Electrostatic Force Microscopy on Organic Photovoltaics

A Dissertation Submitted in Partial Satisfaction of the Requirements for the Degree Bachelors of Science in Physics

By

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Dedicated to Mananya
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1 Introduction

Energy consumption has always been an issue that everyone is concerned about. Currently, fossil fuels consisting of petroleum makes up 36% of the world’s energy consumption followed by coal 27.4%, and natural gas 23.0%, amounting to 86.4% of the world’s energy consumption. However, fossil fuels have much political effect due to security of supply as well as environmental concerns related to global warming and sustainability. Therefore, much research is done on renewable energy such as solar, wind and thermoelectric as a means of much of the new energy sources to replace fossil fuels.

At the moment, much research is focused towards the use of solar energy by means of solar cell. Most solar cells manufactured and in-used are silicon-based solar cells; however research is done on organic solar cell as a means to replace the silicon cells because organic solar cells are cheap, renewable, flexible, light-weight, and environmentally friendly. However, organic solar cells do not have as high power conversion efficiency as silicon cells, to date the highest power efficiency organic photovoltaic cells (OPVC) are ~8%. Due to this, future research on properties of organic solar cell will help develop a more efficient cell that will compete with silicon solar cells for commercial used.

In many scientific research groups, research is being done using different types of polymers, processing techniques and characterization methods in order to improve the efficiency of organic solar cells. One of the ways of characterization of these solar cells is by Electrostatic Force Microscopy (EFM). EFM is a form of Atomic Force Microscopy aim at detecting surface charges and dielectric properties of the organic materials that are used to make solar cells which is essential to the characterization of these materials.

1.1 Organic Photovoltaics

1.1.1 Theoretical

Organic solar cells are semiconductor diodes that convert visible light into direct current. The materials for OPVC are small molecules or polymers that have large conjugated systems. The conjugated systems are formed when carbon atoms bond covalently with alternating single and double bonds. The chemical reactions of these hydrocarbons electrons Pz orbitals delocalized and form the delocalized bonding Π (HOMO: highest occupied molecular orbital) and Π* anti-bonding orbital (LUMO: lowest unoccupied molecular orbital). When light is absorbed the electron is excited from the HOMO level to the LUMO level and the separation between the HOMO and LUMO level is called the band gap of organic electronic materials.
1.1.2 Design of Organic Photovoltaic

The most commonly used junction for OPVC is the bulk heterojunction design. The design of an organic consists of a layer of ITO (tin-doped indium oxide) coated glass, a layer of Poly [3,4-ethylenedioxythiophene]-poly [styrenesulfonate] PEDOT:PSS, a bulk-heterojunction layer of fullerene (donor material) and acceptor material, and a layer of metal electrode.

Sunlight would be absorbed through the transparent ITO layer and hit the bulk-heterojunction. An exciton would be created either in the donor or acceptor region and would diffuse to the interface of the donor and acceptor. There, it would separate into an electron and hole. From there, the electron to would diffuse towards the ITO and the hole would diffuse towards the metal electrode.

Other typical junctions for OPVC are single layer heterojunction in which only one layer of organic material is sandwiched between the two electrode, bi layer heterojunction in which two different types of organic materials are sandwiched in between the metal electrodes and multi-layers ion OPVC with interfacial metallic nanoclusters.
# 2 Techniques for Characterization of Organic Photovoltaics

## 2.1 Introduction to Different Characterization Methods

Currently, much research has been done in the characterizations of Organic Solar Cells consisting of its materials, and properties. Many techniques have been implemented on the characterizations of these cells such as NMR, XPS, Solar Cell Testing, and Scanning Probe Microscopy. Scanning probe microscopy and various adaptations of the scanning probe technique have revolutionized surface science by mapping the features on the topography correlated it to the other features on the surface.

### 2.1.1 AFM (Atomic Force Microscopy)

AFM is called atomic force microscopy (AFM) is a type of scanning probe microscopy with resolution on order of fractions of a few nanometer. The AFM is a tool for imaging, measuring and manipulation materials on a nanoscale. The information is gathered by “tapping” on the surface with a mechanical probe.

