Photoemission Electron Microscopy of Electron Donor and Acceptor Molecules for Organic Photovoltaics.

A Thesis submitted for the degree of Master of Science (By research) by Sinan Kose Bsc

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Abstract

A series of samples based on acceptor and donor molecules used in organic photovoltaics were examined using photoemission electron microscopy (PEEM) in order to examine changes of morphology and to determine if PEEM spectroscopy can be used to determine the difference between acceptor and donor domains in the context of organic photovoltaics (OPVs). Cleaned Indium Tin Oxide (ITO) was examined using PEEM spectroscopy in order to obtain a cutoff value, the cutoff is related to the work function as it indicates the sample bias at which images begin to become detectable in the PEEM meaning electrons have been emitted from the surface. Samples with the acceptor and donor molecules in this case Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM) respectively were examined using PEEM spectroscopy with samples deposited using spin coating. Blends of the acceptor and donor were made by mixing appropriate proportions of the individual solutions of the acceptor and donor together. These mixtures were then spin coated onto a cleaned ITO substrate in order to examine the morphology as well as the cutoff values. The mixtures used were in the ratios: 1:1, 2:1, 1:0.8 P3HT:PCBM. In an effort towards more accurate model OPVs a sample of PDOT:PSS was examined using PEEM spectroscopy. The PEEM was determined to be able to distinguish between different materials on samples where appropriate, however the absolute values of work functions were not the expected values.

1 Introduction to electron donor and acceptor molecules in the context of organic photovoltaics

Electron acceptors are materials with a high electron affinity such as Buckminsterfullerene (C60) and it's derivatives [1]. These materials accept the electron generated in the electron-hole pair (exciton) formed by absorption of radiation by the electron donor [2] which in organic photovoltaics is typically a polymer [3]. In the case of the experiments done in this thesis the electron donor is Poly(3-hexylthiophene-2,5-diyl) (P3HT) and the electron acceptor is Phenyl-C61-butyric acid methyl ester (PCBM) a fullerene derivative. The role of the electron donor is to generate excitons so that they are close enough to the boundary of the acceptor to allow for charge separation and then electron transport [4]. This is the mechanism by which dye sensitised solar cells produce electrical energy that can be used from visible light [5].

Contrast in images obtained using PEEM depends both on topographical features as well as the electronic properties of the material, specifically the work function. Indium Tin Oxide (ITO) is a compound that is used in transparent conducting films and is often used as a substrate in solar cells. ITO has been found to have a work function of 4.4eV [6].

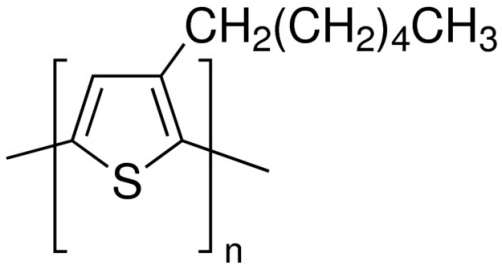


Figure 1: Monomer representation of the chemical structure of P3HT which is used as the electron donor in the series of experiments done.

Figure 1 shows the chemical structure of P3HT, the work function of P3HT has been found to be 3.9eV [7] which is lower than the ITO's work function by 0.5eV. P3HT shown in figure 1 is the most commonly used polymer in commercial OPVs [8].

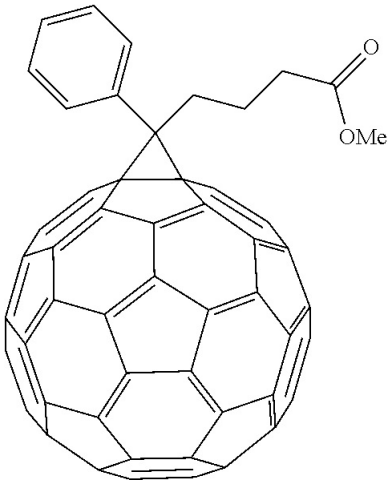


Figure 2: Representation of the chemical structure of PCBM [9] which is used as the electron acceptor in the series of experiments done.

Figure 2 shows the chemical structure of PCBM illustrating that it is a fullerene derivative. Work Function of PCBM, is found to be 4.3eV [7] which is lower than the ITO work function found by Schlaf by 0.1eV.

Early practical solar cells were first found in 1954 where the solar cell was a silicon P-N junction where photons with the energy 1.02eV were able to create electron-hole pairs [10]. Bilayer solar cells are solar cells where the acceptor and donor materials form two separate layers in contact with each other [11].

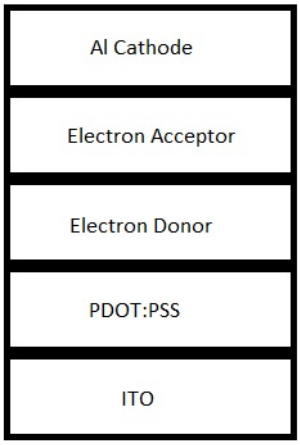


Figure 3: Basic diagram of a typical bilayer solar cell.

A bulk heterojunction is a type of solar cell that instead of being a bilayer structured

solar cell as shown in figure 3 has a more complicated morphology with the acceptor and donor materials separated by phase boundaries across the whole surface rather than in two separate layers [12]. Phase boundaries allow a donor material to give an electron to an acceptor material via exciton (electron hole pair) diffusion, typical exciton diffusion length scale is 10nm [13]. The domain size of the seperated acceptor and donor regions within the active layer has been found to be ideally on the order of the exciton diffusion length scale [14].

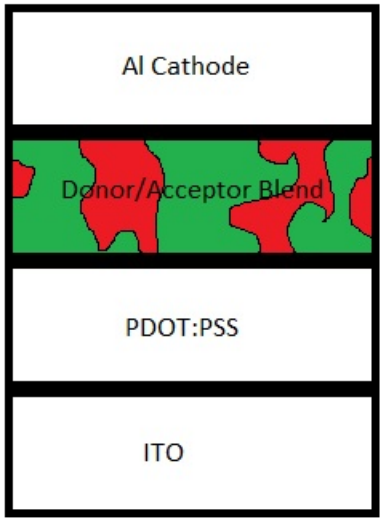


Figure 4: Basic diagram of a typical Bulk Heterojunction solar cell.

Figure 4 illustrates the basic structure of a typical bulk heterojunction including a layer of PDOT:PSS that is seen in both the Bilayer solar cell in figure 3 and in the bulk heterojunction. PDOT:PSS has been found to improve the performance of polymer solar cells [15].

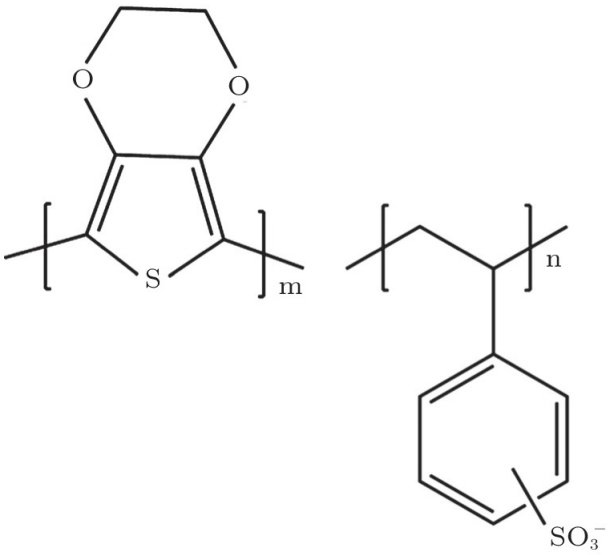


Figure 5: Representation of the chemical structure of Poly(3,4-ethylenedioxythiophene)(PDOT) alongside Polystyrene sulfonate(PSS) [16]

The work function of PDOT:PSS is found to be 5.1eV prior to any treatment of the PDOT:PSS. Thin film PDOT:PSS shows a work function of 4.7-5.4eV [17]. PDOT:PSS is a polymer mixture whose components are shown in figure 5, that is commonly used in solar cells between the ITO and the donor/acceptor layers in solar cells either bilayer or bulk heterojunction [18]. This indicates that thin films of PDOT:PSS will have a lower difference in work function than bulk PDOT:PSS. Other experiments have also found the work function value to be 5eV confirming that this is an established value for the work function [19].

Table 1: A table showing the values of the work functions of the molecules and substrate observed using the PEEM

Material	Work Function (eV)
ITO	4.4
P3HT	3.9
PCBM	4.3
PDOT:PSS	5.1
PDOT:PSS (Thin)	4.7 - 5.4

The values for work function presented in table 1 show that there is a difference be-

tween the materials work function, these can be analysed using the PEEM filter. The work functions of ITO and P3HT in thin films have a difference of 0.5eV meaning that the PEEM should be able to find a difference between the two materials using spectroscopy [20].

Various ratios of the Donor and Acceptor molecules are used in the active layer of the solar cell, ratio's of 1:0.8 were commonly used as well as mixtures of 1:1 ratios in other experiments conducted on OPVs [21] [19]. In commercial OPVs P3HT is commonly used as the absorber in solar cells [8]. The typical concentration of P3HT that has been used is 0.2 weight percentage [22] [23].

2 PEEM theory and instrumentation

Photoemission electron microscopy (PEEM) is a technique used to produce magnified images at a typical resolution of the order of 10 nm [24].PEEM was first pioneered in the 1930's by Ernst Brüche and was used to show that electrons emitted after being bombarded with UV light could be used for imaging once accelerated to higher energies. This original system depended on two apertures that used a simple magnetic lens [25]. The system used for this project operates under UHV, the first efforts towards this began in the 1960's eventually leading to systems that were bakeable in the 1970's and PEEM's usable with clean and controlled samples in the 1980's [25].

PEEM is a surface sensitive imaging method meaning that the electrons measured by the PEEM instrument are primarily from the surface of the material and not from the bulk [26]. The electrons that are used in the imaging process are released from the surface using the photoelectric effect, wherein the sample is bombarded with photons of the threshold frequency induce the emission of electrons from the surface [27]. If the photons are above the threshold frequency the additional energy is converted into the kinetic energy of the electron and increases linearly with the frequency [28]. The photoelectric effect is described by the equation: $h\nu = h\nu_0 + \frac{1}{2}mv^2$ where h is Plancks constant, ν is the frequency of the photons incident on the surface, ν_0 is the threshold frequency, m represents the mass of electron expelled from the surface and v is its velocity.

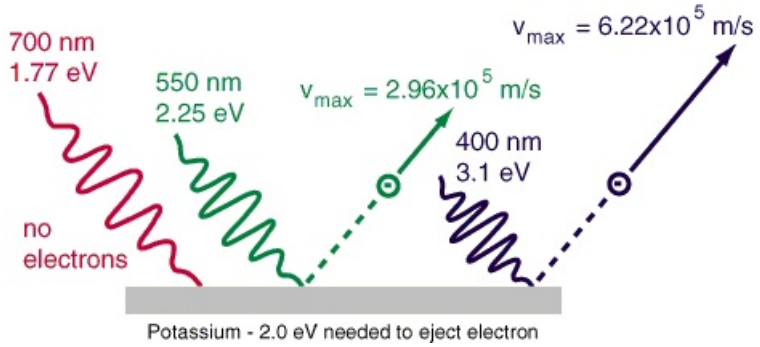


Figure 6: A schematic of the photoelectric effect using potassium as the surface with a work function of 2eV [29].

Figure 6 shows a schematic of the photoelectric effect using potassium, in principle there

is no difference between the behavior shown in the schematic and the OPV's used in these experiments. The only difference is the work functions of the materials used meaning a different wavelength of light will be the threshold frequency.

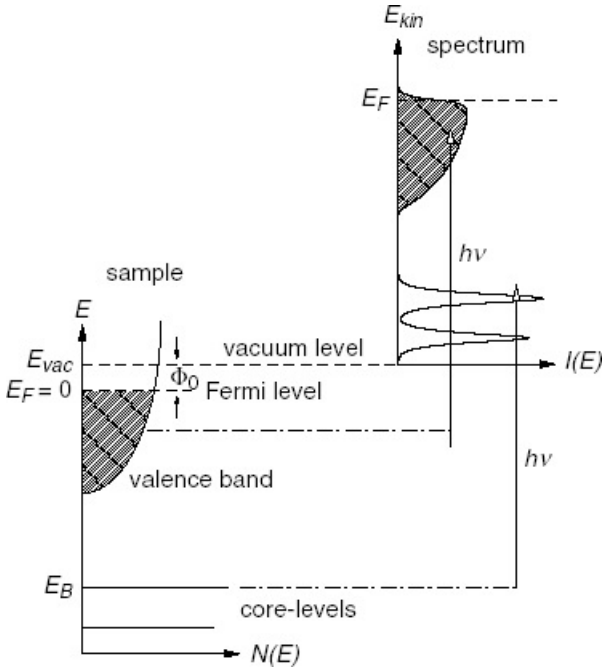


Figure 7: A diagram of photoemission showing the effects of bombardment by a photon of energy hν [30].

Figure 7 shows a diagram of photoemission, in the experiments conducted there was not access to an intense source of x-rays, such as a synchrotron which would allow core-level PEEM. A UV lamp was used and so only electrons from the top of the valence band were emitted from the samples examined.

PEEM devices typically use a lamp in order to produce the photons induced by the photoelectric effect which is how electrons are ejected from the surface of the samples imaged within the PEEM system [31]. A threshold frequency is needed to extract electrons from the samples that the light is incident on and any excess above the threshold is converted into the electrons kinetic energy after its expulsion. The work function is the term hν_0 in the photoelectric equation. The lamp used is a mercury arc lamp that produces UV photons as used with other PEEM based experiments [32] [33]. The energy of the mercury arc lamp used in these experiments is 4.9eV which is represented in the photoelectric equation by hν.

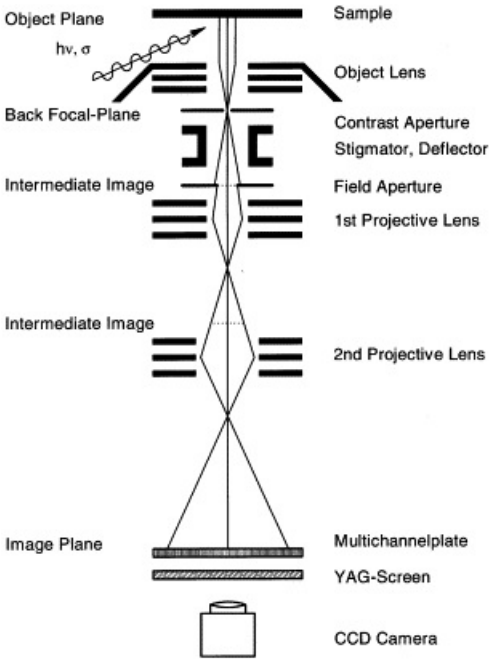


Figure 8: Schematic of a PEEM system adapted from Swiech et al [34].

Figure 8 shows a basic schematic of a typical PEEM system with the first cone closest to the sample corresponding to the extractor in the PEEM used to accelerate electrons into the PEEM.

Images in the PEEM systems are collected by Charged-coupled device (CCD) cameras after they have been focused by the electrical optics within the PEEM. The PEEM operates in three modes: one lens mode, two lens mode and three lens mode. The one that was used for the majority of the images taken in the experiments was one lens mode, this mode keeps the projective lenses at the same value effectively making them unused. The extractor, which is represented by the object lens in figure 8 must be used at a high voltage in order to make the electrons emitted from the sample enter the PEEM and be focused by the elements. PEEMs can provide resolution to the nm scale under the correct conditions [35].

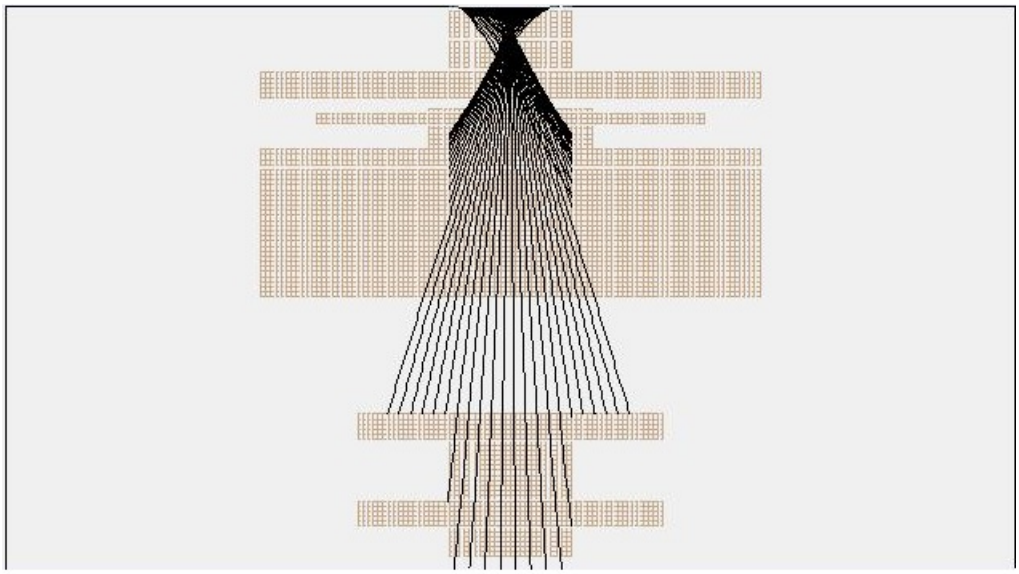


Figure 9: Basic ion optic simulation of a PEEM system using an extraction voltage of 16KV. The electrons had an initial kinetic energy of 1eV.

Figure 9 shows a basic simulation of the PEEM showing the one lens mode of operation. This shows successful extraction of the electrons and their path passing through the elements to where the image plane is located and the image would be formed. The simulation was done in SIMION for the purpose of demonstrating the path taken by electrons within a typical PEEM under basic operating conditions.

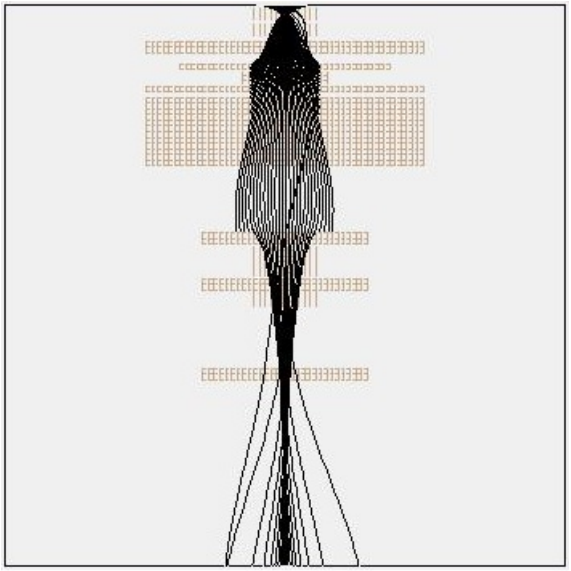


Figure 10: Basic ion optic simulation of a PEEM system using an extraction voltage of 1KV. The electrons had an initial kinetic energy of 1eV.

Figure 10 shows a basic simulation of the PEEM showing the two lens mode of operation. This shows successful extraction of the electrons and their path through the elements. The electrons focus twice within the PEEM.

The PEEM system is capable of energy filtering the electrons that are emitted from the samples. This capability has led to it being used in work function measurements [36]. This is done by applying a sample bias on the sample that gives the emitted electrons additional kinetic energy, this can be used to identify regions with differing work functions. This process is done by moving through a range of kinetic energies causing regions with different work functions to emit electrons at different kinetic energies. In practice this enables the highlighting of different regions and increasing the contrast within images [37].The photons used to bombard the surface are the same energy which from the mercury lamp used in these experiments is 4.9eV. If a material has a higher work function than another the kinetic energy of the emitted electrons will be lower. This means that a more negative sample bias is required in order to get electrons above the vacuum level, a more negative sample bias indicates a region with a higher work function. The PEEM is able to show surface contrasts due to physical features as well as due to different electrical properties [38]. Structural contrast is achieved because the emitted electrons are ejected from the surface at different angles, after focusing within the PEEMs optical systems they cluster in different intensities. In order for a sample to be analysed using PEEM it must ideally be a flat sample so that the resolution is not disrupted by distortions in the accelerating field. There is also the potential for charging which can effect the measures electrical properties of sample and disrupt measurements of the cutoffs and therefore the work functions.

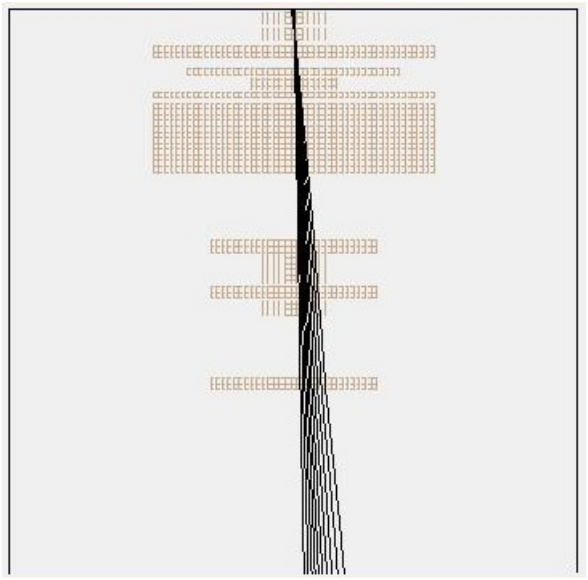


Figure 11: Basic ion optic simulation of a PEEM system using an extraction voltage of 16KV. The electrons had an initial kinetic energy of 1eV

Figure 11 shows a series of electrons emitted from the same point at different angles showing how surface morphology could impact the final image obtained by the PEEM as the path and ending position of the electron is changed.

In some instances it is advantageous to use stigmators in PEEM imaging, the stigmators are a series of cylindrical columns that are set at different voltages in order to change the shape of the incoming emitted electron beam. This can be used to improve image quality and therefore allow images at a smaller scale to be taken. The stigmators can also be used to finesse the position of the image in effect moving the image by small amounts in order to position it over interesting features precisely.

PEEM systems are operated under high vacuum [39] conditions in the series of experiments that have taken place. The PEEM was typically operated at 2×10^{-9} mbar meeting the conditions required for PEEM operation. The PEEM system used was equipped with an energy filter which allowed spectroscopy to be done on samples, this can allow for the identification of different materials that superficially appear similar. PEEMs have been used to identify the work functions of materials using spectroscopy [40] [41]. In a typical spectrum taken by a PEEM the work function of a given material can be identified by the point at which the change in brightness begins to take effect this point

is referred to as the cutoff.

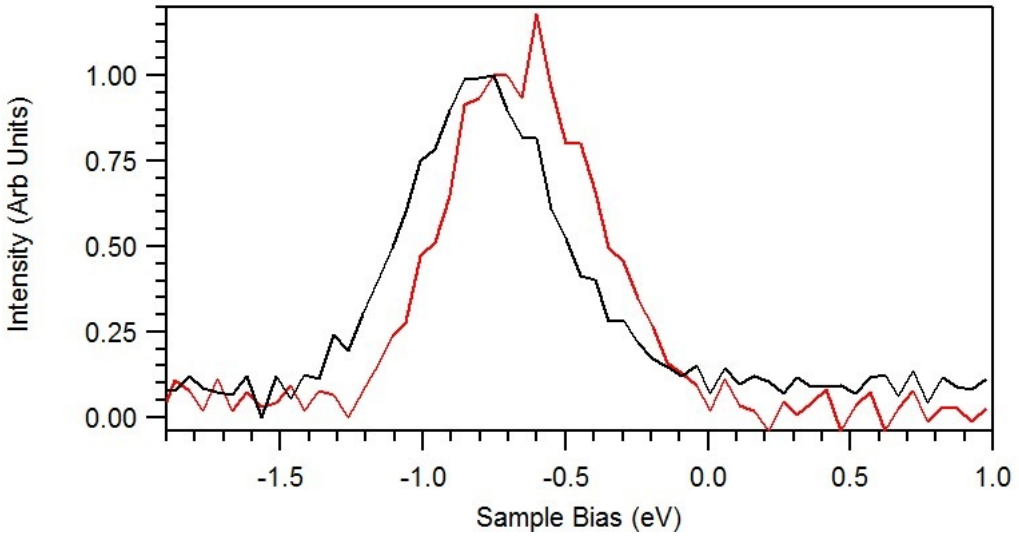


Figure 12: An example of two spectra taken by the PEEM.

In figure 12 there are two spectra taken using the PEEM filter, the work function is related to the low voltage cut off. As can be seen in the figure the cutoff found for the two spectra are noticeably different indicating a difference in work function.

The values in table 1 show the work functions of the materials examined in the PEEM. These show that there should be a noticeable difference in cut off between the ITO and P3HT when examined using the PEEM filter. It also suggests that PDOT:PSS should have a more negative cutoff as it's work function is at a higher value. It also indicates that the PEEM filter will not be able to clearly distinguish between the ITO and PCBM as the work functions difference is only 0.1eV. This means that the expectation is the PEEM will be able to distinguish between P3HT and ITO as well as PDOT:PSS and ITO.

