the lattice planes indeed extend through the bright and dark areas. Small crystal domains are not evident here. The bright and dark regions are likely due to surface damage occurring during FIB milling.

We clearly have a single crystal extending through the thickness of the perovskite layer. This is also evident from high resolution images such as that shown in figure 6.5. These relatively large, single crystal domains help improve the device efficiency by extending the electron and hole diffusion length. Previous studies have shown diffusion lengths for $\text{CH}_3\text{NH}_3\text{PbI}_3$ to be 100-150 nm [Xing et al. \(2013\)](#); [Stranks et al. \(2013\)](#), however, this cannot be the case in our material since we observe very high efficiencies with a perovskite layer of 350-400 nm. [Stranks et al. \(2013\)](#) observed efficiencies of only 4% for a $\text{CH}_3\text{NH}_3\text{PbI}_3$ device where the thickness had been optimized at 140 nm. This was consistent with their measured diffusion lengths however, it seems likely that material imperfections such as grain boundaries and defect states severely limited the diffusion length in their case. Large-scale, single crystal grains appear to increase the diffusion length to at least 350-400 nm, comparable to the thickness of the perovskite material used in this study.

6.6.3 Bulk Heterojunction Structured Perovskite Solar Cell

Another phenomenon that may be contributing to the enhanced photovoltaic performance of these devices is formation of a bulk heterojunction within the perovskite films through infiltration of Spiro-OMeTAD into the perovskite films along the cracks between the grains that are frequently encountered. We use the term bulk heterojunction here to denote simply that we have a heterojunction that is no longer planar but extends into the third dimension. Initially it was assumed that the grains made intimate contact between one another to form typical grain boundaries. However, upon closer examination in the TEM in figures 6.2, 6.4, and 6.6 we can see that the distance between grains can be up to 15 nm. Figure 6.6a shows an HAADF image of a crack. We see that it appears much darker than the surrounding perovskite material. This indicates that the heavier elements Pb and I must be absent in this region. Figure 6.6b shows a high resolution image of the crack, from which we determine that the material within is amorphous.

It seems likely that, upon annealing the perovskite film during fabrication, there is a slight shrinking which manifests as cracks between crystal grains. These cracks are then filled with Spiro-OMeTAD as the device is completed. In order to strengthen this theory a spectrum image was acquired and analyzed according to the procedures laid out in chapter 3. The carbon, nitrogen, and iodine elemental densities are shown in figure 6.6c, d, and e, respectively. The lack of iodine within the crack indicates that it is not perovskite, agreeing with the HAADF image, while the high carbon and nitrogen content are consistent with the presence of Spiro-OMeTAD.

This indicates that Spiro-OMeTAD is indeed pulled into the cracks through capillary action to form a bulk heterojunction-like structure. This increases the surface area for hole extraction and creates more highly active regions throughout the thickness of the film. This also effectively reduces the number of grain boundaries in the perovskite. Moreover, because the valence and conduction band of the Spiro-OMeTAD are higher than those of the TiO_2 , there is no danger of shorting the device through direct contact between them as would be the case if the Ag contact were to extend to the TiO_2 layer. This explains why, despite our observation of cracks extending all the way through the perovskite, we, nevertheless, observe strikingly high efficiencies. The infiltration of Spiro-OMeTAD into perovskite films can substantially enhance the hole collection efficiency, resulting in suppressed carrier non-radiative recombination loss at grain boundaries.

6.7 Degradation in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite materials

In addition to high power conversion efficiency, another major challenge facing perovskite photovoltaics is how to extend the long term stability of these materials and associated photovoltaic devices [Service](#). The stability in organometal halide perovskites is significantly affected by environmental exposure [Bi et al. \(2014\)](#); [Snaith](#)