AFM is a method that uses a cantilever with a sharp tip known as a probe attached at its end to scan over a certain material. The cantilever is usually made of silicon or silicon nitride with a tip radius of curvature on the order of a few nanometers. When the tip is brought to the surface of a sample, certain forces between the tip and the sample caused deflection of the cantilever. From this deflection, a laser’s angle is deflected and this change is detected by a detector which translates into the AFM image. Depending on the situation, some forces that are measured using AFM with the Multimode SPM (Scanning Probe Microscopy):

**Contact AFM** - Measures topography by sliding the probe’s tip across the surface of the Sample

**Tapping Mode AFM** - Determines the topography by tapping the surface with an oscillating tip; with this method, the shear forces which can damage soft samples and reduce image resolution are eliminated. A special quality of Tapping Mode is that it can be used in air or in fluids.

**Phase Imaging** – This method provides image contrast caused my differences in surface adhesion and viscoelasticity.

**Non-contact AFM** – Measures topography induced by Van der Waals attractive forces between the surface and the probe tip held above the surface. However, this method provides lower resolution than contact AFM and Tapping Mode AFM.

**Magnetic Force Microscope (MFM)** – Measures the magnetic force gradient above the sample surface.

**Electric Force Microscope** – Measures the electric field gradient above the sample surface.
Surface Potential Microscopy – Measures differences in local surface potential across the sample surface.

Life Mode – A combined, two-pass technique that separately measures topography (using Tapping Mode) and another selected property using the topographical information to track the probe tip at a constant height above the surface.

2.1.2 SEM (Scanning Electron Microscopy)

The types of signals produced by an SEM include secondary electrons, back-scattered electrons, light, currents and transmitted electrons.

A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition and other properties such as electrical conductivity. The SEM can produce very high resolution images; however the disadvantage of SEM is that it requires the sample to be coated with a conductive substance.

2.1.3 TEM (Transmission Electron Microscopy)

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a very thin film. An image is created by the scattered electrons passing through a magnifier and focused onto a fluorescent screen on a layer of a photographic film or to be detected by a sensor such as a CCD camera. TEMs images are capable of very high resolution scans owing to the small de Broglie wavelength.

However, there are many disadvantages regarding TEM such as extensive sample preparation, and sample damaging during the actual scanning process.

2.1.4 Electrostatic Force Microscopy Technique

Electrostatic Force Microscopy (EFM) is scanning probe technique that measures the long-range electrostatic attraction between a conductive probe and a conductive substrate.

In Electrostatic Force Microscopy (EFM), surface charges (Q) and permanent dipoles (P) generate images in the tip by interacting with the total charge on the EFM tip through Coulomb interactions. The attraction between the cantilever and the substrate is proportional to the square of the voltage difference between them. Thus, application of a sinusoidal voltage $V = V_{DC} + V_{AC}\sin(\omega t)$, yields components of the attractive force at zero frequency, $\omega$ and $2\omega$. The force at $\omega$ gives a local measure of $Q$ and $P$, and the force at $2\omega$ gives information about the dielectric constant of a material.
3 Electrostatic Force Microscopy

3.1 Introduction

Electrostatic Force Microscopy (EFM) is a type of scanning probe microscopy that measures the long range electrostatic interactions between the tip and the sample as well as the topology of the sample.

Although most EFM methods have some quantitative measurements such as electric field distributions and surface potential variations, most applications of EFM have been focused on surface potential and have not distinctly look at the tip-surface capacitance. Therefore, in order to determine static charges and polarizability, we have to characterize the capacitive interactions between the surface of the sample and the probe.

Therefore, we take a given model of a calibrated tip interaction with Au nanoparticle to derive a curvature correction term necessary to capture the relevant parameters for a polarizable particle using a metallic probe. From this model, we can derive the equations to describe the interactions of the EFM with a charged polarizable sphere.

