Thickness and morphology analysis of squaraine based films using advanced AFM and XRD.

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Thickness and morphology analysis of squaraine based films using advanced AFM and XRD.

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A Thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science in Materials science engineering in the School of Chemistry and Material Science College of Science Rochester Institute of Technology Rochester, New York

October 2017

Signature of the Author: __________________________

Kenny Baptiste

Accepted by: __________________________

Casey Miller, Director, M.S. Degree Program
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The M.S. Degree Thesis of Kenny Baptiste has been examined and approved by the thesis Committee as satisfactory for the thesis required for the M.S. degree in Chemistry.

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Date
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The thickness and morphology of squaraine based OPV’s have been explored by our group and the accuracy of their measurement is the focus of this study. The effect of thickness on these squaraine based devices still suffers from a lack of detail. This lack of understanding about the role of thickness in SQ: PCBM devices, specifically, retards optimization efforts. Before we can deduce how active layer thickness affects performance in OPV SQ: PCBM devices, data need to be generated. The determination of the thickness of the active layer and phase domain size in OPV’s is facilitated by instruments that can measure step heights and phase domains on the nanometer scale. Several candidates for each parameter exist and the selection is often based on access and affordability. In our work, we explored several techniques, chief of which were profilometry and Atomic force microscopy for thickness, and X-ray diffraction to explore morphology. In addition, we explored confocal microscopy as a check on our AFM analysis and explored the use of advanced AFM techniques such as peak force QNM and image J to get an approach to the quantification of the phase domains observed.

Our data show that there is promise for the use of AFM to measure thickness of these layers. In addition, XRD and SAXS, can be a good approach to understanding aggregation order in these blended films.
LIST OF ABBREVIATIONS

\( \eta_{OPV} \) ..............Efficiency of the device
\( \eta_A \) .................Efficiency of absorption
\( \eta_{ED} \) .................Efficiency of exciton diffusion
\( \eta_{CS} \) .................Efficiency of charge separation
\( \eta_{CT} \) .................Efficiency of charge transfer
\( \eta_{CC} \) .................Efficiency of charge collection
BHJ .....................Bulk Heterojunction
D-A material ...... Donor – Acceptor material
DCM ..................Dichloromethane
DHSQ(OH)_2 ...... Symmetric aniline-based squaraine with n-hexyl chain on the molecular arm with di hydroxyl substituents on the aniline
FF .....................Fill Factor
FWHM ..................Full Width Half Max
HOMO ..................Highest occupied molecular orbital
ICT .....................Intermolecular Charge Transfer
ITO .....................Indium Tin Oxide
\( J_m \) .............The current at the point where the curve is at maximum power output
\( J_{SC} \) .................Short Circuit Current
\( J-V \) curve ........Current-voltage curve
LUMO ..................Lowest unoccupied molecular orbital
NIR .....................Near infrared
OPV ..................Organic Photovoltaic
P3HT ...............Poly(3-hexylthiophene-2,5-diyl)
PCBM .................Pheny-C61-butyric acid methyl ester
PCE ..................Power Conversion Efficiency
PEDOT:PSS ........ Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
\( P_{\text{incident}} \) .........Power of the incident light
PMMA ...............Poly-(methyl methacrylate)
SQ ..........................Squaraine
TA .....................Thermal Annealing
TEM……………..Transmission Electron Microscopy
$V_m$…The voltage at the point where the curve is at its max power output
$V_{OC}$…………..Open Circuit Voltage
Wt%………………..Weight Percent
XRD………………..X-ray Diffraction
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Chapter 1: Introduction

1.1 Organic Photovoltaic

The desire to replace environmentally unfriendly fossil fuels drives the research needed for the greener technologies of tomorrow[1][2]. In this effort, organic Photovoltaic[3][4] (OPV) cells are being developed. These polymer and small molecule based solar cells[5] are third generation[6] models which can be solution processed allowing for fast, simple, low-cost and large volume processing[7]. This may involve the printing or coating of solar cells using roll-to-roll (R2R)[8] machinery, similar to the way newspapers are made. One class of these films are squaraine dye - fullerene blends which have gained significant interest due to the panchromatic properties[9] of the squaraines, accompanied by their ease of processing and up-scalability of the blends.