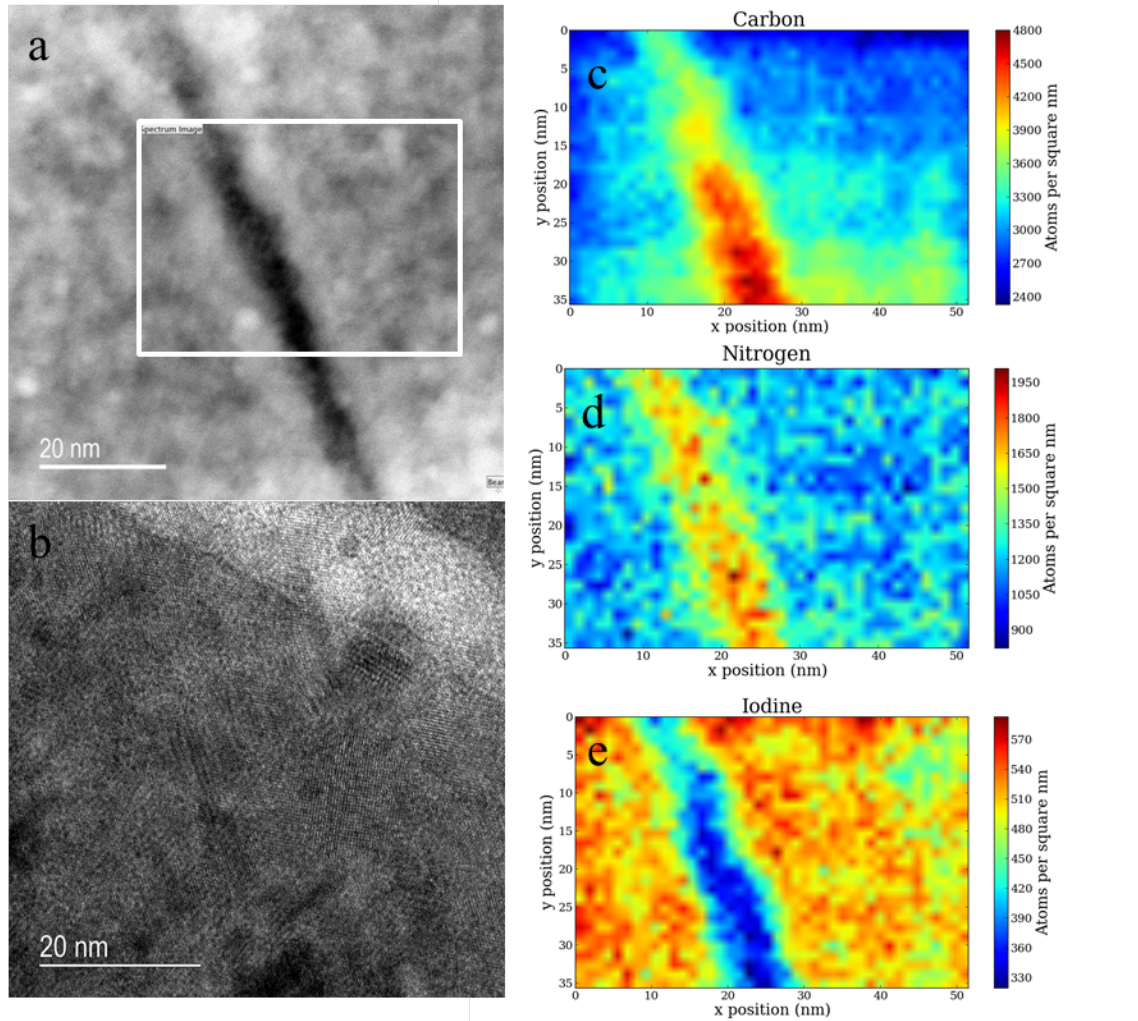


Figure 6.6: a) HAADF image of crack between perovskite grains. The white rectangle indicates the area over which the spectrum image was acquired. b) High resolution TEM image of a similar crack. We see that the crack is filled with an amorphous material. c)-e) analyzed EELS spectrum image produces atomic areal density maps for carbon, nitrogen, and iodine. We observe carbon and nitrogen are rich within the crack, while iodine is deficient when compared to the perovskite. The crack also has low lead concentration as evidenced by its dark appearance in the HAADF image. These findings are consistent with the idea that, upon spin coating, the spiro is pulled into the cracks through capillary action to form a bulk heterojunction like structure.