In order to compare the spectra obtained by the PEEM the cutoff at which the peaks begin to form must be identified, this is done by removing the background and then normalising the spectrum. Then the part of the spectrum where the peak begins to form and the peak is fitted using a straight line then the 20 percent and 80 percent intensity values are taken of the line between the base and the peak, this is because the cutoff would normally be a steep incline as opposed to a slope as shown in the majority of the measurements taken. This is then repeated 3 times different end and beginning

points for the cutoff fit in order to get a value for the cutoff. The spectra for the ITO is used to compare the other materials, in order to reduce the noise ITO spectra with similar cutoffs are added together and normalised. The values for the molecules cutoff is determined by taking an average of the cutoffs found within a 0.1eV range meaning results that are more than 0.05eV apart will be considered different work functions.

3 PEEM of ITO

3.1 Introduction

The first sample that was studied was clean ITO. This was chosen in order to establish what clean ITO's morphology is so that when molecules are deposited on the substrate a direct comparison can be made. Also it was chosen to establish the reliability of the spectroscopy within the PEEM and it's ability to identify regions made of the same material over the same sample.

3.2 Preparation of ITO

The ITO was prepared first by making samples of the ITO glass that were the correct size to fit into the sample holders used in the PEEM system. Then the ITO was cleaned using a three solvent wash, in the order: Acetone, Methanol, Isopropanol in a sonic bath for ten minutes per sample. This was done to ensure that any particles from the air were removed from the sample as well as any dust and other general contaminants on the sample.

3.3 Results and Discussion

The PEEM technique was used on a section of clean Indium Tin Oxide (ITO) glass in order to determine the band gap energy of the ITO and to observe any changes that occur to the surface when it is heated. The image expected from the ITO is a relatively homogeneous and flat surface that has minimal physical faults in the surface.

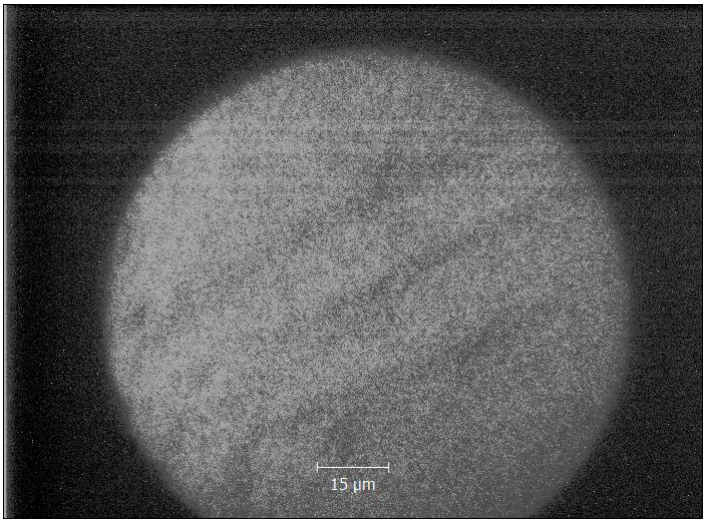


Figure 13: An image of clean ITO glass taken at room temperature at a field of view of 100 µm and a sample bias of -2eV

Figure 13 is of a region of the clean ITO indicating that the surface is relatively homogeneous.

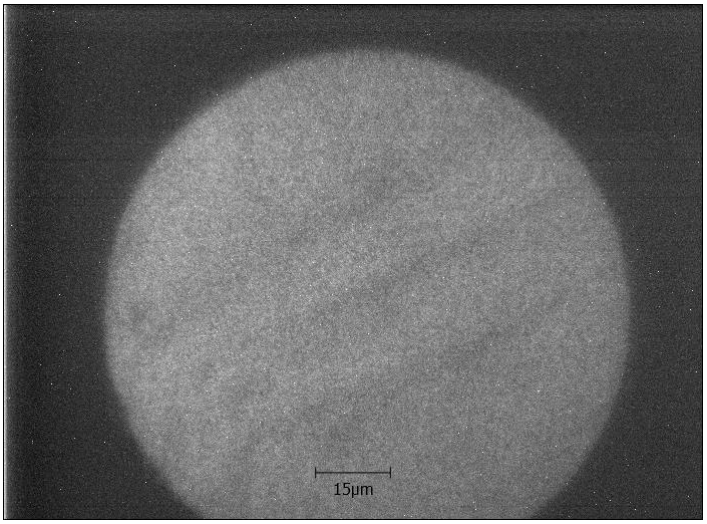


Figure 14: An image of clean ITO glass taken at room temperature at a field of view of 105 µm and a sample bias of -0.6eV. This value of the sample bias is the value at which the sample became visible in the PEEM.

Figure 14 is of the same region with a field of view of 105uM, however the sample bias has been changed to -0.6eV which is the threshold value at which the ITO became just visible.

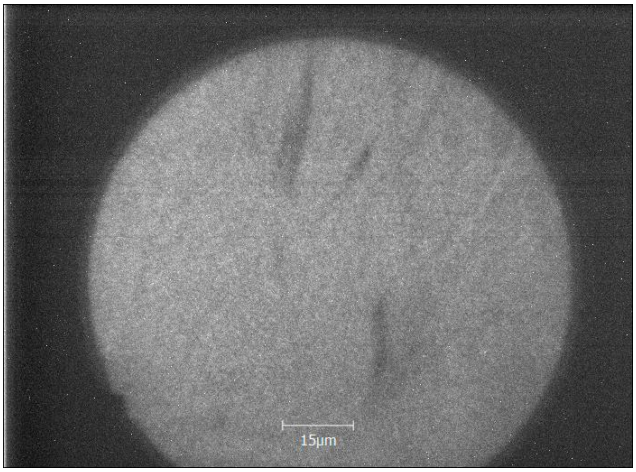


Figure 15: An image of clean ITO glass taken at room temperature at a field of view of 100 µm and a sample bias of -2.0eV.

Figure 15 demonstrated that the surface of clean ITO while generally homogenous can have physical defects on its surface which can be resolved by the PEEM method of imaging. The marks on the surface are possibly scratches on the surface of the ITO glass.

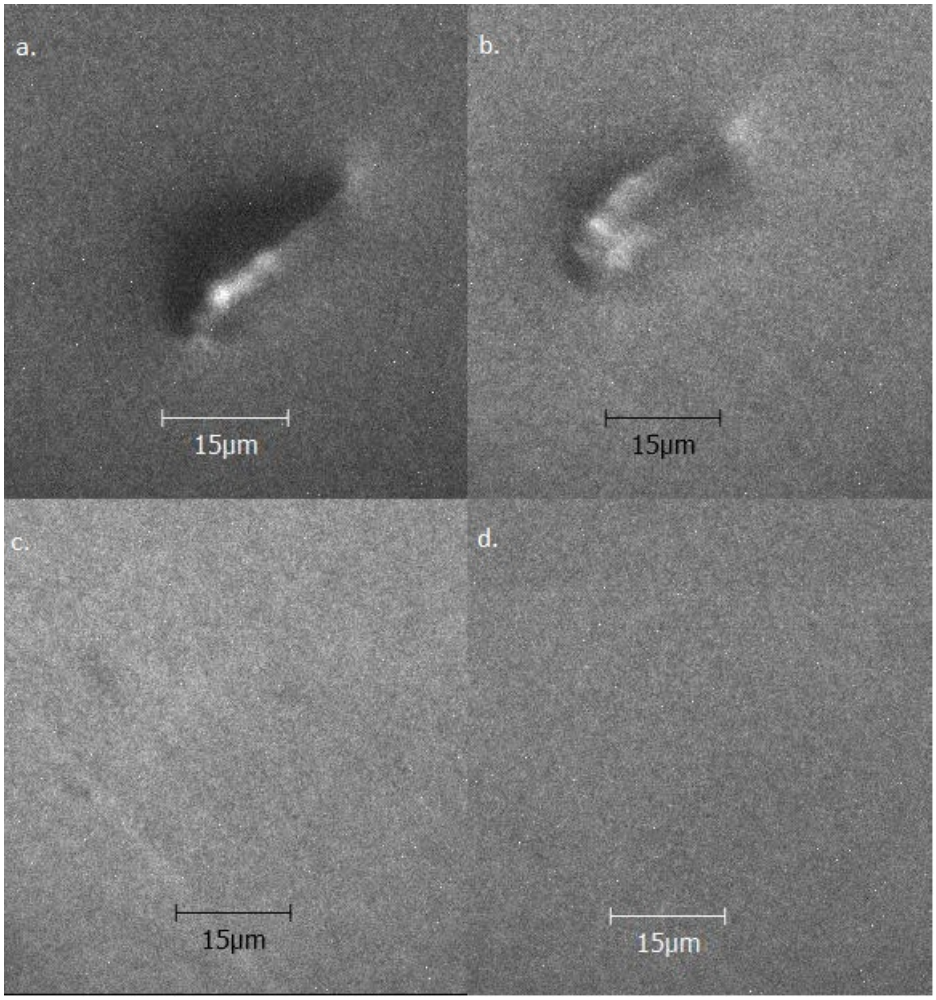


Figure 16: A series of images taken over the same region of cleaned ITO, within the region there is an identified fault. The image was taken at a field of view of 100 µm and a sample bias of -2.0eV. The Image is a region selected from the full images taken. Image a. shows the region prior to heating, image b. shows the region after being partially heated at around 373 K, image c. shows the region after sufficient heating has been applied to remove the potential contaminant at around 474 K, image d. shows the region after cooling.

Figure 16 shows a fault on the surface in order to determine whether this is an example of surface damage or a stray molecule heating must be applied in order to determine this. The PEEM has a heating element as explained above that works by passing a current through the element. Figure 16 shows that the fault has become less pronounced as the heating has been applied indicating that it is not a surface feature since if it was a surface feature heating would not change the morphology of the surface. The image

shows that the potential contaminant has not returned indicating that the fault was a stray molecule as opposed to a surface fault.

The filter can be used for the purposes of spectroscopy by changing the sample bias and measuring the change in brightness between different kinetic energies. This data is differentiated in order to get a spectroscopy curve as illustrated in figure 17 below. Regions of interest can be identified in order to measure the local changes in brightness, this can be used to identify regions that have different properties for example, thick layers of deposited P3HT or monolayers.

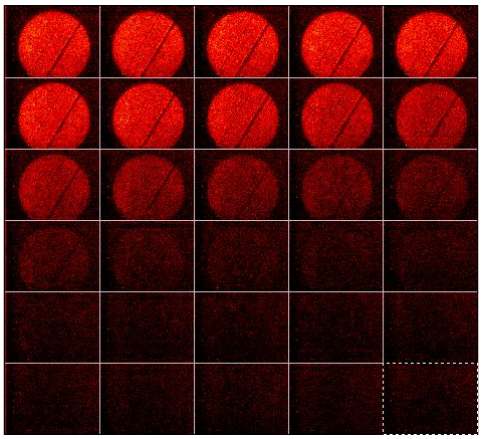


Figure 17: Thirty images taken using varying sample biases, these form the basis of spectra generated by PEEM.

Within the software used to create the spectra there is a capability to highlight specific regions of interest, these are represented by the boxes in the figures that contain spectra. typically for the purposes of obtaining spectra smaller step sizes are used in order to get a more detailed spectra than would typically be obtained by the settings used to obtain figure 17.

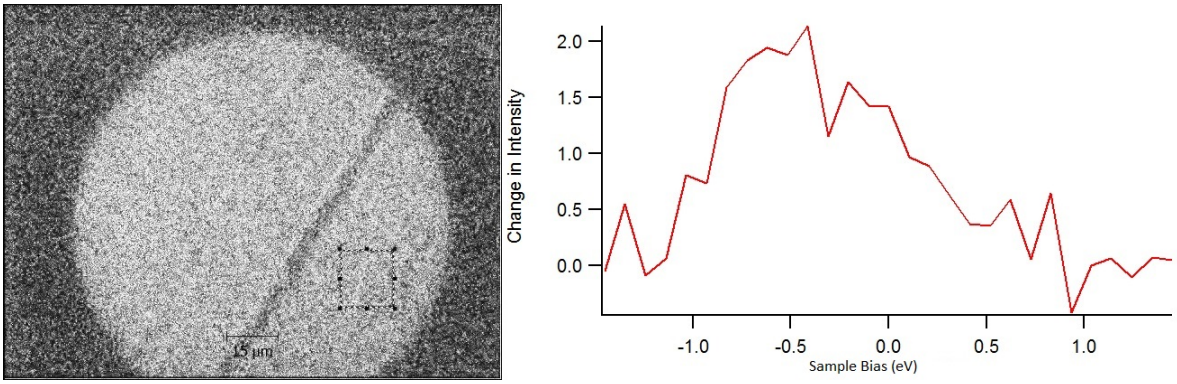


Figure 18: An image of ITO glass at a field of view of 109.7 µm alongside a spectrum corresponding to the region of interest highlighted on the image.

Another ITO sample was placed in the PEEM to explore the spectra and see if across a clean sample of ITO the spectra are similar enough to show that the energy filter is capable of identifying the same material across another sample.

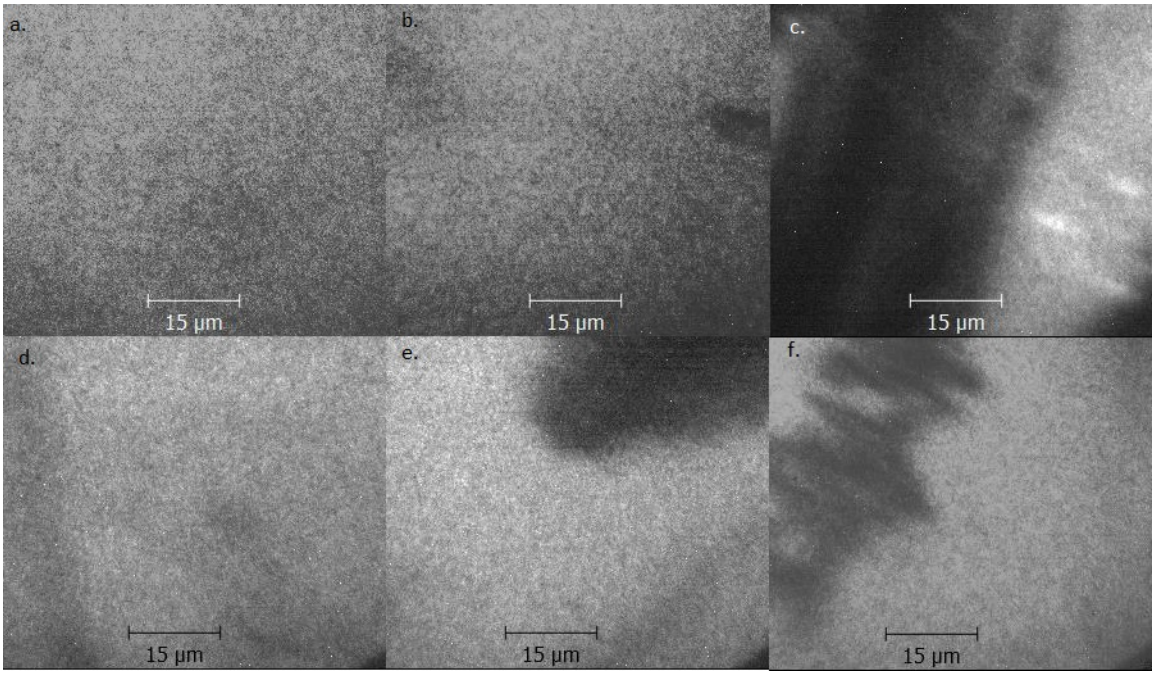


Figure 19: An image of clean ITO glass at a field of view of 109.7 µm of various regions of the same sample, the images are a section taken out of the full images.

Figure 19 shows a region of the cleaned ITO with various regions of the ITO images a., b. and d. show homogeneous regions of the ITO which would meet the expectations of a cleaned ITO surface. Images c., e. and f. show regions that appear to have variations on the surface indicating that while ITO is relatively homogeneous the surface itself

is not completely homogeneous free. The images taken show that ITO is generally homogeneous and the only structure on it are physical faults. Variations on the surfaces impact on the spectrum taken by changing the height of the peaks due to difference in intensity.

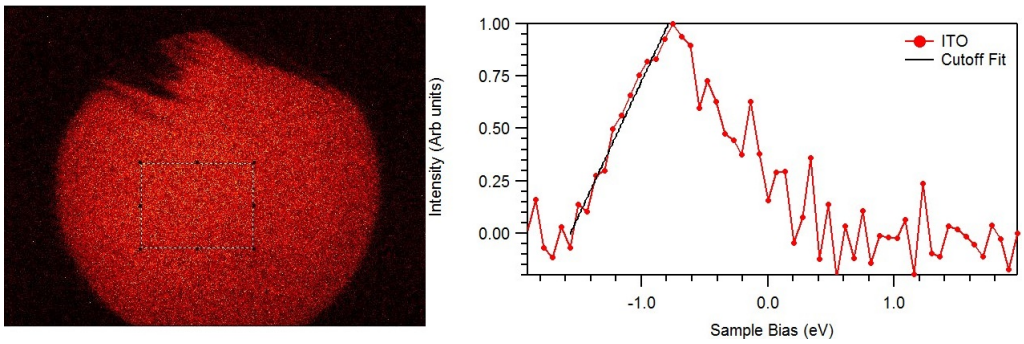


Figure 20: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM. Also the spectrum cutoff has been fitted in order to determine a value of the cutoff.

Figure 20 shows the full image from figure 19 specifically image a. It shows the spectrum taken over the highlighted region, the cutoff value has been determined to be between -1.17±0.05eV.

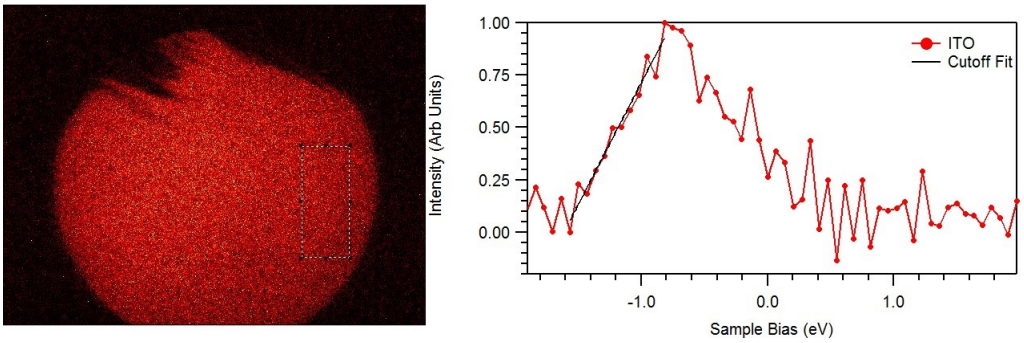


Figure 21: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 21 shows the full image from Figure 19 image a. A different region is highlighted and the spectrum obtained from that regions is displayed, the cutoff value for the beginning of the peak was determined to be -1.18±0.05eV. The cutoffs for both of these regions are similar enough that they indicate that they are made of a material with the same work function. This is what would be expected of a surface with the same material

on it as with clean ITO.

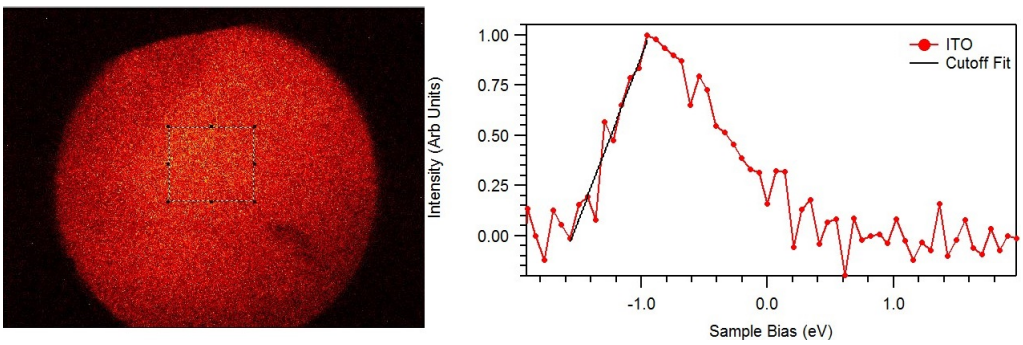


Figure 22: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 22 shows the full image from Figure 19 image b. The spectrum is from the highlighted region on the image, the cutoff values is found to be -1.25±0.05eV.

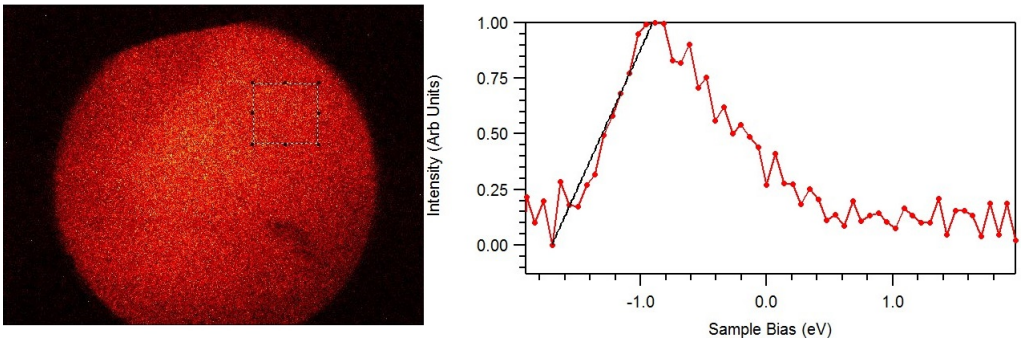


Figure 23: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 23 shows the full image from Figure 19 image b. The spectrum is from the highlighted region on the image, the cutoff values is -1.30±0.05eV. The results from image b do not appear to be the same as image a, in fact there is a significant difference over the same region despite the only superficial difference being brightness.

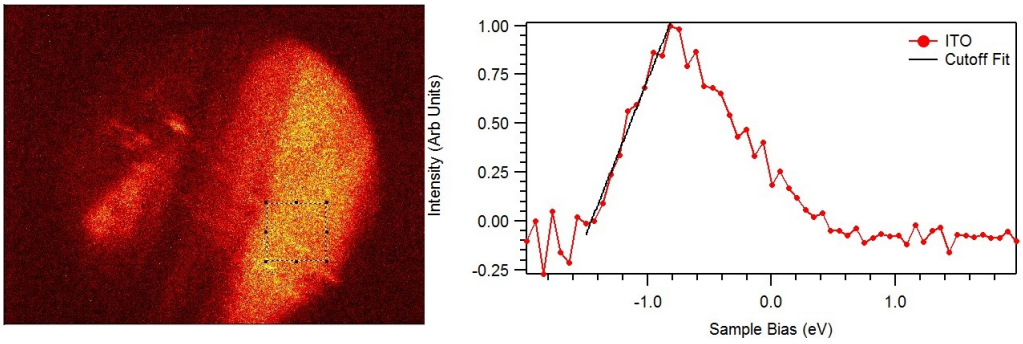


Figure 24: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 24 shows the full image from Figure 19 image c. The spectrum has been taken from the brightest part of the image. This regions cutoff has been determined to be -1.14±0.05eV. This value is more similar to the values found in image a than in image b.

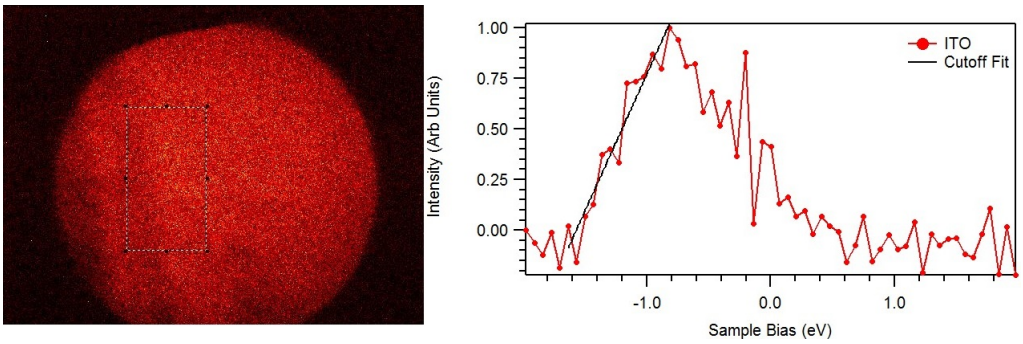


Figure 25: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 25 shows the full image from figure 19 image d. This regions cutoff is -1.19±0.05eV which is similar to the results in region a.