Despite the inadequate power conversion efficiencies (PCE), many researchers are hopeful. Indeed, Varun Sivaram et al. boasted that the solar panels of tomorrow will be transparent, lightweight, flexible, and highly efficient. “we will be able to coat shingles or skylights or windows with them, and it will all be as cheap as putting up wallpaper”[10].

In inorganic Photovoltaics, free electron hole pairs are produced immediately upon photon absorption and produces a voltage at the electrodes. Similarly, in organic Photovoltaics, a photon is absorbed which excites an electron to the LUMO (a form of
conductance band) creating a hole in the HOMO (a form of valence band). Unlike inorganic photovoltaics, however, the hole–electron pair is strongly electrostatically associated. Therefore, the pair is considered as a neutral mobile excited state[11] called an exciton which requires an interface for charge separation.

Light is absorbed by either the donor or acceptor to create an exciton. The excitons diffuse to the interface where they decay by the creation of the charge separated state consisting of the radical cation of the donor and radical anion of the acceptor. The resulting charge separation produces large concentrations of electrons and holes at the junction. They then diffuse down a chemical potential gradient[4] to the electrodes where they produce a current.

For a current to be produced, the excitons must be dissociated at an interface of two materials having different electron accepting and donating properties. In an efficient cell, all excitons generated would diffuse to the interface and separate. However, the lifetime (average diffusion time of excitons) is limited by decay processes that often result in the return of the electron to the ground state before the exciton can reach the interface. This limits the thickness of organic layers, which has to be balanced against the thickness required for the efficient absorption of light. The interface ensures that the process of charge separation is thermodynamically and kinetically favorable.

A gap of 0.3 eV (empirically determined)[12] is required to allow the electron to charge transfer from the donor material to the acceptor material. The coulombically bound charge transfer state must subsequently be separated and there are competing
arguments as to the mechanism by which this separation can occur[13]. The ideal interface ensures that (in the energy change event occurring when the electron or hole is donated from one material to another) enough energy is released to overcome the attraction between these oppositely charged species.

A single bilayer has low efficiencies so bulk heterojunction devices are made to increase efficiencies as donor and acceptor materials are mixed and interpenetrated. The interface surface area is thus greatly magnified in the bulk, producing greater current.

The efficiencies of these organic photovoltaic devices can be predicted by equation 1.1[14]:

$$\eta_{OPV} = \eta_A \eta_{ED} \eta_{CS} \eta_{CC}$$

Equation 1.1

Where $\eta_{OPV}$ is the efficiency of the device, $\eta_A$ is the efficiency of absorption, $\eta_{ED}$ is the efficiency of exciton diffusion, $\eta_{CS}$ is the efficiency of charge separation, and $\eta_{CC}$ is the efficiency of charge collection. Each efficiency is related to each of the steps of the mechanism as stated above.

1.2 The architecture of organic bulk-heterojunction photovoltaics

The bulk-heterojunction(BHJ) structure is rigorously studied in OPV research. This design facilitates a large interfacial area for charge separation and effective pathways for electron transfer. This type of device is relatively easy to make and can be processed in solution. The architecture of the BHJ solar cell is in a “sandwich” geometry as depicted in Figure 1.1.
Experimentally the devices are made to resemble a sandwich, where the bottom layer is commonly the glass or transparent plastic substrate. On top of the substrate, there is a conducting layer, typically Indium Tin Oxide (ITO), acting as an anode for the solar cell. The transparency of ITO allows the solar radiation to be transmitted to the active layer. A thin film of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS, top left in Figure 1.1 is a commonly used buffer layer coated on top of the ITO anode. The effect of PEDOT: PSS is to physically smooth the surface of the ITO, to prepare for the deposition of a uniform active layer. The PEDOT: PSS also acts as an electron blocking layer, which therefore promotes a unidirectional transport of specific charge carriers for what thus becomes a diode.
1.3 Relevant materials used in organic bulk-heterojunction photovoltaic

![Image of [6,6]-Phenyl C61 butyric acid methyl ester. Acceptor molecule.]

Figure 1.2: [6,6]-Phenyl C61 butyric acid methyl ester. Acceptor molecule.

![Image of General structure of Squaraine dye.]

Figure 1.3: General structure of Squaraine dye.