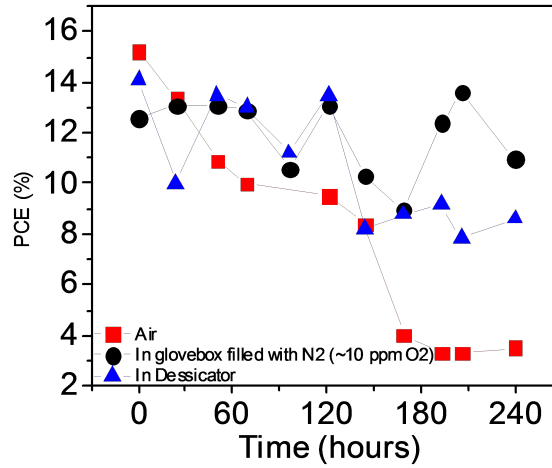


Figure 6.7: Degradation of device power conversion efficiency with different environmental exposure.

(2013), where fundamental systematic studies are needed. It is well known that the perovskite materials used in these devices are especially sensitive to moisture and degrade quickly when exposed to ambient air.

As shown in the Figure 6.7, the devices showed different degrees of degradation with different environmental exposures. The PCE exhibited the fastest decay directly exposed to air, where both water (H_2O) and oxygen (O_2) have a detrimental effect on the perovskite materials. However, when the devices were placed in a desiccator, they decayed slower than in air, which means that O_2 , by itself, induced the perovskite degradation. If the devices were put in the glovebox where both H_2O and O_2 are in low level, the performance of the devices was unchanged. Therefore, water (H_2O) and oxygen (O_2) produce different degrees of degradation, which is due to different degradation mechanisms. Here, however, we observe another (less dramatic) degradation process that occurs in vacuum.

Previous studies have investigated the mechanisms of degradation and concluded that the $CH_3NH_3PbI_3$ decomposes into polycrystalline PbI_2 and I_2 Niu et al. (2014); Burschka et al. (2013). A cursory investigation of a TEM sample exposed to air for a few days reveals bright polycrystalline regions that are iodine rich, consistent

with degradation into PbI_2 and I_2 . In figure 6.8 the areas devoid of iodine appear dark. This implies they are devoid of lead as well. High resolution TEM images show the dark area to be amorphous (not shown). Also of note is that the iodine rich region overhangs the TiO_2 in some areas which suggests it has migrated and grown. The presence of oxygen in the amorphous region is consistent with the idea that the absorption of moisture plays a role in breaking down the perovskite, which is consistent with the fastest degradation of PCE of devices left in the air.

What is quite interesting is that samples with very little exposure to air (<5 mins) that have been stored in the vacuum of the TEM still show signs of degradation. Figure 6.9 shows a typical sample. We see accumulations of lead rich particles that are devoid of both carbon and iodine. These particles were not present upon initial examination. Further experimentation needs to be conducted to determine precisely what these are, nevertheless, this degradation appears completely different from that of an air exposed sample and suggests that even in the absence of moisture and oxygen, in the vacuum of the TEM, degradation still occurs. This appears to act more slowly than a sample exposed to air (where we see the entire film has decomposed) and has not been observed to destroy the entire perovskite film. Moreover, this degradation either does not exhibit itself in the glovebox where no PCE degradation was observed, this degradation mechanism only effects PCE after very long times, or this degradation mechanism has no effect on PCE and will not continue to consume the active layer perovskite material. This has uncertain implications for the hope of encapsulation preventing degradation. More experimentation is needed to precisely determine the degradation mechanisms and what can be done to suppress them.