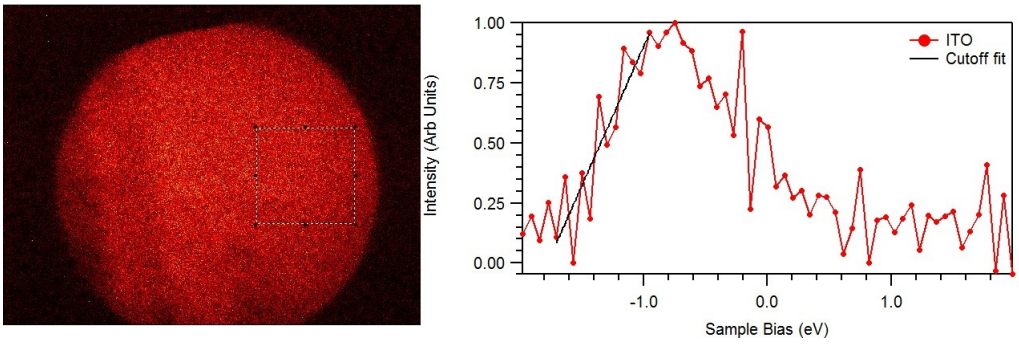


Figure 26: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 26 shows the full image from figure 19 image d. This regions cutoff is -1.34±0.05eV. The two regions from the same image have very different cutoffs with the difference being 0.15eV. This would indicate that they have significantly different properties however as they are both ITO this is a very unusual result.

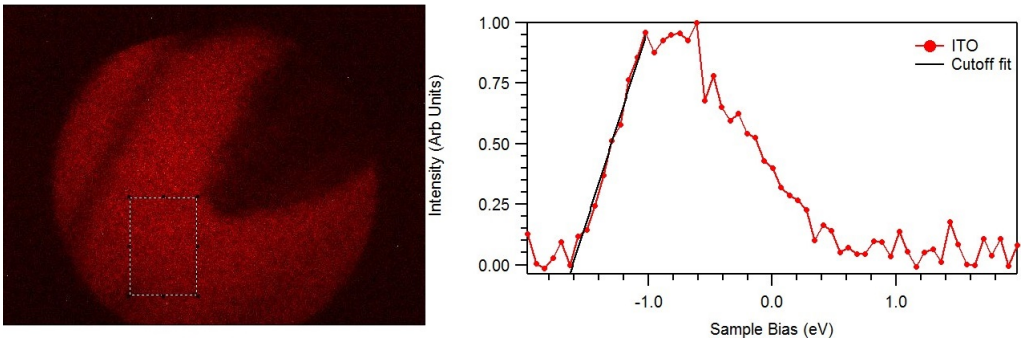


Figure 27: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 27 shows the full image from figure 19 image d. This regions cutoff is -1.30±0.05eV.

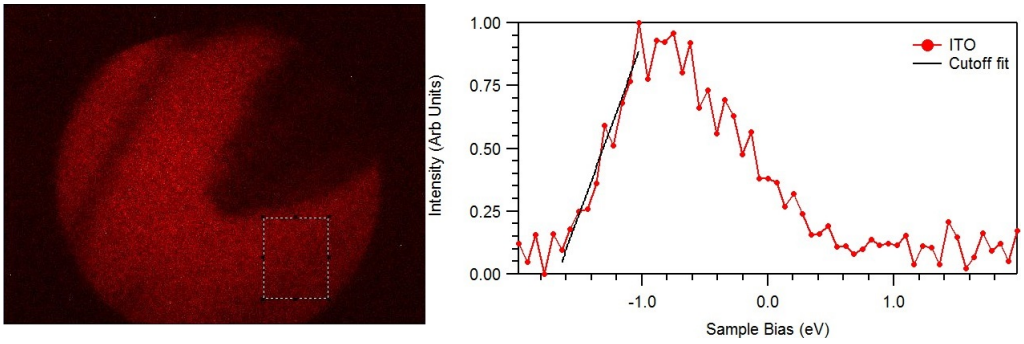


Figure 28: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 28 shows the full image from figure 19 image d. This regions cutoff is -1.30±0.05. The regions from image d show the same cutoff which indicates if if the surface is just clean ITO in this region that it has shown the same result for the work function.

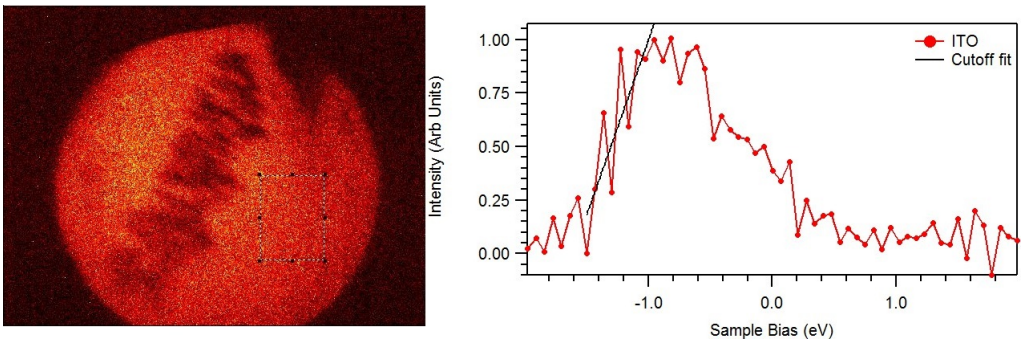


Figure 29: An image of clean ITO glass at a field of view of 109.7 µm alongside a spectrum of the highlighted region taken by the PEEM.

Figure 29 shows the full image from figure 19 image e. This regions cutoff is 1.32±0.05eV.

The values for the cutoff where the peak is determined to begin and relate to the work function has regularly been found to be centered around -1.30eV in terms of sample bias on the PEEM filter with the exception of two regions around -1.15eV in terms of sample bias shown in figures 24 and 25. These differences can either due to there being molecules in these regions. Alternatively that the PEEMs filter cannot properly be used to determine the region has the same material on the surface.

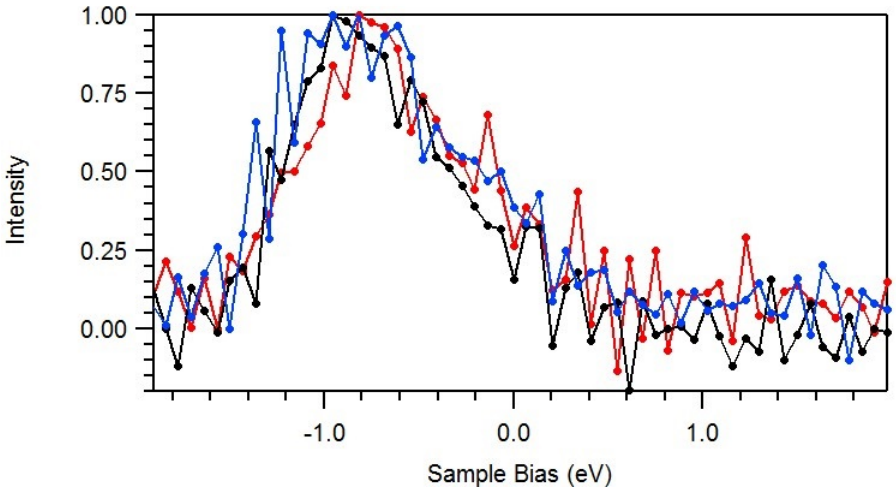


Figure 30: A comparison of the two regions of the clean ITO comparing 3 regions from selected spectra for cleaned ITO.

The comparison of these spectra shows that in the regions highlighted, the point at which the peak begins to form is at the same sample bias indicating that they are the same material. These images were taken across the same sample of cleaned ITO indicating that across the same sample, spectra measurements are consistent, indicating that it can be used as a means to identify regions of the same material as long as the discrepancies in region a is anomalous or the result of a contaminant covering that area of the sample. Otherwise it would indicate the PEEM is not capable of identifying the same region of the same material, however since the other regions cutoff values for the work function agree with each other it seems unlikely to be the case.

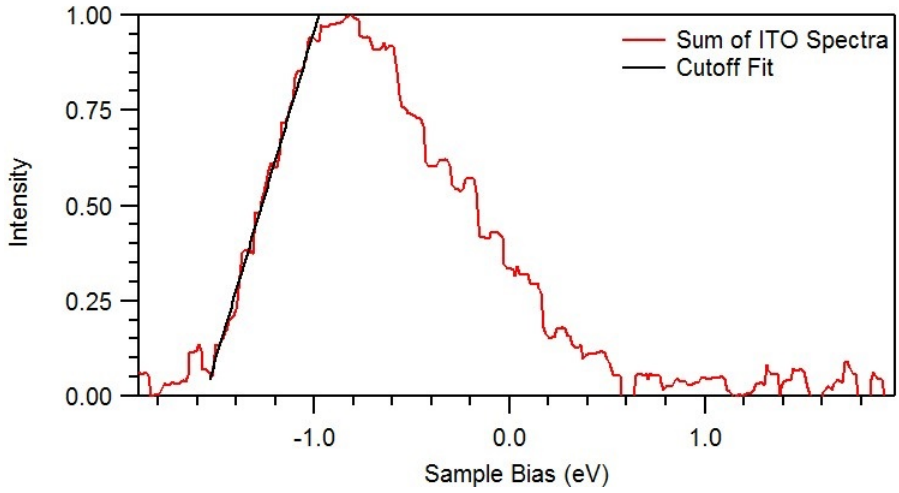


Figure 31: A summation of the spectra of ITO normalised and taken from figures determined to have the same cutoff with a cutoff taken from the normalised spectrum generated.

The cutoff was found to be -1.28±0.05eV this spectrum will be used as the reference to compare other materials deposited on ITO to.

3.4 Conclusion

The PEEM has been used to assess the morphology of cleaned ITO showing that aside from features which can be identified as surface faults, it is a relatively homogeneous surface. The PEEM filter was used in order to identify a cutoff value which is related to the work function of ITO, the value of the cutoff for ITO has been determined to be -1.28±0.05eV. The uncertainty represents the step size used when obtaining the results in each spectrum.

4 PEEM of P3HT and PCBM on ITO

4.1 Introduction

A series of samples were examined with molecules deposited onto cleaned ITO, firstly samples with just P3HT and PCBM were made in order to observe changes in morphology observed by the PEEM as well as determine if the filter on the PEEM could determine if there was a different material on the surface. All of these samples were made using spin coating which is a process where a substrate is revolved at high speed in order to ensure uniform film thickness across a sample. The sample is placed onto a rotating piece which can rotate typically between 1000 and 6000 revolutions per minute.

4.2 Preparation of Samples

A spin coated sample of the 0.2 weight percentage P3HT was made in order to compare the morphology. The sample was made by drop depositing the solution and spinning at 2.5 KRPM for around 30 seconds in an effort to create an even morphology across the sample. This angular velocity yields a film thickness of approximately 600nm which means that emission from the surface of the substrate will not be detected. In the case of the samples imaged in this series of images the sample was rotating as the solution was drop deposited. The aim is to create a film of uniform thickness across the substrate so that the features which have images taken are of similar morphology allowing for direct comparisons of their spectra with the knowledge that film thickness is not effecting the results. The ITO was cleaned by submerging it in: Acetone, Methanol and Isopropanol while being place in a sonic bath for 10 minutes per solvent. The same process was used for the substrates used in the PCBM samples. The mixtures were made by adding the required ratio of each solution in a third container and then following the same spin coating method used for the individual molecules they were deposited onto cleaned ITO.

4.3 P3HT on ITO results

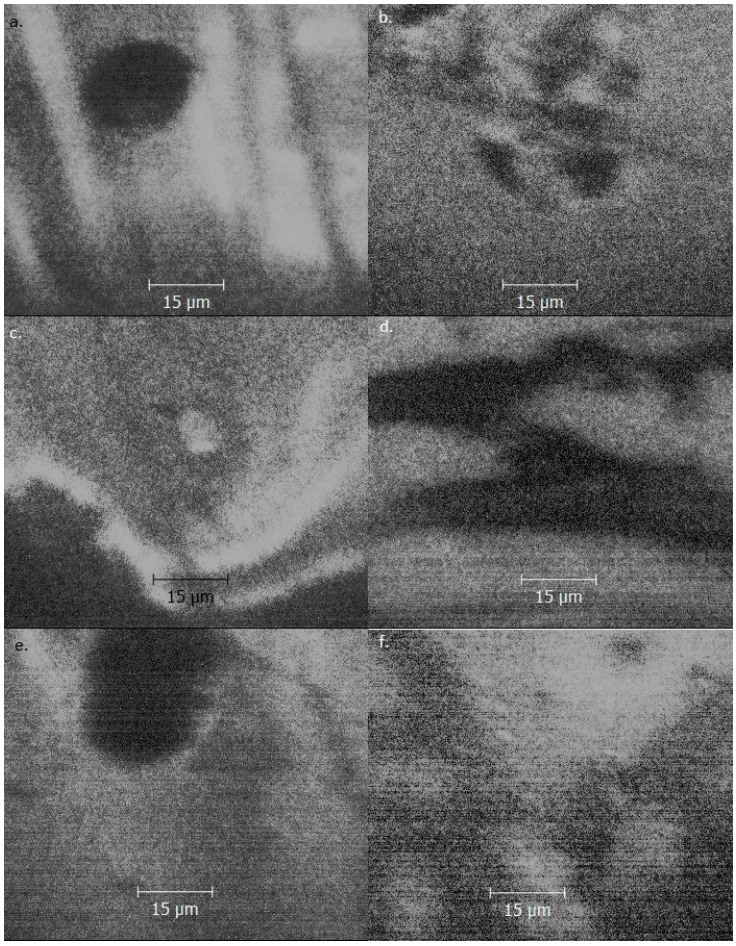


Figure 32: A series images taken of an ITO sample spin coated with P3HT dissolved in chlorobenzene taken at a field of view of 109.7 µm. The images are selected sections of the whole image presented together. The images are in gray-scale because it more clearly showed definition in the morphology.

Region a. shows a series of ridges that appear to be surface defects where the P3HT has collected and formed thicker depositions along the ridges, these are represented by the brighter regions. There is a also a dark region that could be a very thick region of P3HT due collecting between ridges or simply a surface fault. Region b. shows a homogeneous region interrupted by what appear to be surface features, as there is a brighter region surrounding the dark spots that can be seen on the figure indicating that the P3HT may have collected around these faults as with the ridges seen in other areas of the sample. Region c. shows a section of brightness neighboring a darker area, the bright region appears to be homogeneous within itself. The region in region c. may

represent an edge of the P3HT film meaning the darker region is the ITO substrate or possibly a thinner layer of P3HT, though this is unlikely due to the spin coating used to deposit the solution. Region d. shows a region of the spin coated sample that appears inhomogeneous, this could be because of surface features on the ITO surface. The regions of the image that are bright are homogeneous indicating that the spin coating achieved homogeneity in this region, with the exception of the surface faults. Region e. shows a relative homogeneous region with two major dark spots, these display similar behaviour to the dark region in region b. indicating that it may also be surface faults. The region imaged in region f. is very inhomogeneous compared to the other regions with significant dark regions surrounding bright regions indicating that the spin coating may have limitations with regards to creating a perfectly homogeneous film. The filter was used on various regions of the P3HT sample and compared to the ITO in order to determine if the filter can distinguish between ITO and P3HT on ITO.

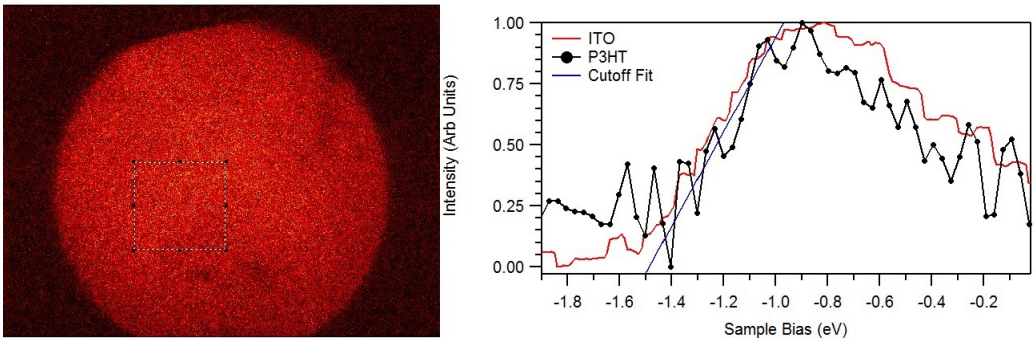


Figure 33: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm. The ITO line corresponds to the spectrum in figure 31.

Figure 33 shows a homogeneous region of the sample over which the P3HT was spin coated, the filter was used on this region and compared to the ITO spectrum taken in figure 31. The cutoff was found to be -1.22±0.05eV This is slightly lower than the value found for the ITO spectrum in the figure which is -1.28±0.05eV, this is in line with the expectations of the result as it is a lower work function indicated by higher sample bias at which the cutoff is found.

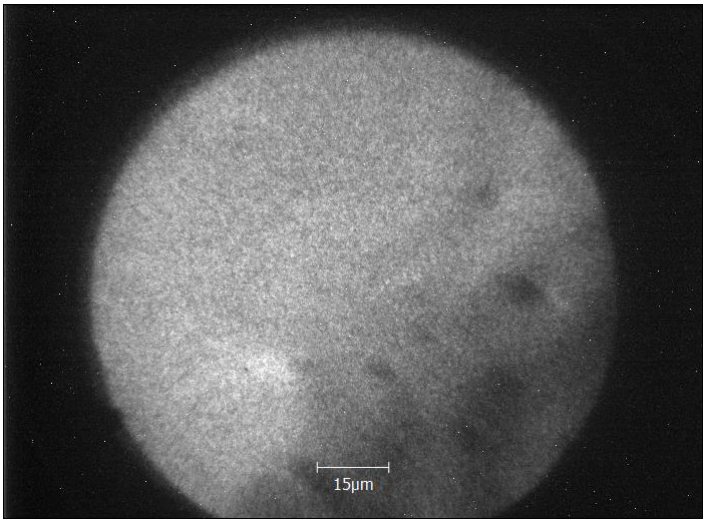


Figure 34: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm.

Figure 34 shows a region of the sample that has a large homogeneous region alongside a darker less homogeneous region, a spectrum was taken of this region and compared to ITO.

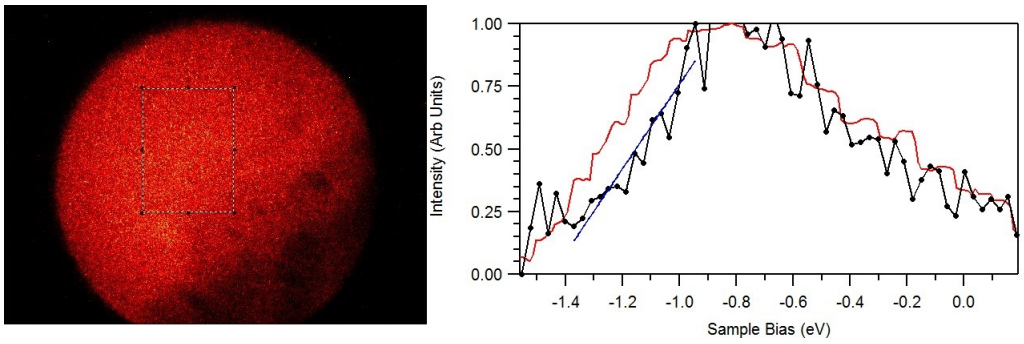


Figure 35: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm. The red line is the spectrum for ITO.

Figure 35 shows the same area as in figure 34 alongside a spectrum taken of the region, once again this region shows that the peak begins at a higher sample bias consistent with the previous obtained results for P3HT when compared to clean ITO. The cutoff was found to be -1.06±0.05eV this is not only significantly different from the ITO result but also different for another sample of P3HT on ITO, this may indicate that the PEEM is not consistently able to identify the same material. However the region could also be subject to local morphologies on the ITO causing the P3HT to form thicker or

thinner regions affecting the work function found by the PEEM. This result is closer to the experimentally determined difference between P3HT and ITO though it is still significantly different from these values.

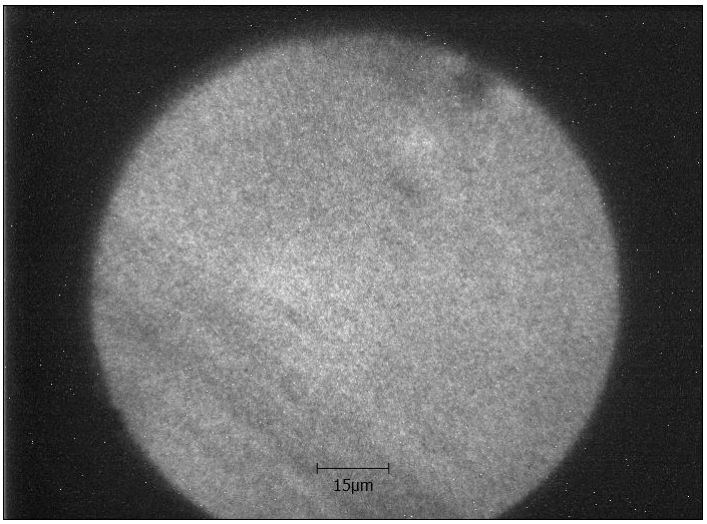


Figure 36: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm.

Figure 36 shows a homogeneous region that may not be distinguishable from clean regions of ITO, the spectrum taken here will illustrate whether the PEEM filter can be used to determine the difference between regions that are visually similar but are different materials.

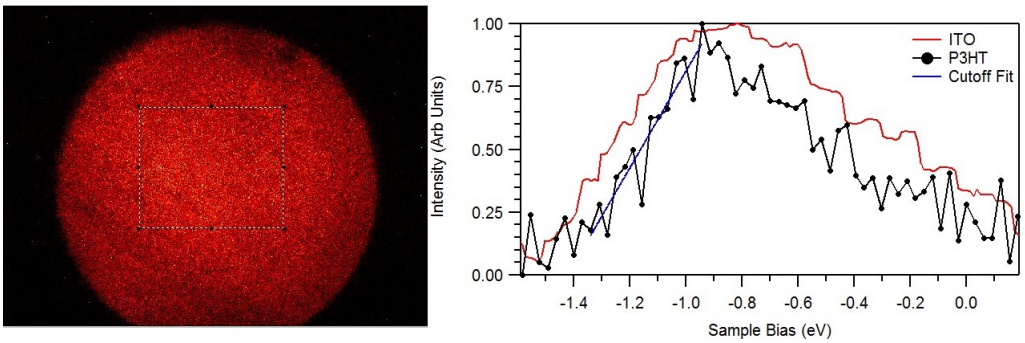


Figure 37: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm.

Figure 37 shows the region in figure 36 with a spectrum taken from the region highlighted. The cutoff has been found to be -1.17±0.05eV this is substantially different from the ITO cutoff found and is consistent with the other P3HT spectra taken showing that the cutoff

value is higher than the ITO. This has shown that the PEEM can identify differences in regions that look similar across different samples as the region shown is not very different morphologically from cleaned ITO and has been shown to have a different work function. The value of the cutoff is different from the others found for P3HT though it is closer to the value found for the spectrum in figure 33 indicating these regions have met similar conditions.

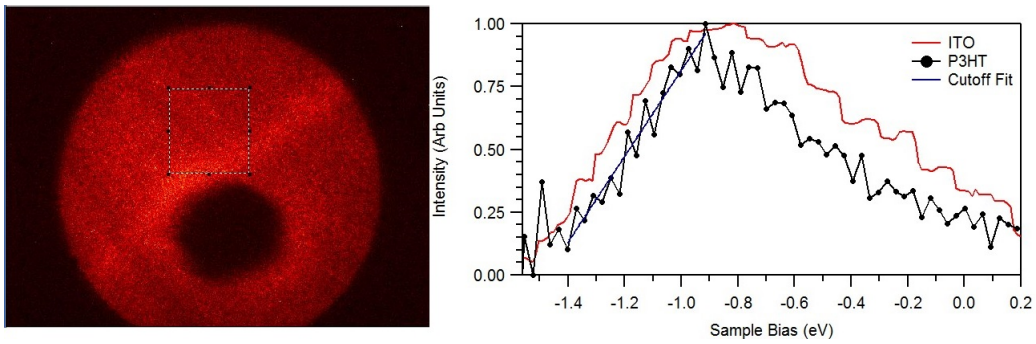


Figure 38: An image taken of clean ITO with P3HT dissolved in chlorobenzene spin coated onto it taken at a field of view of 109.7 µm.

Figure 38 shows a region with a substantial dark circular region surrounded by a homogeneous region, the dark patch could be a result of surface features. The cutoff has been found to be -1.19±0.05eV which is consistent in that it is higher than the ITO cutoff, the cutoff is also similar to the cutoff found in figure 37 indicating that these regions have met similar conditions with the deposition regarding the ITO in that region and how it affects the P3HT.

Drop deposited sample of P3HT in chlorobenzene were made in order to see if different morphologies could be identified that did not arise in the spin coated samples.