Squaraine dyes[8], [15]–[18] have evolved as an important group of materials for OPV device construction. The squaraine molecular structure is comprised of a central four membered carbon ring bracketed by two anilino groups forming a donor – acceptor –donor (D-A-D) template. This type of molecule has lower energy band gaps allowing more overlap of the near IR region of the solar spectrum. This improves device efficiency as the panchromaticity (the molecule absorbing more sunlight over a broader range of wavelengths) is enhanced in the solid state. DHSQ(OH)2 (Figure 1.3) was used[19] in this work due to its high extinction coefficients (>10^5 Lmol^{-1}cm^{-1})[20], sharp absorption bands and broad and varied absorption spectra in the solid state[15]. The increase in absorption in the solid state is due to self-aggregation of the dye molecules due to the high intermolecular forces between them.
For our OPV devices, we made blended films of squaraine and PCBM (Figure 1.2) to create the bulk heterojunction structure and exploit squaraine panchromaticity. In their seminal work on conjugated polymer based OPVs, Sariciftci et al. [4] observed that in BHJ the phases are intimately intermixed with no preset or preferred orientation or symmetry within the bulk. The internal fields exhibit no preferred direction for the separated charges, so the electrons and holes are free to move along any vector.

After separation, the charges require percolated pathways for the electron and hole to travel to their respective electrodes. The BHJ design offers this continuous network of interpenetrating highways on the nanoscale. Consequently, these BHJ’s are much more sensitive to the nanoscale morphology in the blend.

To study the relationship between morphology and performance, BHJ, polymer/PCBM blends were rigorously examined by the Sariciftci group and six critical parameters were identified as influencing the nanomorphology in the polymer:PCBM blend matrix. The six critical parameters are 1. Solvent used. 2. Processing temperature 3. Relative ratio of donor:Acceptor. 4. Solution concentration. 5. Thermal annealing, and 6. The primary chemical structure of materials determining tertiary organization structure.

From their work, they postulated that the ideal BHJ should have a structure in which the two phases of Donor and Acceptor are interspaced with an average length scale of ~10 to 20 nm equal to or less than the diffusion length (D_L) to ensure charge transfer. For efficient device function the donor and acceptor materials should exist
interpercolated and interdigitated, having pathways that ensure high mobility charge
carrier transport with minimal recombination.

In this work, we attempt to develop a method to measure thickness of the films
that we make by spin coating SQ: PCBM blends, create a step and measuring the
thickness accurately using atomic force microscopy (AFM) and stylus profilometry.
Will the thickness increase if the spin speed change or will the thickness change if the
initial concentration of the blends change? We hope to answer questions about what
exactly causes the thickness to change. In addition, we use X-Ray diffraction (XRD)
to monitor the morphology of the SQ:PCBM films.
Chapter 2  Experimental Methods

2.1 Materials and film preparation

Dr. Jeremy Cody’s research group at the School of Chemistry and Material Science at RIT was the source for our Squaraines. Phenyl-C$_{61}$-butyric acid methyl ester (PCBM) was purchased from Solenne b.v. and was used as received. The reagent solvents purchased from Sigma Aldrich, were used as received without any further purification.

The Squaraines and PCBM materials were kept in a N$_2$-filled glove box with O$_2$ levels $\leq$ 20-40 ppm and H$_2$O levels $\leq$ 50 ppm.

All the solutions were prepared in pre-cleaned 20 mL scintillation vails, which were capped using a lid and parafilmed after the solvent was added to prevent any change in concentration of the solution due to evaporation of the solvent. The solutions were examined to make sure the materials were fully dissolved.

The solution was then spin coated on a microscope slide which was used as the substrate. The microscope slides were sonicated in Acetone for 15 minutes and then sonicated in Isopropanol Alcohol for 15 minutes and then rinsed in hot deionized water again before spin coating. The slides were then blown dry with pressurized nitrogen. The solution was spin coated using a Chemat spin coater (model KW-4A). The spin speed used was 1500 RPM for 18 seconds unless otherwise specified.