6.8 Conclusion

We have demonstrated repeatable, solution processed solar cells with efficiencies up to 17.9% and routinely achieve efficiencies above 16%. This is done without a mesoporous TiO_2 layer, making the fabrication process simpler. The likely reasons

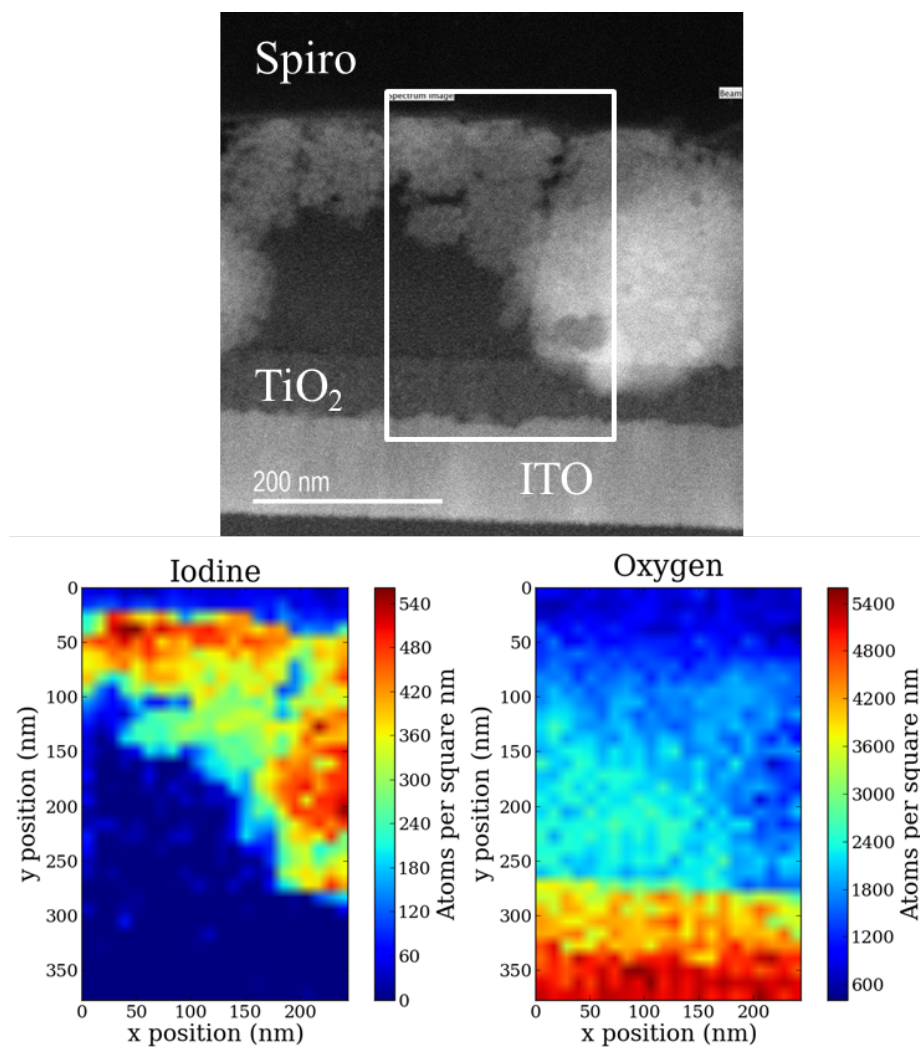


Figure 6.8: Top: HAADF image of sample degraded with exposure to air. An EELS spectrum image was acquired over the area indicated by the white square. The iodine and oxygen atomic areal density maps are shown below.