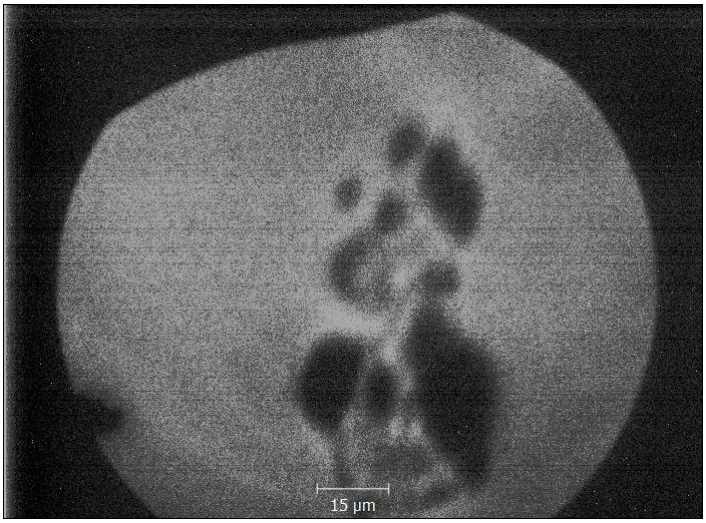


Figure 39: An image taken of P3HT dissolved in Chlorobenzene drop deposited onto ITO. This image was taken in high magnification mode with a field of view of 109.7 µm.

This region has a series of dark regions containing bright regions, this is in line with what would be expected as it is typical of polymer depositions, though it does not have the particular complexities that might otherwise be expected. The dark spots are often neighboring brighter regions that the typical homogeneous region surrounding it indicating that they may have formed as a result of a fault on the surface as in the spin coated sample.

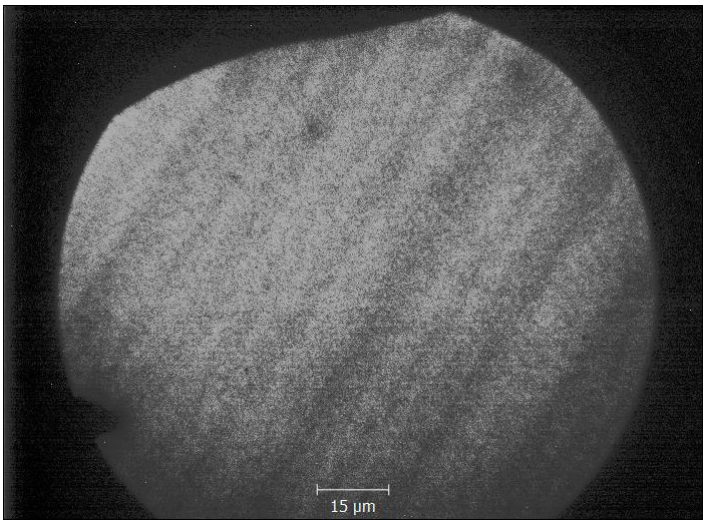


Figure 40: An image taken of P3HT dissolved in Chlorobenzene. This image was taken in high magnification mode with a field of view of 109.7 µm.

Figure 40 shows a region where there doesn't appear to have had P3HT deposited on it

showing the features of clean ITO. The features in the image are likely to be ridges on the substrate. This can be expected with drop deposition as there was not any measures taken to ensure even distribution. This can be checked using the filter though it was not done in this case, the filter could be used to compare it to different regions on this sample and confirm that there is a different work function here.

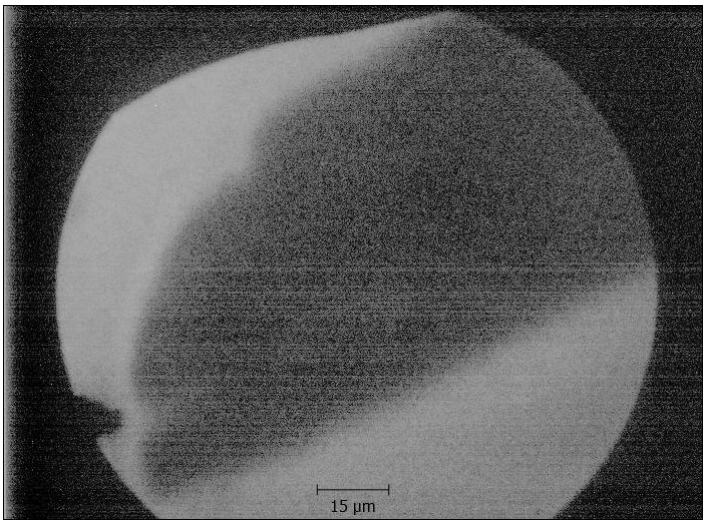


Figure 41: An image taken of P3HT dissolved in Chlorobenzene. This image was taken in high magnification mode with a field of view of 109.7 µm.

This region appears to have a large and thick deposition of P3HT on the ITO as the regions surrounding it are bright as is consistent with other P3HT depositions. Also the thickness of the P3HT may be effected by the concentration of the solution leading to large areas that are unable to conduct. These may also be surface faults though it does not appear to be consistent with other surface faults as there isn't a build up of brighter/f material around the darker region.

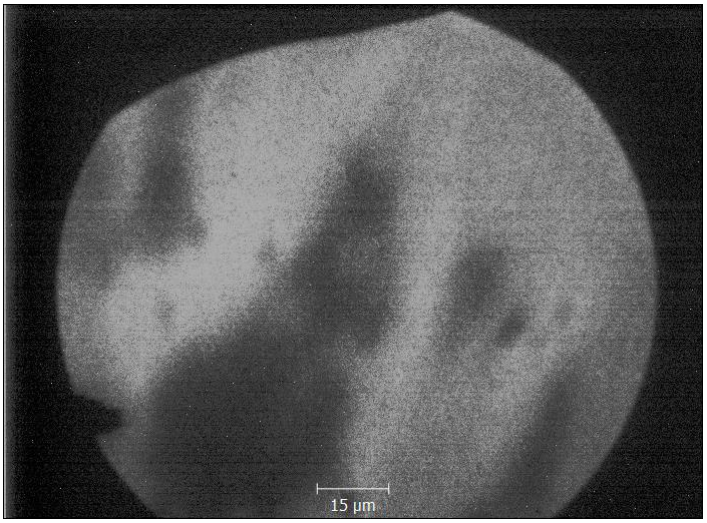


Figure 42: An image taken of P3HT dissolved in Chlorobenzene drop deposited on ITO. This image was taken in high magnification mode with a field of view of 109.7 µm.

This region has the features of most of the other regions imaged in the other figures for P3HT in Chlorobenzene that has been drop deposited onto ITO. This region also appears to have similar structure to figure 41 however in this case the dark region borders a region that is noticeably brighter than the more homogeneous areas in the image. This may indicate that a there has been a build up of P3HT alongside a thicker region of the deposition as opposed to being the result of surface features.

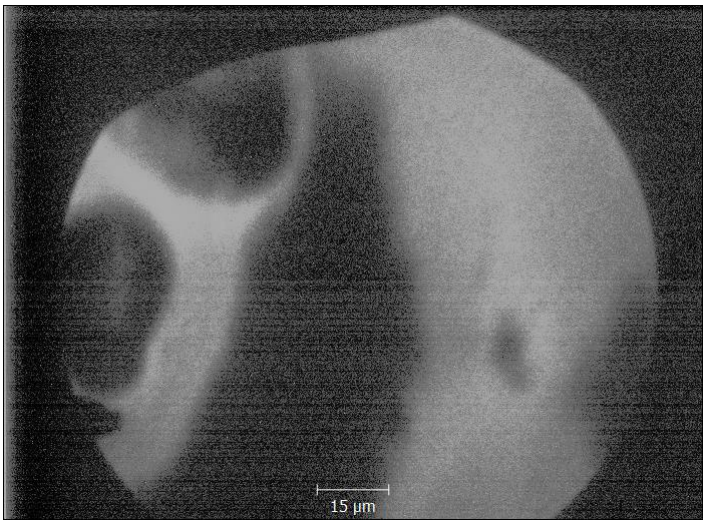


Figure 43: An image taken of P3HT dissolved in Chlorobenzene drop deposited on ITO. This image was taken in high magnification mode with a field of view of 109.7 µm.

Figure 43 shows similar features to the other images taken on this sample indicating it

has dark regions bordered by lighter regions as in other areas of the samples with P3HT deposited on them. This may indicate that the P3HT has collected next to thicker depositions.

The P3HT dissolved in Toluene was drop deposited onto the clean ITO and was imaged using the PEEM. The most interesting structure that was observed was a fractal structure an example of which is shown in figure 44, that was not observed when spin coating was used, this is because the P3HT when spin coated is not allowed to form drying patterns that could result in such complex structures. Also the Toluene did not dissolve all of the P3HT indicating it may have only dissolved the shorter chain lengths which may favour the formation of fractal and other complex structures.

Spectra were obtained using the same process as for clean ITO and the spin coated P3HT in order to determine if the regions inside and outside the fractal are the same material or if the thickness of the film impacts work function enough to be detected by the PEEM filter. This sample was made by drop depositing P3HT in toluene onto cleaned ITO, the toluene was not able to dissolve all of the P3HT indicating that it was unable to dissolve longer chain lengths of P3HT.

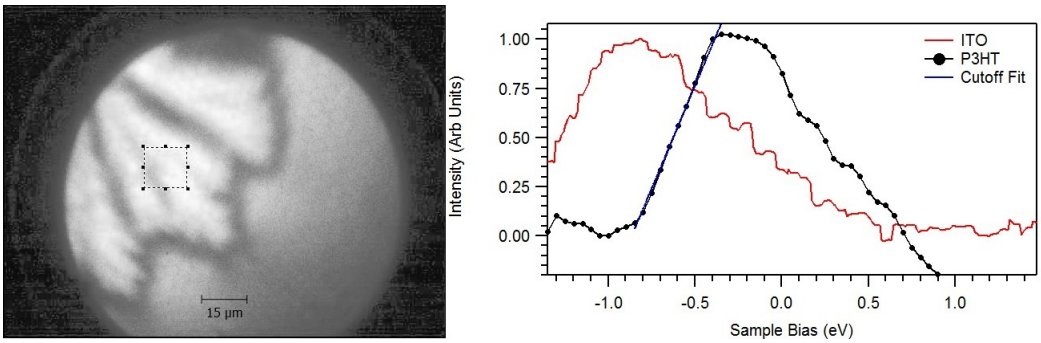


Figure 44: An image of P3HT dissolved in toluene drop deposited on ITO.

The P3HT has formed a fractal like structure on the surface of the ITO due to specific conditions being met that allow for these structures to form. The region of interest is within the structure of the fractal and shows a different sample bias at which the peak begins to form to clean ITO. The cutoff has been found to be -0.63±0.05eV this is significantly different from both the values found across the spin coated sample as well as from ITO. The difference between the ITO and this region of P3HT is 0.65eV less negative, which is consistent as it shows that P3HT has a lower work function like the

other results for P3HT. The result is also closer to the absolute difference that would be expected between P3HT and ITO.

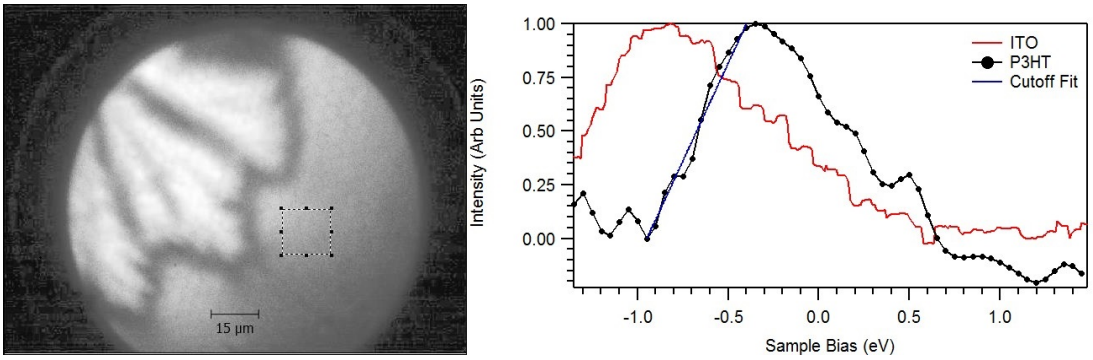


Figure 45: An image of P3HT dissolved in toluene drop deposited on ITO. The P3HT has formed a fractal on the surface.

The region outside of the fractal shows a similar cutoff at 0.63±0.05eV which is the same as the region within the fractal this means that the regions are made of materials with the same work function.

This demonstrates the ability of the PEEM to identify regions that while superficially different are made up of the same material. Overall it has been demonstrated that the PEEM filter can be used to identify regions of the same material across the same sample while also being able to distinguish between specifically cleaned ITO and P3HT, the next step is to test this capability with PCBM in order to determine if the PEEM filter could potentially be used to identify different regions in mixtures of P3HT and PCBM.

4.4 PCBM Spin Coated Results and Discussion

A solution of PCBM in Chlorobenzene was created with a concentration of 0.2 weight percentage and then spin casted onto ITO at a rotation speed of 2.5KRPM. The PCBM solution was spin cast onto a clean ITO substrate and imaged using PEEM. The speed of the spincasting was 2.5 KRPM and the spinning began after the deposition of the solution.

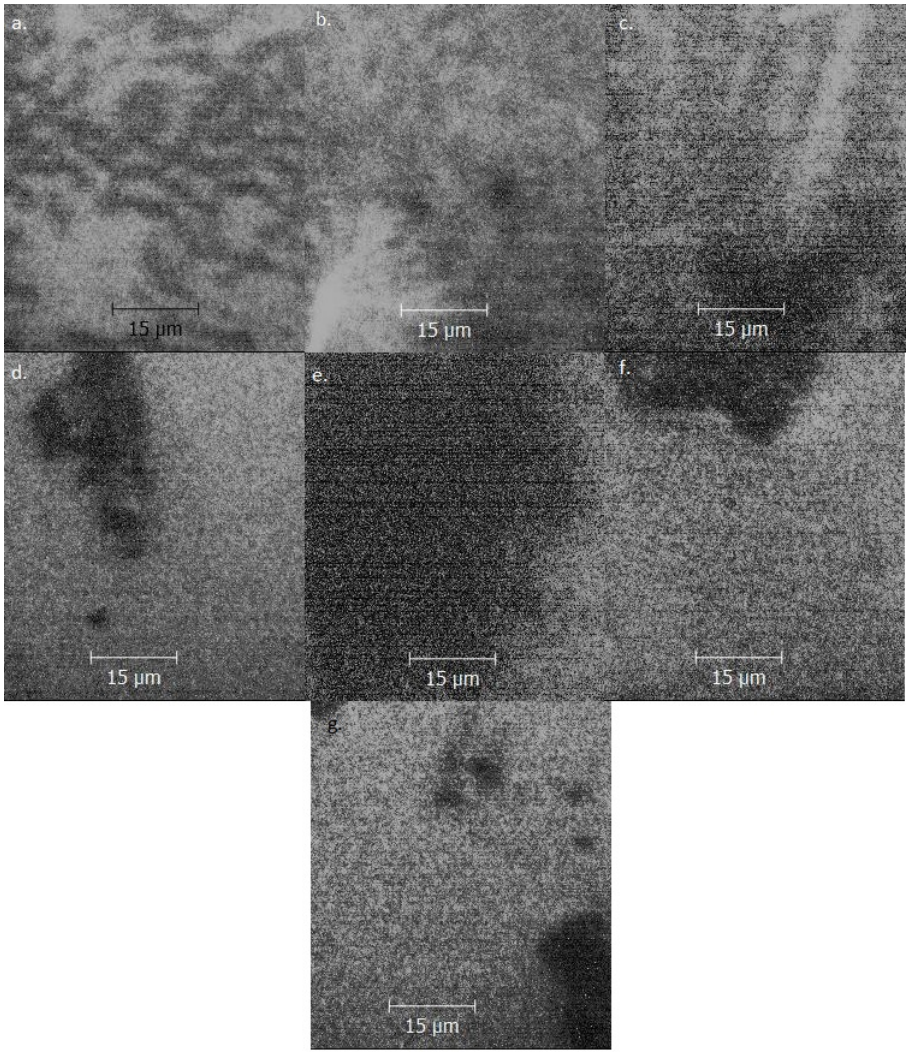


Figure 46: A series of images taken at 109.7 µm of ITO spin coated in PCBM with Chlorobenzene on the same sample. All of the images are sections of full images taken by the PEEM.

Region a shows an area that is covered in both dark and bright regions, the dark regions most likely correspond to thicker PCBM depositions on the surface. Region b shows a region that is covered in both dark and bright regions, as in region a the dark regions are likely to correspond to thicker PCBM depositions. Region c also shows a similar pattern to regions a and b. Regions a b and c do show somewhat complicated patterns on the surface of the ITO this is in contrasts to regions d, e, f and g which show relatively homogeneous regions with large regions of darkness on them, these might be as a result of a less even surface in the regions where these images were taken as in the P3HT being affected by surface defects.

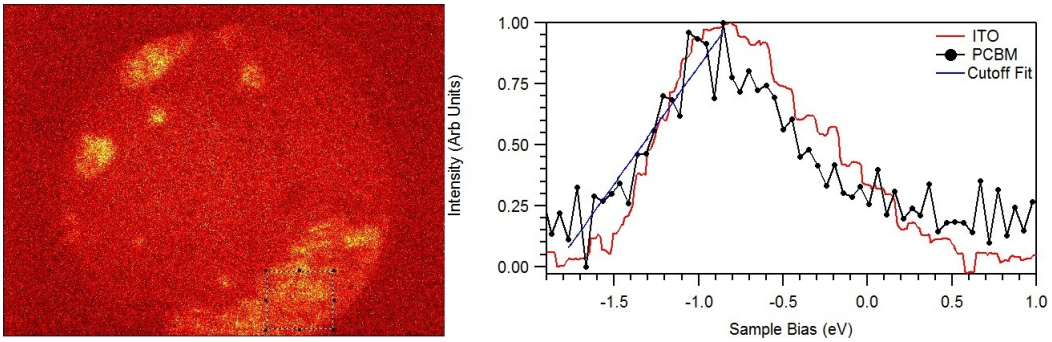


Figure 47: An image taken at 109.7 µm of ITO spin coated in PCBM in Chlorobenzene. Alongside it is a spectrum taken of the highlighted region compared with ITO and the Cutoff Fit for the PCBM spectrum.

Figure 47 shows the full image from the sample of spin coated PCBM. It shows the spectrum taken over the highlighted region, the cutoff value has been determined to be -1.34±0.05eV This is similar to the ITO cutoff with a difference of 0.6eV which doesn't fit with the expected results as the difference is too large between the ITO and PCBM cutoffs.

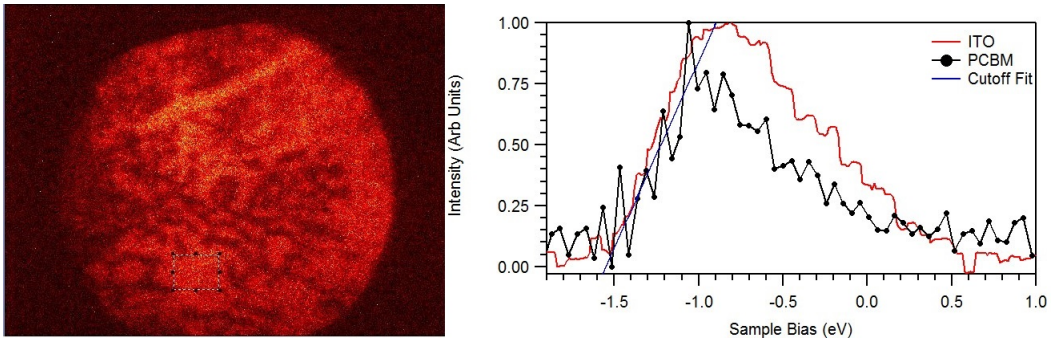


Figure 48: An image taken at 109.7 µm of ITO spin coated in PCBM in Chlorobenzene. Alongside it is a spectrum taken of the highlighted region compared with ITO and the Cutoff Fit for the PCBM spectrum.

Figure 48 shows the full image from the sample of spin coated PCBM specifically from region a in figure 46. It shows the spectrum taken over the highlighted region, the cutoff value has been determined to be -1.22±0.05eV. This value is very different from the spectrum taken over the same sample in figure 47, this either indicates that one of the regions is bare ITO or a thinner deposition of PCBM or that the PEEM is not able to identify the regions assuming they have the same material spread over them as would be

expected of a sample of cleaned ITO spin coated in PCBM. This result is also similar to the P3HT results which may indicate the PEEM has difficulties differentiating between the two.

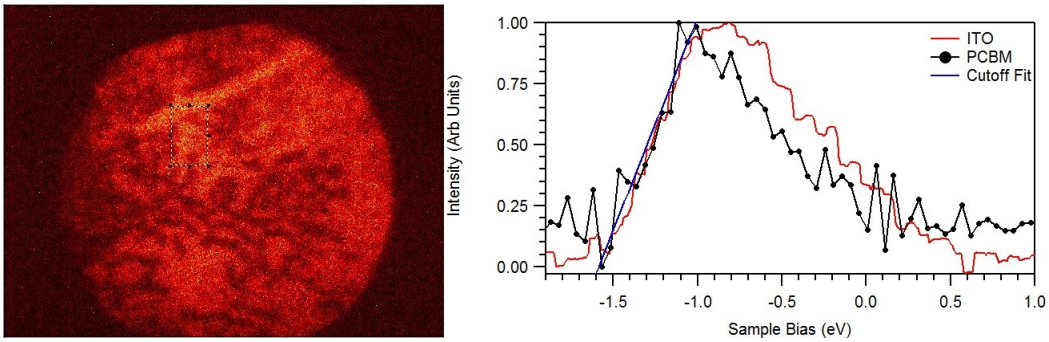


Figure 49: An image taken at 109.7 µm of ITO spin coated in PCBM in Chlorobenzene. Alongside it is a spectrum taken of the highlighted region compared with ITO and the Cutoff Fit for the PCBM spectrum.

Figure 49 shows the full image from the sample of spin coated PCBM specifically from region a in figure 46. It shows the spectrum taken over the highlighted region, the cutoff value has been determined to be -1.31±0.05eV. This value is more in line with the value found in figure 47 indicating that this region and the region in figure 47 are covered in a material with the same work function as opposed to the cutoff found in the same region which is higher by 0.09eV. This cutoff also more closely resembles expected results in terms of the difference between the work functions of ITO and PCBM however the cutoff is lower representing a higher work function which is not consistent with expected results.

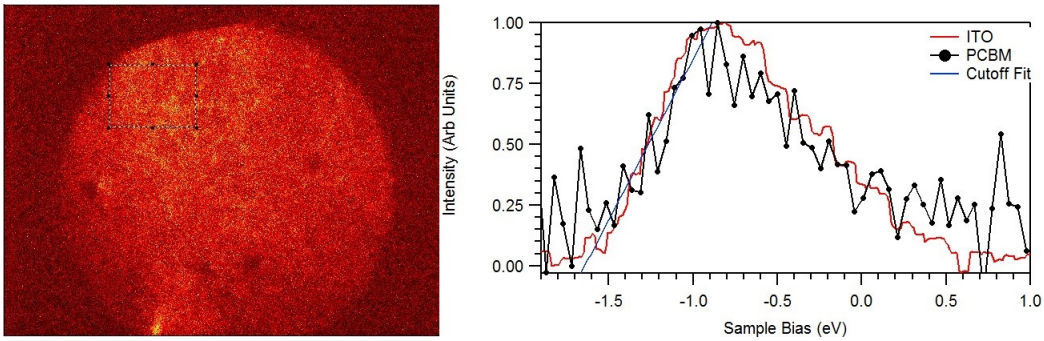


Figure 50: An image taken at 109.7 µm of ITO spin coated in PCBM in Chlorobenzene. Alongside it is a spectrum taken of the highlighted region compared with ITO and the Cutoff Fit for the PCBM spectrum.

Figure 50 shows the full image from the sample of spin coated PCBM specifically from region a in figure 46. It shows the spectrum taken over the highlighted region, the cutoff value has been determined to be -1.27±0.05eV. This cutoff is within the uncertainty of the ITO cutoff indicating that the PEEM may not be able to tell the difference between PCBM and cleaned ITO.

These results are typically over the same range of the ITO this does not indicate that the PEEM can determine between cleaned ITO and PCBM on ITO.

4.5 PCBM drop deposited on ITO results

A solution of PCBM in Toluene was prepared and drop deposited onto a piece of clean ITO. The preparation of it was the same as the P3HT in Toluene solution, the PCBM totally dissolved as in the case of using chlorobenzene.