3.2 Theory

A conductive AFM probe is connected to a conductive sample which creates a capacitor. The variations in distance from the probe to the sample cause different electrostatic forces and therefore differences in surface charges and dielectric properties. The forces are then separated into two parts: the columbic forces due to the static charges and multipoles and capacitive forces due to surface potential and dielectric screening. Because of the principle of superposition we can separate the forces due to the sample from the forces between the plates as an empty capacitor. We can write the force due to the sample as the product of the total electric field from the sample and the charge on the tip:

\[ F_{\text{coul}} = E_z Q_{\text{tip}} \]

Here, \( E_z \) is the z-component of electric field that is due only the charges and/or multipoles on the surface. The force between the plates of the empty capacitor is given by

\[ F_{\text{cap}} = \frac{1}{2} \frac{dC}{dz} V^2, \]

Where \( V \) is the voltage applied between the surface and the probe and \( \frac{dC}{dz} \) is the derivative of the empty probe-substrate capacitance with respect to \( z \), the separation of the probe apex from the conductive plane of the sample. The potential has the form
\( V = V_{\text{DC}} + V_{\text{AC}} \sin(\omega t) \) and

\( F_{2\omega} = \frac{1}{2} \frac{dC}{dz} V_{\text{tot}}^2 + E_z Q_{\text{tip}} \)

\( Q_{\text{tip}} \) is the sum of the charge on the capacitor, \( CV_{\text{tot}} \) plus the image charges \( Q_{\text{im}} \) induced by the static charge distribution on the surface. \( E_z \) has two components: \( E_z^S \) – due to static charges and multipoles and \( |E_z^d| \sin \omega t \) – due to oscillating polarization induced in the sample by the AC field. Thus \( E_z = E_z^S + |E_z^d| \sin \omega t \). \( |E_z^d| = f(\varepsilon, \{g\}) V_{\text{AC}} \) where \( f \) is determined constant \( \varepsilon \) and the geometric parameters \( \{g\} \) of the system.

We can write the total force on the tip as

\( F_{\text{EFM}} = \frac{1}{2} \frac{dC}{dz} \left( (V_{\text{DC}} + \varphi) + V_{\text{AC}} \sin(\omega t) \right)^2 \)
\( + \left( E_z^S + |E_z^d| \sin \omega t \right) (Q_{\text{im}} + C(V_{\text{DC}} + \varphi) + CV_{\text{AC}} \sin(\omega t)) \)
\( = \frac{1}{2} \frac{dC}{dz} \left( (V_{\text{DC}} + \varphi)^2 + \frac{1}{2} V_{\text{AC}}^2 \right) + E_z^S (Q_{\text{im}} + C(V_{\text{DC}} + \varphi)) + \frac{1}{2} |E_z^d| CV_{\text{AC}} \)
\( + \left( V_{\text{DC}} + \varphi \right) \frac{dC}{dz} + E_z^S C + f(\varepsilon, \{g\}) V_{\text{AC}} (Q_{\text{im}} + C(V_{\text{DC}} + \varphi)) \) \( V_{\text{AC}} \sin(\omega t) \)
\( - \left( \frac{1}{2} f(\varepsilon, \{g\}) C + \frac{1}{4} \frac{dC}{dz} \right) V_{\text{AC}}^2 \cos(2\omega t) \)

In Equation there are 3 terms; a static term which shows how the amplitude oscillates at the frequency of the applied voltage \( \omega \) and a term whose amplitude oscillates at twice that frequency \( 2\omega \).

Therefore

\( F(\omega) = \frac{dC}{dz} (V_{\text{DC}} + \varphi) V_{\text{AC}} \)

and

\( F(2\omega) = \frac{1}{4} \frac{dC}{dz} V_{\text{AC}}^2 \)

Represent the empty capacitor with no sample present. The apparatus then detects shifts in the AFM probe’s frequency due to the force gradients. Because the motion of the AFM probe represents that of a harmonic oscillator in a force field, the resonant frequency \( \nu' \) represents

\( \nu' = \nu \sqrt{1 - \frac{1}{\kappa} \frac{dF}{dz}} \)

Where \( \kappa \) is the force constant of the probe and \( \nu \) is the resonant frequency. If we approximate the Taylor expansion, we reduce our form to
\[ |\Delta \nu| = |\nu - \nu'| \approx \frac{\nu \frac{\partial F}{\partial z}}{2k} \]

Which we will use to analyze surface charge and dielectric properties.