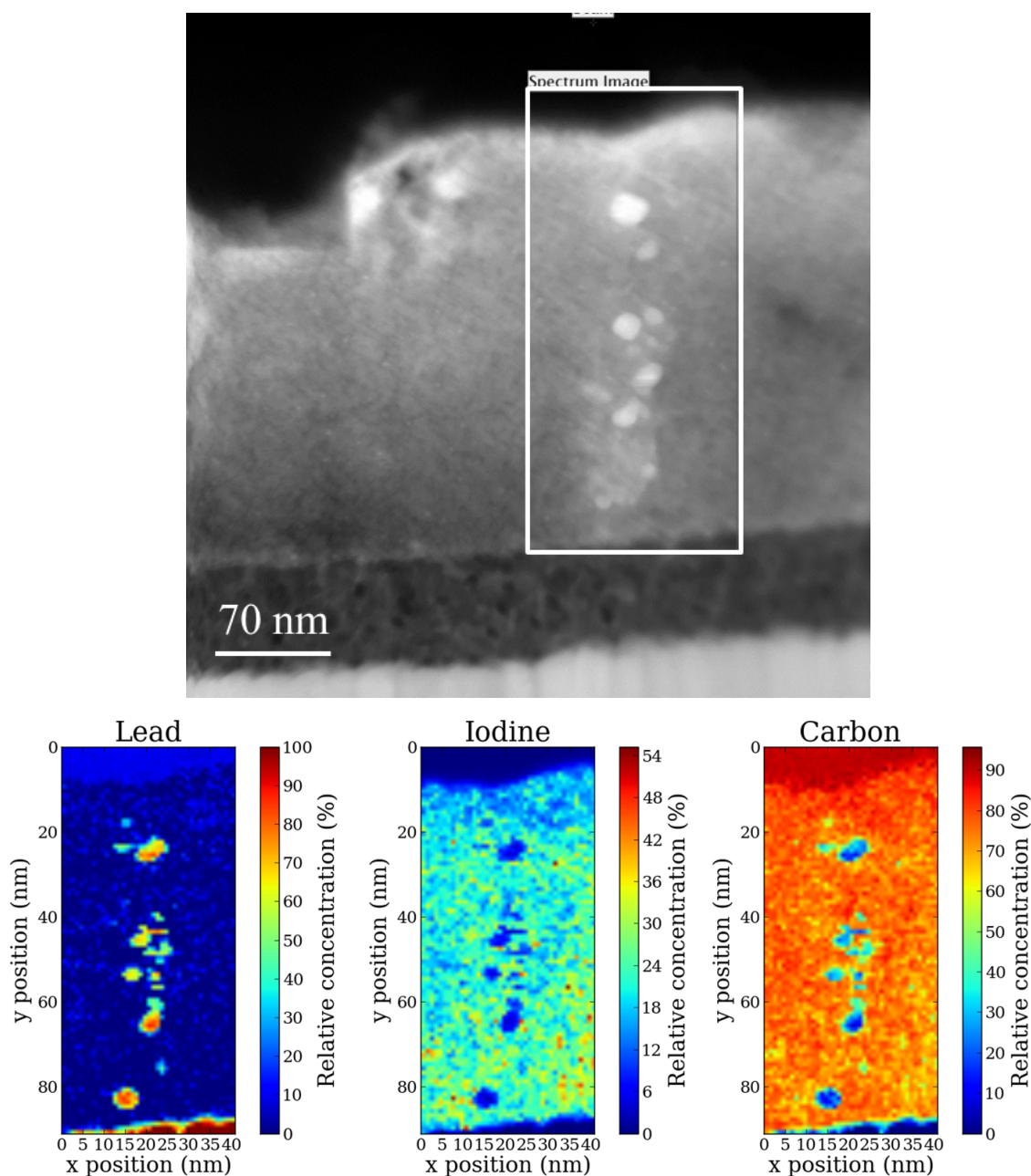


Figure 6.9: Top: HAADF image of a perovskite cross-section sample that degraded in the vacuum of the TEM. Bottom: relative concentrations of elements determined from an EELS image acquired over the area indicated by the white rectangle. The bright particles are lead rich and iodine deficient which precludes the possibility of PbI_2 . Further experimentation is needed to determine precisely what this material is, however, it is already clear that this degradation is not the same as the sample degraded in air.

for our high efficiencies are that we see large (>300 nm) single crystal domains that extend through the full thickness of the perovskite film coupled with HTM filled cracks between the single crystal grains that form a bulk heterojunction-like structure. This increases the active volume of the device over the same macroscopic area, decreases the number of grain boundaries (i.e. charge carriers do not have to cross a grain boundary that is filled with HTM), and does not short the device if the Spiro-OMeTAD and TiO_2 come into contact. These features work together to improve device performance. Control and optimization of the BHJ structure has yet to be explored and offers the possibility of further enhancements. Finally, we observed what appears to be a new degradation pathway occurring in a sample stored in the vacuum of the TEM. Further investigations are ongoing.

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Vita

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