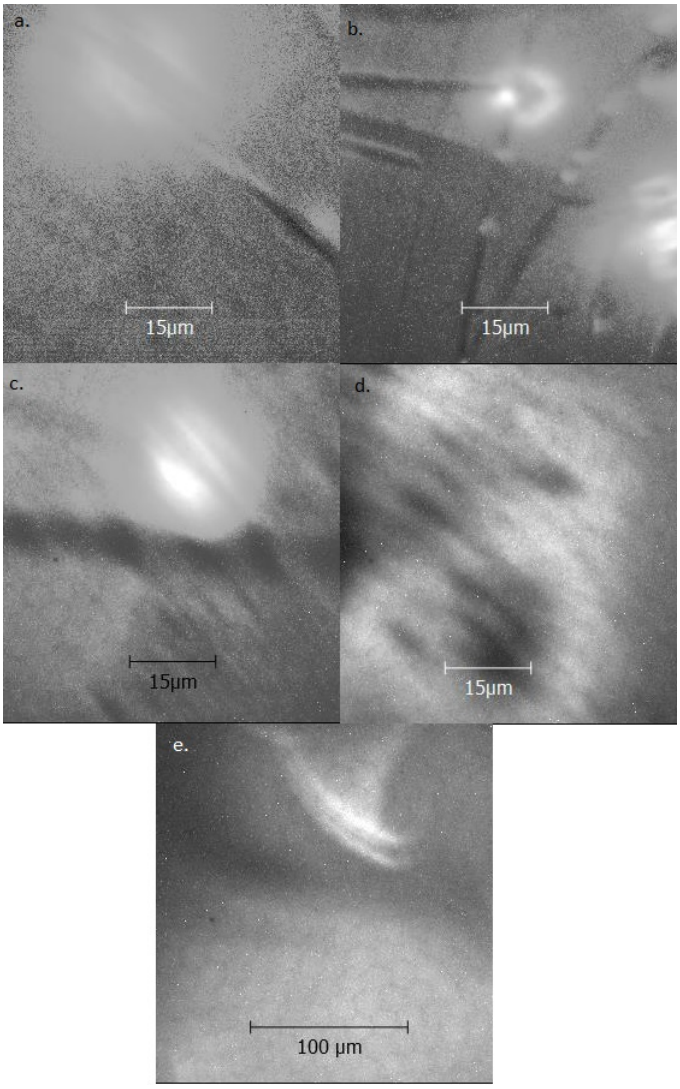


Figure 51: A series of images taken of drop deposited PCBM across the same sample. region a shows a significant surface feature with a bright region on it. Region b shows a similar region to a but with more features and bright spots. Region c shows another bright spot that appears to have formed at another surface feature. Region d shows a region with significant dark regions surrounded by brighter regions. Regions a, b, c, d are parts of full images taken at 109.7 µm and a sample bias of -2eV. Region e shows a section of an image taken at 400 µm with the filter off.

The brightness shown in region a is not only limited to large surface features. These bright region can be observed around dark regions on the sample which could be multilayer depositions of PCBM. The bright region around one of these features could be PCBM as these features are repeated along large scale surface features and were not present before deposition of PCBM onto the ITO surface. In regions a, b and c there

is a tendency demonstrated on this sample that bright regions tend to be found near surface faults, in this case scratches, these could be a result of PCBM that has collected around the scratches. The bright regions in region d surround the darker region which could be a multilayer deposition of the PCBM on the surface, possibly indicating that the bright regions are much thiner depositions on the surface of the ITO. Region e shows large scale 'scratches' that are curved slightly, one of these features is significantly brighter than the others perhaps indicating that a large amount of PCBM has collected in this region. This could also indicate the PCBM tends to form circular patterns. A lot of these features were not observed in spin coated PCBM this is likely because it resulted in more uniform film thickness across the sample leading to the PCBM being unable to collect at surface faults on the surface. Though large dark regions are still present on the spin coated PCBM this may mean that the regions in the spin coated and drop deposited PCBM samples that show these features have met similar conditions for the formation of these structures.

4.6 Conclusion

The PEEM has been used to compare the morphologies of P3HT and PCBM with each other and ITO, the results show that P3HT forms more complicated and structured patterns across the surface of ITO as well as regions that appear homogeneous. The regions which appear complicated appear to be as a result of surface faults as well as the P3HTs tendency to form these patterns. The P3HT has also met the conditions to form fractal patterns which do not appear on spin coated samples indicating that the spin coating succeeds in ensuring more even distribution of the solution across the substrate. The cutoffs found for P3HT were found to be -1.20±0.05eV indicating there is a difference that exists between the P3HT and ITO, one cutoff was found to be -1.06eV this result is distant from the typical results found for P3HT. The cutoff for P3HT is less negative indicating its work function is lower than that of ITO which is consistent with what would be expected, however the difference found between the values is not as large as that found in the expected values which is 0.1eV. PCBM was found to be largely homogeneous with large dark regions across the sample of PCBM on ITO. Both molecules show round dark regions on their surfaces these may be as a result of the underlying ITO. The cutoffs for the PCBM were typically found to be -1.31±0.05eV which is close

to the value of the ITO, which would be what is expected as the expected difference would be 0.1eV which the PEEM is not expected to be able to differentiate between. The morphologies of the P3HT and PCBM have been found to be quite different by the PEEM as the P3HT has shown capacity to form complicated structures on the substrate whereas PCBM does not form these structures.

5 P3HT and PCBM Mixtures deposited on ITO

5.1 Introduction

Mixtures of P3HT and PCBM solutions were made in varying ratios to determine how this changes the morphology of the surface. A series of mixed samples were made with the ratios, 1:1 in in order to get a reference for an equal mixture of the two solutions. A 2:1 blend was made and then a 1:0.8 P3HT:PCBM sample was made. The samples were made by spin coating cleaned ITO at 2500 RPM to ensure uniform thickness of the film.

5.2 Preparation

The ITO was prepared in the same way as in the other series of experiments using a three solvent wash to make sure any dirt is removed from the surface and does not effect the morphology. The mixtures were made by mixing the original solutions with the weight percentage concentration of 0.2 percent to the desired ratios. The cleaned ITO was rotated at 2.5KRPM when drop depositing was carried out. In the preparation of the solutions the P3HT in chlorobenzene was heated up to 50 degrees over an hour to ensure total dissolution.

5.3 1:1 P3HT:PCBM Results and Discussion

The PEEM was used on a 1:1 mixture of P3HT:PCBM and used to get images and spectra in order to determine if the PEEM can observe the difference between these molecules on the same surface.

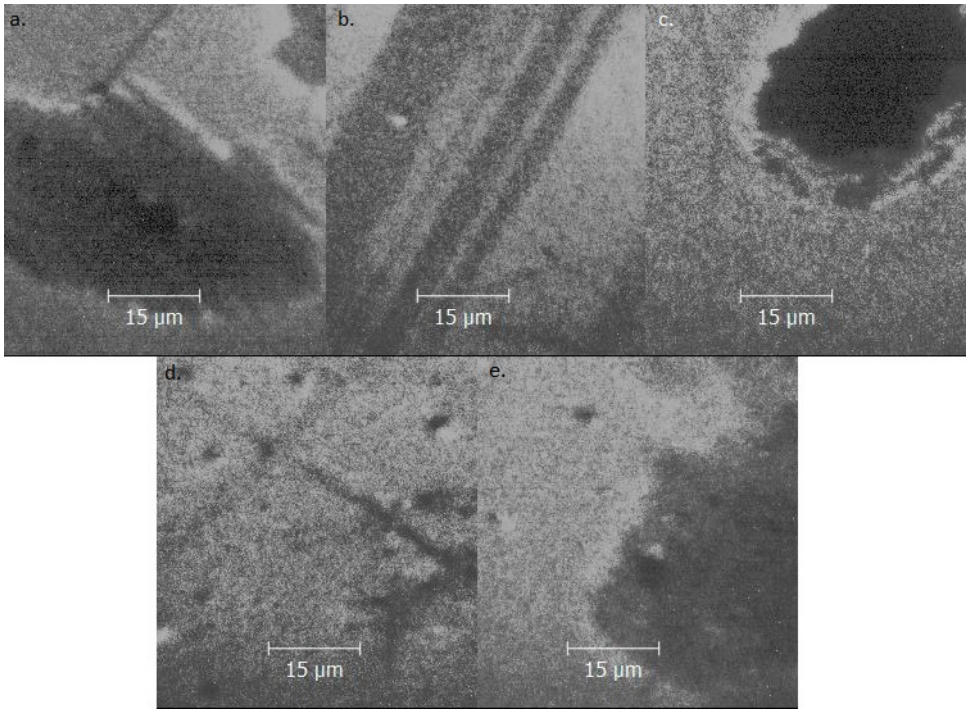


Figure 52: A series of images taken of a cleaned ITO sample spin coated with a 1:1 mixture of P3HT:PCBM in chlorobenzene. Images are selected sections of the full images taken at 109.7 µm with a sample bias of -2eV in order to ensure all of the features on the surface are made visible. Regions a, c and e show areas of the sample that contain larger dark regions. Region b shows an area of the sample that appears to have surface faults and the solution has spread evenly around the faults. Region d shows an area with the solution distributed evenly across the surface around the surface faults on the ITO.

The morphology of the 1:1 mixture spin coated onto ITO shows that it is a mostly homogenous surface apart from the areas in which the solution interacted with surface faults. The mixture displays some of the signs of PCBM morphology with large dark regions on the surface of the ITO when looked at with the PEEM. The regions in figure 52 don't display the complicated morphology seen in P3HT such as the fractal structures seen in figures 44 and 45. As expected there aren't any complicated drying patterns on the surface of the ITO as it was spin coated with the intent of creating of uniform surface on the ITO.

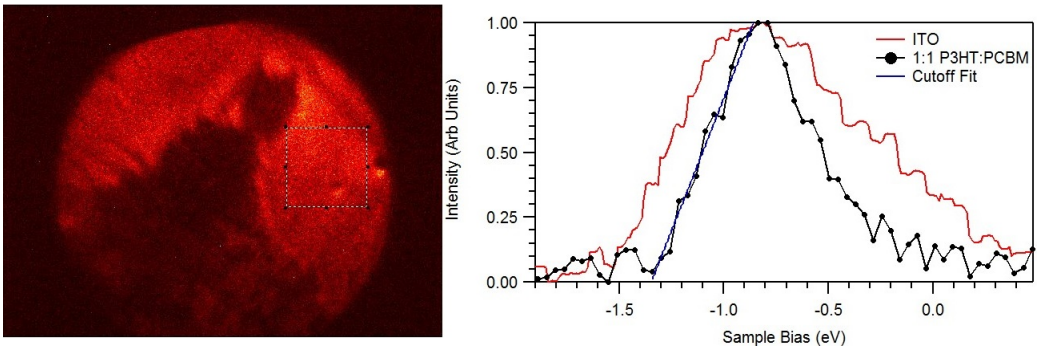


Figure 53: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. The region shows a substantial dark region neighboring a brighter region. The spectrum was taken from the highlighted region within the brighter region.

The region in figure 53 shows a substantial area region neighboring a bright region, the cutoff for the bright region was found to be -1.10±0.05eV. This result is substantially different from the ones found for the solutions of the molecules and from the cleaned ITO, this indicates that the PEEM has been able to identify a difference between typical ITO regions and this particular region of the 1:1 mixture spin coated onto ITO.

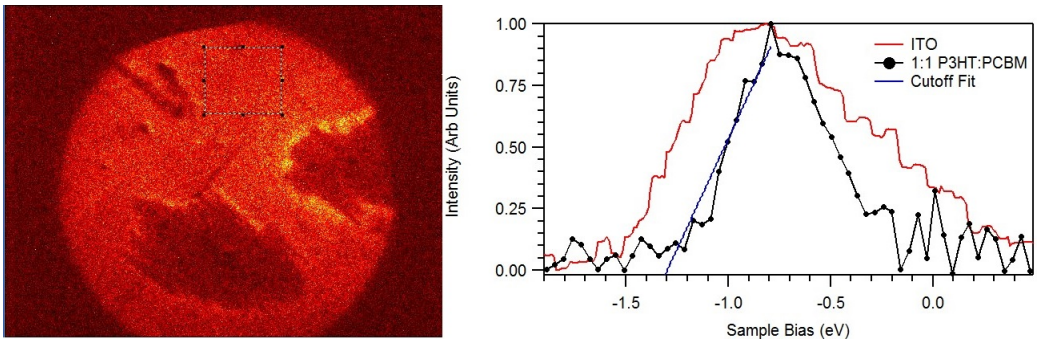


Figure 54: A region of the 1:1 mixture of P3HT:PCBM on cleaned ITO, this region is the full image for figure 52 region a. The image was taken at 109.7 µm. This region is placed alongside a spectrum taken from the highlighted region

In this region there are substantial bright regions surrounding darker regions, the bright region is homogeneous up to the edge of one of the dark regions indicating that this may be the result of the morphology of the underlying cleaned ITO. The cutoff was found to be -1.02±0.05eV this is substantially different from the region in figure 53 indicating that the regions are coated in materials with different work functions despite having

fundamentally similar morphologies. It is unclear at this point if this indicates that it is a separation of the constituent materials or if it is simply the PEEM filter not being able to to be consistent across the same sample. The expectation would be that in a mixed region an average work function would be found by spectroscopy. In regions that have phase boundaries with the different materials in the blend would be in each region the work function observed would be the same as found in the individual solutions.

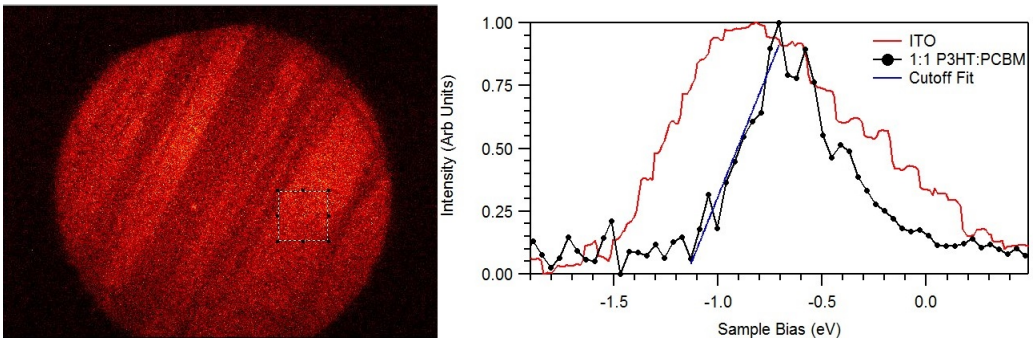


Figure 55: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. The region shows a a series of alternating bright and dark streaks across the surface. The spectrum was taken from the highlighted region within the brighter region.

Within this region there is a streak pattern with alternating bright and dark regions, in figure 55 the bright regions spectrum is investigated. The cutoff value of the bright region is found to be -0.90±0.05eV, this is not consistent with either of the previous regions investigated on this sample, indicating the region has a substantially different work function. The reason for this may be because of how the blend of the materials interacted with each other resulting in a less negative cutoff value found by the PEEM. Though this would not be in line with the expectation of an average cutoff being measured.

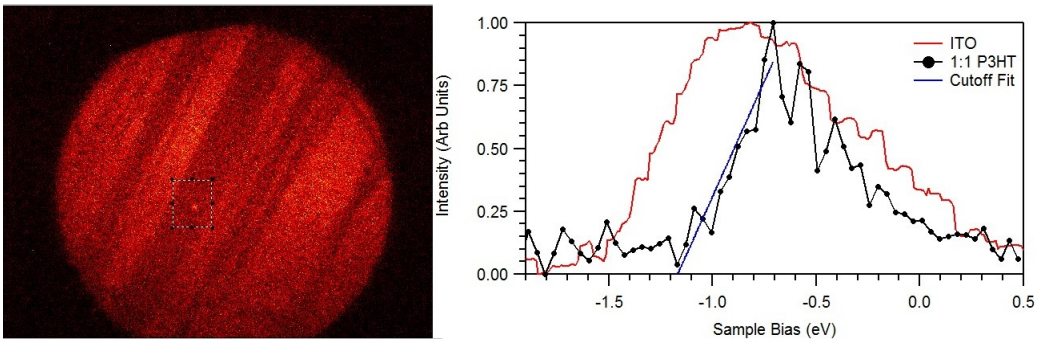


Figure 56: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. . The spectrum was taken from the highlighted region within the darker region.

In figure 56 the region shows a a series of alternating bright and dark streaks across the surface the spectrum of the darker region is taken to see if the work function is substantially different from the brighter region. The cutoff of was found to be -0.90±0.05eV indicating that the regions have similar work functions. This is consistent with the brighter region of the region indicating they are coated in a material of the same work function.

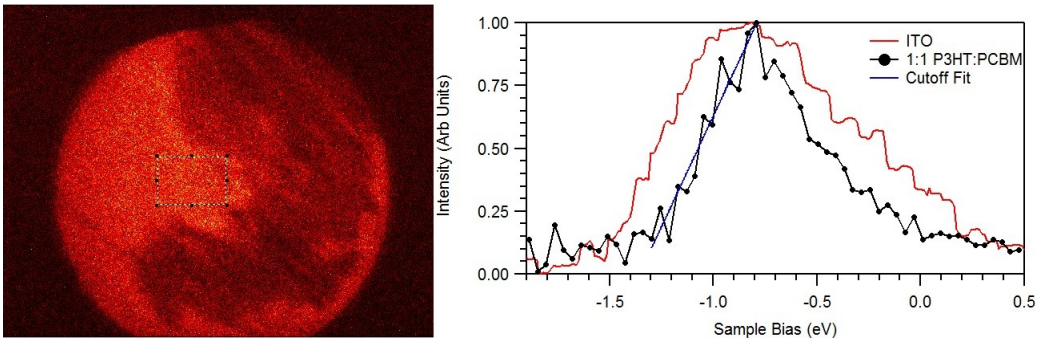


Figure 57: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. The shows a substantial homogeneous bright region neighboring a dark region. The spectrum was taken from the highlighted region within the bright area on the surface.

In figure 57 the spectrum is taken from the bright homogeneous region neighboring a darker region with more complex structures within it. The cutoff is found to be -1.07±0.05eV placing it more in line with the first region taken on this sample with a cutoff point of 1.10±0.05eV indicating these regions may have similar work functions

when compared to the other regions analysed so far.

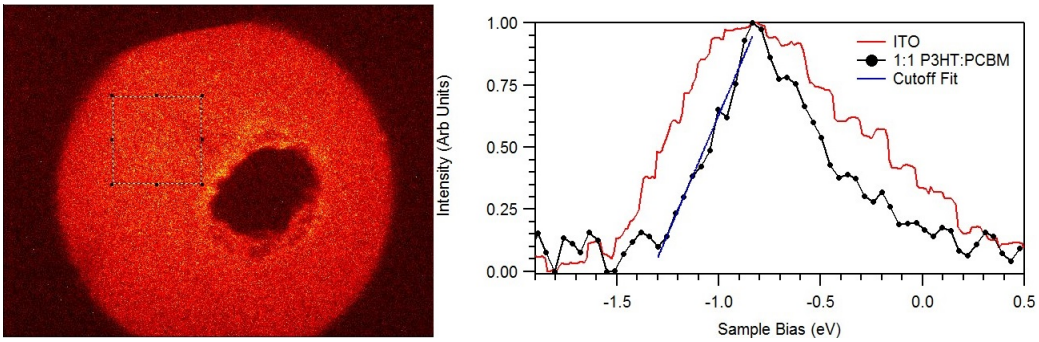


Figure 58: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. The shows a substantial homogeneous bright region surrounding a dark circular region. The spectrum was taken from the highlighted region within the bright area on the surface

The region analysed in figure 58 shows some of the morphological features that were seen in previous images taken by the PEEM such as the large circular dark region. The bright region is almost entirely homogeneous. The cutoff value was found to be -1.07±0.05eV which is the same as the previous region indicating that these regions which are both homogeneous within their bright regions are made of materials with the same work function.

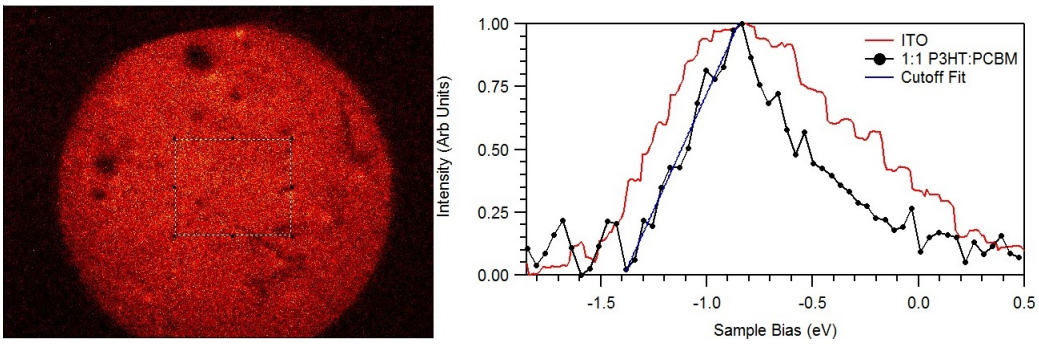


Figure 59: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. The image is a full version of the one in figure 52 region d.

This region is largely homogeneous but has a series of small dark circular areas on the surface as well as appearing to have a ridge like structure, this may be due to the underlying morphology of the ITO used. The cutoff was found to be -1.13±0.05eV

indicating it is also different from the other regions on this sample.

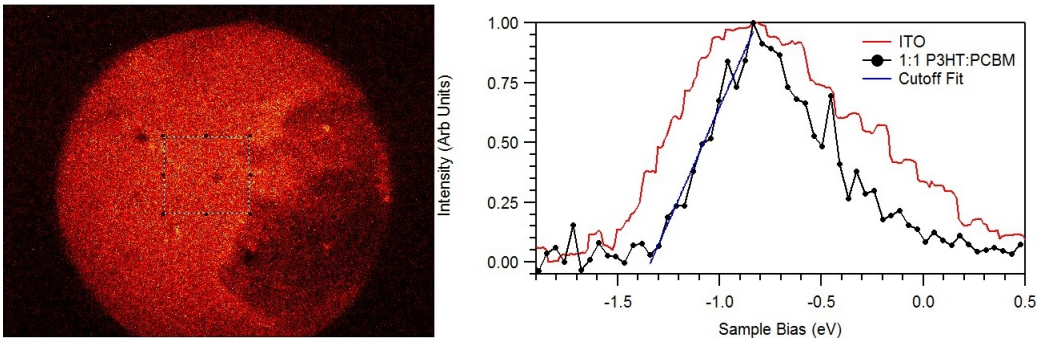


Figure 60: A region of a 1:1 mixture of P3HT:PCBM on cleaned ITO from the sample shown in figure 52, the image was taken at 109.7 µm. This region shows a relatively homogeneous region neighboring a darker region, the spectrum was taken from the highlighted region within the brighter region.

The region in figure 60 shows similar morphology to a lot of the other regions examined with the PEEM filter including the presence of a large dark region. The cutoff was found to be -1.06±0.05eV placing it within uncertainty of the regions in figures 57 and 58 with cutoffs of 1.07±0.05eV indicating these regions are likely to have the same work function if the PEEM filter operates as expected.

The PEEM has shown it can distinguish between regions across the same sample, however it isn't clear that it is distinguishing between the workfunctions of different regions. The fact that regions across the same sample are showing similar work functions with similar morphologies indicates that it is able to identify these regions to some extent however these do not have the desired morphology of a bulk heterojunction.

A mixture of 1:1 P3HT:PCBM solution used and drop deposited onto cleaned ITO in order to examine if different morphologies arise when the solution is drop deposited as opposed to spin coated.

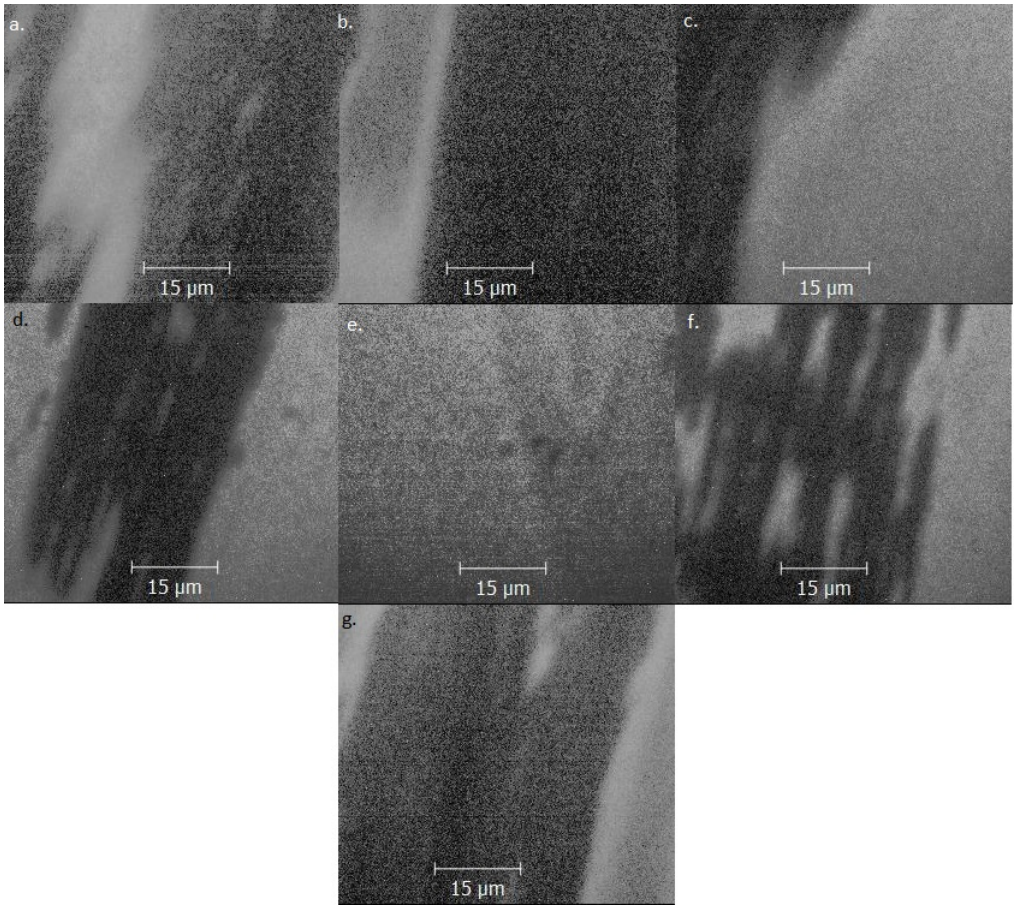


Figure 61: A series of images taken of the 1:1 mixture of P3HT and PCBM across the same sample, these regions show similar features primarily streaking patterns of light and dark regions. Though region e shows a relatively homogeneous region on the surface The images here are sections taken from full images from the PEEM. The field of view for the full images are 109.9 µm with the filter off

A mixture of P3HT and PCBM was dissolved in Toluene and drop deposited onto a cleaned piece of ITO glass. This led to interesting morphologies that were not present in the chlorobenzene based solutions and the spin coated solutions. The solution appears to have dried in streaking patterns with bright regions surrounding darker regions, the bright regions are likely to be the mixed solution deposited on the surface, the cause of the general streaking pattern may be that there are surface faults that prevent the solution from covering certain areas. In region e there is a homogeneous region similar to the spin coated sample indicating that these regions have met similar conditions such as film thickness and the ITO substrates morphology.