In an EFM experiment, we get three images involving topology, surface charge; \( \omega \), and dielectric properties; \( 2\omega \). The probe first taps the sample to get the tapping-mode topography in the first pass with no voltage applied, and on the second pass the probe is lifted at a \( z_{\text{lift}} \) above the sample and scanned at a constant height. As the probe passes over the sample it remains oscillating at its resonant frequency and deflects as it senses charge on the sample. The signal of the deflection is then modified by the two lockin amplifiers, one for \( \Delta \nu(\omega) \) and the other for \( \Delta \nu(2\omega) \) and from these values we can relate it to \( |\Delta \nu| \approx \frac{\nu \frac{\partial F}{\partial z}}{2k} \)

which gives us the capacitance and electrostatic relations by writing the derivatives of 3.6 and 3.7.

To determine \( \varphi \), we vary \( V_{\text{dc}} \) to eliminate the signal at \( \omega \) over an empty sample region.

### 3.3 Components of Electrostatic Force Microscopy

Computer and DC power supply

(From Top to Bottom) Signal Access Module, Function Generator
(From Top to Bottom): Voltmeter, Oscilloscope, Lock-in Amplifier 1, Lock-in Amplifier 2

Scanning Probe Microscope in Glove Box
Nanoscale Morphology for DATA extraction using EFM technique
In order to correctly establish quantitatively the interaction of the probe and the sample, a model to represent probe’s dependence on curvature and how probe and sample interactions were affected by its curvature. The best fit model established was taken from Brus et al. 2003. The model given for the field felt by the tip due the AC polarization for a point charge is represented the distance at the center of the sphere. In Brus et al.’s model, the capacitance interactions where derived from the interaction between the probe and gold nanoparticles therefore $\varepsilon$ was set to infinity. The $\varphi_q$ equation is taken to the second expansion, $P_n(\cos\phi)$ which represents the Legendre polynomials is expanded to the 2nd expansion with $\phi$ set to 0. However, we plan to modify this model to fit the parameters of our material.

We also write the expression to describe the potential due to a sphere polarized by a line charge in the probe such as:

We expressed the total potential

$$\varphi_{tot}(r) = \varphi_{Q\text{sphere}}(s_1) + \varphi_{q\text{sphere}}(s_2) + \varphi_{l}(-s_3) + \varphi_{L\text{im}}(-s_4)$$
Where $s_i$’s are the distances from the charge (line and spherical) centers to the center of the nanoparticle such that

\begin{align}
S_1 &= z + \rho - (d/2) - (h/\varepsilon_h) \\
S_2 &= z + \rho + (d/2) + (h/\varepsilon_h) \\
S_3 &= z_1 - (d/2) - (h/\varepsilon_h) \\
S_4 &= z_1 + (d/2) + (h/\varepsilon_h)
\end{align}

Then we write the total force on the sphere and cone at $2\omega$ due to the particle by

\begin{equation}
F_{2\omega}(z) = -2 (\nabla \varphi_{tot}(s_1) Q_t + \int_{S_3}^{S_3+L} \nabla \varphi_{tot}(z) \lambda dz + \nabla \varphi_{tot}(s_2) Q_t + \int_{S_4}^{S_4+L} \nabla \varphi_{tot}(z) \lambda dz)
\end{equation}

Brus et al. then take the best model given such that $p$, $z$ and $d$ are 18, 30 and 10 nm and establish an offset term to fit the model predicted with the data given for the interactions such that

\[ \frac{dF_{2\omega}(z-z_{off})}{dz} \]

which we imposed as our model for our experiment,

Where $z_{off} = 1.02\rho - 1.32d + 0.707z - 0.02pz + 12.28(d/\rho) - 19.43$ where the offset averages to 2.81. For the rest of our experiment, this simulation is taken from Brus et al., however variations may occur since our probes do not exactly represent Brus et al.