For thickness measurement, edge creation was required to obtain the relative difference between the substrate and the top of the film. Different approaches were undertaken with varying degrees of success. This proved to be one of the most frustrating aspects of this study as the next following chapters will detail.
2.2 Annealing in organic bulk-heterojunction photovoltaic

Annealing using heat is one way to control the morphology of the BHJ active layer. Thermal energy can facilitate the orderly packing of constituent molecules in a blended film such as ours. With knowledge of the Differential scanning spectroscopy (DSC) data for our DHSQ(OH)$_2$ dye, we use a hotplate to set the temperature below the melting point but higher than its glass transition temperature. This temperature permits molecular motion and reorientation into more orderly arrangements. This temperature selection is important as McGehee et al.[21] acknowledged, for there are difficulties in optimizing OPV material design. High temperatures change the morphology of the BHJ but may also retard cell energy output. In another critical work, Shafari et al. using P3HT/PCBM models, show that at temperatures >150$^\circ$C, more phase separation occurs resulting in the creation of highly isolated PCBM aggregates [22]. This hurts cell Power conversion efficiencies (PCE) due to the production of more e-h traps. At these trap sites recombinations between electrons and holes can occur. With increased thermal annealing the ratio of the hole mobility overtakes electron mobility because of the formation of PCBM clusters. This promotes disruption of the transport pathways so the cell PCE is deteriorated[15].

The BHJ design allows much more of the available solar energy to be absorbed but there is an optimal morphology that allows effective exciton travel. However, if the clusters are too large then the diffusion lengths are too long and the charge may decay. Thus, exciton dissociation rate and recombination rates are competing processes and PCE is increased as a function of increased charge carrier mobilities. The more charges are created and survive the transport phase, the more
efficient is the charge extraction. Blend morphology governs the effective export of
these generated charges to the electrodes.

Finally, for efficient charge extraction, pure phases are beneficial at the
electrodes. Pure phases along with compatible buffer layers will ensure that charges
with the wrong sign at the electrodes, do not result in recombinations.

The analysis of the molecular packing and arrangement (tertiary
organizational nanostructure) of the DHSQ(OH)$_2$ and how that is affected by
morphology, is a focus of our research paper.

2.3 Squaraine aggregation:

Aggregation is important to OPV devices as it broadens the absorption band
and subsequently changes the extinction coefficients. My colleagues have
investigated aggregation in Squaraine dyes and have noted that our dyes self-
aggregate due to Van der Waals forces between them, to form H and J-aggregates[23]
based on exciton theory. Exciton theory establishes that the dye molecule splits into
two bi-level electronic states due to the influence of neighboring interacting dipoles.
In one case the packed molecules line up face to face while others line up head to tail.
The former is the case of H- aggregation while the latter is known as J-aggregation.
Lower energy is associated with the plane to plane oriented H-aggregates which have
oppositely oriented transition dipole moments and these states cannot be populated
directly through absorption unlike the higher face to face arrangements of similar
transition dipole moment orientation. Higher energies are observed due to the
repulsive coulombic forces between adjacent dipoles. J-aggregates have higher energies with the head to head orientation of transition dipole moment, with no oscillator strength from the ground state, and lower energy when the head to tail orientation dominates, with high oscillator strength from the ground state. For every molecule, there is an oscillation of the electron density around the molecule. Symmetric molecules have equal density fluctuation on both sides of the long axis. However, a transition dipole moment can point in any direction. The probability of a molecule absorbing light is directly correlated to the magnitude of the transition dipole moment. Squaraine molecules typically absorb in the red region of the spectrum, so the dyes are various hues of green.

Some dyes have side chains which can impact the absorption spectra to different degrees. Our studies[24] show that the steric hindrance from packing influences the slip-stack angle (the angle of tilt of the deck of molecular “cards”. In addition, the suppression of torsional motion results in an increase in effective conjugation length and hence redder emission spectra.