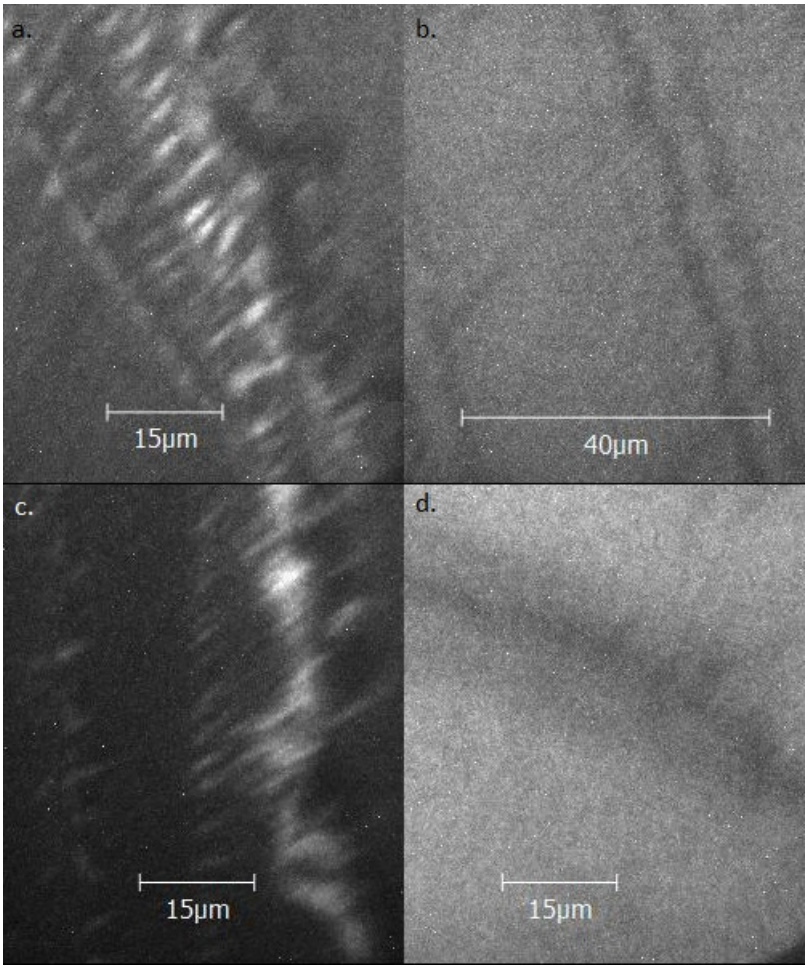


Figure 62: A series of images taken from full PEEM images of a mixture of P3HT and PCBM in toluene on cleaned ITO glass. Regions a and b were taken at 109 µm and a sample bias of -0.8eV. region c was taken at 109.7 µm with the filter off. region d. was taken at 109.7 µm and a sample bias of -0.8eV.

The series of images in figure 62 shows structure formation within what appears to be large scale surface faults. This leads to interesting structures in regions a and c where there are clear surface faults where the solution has collected and formed more complicated drying patterns than in the other drop deposited regions such as regions b and d in figure 61. These are also more complicated than a lot of the structures found in the spin coated samples which shows relatively homogeneous regions with some medium sized dark regions on them.

5.4 2:1 P3HT:PCBM Results and Discussion

A solution of 2:1 P3HT:PCBM was made with a concentration of 0.2 weight percentage, this was drop deposited onto cleaned ITO and then imaged using PEEM.

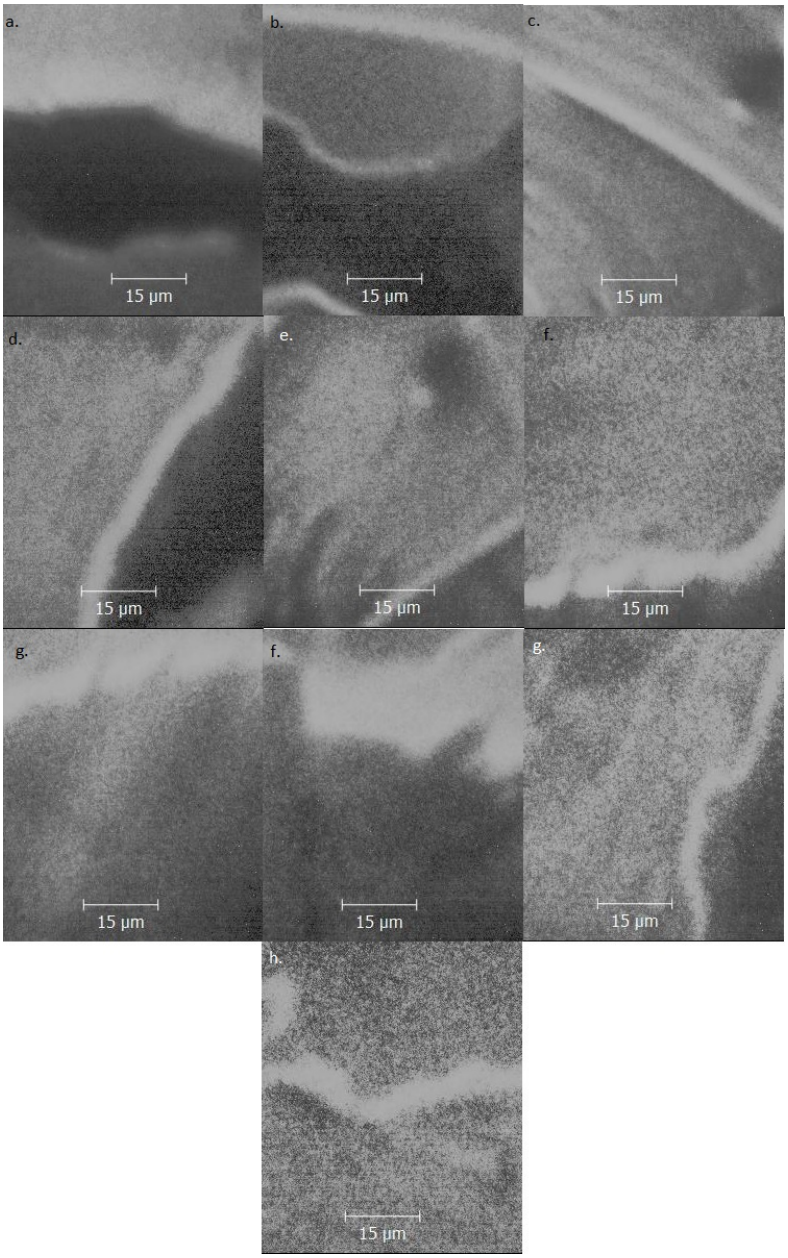


Figure 63: A series of images taken across the same sample of a cleaned ITO sample spin coated in a 2:1 P3HT:PCBM solution. These images are sections of full images taken at 109.7 µm.

The images taken from the 2:1 mixture show areas with clear diversity across them demonstrated especially in regions a and b where there are clearly brighter regions

adjacent to dark regions. These dark regions are not consistent with the dark regions seem in other samples which more closely resemble surface faults where as these appear to represent boundaries between either different molecules or the solution and the cleaned ITO. The areas that are brighter appear uniform within their own areas indicating that if they are the solution it has been distributed evenly in these areas.the substrate was rotated at 2.5KRPM.

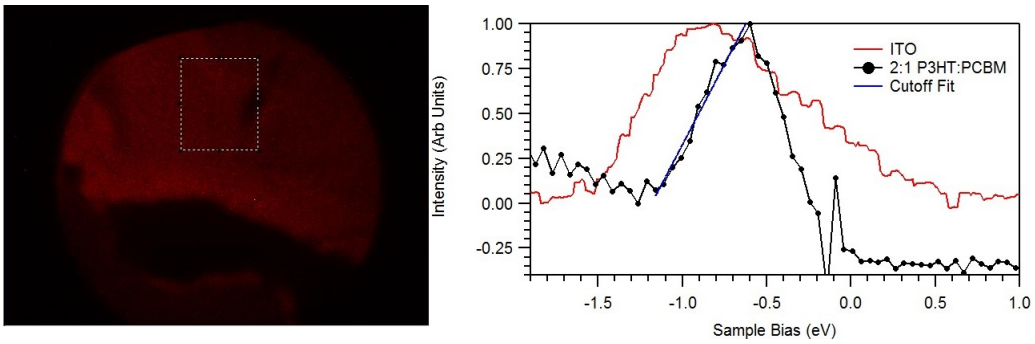


Figure 64: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene representing region a in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region in figure 64 shows an area of the sample with a substantial dark region between two brighter regions, the spectrum is taken from the brighter region which also appears homogeneous. The cutoff was found to be -0.90±0.05eV this is similar to several of the regions observed in the 1:1 mixture indicating that these regions have the same wave function despite being made from solutions with different ratios of P3HT and PCBM. The expected result would have been a cutoff value closer to P3HT than PCBM as opposed to one less negative than both.

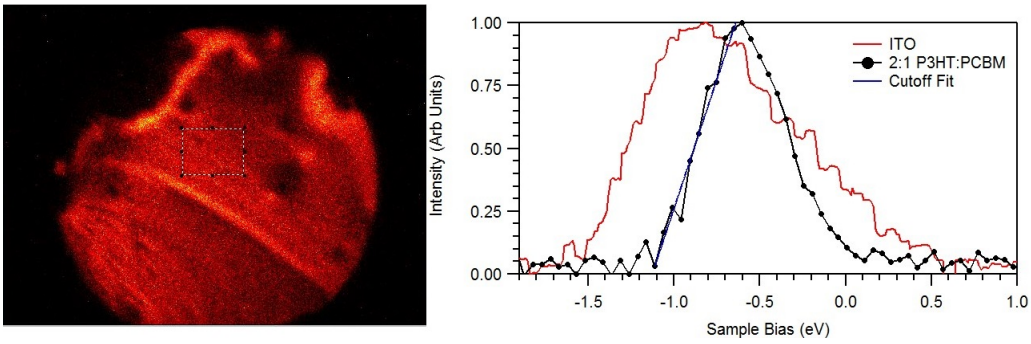


Figure 65: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region in figure 65 shows an area of the sample with a section of the deposition that is less homogeneous than the others shown with features seen elsewhere such as circular dark spots as well as physical features such as a ridge running through the region. The cutoff for the highlighted region was found to be -0.89±0.05eV which is within the uncertainty of the region in figure 64 meaning it is also similar to the other regions in the 1:1 mixture in terms of work function.

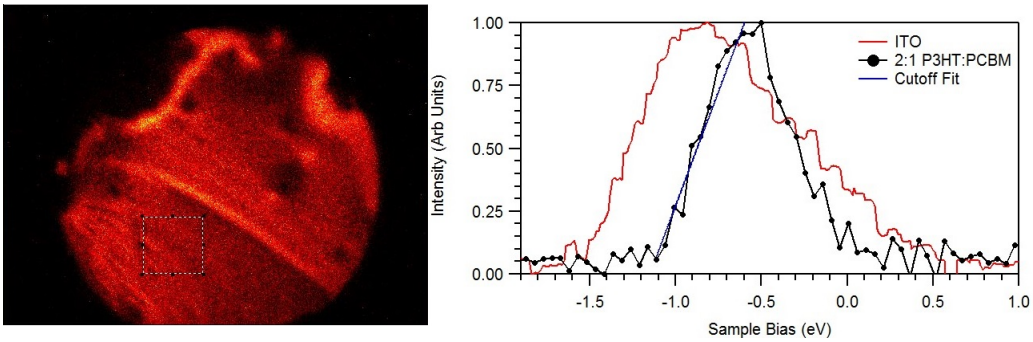


Figure 66: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region in figure 66 shows a region in the same reason of figure y in order to see if the region with more ridges within it has a similar work function to the rest of the sample. The spectrum's cutoff is found to be -0.88±0.05eV which indicates the regions on opposing sides of the ridge through the region are made of materials with the same materials as the cutoffs were found to be within uncertainty of each other.

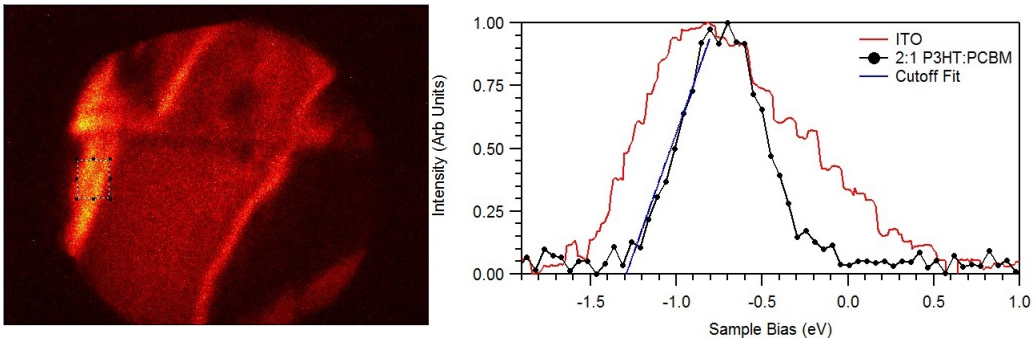


Figure 67: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene representing region d in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region in figure 67 shows the full image of region d in figure 63, the region itself had a long section of relatively homogeneous molecule alongside a darker section of the sample, as well as this the edges of the bright homogeneous region are brighter than the centre. The spectrum taken is of one of the brighter regions on the edge. The cutoff was found to be -1.02±0.05eV this is substantially different from the other regions seen so far on the 2:1 sample though it falls within the range of found cutoffs across other samples.

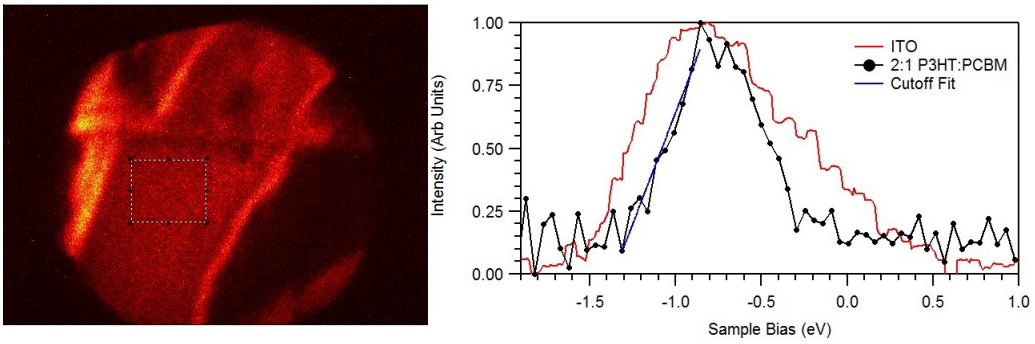


Figure 68: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene representing region d in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

This spectrum for the same region was taken within the dimmer region that the brighter regions border, the cutoff found was -1.08±0.05eV which shows a difference between the bright border regions and the dimmer homogeneous region. This may indicate that the thickness of the region affects the cutoff observed by the PEEM.

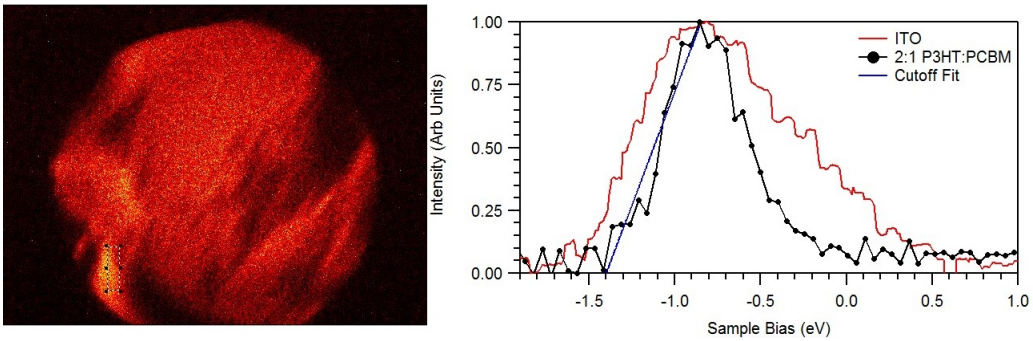


Figure 69: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene representing region d in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

Figure 69 shows a region which has a darker regions within moderately bright areas as well as a bright area. The morphology appears to be more complicated in this region, this may be because of the underlying ITO's morphology. The spectrum was taken from the bright region in order to compare it to the dimmer region, the cutoff was found to be -1.12±0.05eV which is similar to other regions in the 1:1 samples.

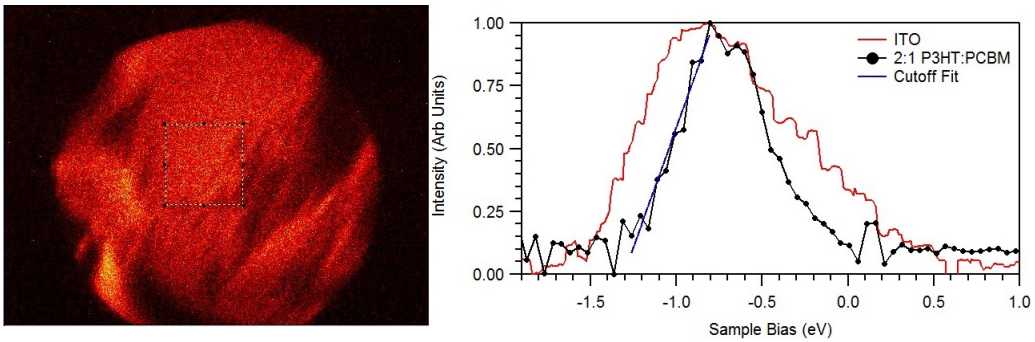


Figure 70: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The spectrum in the dimmer region was taken and compared to ITO. The cutoff was found to be -1.04±0.05eV which is substantially different from the bright region in the same region. This indicates that the thickness of the deposition on the sample may have a consistent impact on the cutoff found by the PEEM as the value of both regions are outside of the uncertainties of the results found for the cutoff. However in this case the cutoff found in the brighter is lower than in the dimmer region.

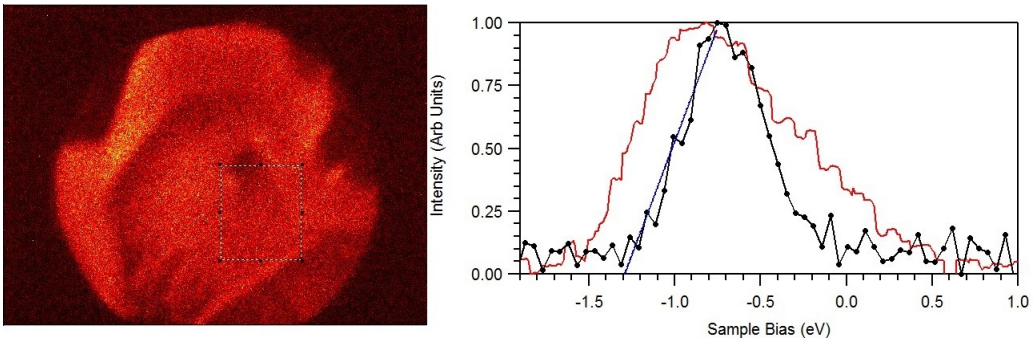


Figure 71: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region shown in figure 71 is one that appears to have ridge like structures on it likely the result of the underlying ITO. The spectrum was taken over a substantial region the cutoff found was -1.02±0.05eV which is similar to the region highlighted in figure 70.

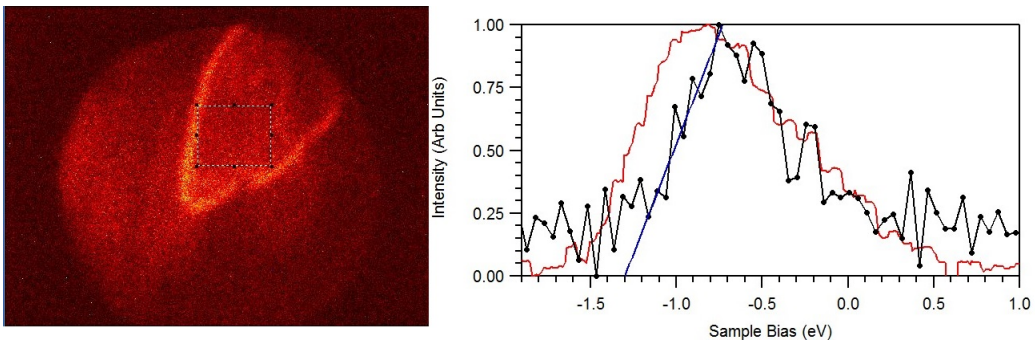


Figure 72: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region shown in figure 72 is a a relatively homogeneous region with a brighter region within the bright outline, the spectrum is taken from within the bright outline. The cutoff found was -1.03±0.05eV which is similar to the region found in other figures of the 2:1 mixture indicating that this cutoff is common across the surface.

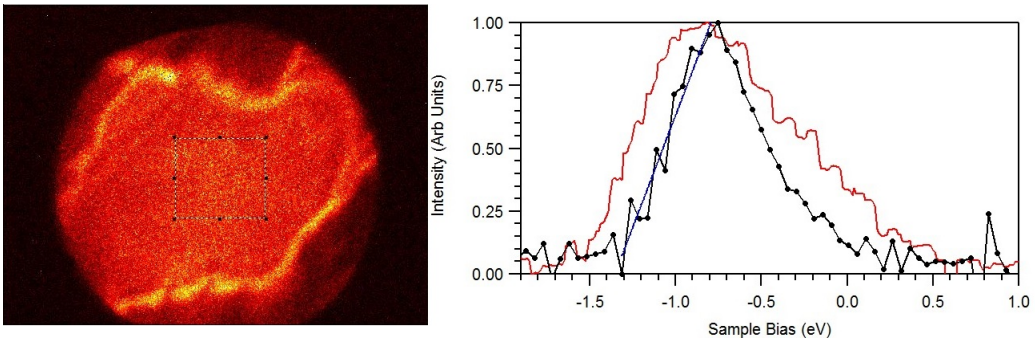


Figure 73: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region in figure 73 is another region surrounded by bright edges with darker regions beyond the bright edges, these types of formations appear to be relatively common across the sample. The cutoff found in the highlighted region within the homogeneous region was -1.08±0.05eV this is the same as in figure 68 which is another region with bright boundaries.

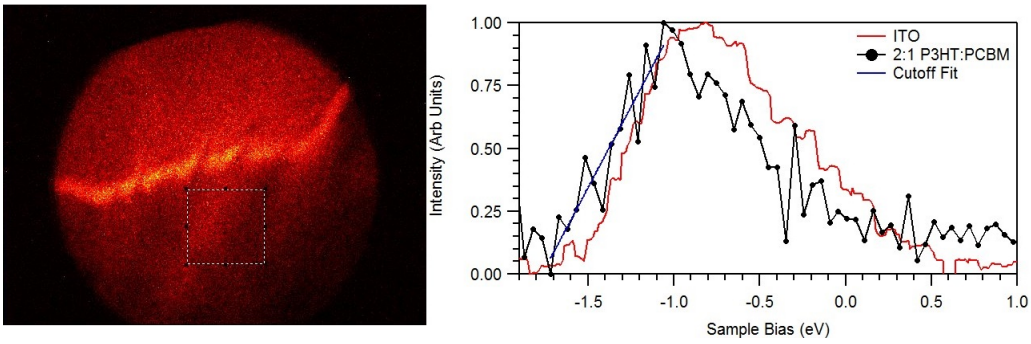


Figure 74: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

Figure 74 shows a bright and dark areas separated by a bright edge both regions appear to be internally homogeneous. The spectrum in this figure was taken from the darker section and was found to have a a cutoff of -1.39±0.05eV which is significantly different from all of the other regions of interest assessed using the PEEM filter on this sample this value is closer to the ones found on the cleaned ITO glass indicating that this region has similar properties to the cleaned ITO sample. This would be unusual as the sample

was spin coated in order to ensure the entire surface was covered by the solution.