### 3.5 Interpreting $F(\omega)$ – Charge Distribution in Small Dielectric Spheres

We then use Brus et al. model for surface charge for $F(\omega)$. $F(\omega)$ is composed of three terms as given in

\begin{equation}
F(\omega) = ((V_{DC} + \varphi) \frac{dC}{dz} + f(\varepsilon, \{g\})V_{AC}(Q_{im} + C(V_{DC} + \varphi)) + E_z^SC)V_{AC}
\end{equation}

The first term is due to the contact potential difference between the probe and the substate which can be zeroed when setting $V_{DC} = -\varphi$. The second term is due to the interaction of the oscillating dipole in the sample with the static image charges in the tip. The third term is dominant in determining the forces on the tip and the effective observed force at $\omega$ which becomes

\begin{equation}
F(\omega) = E_z^SCV_{AC}
\end{equation}

The potential due to a charge within nanoparticle we consider the as polarizable spheres. The equation

\begin{equation}
\varphi(x, \zeta) = \frac{q}{4\pi\varepsilon_0} \sum_{n=0}^{\infty} \left( \frac{s^n}{(x^2+\zeta^2)^{n+1}} \right) \left( \frac{2n+1}{\varepsilon n+n+1} \right) P_n(\cos\phi_1)
\end{equation}

represents the potential at point $(x, \zeta)$ given by 3.16, such that if charge $q$ is located within a particle a distance $s$ from the particle center at an angle $\phi$ to the substrate normal where $x$ is a radial distance from the surface normal axis going through the center of the particle and $\zeta$ is the
height above the nanoparticle center, $\varepsilon$ is the dielectric constant of the spherical particle, and $P_n(a)$ is the $n^{th}$ Legendre polynomial in $a$.

The potential of the image charge is given as 3.28

\[(3.17)\quad \varphi_{im}(x, \zeta) = \frac{q}{4\pi\varepsilon_0} \sum_{n=0}^{\infty} \left( \frac{s^n}{(x^2 + \zeta^2)^n+1} \right) \left( \frac{2n+1}{k_{\varepsilon n+n+1}} \right) P_n(cos \phi_2) \]

\[(3.18)\quad \zeta_2 = \zeta + d + 2\frac{h}{\varepsilon} \]

and

\[(3.19)\quad cos \phi_2 = \frac{-x \sin[\pi-\phi]+\zeta_2 \cos[\pi-\phi]}{\sqrt{(xcos[\pi-\phi]+\zeta_2 \sin[\pi-\phi])^2+(-x \cos[\pi-\phi]+\zeta_2 \sin[\pi-\phi])^2}} \]

from this we derived the model

\[(3.20)\quad \varphi_{total}(x, \zeta) = \Sigma_l(\varphi_l(q_i,s_i,\phi_i,x,\zeta) + \varphi_{im,l}(q_i,s_i,\phi_i,x,\zeta)) \]

and take the force

\[(3.21)\quad F_\omega(x,z) = -2\left[ \frac{d}{ds_1} \varphi_{total} \right](x, s_1) Q_{sphere} + \int_{s_2}^{s_1} \frac{d}{d\zeta} \varphi_{total}(x, \zeta) \lambda d\zeta = -2\left[ \frac{d}{d\zeta} \varphi_{total} \right](x, s_1) Q_{sphere} - \varphi_{total}(x, \zeta) \lambda \]

where

\[(3.22)\quad s_1 = z + \rho - \frac{d}{2} - \frac{h}{\varepsilon_h} \]

and

\[(3.23)\quad s_2 = z_1 + \rho - \frac{d}{2} - \frac{h}{\varepsilon_h} \]

Now we can substitute 3.21 into 3.9 and using experimental data for $\Delta \nu(\omega)$ and from this we can get the charge distribution of the particle. By using these tools we can analyze the $z$ dependence as well as cross-sections of the observed electrostatic force gradients.

These equations will be used to help calculate the charge distributions on MDMOPPV/PCBM balls in toluene.

### 3.6 Surface Charge Measurements

To get some generalized results directly from our surface charge measurement, we know that

\[(3.24)\quad |\Delta \nu| = |\nu - \nu'| \approx \frac{\nu}{2k} \frac{\partial F}{\partial z} \]

And from electrostatics theory
\[ (3.25) \sigma = |\varepsilon_0 \frac{\partial \nu}{\partial z}|. \]

Therefore in order to find surface charge, we integrate the force with respect to \( z \) and substitute it for \( \frac{\partial \nu}{\partial z} = -F \), we can find a value for surface charge with respect to lift height.
3 Experimental