Understanding the relationship between aggregation and phase separation is critical to the production of efficient solar OPV cells[25]. Pure domains, mixed aggregated donor-and-acceptor domains and mixed amorphous regions make up the three main phases in our devices. A hybrid state in which these phases exist is considered ideal. However, the optimal morphology depends on the degree of aggregation and domain size. Correspondingly these effects are in turn predicated on the purity of the domains and phase separation. In addition, a homogenous mix of Squaraine and PCBM will allow for good exciton quenching and charge production.
but shortened diffusion lengths. However, the mixed state will have a negative impact on charge mobility. There is necessarily a balance required between domain size and efficient charge transport. If the domain size is too large the charge can be lost because recombination to the ground state will occur before the charges can reach the electrodes. On the other hand, if the size is too small the dissociation is rapid but the path to the electrode becomes more treacherous and tortuous and the opportunity for encountering hazards like charge neutralizing traps rises significantly. According to Credgington et al.,[26] the losses within any heterojunction solar cell may be grouped into three categories: a) relaxation of excitons that fail to diffuse to, and separate at, a suitable molecular inter-face, b) recombination of geminate pairs formed at that inter-face which fail to fully dissociate (geminate recombination) and c) recombination of dissociated carriers generated by different absorption events (non-geminate recombination). In these trap sites, geminate and non-geminate recombinations problems can result if the domains are not pure[27].

Our group has made several OPV’s using squaraine and fullerene blends, employing the BHJ architecture. In this work DHSQ(OH)$_2$:PCBM blends are used to create thin films whose thickness and morphology are varied so that the effects of annealing and the impact of thickness variations may be studied. Much discussion surrounds these parameters and their effect on OPV, solar cell effectiveness. Annealing is important because it enhances phase separation. Phase separation creates the interdigitated morphology and the continuous percolation pathways necessary for efficient charge migration. Ultimately, we want to understand the correlation between optical absorbance and thickness. If we know the thickness and
the optical absorbance we may then calculate the unique “extinction coefficients” for each squaraine dye moiety.

To measure thickness, it is necessary to create a step. The step is a relative measure of film thickness from a flat substrate baseline to the top of the film. We plan to use a small piece of tape prior to spin casting, or sharp blade post spin casting, to create such a step. The quality of the step is critical to this study. If we cannot create a profile that represents a step function. Then this can add significant errors to our method.

Many techniques exist and many have been tried but there is no established, universal approach. We hope to explore these parameters using a variety of techniques at our disposal. This study should help us better understand the future role of thickness and morphology in OPV efficiency optimization.
Chapter 3 Thickness

3.1 Thickness in spun cast films

The first parameter we explored was thickness. Thickness of the BHJ active layer directly affects device mechanism. Thickness measurements coupled with absorbance measurements allow us to characterize the extinction coefficient of any squaraine that we make. Thicker samples can absorb more light and absorption is directly related to the product of extinction coefficient ($\varepsilon$) times height (h) for the Squaraine films Equation 3.1.

$$A = \varepsilon h$$

Equation 3.1 Beer –lambert law for solid solutions (films)

The exciton diffusion rate is equal to the distance travelled (film thickness) divided by the time taken. If the distance travelled must be large, then longer times and greater rates are required. If the rate is too slow or the pathway to electrodes too tortuous the chance for charge quenching is increased. The extinction coefficient is an intrinsic property of a given material defined by how strongly a substance absorbs light at a given wavelength, per centimeter of penetration (and per molar concentration in thin films (or solution).

We do not yet know the extinction coefficients for either monomers or aggregates in our thin films because we don’t know the thickness of our thin films. This is a problem that we would like to solve. Thickness and morphology are the only property our BHJ system that we can control. Knowledge of the thickness can help us measure extinction coefficients for a variety of our dyes based on their constituent R-
group chain length (e.g. -C\textsubscript{2}H\textsubscript{5} to -C\textsubscript{6}H\textsubscript{13}). From this information, we hope to be able to identify trends in chemical structure that chemists can use to tailor materials with optimal absorbing power.

3.2 Mathematical modeling on spin cast films

Our samples are ultra-thin, which means less than 200nm thick. The factors affecting thickness of ultra-thin spun cast films have been extensively studied by Torkelson et al.[28] Their work (summarizing the contributions of several pioneers[29] in the field) discussed in detail models for how the thickness is controlled.

Using a one dimensional model and finite element methods Bornside et al[29] had earlier established that film thickness is governed by solution density, spin speed and spin time. During spin coating the solution is first deposited onto the glass substrate using a pipette. The spin coater is then started and the rotation is accelerated to the set rate, typically 700 to 1500 rpm, for our work. Centrifugal forces push the solution out radially to cover the entire substrate. The excess is flung off. The film thins slowly until some equilibrium thickness (E) is achieved. As the solution becomes more solid-like the viscosity increases. The thinning rate is given in Equation 3.2

\[
\frac{\delta h}{\delta t} = \frac{(2\rho \omega^2 h^3)}{3\eta_0}
\]

Equation 3.2
Here \( h \), is thickness, \( t \) is the spinning time, \( \rho \) is the solution density, \( \omega \) is the spin speed, and \( \eta_0 \) is the initial concentration. At this point in the Bornside model the film concentration is assumed constant so solvent evaporation is ignored.