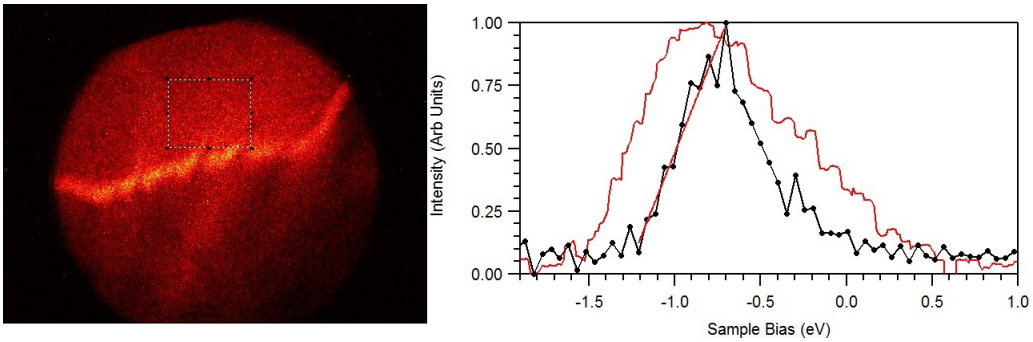


Figure 75: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The spectrum in this figure was taken from the bright region, the cutoff in this region was found to be -1.00±0.05eV which is 0.39eV higher than the cutoff for the dark region indicating that this region has a substantially different work function from the dark region and is therefore considered to be covered in a different material.

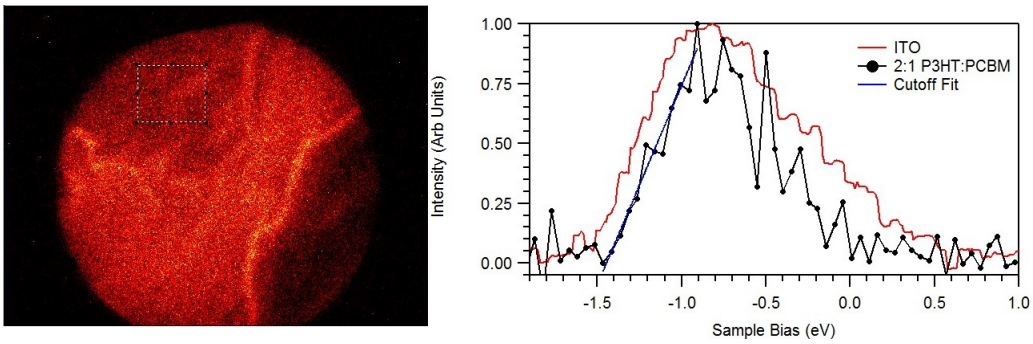


Figure 76: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The region shown in figure 77 is one that is similar to the others on the sample where there are regions surrounded by a brighter edge, in this case the spectrum was taken from the dimmer region. This region was found to have a cutoff of -1.14±0.05eV which closely resembles the cutoff found in the region in figure 69.

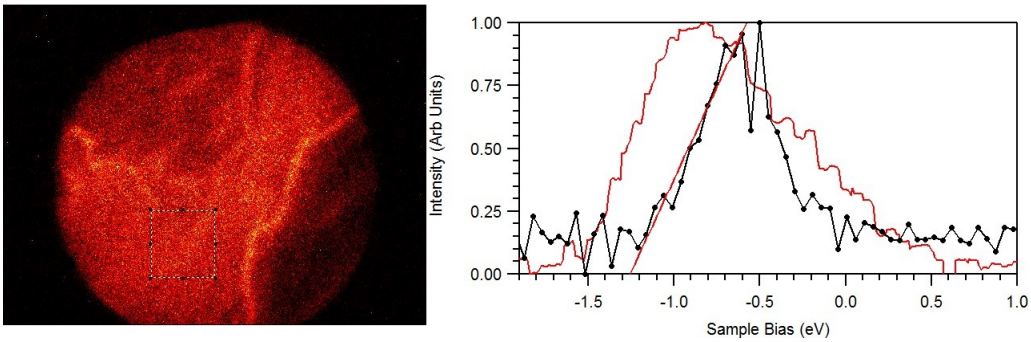


Figure 77: An image of 2:1 P3HT:PCBM dissolved in chlorobenzene from the same sample as in figure 63 taken at 109.7 µm alongside a spectrum of the highlighted region in the image. The spectrum is compared to the ITO spectrum.

The brighter regions spectrum was taken in this case and the resulting cutoff was found to be -0.93±0.05eV which is significantly different from the dimmer region, this may once again indicate that there are different molecules covering those regions or that the morphology of the ITO is affecting the cutoff found by the PEEM.

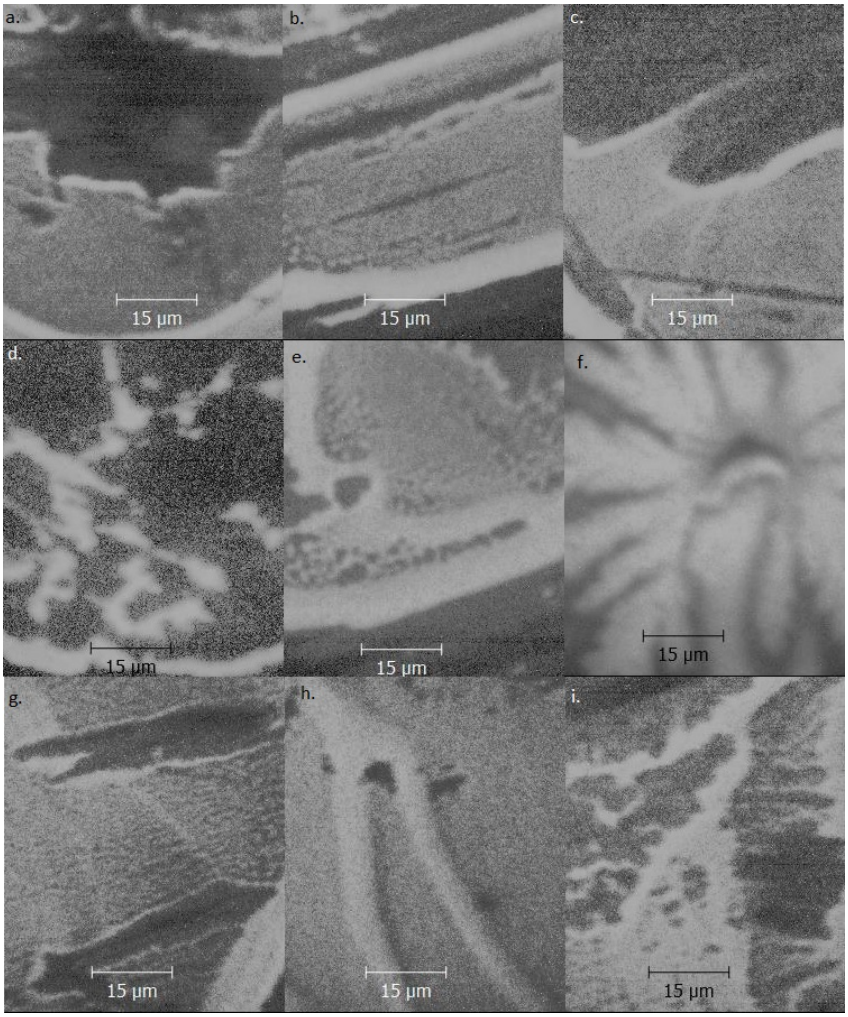


Figure 78: A series of images taken of the same sample of cleaned ITO with a 2:1 solution of P3HT:PCBM drop deposited onto the surface. The original images were taken at 109.7 µm the regions represented here are sections taken from full images.

The regions in figure 78 show that drop depositing has allowed more complicated structures than the spin coated 2:1 solution. Substrates of ITO had a 2:1 solution drop deposited on them with the same solution used. On this sample there were regions like a where the bright area surrounds a darker area as in figure 63 regions a and b. Also across the sample it appears that finer structure had formed within the brighter regions as in regions d, e, g and i where there are darker regions with the greater bright region. Another interesting feature that arose as a result of the solution being allowed to dry rather than spread across the sample is a fractal structure that formed as with the P3HT on ITO sample, this may be because the conditions for fractal formation were met and due to the higher amount of P3HT in the solution allowing for these conditions to be

met more easily. The fractal formation was likely an anomaly as it was not observed in any of the other mixed solutions and only seen infrequently in pure P3HT solutions. There is also the appearance of ridged formations in region h.

5.5 1:0.8 P3HT:PCBM Results and Discussion

A solution of 1:0.8 P3HT:PCBM was made with a concentration of 0.2 weight percentage. This solution was then spin coated onto a sample of cleaned ITO then imaged in the PEEM.

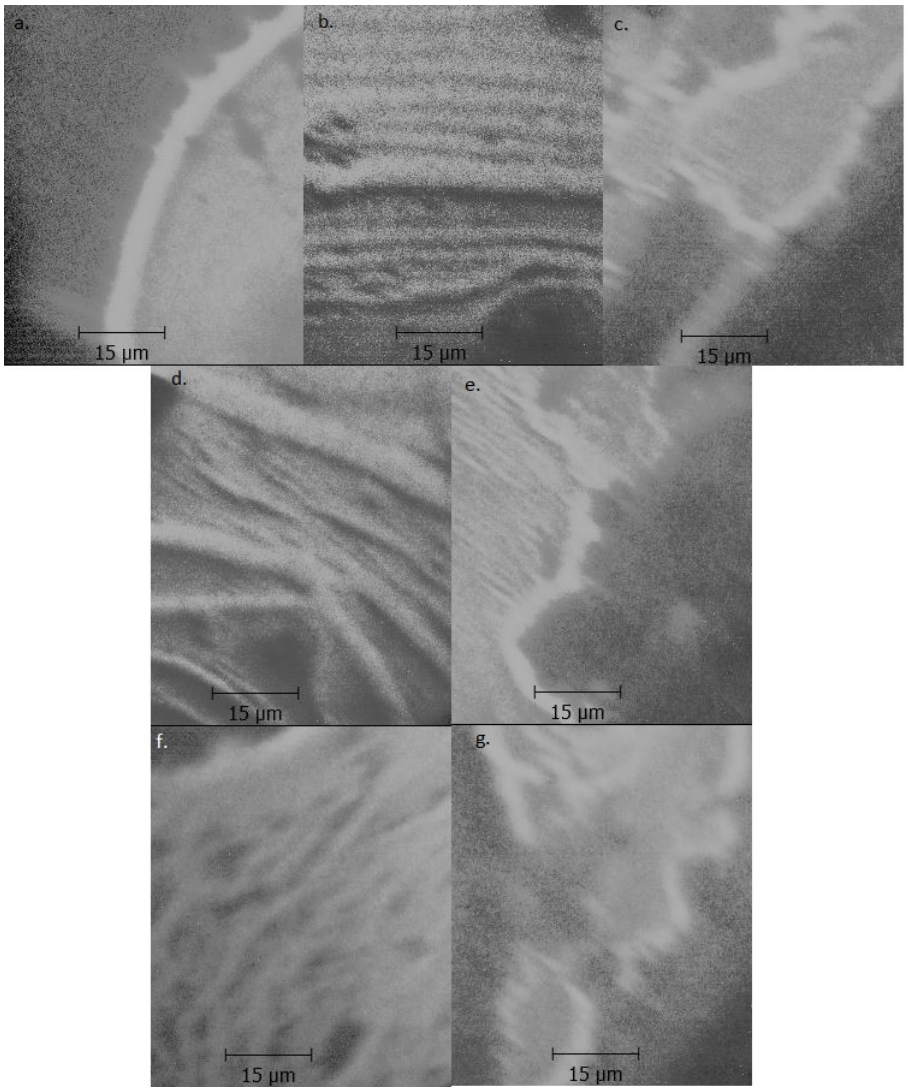


Figure 79: A series of images taken of a sample of cleaned ITO with a solution of 1:0.8 P3HT:PCBM spin casted onto the surface at a speed of 2.5KRPM. The regions are sections of full images which were taken at 109.7 µm with the filter off.

The regions in figure 79 show various areas on the same sample of 1:0.8 P3HT:PCBM. Region a shows a very bright circular region next to an area that is darker. Region b shows a section of the sample that has formed many ridges over the surface with a circular fault among the ridges, a similar morphology is seen in region d. Regions c, e and g show bright and dark regions neighbouring each other with bright edges between them, this is similar to the morphology observed on other samples but in particular in the 2:1 mixture indicating that the increased presence of P3HT enables the conditions for these formations. Region f shows another section of the sample that also formed ridges though these have either not been imaged as well by the PEEM or are not as defined as in regions b and d.

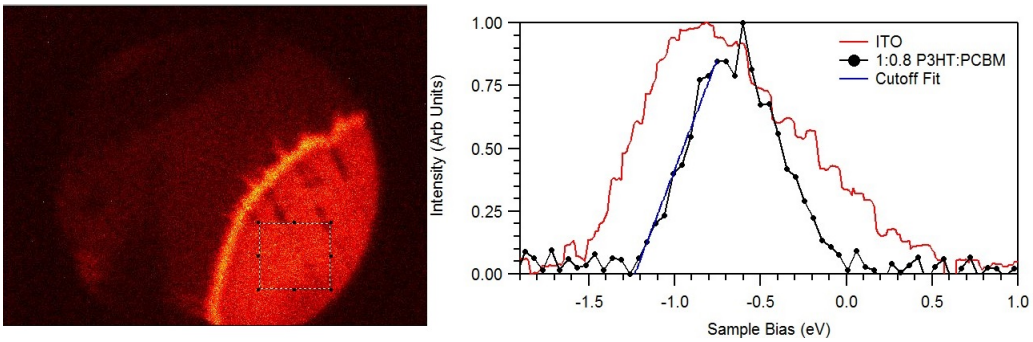


Figure 80: An image of the full image of region a in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

This region shows the circular feature in figure 79 region a in this region there is a very bright region adjacent to a dimmer part beyond the circles boundary. This spectrum was taken from within the circle and the cutoff was found to be -0.95±0.05eV this is similar to measurements made within the 1:1 mixtures indicating these regions have similar work functions.

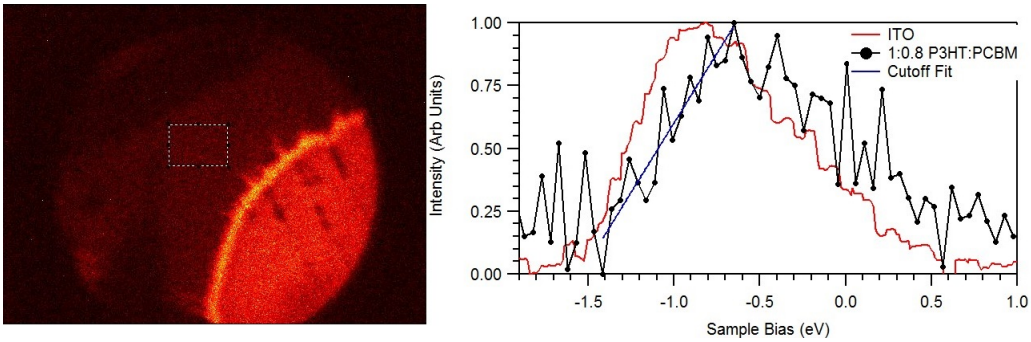


Figure 81: An image of the full image of region a in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

This spectrum was taken from the darker region on the region, the cutoff value was found to be -1.10±0.05eV this is significantly different from the value found from the bright region, this may be because it is not coated as thickly in the solution despite it being spin coated or that the regions are coated in materials with different work functions.

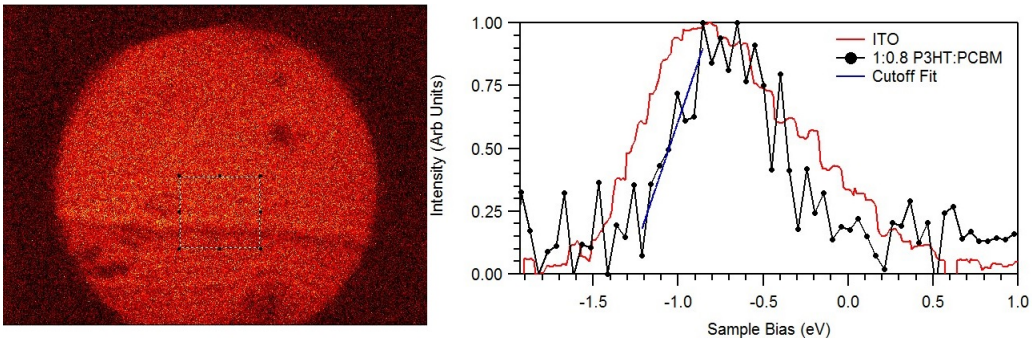


Figure 82: An image of the full image of region b in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

This spectrum was taken from a region containing the prominent ridge on the surface, the cutoff found was -1.07±0.05eV this is similar to the darker region in figure 81 indicating that they may be made of materials with the same work function.

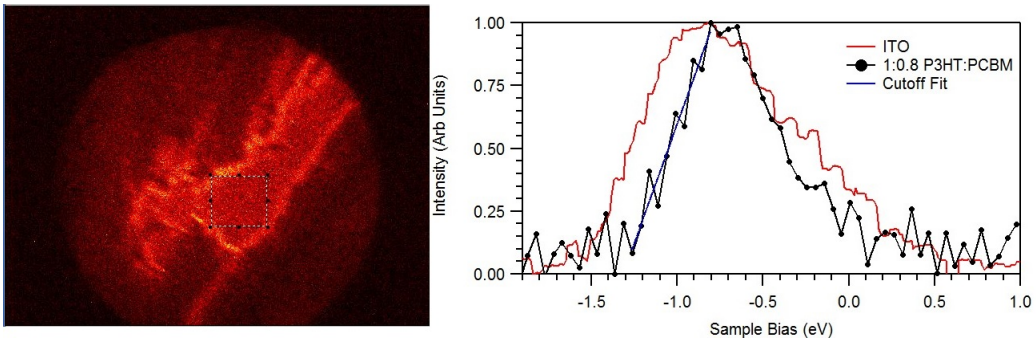


Figure 83: An image of the full image of region c in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

This region shows a bright structured region surrounded by a dimmer region which is similar to many of the other regions seen in the 1:0.8 mixture. The cutoff found was -1.05±0.05eV which is similar to other regions on the 1:0.8 sample.

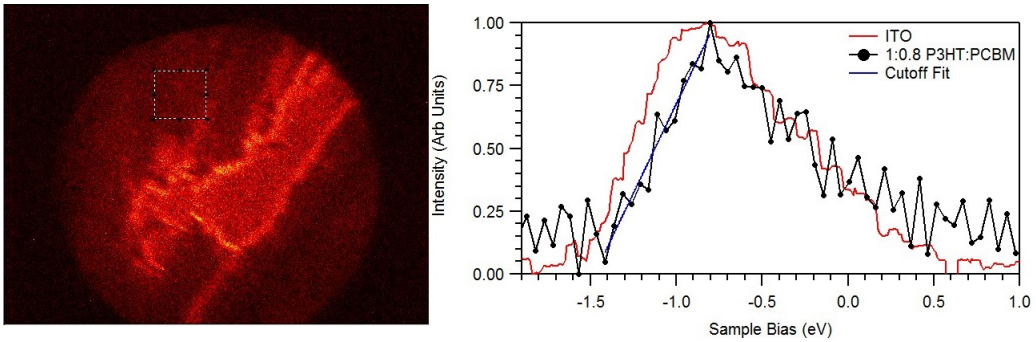


Figure 84: An image of the full image of region c in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

This spectrum was taken from the darker region surrounding the brighter region, the cutoff was found to be -1.12±0.05eV representing a difference from the bright region. The difference shown between these regions is consistent with the other differences shown in other spectra taken in that the bright regions cutoff is lower than the dark regions.

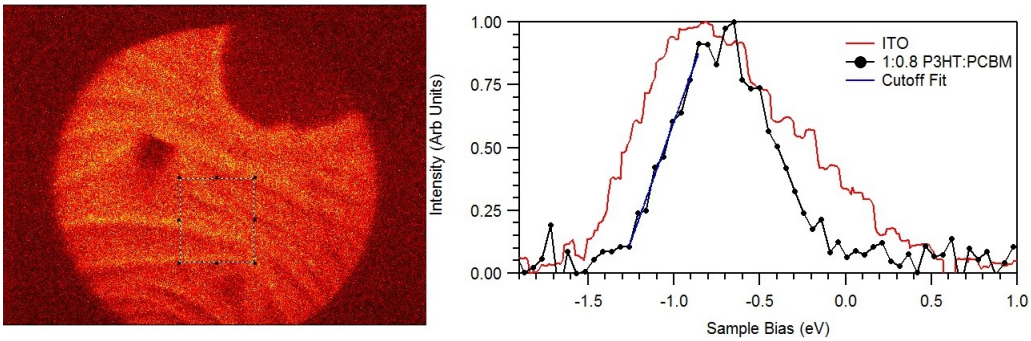


Figure 85: An image of the full image of region d in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

The region shown in figure 85 is of one of the ridged regions found on the surface. The spectrum was taken from the ridged region in order to compare it to the other ridged region. The cutoff was found to be -1.05±0.05eV which is within the uncertainty of the other ridged region found on the sample indicating that they are covered by a material with similar work functions that have met similar conditions to create similar morphologies.

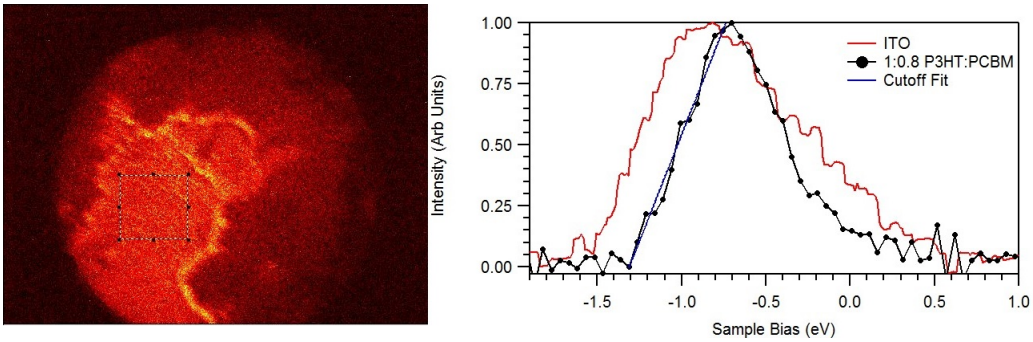


Figure 86: An image of the full image of region e in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

The region shown in figure 86 is similar to those seen on other mixtures of P3HT and PCBM, a bright region is surrounded by a dimmer region. The spectrum taken in the highlighted region within the brighter area showed a cutoff of -1.02±0.05eV.

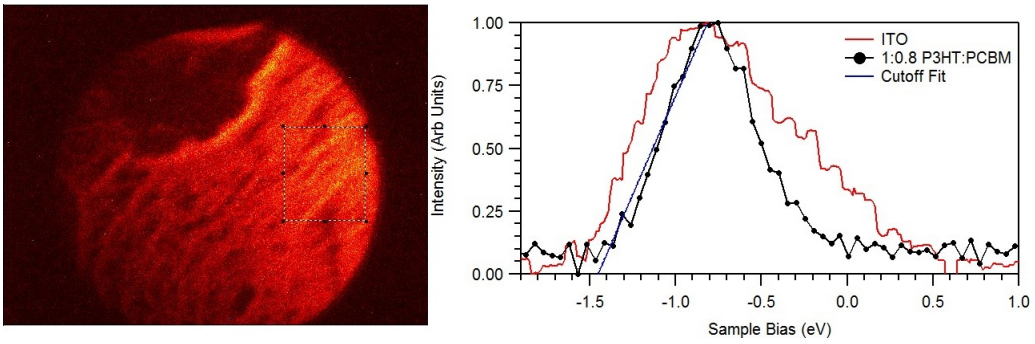


Figure 87: An image of the full image of region f in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

The region shown in figure 87 shows a regions which has less pronounced structures on it than in figures 82 and 85 but clearly has structure. The spectrum was taken from the highlighted region. The cutoff was found to be -1.13±0.05eV.