Images at room temperature under nitrogen atmosphere were obtained with a Digital Instruments (Santa Barbara, CA) Nanoscope IIIa Multimode AFM with Extender module. Pt-Ir coated EFM tips (Nano World Innovative Technologies) and Veeco (Camarillo, Ca). Their resonant frequency was around 65 kHz and spring constants ranged from 1.2-5.5 N/m (in our model we assume spring constant to be 1 N/m for simplicity). During image scanning, the tip taps across the surface applying no voltage and then lifts on the second pass over the same topography but with an external applied bias. During the second pass, the tip is scanned above the surface at constant height while oscillating at its resonant frequency. The frequency shift stream from the phase-lock look is fed into two lock-in amplifiers where the \( \omega \) and \( 2\omega \) components of the signal were isolated. The signal is then fed back to the imaging software and the frequency shift can be seen in the changes on the EFM images for \( \omega \) and \( 2\omega \). In all experiments, \( \omega \) was set to 400 Hz, \( V_{ac} \) was set to 3V, lock-in time-constant \( \tau \) was set to 3ms, topographic feedback set point 0.35-0.4V and the scan rate was 0.75 Hz. An external power supply applied on the tip gives the \( V_{dc} \) was set to cancel out the contact potential between the substrate and the tip.

Images were taken under 3 conditions: no light exposure, blue monochromatic laser (Crystalaser BCL-405-40-S 40 mW, 407 nm diode laser), and fiber optic light(Fiber-Lite® Illuminator System); the light sources were shown at a grazing angle.
4 Results

4.1 $V_{dc}$ Applied on ITO (Indium Tin Oxide) To Cancel Contact Potential

In order to cancel out the contact potential, bias is applied on the tip. These are the images resulted from different biases applied on the tip. For all our following experiments, we applied 0.2 V to cancel out the contact potential between ITO and the probe.

Figure (a)

Images shown are of ITO substrates applied at 0.2V to cancel out the contact potential.
4.2 Solvent Effects

The main characteristic of a bulk heterojunction is the interfacial area between the donor and acceptor phases which enables charge separation with the bulk. Bulk heterojunction device makes use of photo absorption throughout the bulk mixture layer.

The solvent from which the blend film is cast influences the solar power conversion dramatically seen in many papers.

Our results consist of MDMO-PPV:PCBM-based bulk heterojunctions (MDMO-PPV:PCBM:poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylene-vinylene; PCBM: 1-(3-methoxy carbonyl) propyl-1-phenyl[6,6]C70) for the AFM and EFM images obtained on ITO (Indium-Tin-Oxide) films.

Our conditions consist of 1 wt.% 1:3 MDMO-PPV/PCBM in Toluene, stirred at 55 degrees overnight, spin coated on bare ITO (indium tin oxide) on glass substrate at 1500 rpm (revolutions per minute), and annealed at 150 degrees for 15 minutes; and 0.5 wt.% 1:4 MDMO-PPV/PCBM in Chlorobenzene, stirred at 50 degrees overnight, spin coated on APTMS (aminopropyltrimethoxysilane)-modified ITO on glass substrate at 2000 rpm (revolutions per minute), and annealed at 120 degrees for 10 minutes.

4.3 Toluene-Cast Films

In toluene cast films, we see very high surface features on round MDMOPPV/PCBM mixtures. There are very large phase separations of the MDMOPPV/PCBM in toluene with a diameter of 500 nm.

Images were taken at different lift heights to show the change in frequency shifts with respect to change in distances from the surface and the tip.

4.4 MDMOPPV/PCBM in Toluene under No Light

In these images, scans per lift height take 23 minutes and for 20 to 40 nm lift heights increments of 2nm, the total time takes about 4.5 hours for each experiment.

For these experiments, we can see the photo-excited charge transfer of holes interacting with the tip and the film. During these experiments, no light is shown on the material, but however there is some surface charge available due to errors in instrumentation and thermal effects.