The Torkelson et al. model involved two distinct steps. The first is a mass transfer expression which occurs early during the process described in Equation 3.3.

\[
E = k (\chi_1^0 - \chi_{1\infty})
\]

Equation 3.3

The initial step defines an equilibrium thickness \( E \), \( k \) is the mass transfer coefficient, and \( \chi_1^0 \) is the initial solvent mass fraction. \( \chi_{1\infty} \) is the solvent mass fraction that would be in equilibrium in the gas phase (above the liquid phase).

Combining Equation 3.2 and Equation 3.3 can give a wet film thickness \( h_w \), Equation 3.4. At this point the film is now immobile.

\[
h_w = \left[ \left( \frac{3 \eta_0}{2 \rho \omega^2} \right) k (\chi_1^0 - \chi_{-\infty}) \right]^{1/3}
\]

Equation 3.4 wet film thickness

If all but the initial concentration is kept constant, then the equation becomes:

Wet film thickness: \( h_w = [A \eta_0]^{1/3} \)

Where \( A = \left[ \left( \frac{3}{2 \rho \omega^2} \right) k (\chi_1^0 - \chi_{-\infty}) \right]^{1/3} \) is a constant.
Using concentration values from 0 to 45 mg/mL the curve produced, Figure 3.1, show a decrease in the slope of the film thickness as the concentration increases. This is due to a reduction in centrifugal force as the resistance to rotation increases with the increased mass. Consequently, the drag on the chuck increases and less material is thrown off. This leads to a thicker film being formed as the concentration increases. Eventually, after a certain concentration the effect of the drag becomes less significant as the factors affecting the thickness depends more on other factors, and the rate of increase slows.

Alternatively, if the spin speed is the only variable, then the curve show an exponential decrease followed by a plateauing in the film thickness, Figure 3.2. The wet film thickness expression becomes:
\[ h_w = \left( \frac{B}{\omega^2} \right)^{1/3} \], where \( B = \left( \frac{3 \eta_0}{2 \rho} k(x_1^0 - x_{-\infty}) \right)^{1/3} \) is a constant.

Figure 3.2 Thickness trend if spin speed is only variable.

This thinning trend may be explained as the effect of the increase in centrifugal force as the spin speed increases. This causes more material to be flung off the substrate so less material remains to form the film.

The last stage of film thinning is due to evaporation which is given as:

\[ h_f = (1 - \chi_1^0)h_w \]

Equation 3.5

This \( h_f \) Equation 3.5 is thus the dried film thickness which incorporates all the previous processes that yields a dried thin film with stable dimensions. The thicknesses of three films having three different concentrations are plotted using Torkelson’s model.
Using thickness \((h_f) = [C \eta_o]^{1/3}\), (model-1), and assuming all but the concentration is constant, we obtain a relationship to thickness. \(C\) is thus a constant equivalent to all the other precursor processes.

**Table 3.1 Measured AFM Thickness compared to thickness obtained using Torkelson model when concentration is the only variable. Solver calculates a best fit constant from the SSD (square of the standard deviations).**

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>Model (H_i = Ax^{1/3})</th>
<th>real data</th>
<th>SSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>131.374647</td>
<td>113</td>
<td>337.6</td>
</tr>
<tr>
<td>12</td>
<td>150.384397</td>
<td>156</td>
<td>31.5</td>
</tr>
<tr>
<td>16</td>
<td>165.5178589</td>
<td>175</td>
<td>89.9</td>
</tr>
<tr>
<td>Constant</td>
<td>283844.3909</td>
<td></td>
<td>459.1</td>
</tr>
</tbody>
</table>

**Figure 3.3 SQ:PCBM film thickness graph of real data compared to Torkelson model-1 where \(C\) is all but the varying concentration.**

Using the solver function in excel we can generate models to determine how well the data fits the Torkelson thickness relationship. Model -1, Figure 3.3, shows the correlation with the observed deviations from Torkelson’s model. Since we know the density of the solvent, chloroform, to be 1.49g/mL, and the spin speed 700 rpm we
modified the thickness equation to model-2. This curve show a much better fit to the data, Table 3.1. Here only the thinnest film show significant deviation from the model.

\[
(Model - 2) \quad h_f = \left[ \frac{\frac{3 \eta_o}{2(1.49)(700)^2}}{3} \right]^{1/3}
\]

Equation 3.6  Thickness model 2, modified equation incorporating spin speed and density.