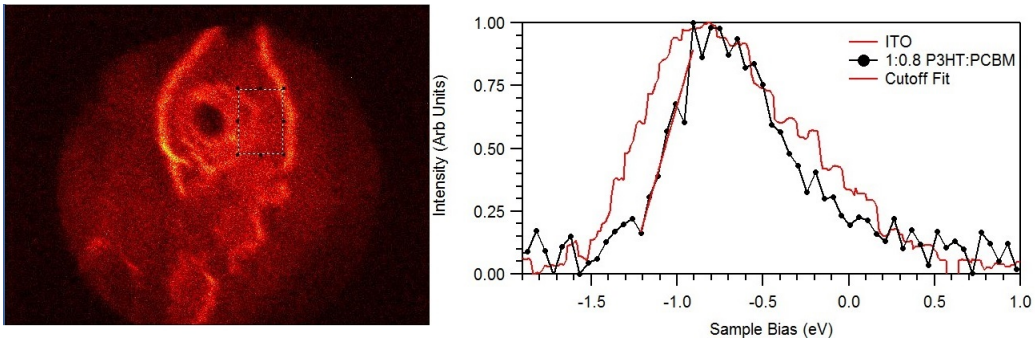


Figure 88: An image of the full image of region g in figure 79 taken at a field of view of 109.7 µm. Alongside the image is a spectrum taken of the highlighted region compared to the ITO spectrum.

The region shown in figure 88 shows an area of the sample that appears to have regions that have circular patterns formed with a bright edge around the almost circular region. The spectrum was taken from within the almost circular region and the cutoff was found to be -1.08±0.05eV.

A cleaned sample of ITO had the 1:0.8 mixture drop deposited onto it in order to assess the morphologies that arose as a result of the sample not being spin casted like the other 1:0.8 sample.

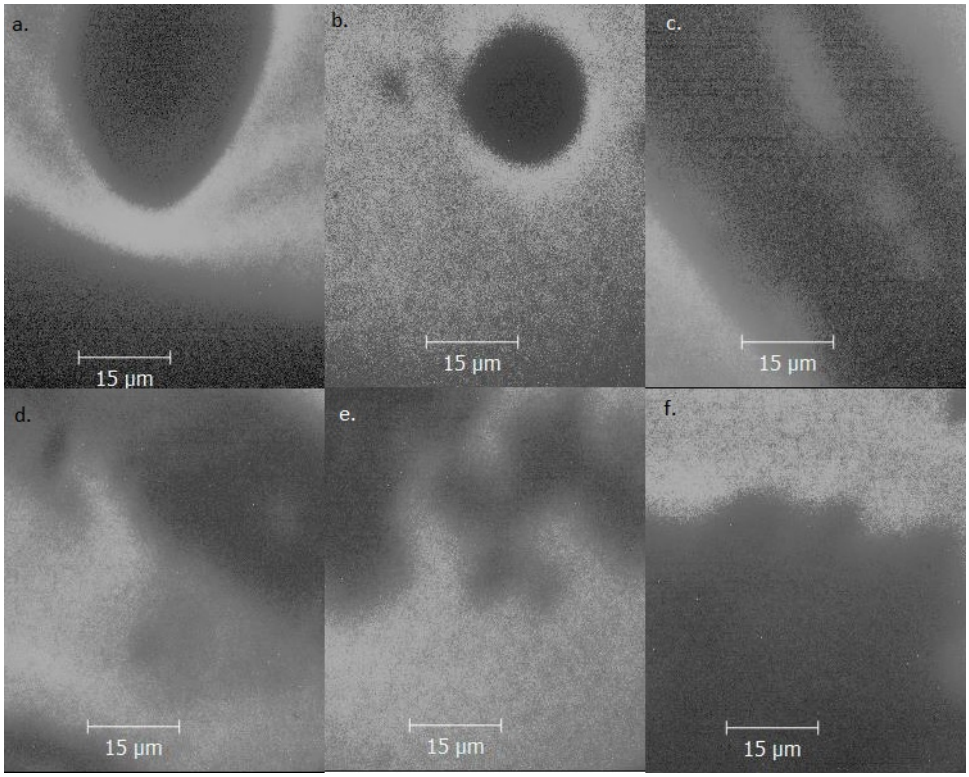


Figure 89: A series of images taken of 1:0.8 P3HT:PCBM drop deposited onto ITO taken at 109.7 µm. The images are sections taken from full images taken at a sample bias of -2eV

Regions a and b show regions of the sample with large circular dark spots in the image, these have been consistent features across most of the samples imaged by the PEEM that contain PCBM indicating that this is a property that can be associated with the presence of the PCBM. The other regions show morphologies similar to those found on the spin coated sample of the 1:0.8 mixture. The primary shared feature is that there are well defined boundaries between light and dark regions that are adjacent to each other on the surface. No spectra were taken of this region as this sample was used to compare the morphologies between spin coated and drop deposited samples.

5.6 Conclusion

The various blends were examined using the PEEM, the 1:1 spin coated sample has a morphology that is generally homogeneous aside from surface faults and dark regions that occur across the surface. The drop deposited 1:1 sample also shows large dark regions on the surface adjacent to homogeneous bright regions, however the dark regions

on the drop deposited sample resemble streaks. Also images taken in regions with large surface faults show that the solution can form structures within the faults when drop deposited. The cutoff for the 1:1 blend was found to be -1.08±0.05eV with a region showing cutoffs at -0.90eV this blend shows a significantly higher cutoff than both the ITO and the individual molecules deposited onto ITO. The 2:1 blends morphology shows bright regions directly neighboring darker regions, these regions do not resemble the other ones observed in the 1:1 blend and the individual molecules which have the appearance of surface faults. The cutoff for the 2:1 blends were typically between -1.05±0.04eV within the bright regions on the sample, a darker area was analysed and showed a cutoff of -1.39eV. Once again it appears that the blend of materials has a lower work function that the individual molecules and the ITO itself. The drop deposited 2:1 blend showed varied morphology ranging from homogeneous regions adjacent to dark regions as in the spin coated sample as well as large ridged regions and a fractal which is an unusual occurrence and is likely caused by very localised conditions that allowed the fractal to form. The 1:0.8 blend showed a morphology similar to the ridged region of the drop deposited 2:1 blend as well as further dark regions adjacent to bright regions as seen in the other blends. The cutoff found for the 1:0.8 blend was -1.07±0.05eV this is in line with the results found for the other blends in that the cutoff is significantly higher than the individual molecules and the ITO.

Table 2: Table showing the cutoff values of the various blends and individual molecules. The values shown are averages taken across the whole of the samples.

Material	Cutoff Value (eV)
ITO	-1.28±0.05
P3HT	-1.19±0.05
PCBM	-1.31±0.05
1:1 P3HT:PCBM	-1.08±0.05
2:1 P3HT:PCBM	-1.05±0.05
1:0.8 P3HT:PCBM	-1.07±0.05

The cutoff values can be converted into work function values using the photoelectric equation, treating the cutoffs as the kinetic energy of the electrons within the PEEM

the following values are obtained.

Table 3: Table showing the converted values for work function found using the photoelectric equation and the cutoffs as the kinetic energy.

Material	Work Function (eV)
ITO	3.62±0.05
P3HT	3.71±0.05
PCBM	3.59±0.05
1:1 P3HT:PCBM	3.82±0.05
2:1 P3HT:PCBM	3.85±0.05
1:0.8 P3HT:PCBM	3.83±0.05

The values found for the work function do not agree with previously found values. This may be because of charging that can occur due to the organic nature of the samples used in the case of ones containing P3HT. However this does not explain the discrepancy found with ITO samples leading to the possibility that PEEM may not be suitable in this instance for direct measurement of the work function.

6 PDOT:PSS on ITO

6.1 Introduction

A solution of 1 weight percentage PDOT:PSS was deposited onto ITO, this is because PDOT:PSS is widely used in solar cells and part of future experiments modeling an OPV would involve making a model solar cell more similar to the one shown in figure 4. PDOT:PSS is regularly used in solar cells and has been shown to improve the performance. The purpose of the experiment is to observe the morphology of the PDOT:PSS sample and as a further examination of whether the PEEM can be used to determine the cutoff of PDOT:PSS and if it agrees with other experimental data.

6.2 Preparation of PDOT:PSS

A spin coated sample 1 weight percentage PDOT:PSS was made in order to make progress towards better modeling an OPV, the sample was made by spin coating a cleaned ITO sample at 2.5KRPM in an effort to create an even morphology across the surface. The solution was too viscous to be drop deposited onto ITO and so no drop deposited samples were imaged by the PEEM.

6.3 Results

The solution of 1 weight percentage PDOT:PSS was deposited onto the clean ITO and the PEEM was used to take images of various areas of the surface.

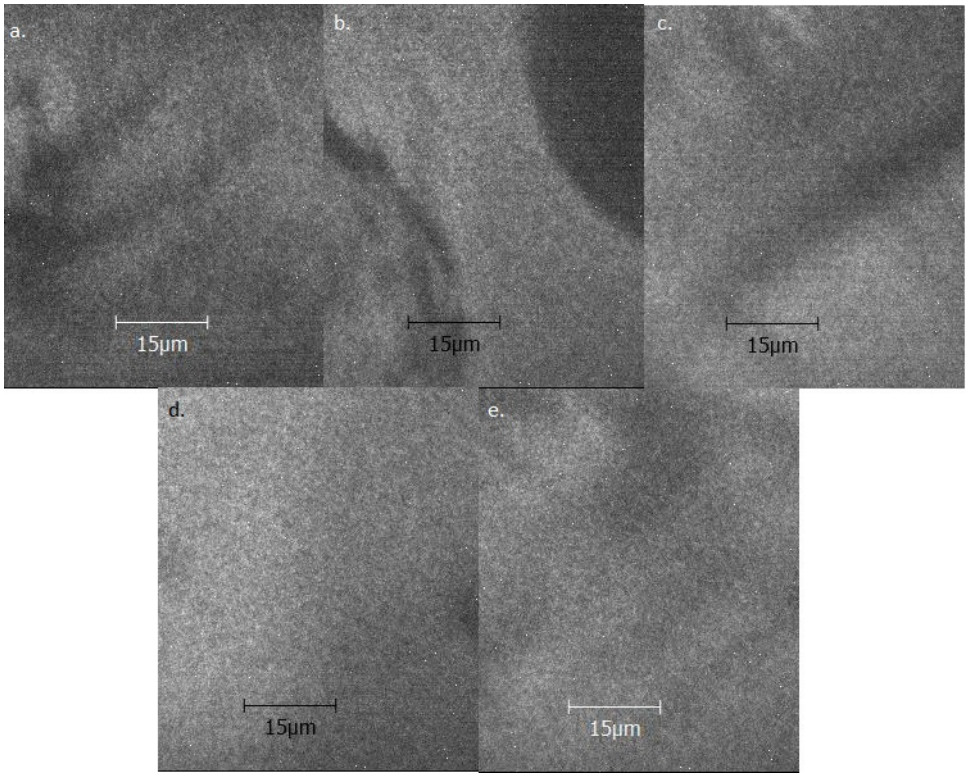


Figure 90: A series of images taken of PDOT:PSS spin coated onto ITO taken at 109.7 µm. The images are sections taken from full images taken at a sample bias of -2eV.

The morphology of the PDOT:PSS sample is typically homogeneous across the sample indicating that the spin coating has achieved the desired effect of evenly spreading the solution. Region a shows a homogeneous region with a darker structured region which is likely the result of the ITO's underlying structure. Region b shows a more structured area adjacent to a homogeneous part of the sample which is also next to a dark region which resembles the mixtures of the P3HT and PCBM solutions. Region c shows a relatively homogeneous image from the PEEM with a dark region across it which is similar to regions d and e. This indicates that the morphology is generally homogeneous with occasional areas with structure.

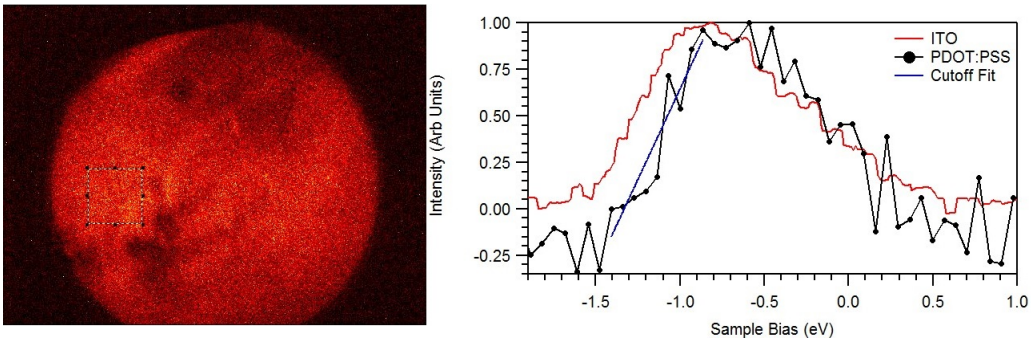


Figure 91: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at 109.7 µm and is a full image of region a in figure 90

The region shown in figure 91 is generally homogeneous region; a spectrum was taken using the PEEM from this homogeneous region. The cutoff was found to be -1.07±0.05eV which is different from the values found for clean ITO.

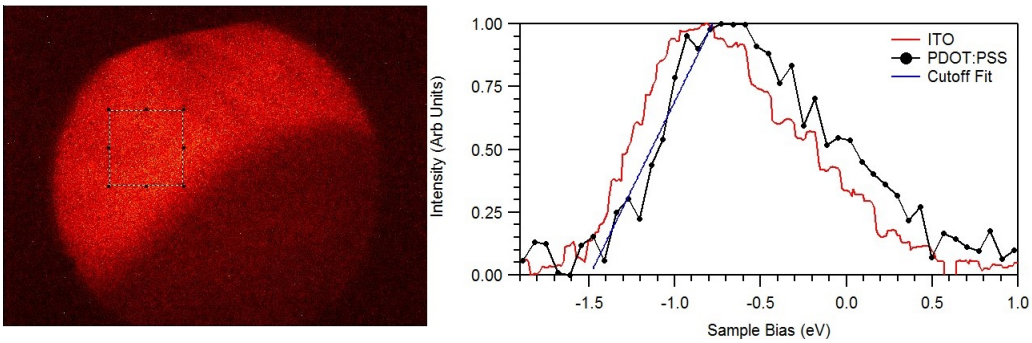


Figure 92: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at 109.7 µm.

The region shown in figure 92 is a region with a bright homogeneous region neighboring a dark region, unlike in the mixtures of P3HT and PCBM where the edges of the brighter regions tend to result in brighter edges in this case there is no obvious boundary between the two regions. The cutoff found in the bright region was -1.14±0.05eV a substantially different value from the other spectrum taken on the surface.

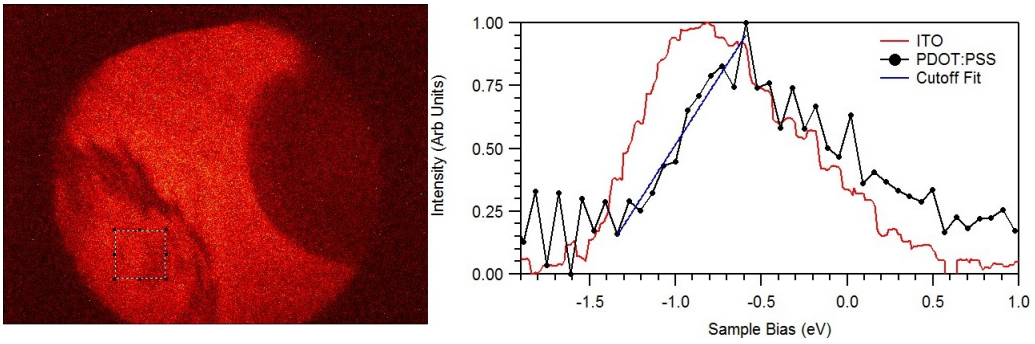


Figure 93: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at 109.7 µm. This region is a full image of region b.

Figure 93 shows a region with a dark circular section neighboring a large homogeneous which has a boundary with a less homogeneous area. Once again this image does not show bright edges between the dark and bright regions. The spectrum was taken from the highlighted region, the cutoff was found to be -1.01±0.05eV this value is also inconsistent with the others found for the PDOT:PSS samples.

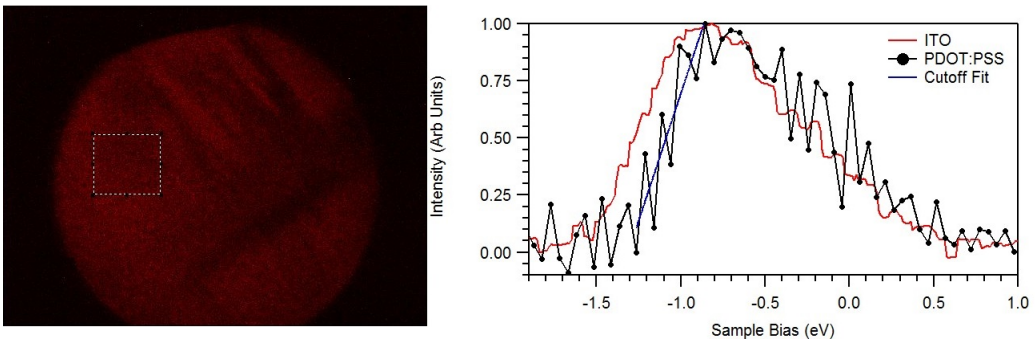


Figure 94: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at 109.7 µm. This region is a full image of region c.

The region in figure 94 is a region which is distinctly less homogeneous than the previous images taken from PDOT:PSS as shown by the large surface fault seen on the image disrupting the homogeneity of the PDOT:PSS. The spectrum in this image was taken from the region above the large surface fault and the cutoff was found to be -1.09±0.05eV which is within the uncertainty of the broadly homogeneous region found in figure y.

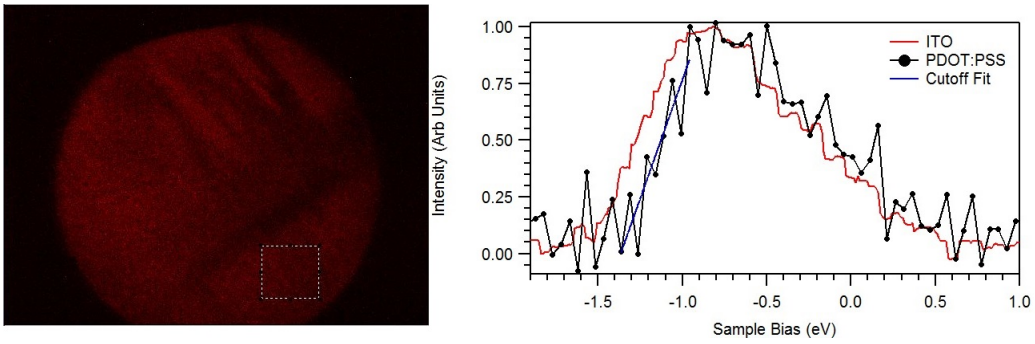


Figure 95: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at 109.7 µm. This region is a full image of region c.

The spectrum taken from the highlighted region below the surface fault finds a cutoff value of -1.14±0.05eV which is significantly different from the value found on the other region of interest across this image indicating that they are covered in materials with different work functions. The cutoff found in this region is the same as the cutoff found in figure 92 indicating that these regions have the same work function.

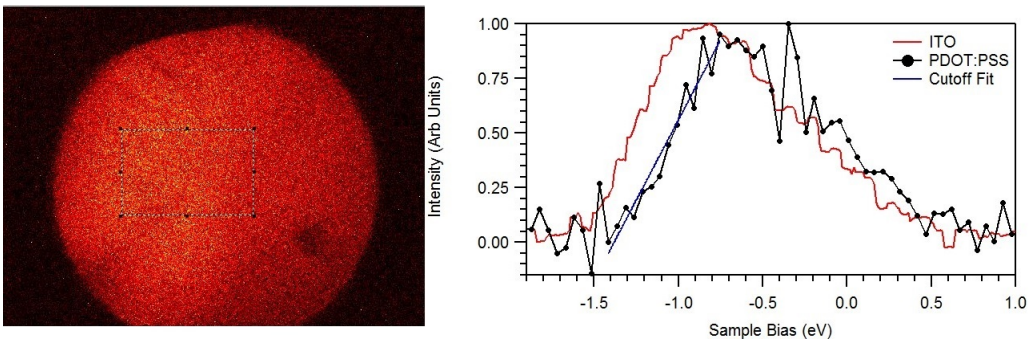


Figure 96: An image of PDOT:PSS deposited onto ITO next to a spectrum taken from the highlighted region. The image was taken at a field of view of 109.7 µm.

The image in figure 96 is of a homogeneous region on the PDOT:PSS sample, the spectrum has been taken from a broad region of the sample. The cutoff found by the PEEM was -1.05±0.05eV which is within the uncertainty of the other large homogeneous region indicating that the morphology found by the PEEM effects the cutoff found by the filter.

6.4 Conclusion

The PDOT:PSS sample shows a generally homogeneous morphology with occasional regions with more complex morphologies probably as a result of the ITO's structure beneath the PDOT:PSS layer on the substrate. The cutoff for the PDOT:PSS was found to be -1.10±0.05eV which is an unusual result as the PDOT:PSS has been shown to have a work function that is higher than ITO which would require a more negative result for the cutoff. This leads to a work function value of 3.8±0.05eV. This may indicate that the PEEM is able to detect and display a difference between ITO and PDOT:PSS however in this case the result found is not what would be expected.

For future experiments, the next step would be to spin coat ITO with PDOT:PSS and then spin coat mixtures of P3HT and PCBM on top of the PDOT:PSS layer to better model a solar cell and to observe changes in the morphology that might occur as a result as well as changes in the cutoffs found by the PEEM.

7 Conclusions

The Thesis has presented several experiments undertaken in order to determine the suitability of PEEM in observing changes in morphology in model OPVs as well as differences in work functions between acceptor and donor materials. This was done first by simply obtaining images of select regions of interest, then by using the PEEM systems spectroscopy capabilities in order to determine if the PEEM was capable of showing a difference between the cutoff values of the ITO, P3HT, PCBM, blends of the acceptor and donor in line with standard OPVs and finally PDOT:PSS.

The cutoff value for ITO was found to be at a sample bias of -1.28eV and the morphology of the cleaned ITO was found to be homogeneous with the exception of surface defects such as scratches.

The morphology of P3HT was found to be substantially different from that of clean ITO, with structured and complicated patterns forming across the surface. The cutoff for P3HT was found to be -1.20eV which is less negative than the value for ITO meaning it has a lower work function which is in line with expectations. The difference between the values is not as large as expected, however this may be because of film thickness affecting the result as in the experiments by Schneider et al [20]. The morphology of PCBM was found to also be homogeneous but PCBM did not form any complicated structures such as the fractals shown in figures 44 and 46, instead there were no complicated structures formed by the PCBM in either spin coated or drop deposited samples. The cutoff for PCBM was found to be -1.31$\pm$0.05eV which is more negative than ITO which contradicts what would be expected given the known values of the work functions, however the results are less than 0.05eV apart indicating that they have similar work functions, this is in line with predictions for PCBM in relation to ITO as the difference in the work function is 0.1eV [7].

The blends yielded similar morphologies to each other, they each showed homogeneity when spin coated onto ITO, however the 2:1 and 1:0.8 blends each showed ridge like formations across the surface indicating an ability to form complex morphologies on the substrate. There was an instance of fractal in the drop deposited 2:1 blend indicating that the conditions for fractal formation was met as it was with the pure P3HT on

ITO. The blends also showed cutoffs that were less than 0.05eV apart indicating that they each showed similar electrical properties. The blends all showed significantly less negative cutoffs than either the ITO or the individual molecules deposited onto ITO which indicates that the blends of the acceptor and donor molecules in this case have a lower work function than either of the individual molecules.

The PDOT:PSS showed generally homogeneous morphology across the sample. The cutoff for PDOT:PSS was found to be -1.10±0.05eV which is distinct from ITO. However the result contradicts expected results as it indicates a lower work function whereas experimental data shows that the work function of PDOT:PSS is higher. This result may indicate that the results taken from PDOT:PSS have been effected in someway by the thickness of the deposition or that the PEEM is not able to correctly distinguish between PDOT:PSS and ITO.

It has been demonstrated that the PEEM can be used to identify differing morphologies across various samples, though none of the samples yielded the morphology of a typical OPV the potential exists that the PEEM can be used to identify these morphologies. The experiments using the spectroscopy yielded mixed results, in the case of the pure molecules it yielded results that were expected given the context of the experiment however the blends showed much less negative cutoffs than the individual molecules when it might be expected that they would give an average value. Furthermore the results with PDOT:PSS cast doubt on the suitability of PEEM to identify correctly between PDOT:PSS and ITO.

For future work in this area steps should be taken to better model the OPVs this should be done by creating model OPVs more similar to those found in figure 4 with PDOT:PSS being deposited onto the ITO first followed by blends of the molecules. This has the possibility of yielding different morphologies as well potentially effecting the work functions of the donor/acceptor layer and the PEEMs ability to distinguish between regions on the same sample. The goal would be to get morphology more similar to typical OPVs with clearly distinguishable phase boundaries.

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