The film was annealed at 150 degrees for 15 minutes, has a scan size of 5 um, and was biased at 0.2V.
Lift  
28 nm  
0.2V  
Height  
Surface Charge  
Dielectric Properties

30 nm  
0.2V  
S -22.4 d -177.4

32 nm  
0.2V  
Height  
Surface Charge  
Dielectric Properties

34 nm  
0.2V  
S -22.4 d -177.4
Lift 36 nm  
Height  0.2V  
Surface Charge  S -22.4 d -177.4  
Dielectric Properties

Lift 38 nm  
Surface Charge  S -22.4 d -177.4

Lift 40 nm  
Height  0.2V  
Surface Charge  S -22.4 d -177.4  
Dielectric Properties
We notice that in higher regions, there are more surface charges and capacitance signals. However, there is a crease in the middle of the round features indicating some sort of deformity in the round features due to it being an old sample. Therefore, it is better to analyze the surface charge from our model than just the morphology alone.
4.5 MDMOPPV/PCBM in Toluene under Monochromatic Light

Then we analyzed the MDMOPPV-PCBM solution under monochromatic light to see the photo-charge transfer of holes interaction between the tip and film, as light is shown on the film.
In these images for surface charge, there seem to be more signal at lift lower heights seeing that the columbic force decreases as $1/r^2$. For the surface charge and dielectric images, more signals are seen on the rings on the round MDMOPPV/PCBM shaped blob. Therefore, we interpret it as areas where holes and electrons have the highest interaction since it’s the region closest to the ITO electrode.
4.6 MDMOPPV/PCBM in Toluene under White Light

We then tested the MDMOPPV-PCBM in Toluene film under white light conditions to see the contrast between different light conditions.

This film was annealed for 15 minutes, 5 um scan size, 1% MDMOPVV/PCBM in Toluene, and biased at 0.2V.
For the film shown under white light, the morphology shows charges of the large round domains. Also, in the surface charge image as opposed to the height image shows the small features of the smaller domains in the MDMOPPV PCBM, not clearly seen in the height images. Therefore, we can see surface charge interactions in small domains as well as large domains.
4.6 Measured Surface Charges in MDMOPPV/PCBM in Toluene Different Conditions

4.6.1 MDMOPPV/PCBM in Toluene under No Light

MDMOPPV PCBM in Toluene No Light
Surface Charge

Data Set 1

MDMOPPV PCBM in Toluene No Light
Surface Charge

Data Set 2
MDMOPPV PCBM in Toluene No Light
Surface Charge

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Data Set 1</th>
<th>Data Set 2</th>
<th>Data Set 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0375e</td>
<td>0.474e</td>
<td>0.153e</td>
</tr>
<tr>
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<td>24</td>
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<td>0.33107e</td>
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<tr>
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<td>0.359e</td>
<td>0.189e</td>
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<td>0.29975e</td>
<td>0.181e</td>
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<td>30</td>
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<td>0.174e</td>
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<td>0.185e</td>
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<td>0.223e</td>
<td>0.0979e</td>
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<td>0.193e</td>
<td>0.114e</td>
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<tr>
<td>38</td>
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<tr>
<td>40</td>
<td>0.0375e</td>
<td>0.183e</td>
<td>0.158e</td>
</tr>
</tbody>
</table>
4.6.2 MDMOPPV/PCBM in Toluene under Blue Light

MDMOPPV PCBM in Toluene Blue Light

Data Set 1

MDMOPPV PCBM in Toluene Blue Light

Data Set 2
MDMOPPV PCBM in Toluene Blue Light

Data Set 3

Lift Height (nm)

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Data Set 1</th>
<th>Data Set 2</th>
<th>Data Set 3</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.243e</td>
<td>0.099e</td>
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<tr>
<td>22</td>
<td>0.195e</td>
<td>0.195e</td>
<td>0.135e</td>
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<tr>
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<td>0.117e</td>
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<td>26</td>
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<td>0.042e</td>
<td>0.098e</td>
<td>0.104e</td>
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<td>0.082e</td>
<td>0.204e</td>
<td>0.108e</td>
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<td>0.109e</td>
<td>0.202e</td>
<td>0.111e</td>
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<td>0.157e</td>
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<td>38</td>
<td>0.042e</td>
<td>0.070e</td>
<td>0.077e</td>
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<td>40</td>
<td>0.077e</td>
<td>0.182e</td>
<td>0.091e</td>
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</tbody>
</table>
4.6.3 MDMOPPV PCBM in Toluene under White Light