Table 3.2 Measured AFM Thickness compared to thickness obtained using Torkelson model-2 that incorporates density and spin speed, but with concentration as the only variable. Solver calculates a best fit constant from the SSD (square of the std. dev.)
This relationship may be expressed such that,

\[
\text{Thickness (nm)} = 16106127660.0 \cdot \text{Concentration mg/mL}^{0.33}
\]

The authors reported data that were within 10 % of the model predicted. The discrepancies observed were explained as:

i) under-predictions for films spun from solutions having high initial polymer concentrations or highly volatile solvents and

ii) over-predictions for those made from dilute solutions and solutions containing low volatility solvents.

Our films were made in a highly volatile solvent chloroform so a model based on \( h_f \) may underpredict our thickness data. In any event, we have an Atomic Force Microscope instrument which can measure thickness directly so we focused on obtaining our own empirical data. Nevertheless, we hope to also use this model to predict our film thickness to save time and eliminate expensive analytical costs as we explore the behavior of these small molecules: PCBM blends.

3.3 Thickness in spun cast films using various techniques.

In addition to AFM, researchers have employed many different approaches to thickness measurement in thin films. Lobo and colleagues [30], who have studied thickness analysis extensively, concluded that determining nanometer thickness dimensions in thin films is difficult and no unique approach exists to yield consistent and accurate data. Nevertheless, several techniques exist that have been used
successfully to measure film thickness. Each with varying degrees of success. Four prominent options are Variable Angle Spectroscopic Ellipsometry (VASE), X-Ray diffraction, Confocal microscopy, and stylus profilometry. Lobo concedes that these techniques work but, they are often expensive, time consuming, may slowly lose sensitivity or require the measurement of additional physical properties. For instance, VASE analysis will require either the refractive indices of the materials under consideration or time consuming and complicated modelling. Confocal microscopy has great vertical resolution, employing white light interferometric techniques to measure thickness, but the lateral resolution suffers. Stylus profilometry is excellent for step height measurement however the technique quickly becomes inadequate as the thickness approaches 100nm.

AFM, by contrast, shines in its ability to measure heights directly especially for dimensions less than 100nm. Indeed, AFM has been used to study the thickness of thin films with dimensions even less than10nm[31]. Our films are nominally in the 50-to 200nm range depending on coating parameters; a virtual sweet spot for this technique.
Chapter 4  Stylus profilometry

4.1 KLA Tencor P-2

The easy access to our profilometer and the potential for rapid turnaround times made this technique an easy option to measure our film thickness.

Profilometry was performed using a KLA Tencor P-2 profiler with a 12.5micron radius stylus. The applied load was 3mg. An Instrument Calibration check (Table 2.1) was done using a silicon wafer with etchings. These etchings comprised structures with height features nominally 95.2nm.

Table 4.1 Calibration data for stylus profiler. Showing good correlation and standard error

<table>
<thead>
<tr>
<th>Replicates</th>
<th>Thickness (angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>955</td>
</tr>
<tr>
<td>2</td>
<td>960</td>
</tr>
<tr>
<td>3</td>
<td>947</td>
</tr>
<tr>
<td>4</td>
<td>954</td>
</tr>
<tr>
<td>5</td>
<td>946</td>
</tr>
<tr>
<td>6</td>
<td>948</td>
</tr>
<tr>
<td>7</td>
<td>970</td>
</tr>
<tr>
<td>8</td>
<td>965</td>
</tr>
<tr>
<td>9</td>
<td>943</td>
</tr>
<tr>
<td>10</td>
<td>948</td>
</tr>
</tbody>
</table>