MDMOPPVPCBM under White Light

Data Set 1

110425-TUMDMOPPVPCBM under White Light-data set 2

110425-TUMDMOPPVPCBM under White Light-data set 3
Lift Height (nm) | Data Set 1 | Data Set 2 | Data Set 3
---|---|---|---
20 | 0.556e | 0.3631e | 0.117e
22 | 0.3656e | 0.3976e | 0.128e
24 | 0.4429e | 0.3834e | 0.138e
26 | 0.442e | 0.4245e | 0.214e
28 | 0.354e | 0.4303e | 0.0923e
30 | 0.4716e | 0.2965e | 0.1907e
32 | 0.4151e | 0.3326e | 0.1418e
34 | 0.535e | 0.3401e | 0.1209e
36 | 0.517e | 0.3657e | 0.1552e
38 | 0.476792e | 0.324e | 0.119e
40 | 0.61972e | 0.2513e | 0.14026e

4.7 Chlorobenzene-Cast Films

In chlorobenzene cast films, the morphology represented were more homogenous than toluene mixed films. However we still see phase separation of smaller nanospheres around 20 nm in diameter.

4.7.1 MDMOPPV PCBM in Chlorobenzene under Blue Light

Experiments were also done on MDMOPPV/PCBM in Chlorobenzene, the data for surface charge is given.
<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Surface Charge</th>
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</thead>
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<td>0.01244e</td>
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<td>0.006133e</td>
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<tr>
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<td>0.010031e</td>
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<tr>
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<td>0.0120e</td>
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<tr>
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<td>0.01564e</td>
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<td>0.01590e</td>
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<td>0.00698e</td>
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<td>38</td>
<td>0.012176e</td>
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<td>40</td>
<td>0.00826e</td>
</tr>
</tbody>
</table>

4.7.2 MDMOPPV/PCBM in Chlorobenzene under White Light

CB MDMOPPV PCBM WHITE LIGHT

<table>
<thead>
<tr>
<th>Lift Height (nm)</th>
<th>Surface Charge</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.01719e</td>
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<tr>
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</tr>
<tr>
<td>24</td>
<td>0.01800e</td>
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<tr>
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<td>0.01677e</td>
</tr>
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<td>28</td>
<td>0.01770e</td>
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<td>0.01636e</td>
</tr>
<tr>
<td>32</td>
<td>0.01780e</td>
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<td>0.01032e</td>
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<td>0.01858e</td>
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<tr>
<td>40</td>
<td>0.02427e</td>
</tr>
</tbody>
</table>
6 Discussions

6.1 Analysis of Surface Charges

Comparatively, out of all the experiments, surface charges are seen more profoundly in solutions when toluene is the solvent than when chlorobenzene is the solvent using the model created. This more charge accumulation seen on the surface of the toluene solution than chlorobenzene may be due to the much higher topology of solutions in toluene than solutions in chlorobenzene, since columbic forces fall off as $1/r^2$ as a function of distance. Out of all the light conditions, more surface charges are extracted under white light than all other conditions. Since a larger of spectrum of wavelengths is used for photo-excitations, it is a clear indicator why white light gave more surface charge.

The model for surface charge was not used in results but the code is written on Mathematica. The analysis of this model could be very useful in the future.

6.2 Analysis of Capacitance Interactions

For the Capacitance interactions between the MDMOPPV PCBM and the tip, we see the highest interactions in solutions containing toluene as the solvent under blue and white light conditions. The reason for this might be that $\frac{\partial^2 C}{\partial z^2}$ is proportional to $1/z$ as $z$ is a function of distance pertaining to lift height. The highest capacitance interaction is seen under blue light in toluene solution however, under white light, surface charges in toluene solution do show about the same values as well. Overall, solutions in chlorobenzene do not show much capacitance interactions as solution in toluene but this may be due to the big difference in the topography among the two blends.

7 Conclusion

The method of EFM is useful in many respects such as to see the transfer of holes and electrons to their proper electrodes. With the data collect and the information given, models could be made and used that would be useful for not just figuring out such electrostatic properties but the movement of electrons and holes in their processes as the image is scanned. From our results, we would be able to get useful data that would help us understand Organic Solar Cells more efficiently which would lead to a more efficient solar cell.
8 Bibliography