| AVG        | 953.6                 |
| STDEV      | 8.9                   |

\[
\text{SiO}_2 \text{ wafer with etched features nominally } 952\text{A deep.}
\]
Both water treated and wiped samples (using Lens cleaning tissue) were analyzed. The data obtained using profilometry were extremely noisy as Table 2 below indicates. The profiles were inconsistent and the baseline was difficult to determine even after employing the levelling/flattening protocols on the instrument. The large stylus used and the relatively small dimensions of the films conspired to make the analysis much more challenging and less precise.
Table 4.2 Table of profilometer thickness measurements for SQ blend films with lens cleaning tissue and water treated edges. Note even larger standard deviations for the lens cleaning tissue samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Edge treatment</th>
<th>AVG</th>
<th>stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (8 mg/ml)</td>
<td>water Treated</td>
<td>92.35</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>lens cleaning tissue</td>
<td>104.15</td>
<td>1.5</td>
</tr>
<tr>
<td>2 (16 mg/ml)</td>
<td>water Treated</td>
<td>170.15</td>
<td>51.1</td>
</tr>
<tr>
<td></td>
<td>lens cleaning tissue</td>
<td>117.4</td>
<td>15.2</td>
</tr>
<tr>
<td>5 (8 mg/ml)</td>
<td>water Treated</td>
<td>85.13</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>lens cleaning tissue</td>
<td>64.6</td>
<td>26.4</td>
</tr>
<tr>
<td>6 (16 mg/ml)</td>
<td>water Treated</td>
<td>255</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>lens cleaning tissue</td>
<td>101.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Given recent encouraging thickness data using the water treated approach (discussed later in chapter 5 we tried edges of both lens wiped and water treated edges. The analyses were disappointing in the significant errors generated. This problem appears to be a function of errors involved in the creation of the sample edge and the fact that the profilometry technique struggles at thicknesses towards the lower end of its operational range. In the future, there can be investment in understanding how sample load and stylus type can improve this analysis. Nevertheless, Lobo warned that with profilometry there will always be serious limitations for ultra-thin layers, for the technique struggles to measure dimensions less than 50 nm and the associated error approaches a whopping 100%[30].
Chapter 5 Atomic force Microscopy

5.1 The Atomic force instrument

The idea for the Scanning probe microscopy was pioneered by Binning, and Rohrer in 1982 [32]. In this initial approach a sharp metallic needle was scanned over the surface of a sample which at a separation of less than 1 nm[33]. The separation distance is controlled by the tunneling current between the probe and the conducting surface. Meyer et al. explained that this quantum mechanical effect incorporates two important properties:

i) of electrons flowing between two electrodes through a thin insulator or a vacuum gap,

ii) the current decaying as a function of the gap distance on the length scale of one atomic radius.

Force microscopy is based on maintaining forces at a constant level between a sharp tip and a sample surface. Usually the tip is mounted at the end of a cantilever which serves as a force sensor. Either the static deflection of the cantilever or the change in its dynamic properties due to tip-sample interactions is exploited. Since the limit of force detection is far lower than the force between atoms in the lattice positions the term Atomic force microscopy is used[34].

The basic physical principle of most scanning probe techniques is the sample–tip interaction. The resolution is often on the atomic scale in the vertical plane, but limited by the geometric shape of the tip. Lateral resolution is governed by the
vertical amplitude of the surface features. A tip can be considered as a cone with a finite radius at the apex, so surface structures with walls steeper than the opening angle will be smeared out. In addition, holes deeper than the vertical range or with diameters smaller than the tip radius will most likely not be imaged or will have significant distortion.

Tunneling current across the vacuum gap is the most significant near field interaction but in Force microscopy longer range forces interfere. Chemical forces also exist between the tip and the sample at ranges similar to that for tunneling. However, for atomic force microscopy the principal longer range forces are dipole-dipole, or Van Der Waals. These forces, can be attractive or repulsive depending on the tip-sample interaction.

Another important force in AFM is the electrostatic force created during sample preparation. These trapped charges induce coulombic forces between insulating tips and samples. These localized charges can be detected by conductive-AFM.

Ferromagnetic materials can be analyzed and the magnetic domains of their surfaces can be mapped. Magnetic dipoles located in a magnetic field generate magnetic forces. The range of the magnetic forces depend strongly on the decay of the field outside the sample and on the size of the magnetic domains in the sample and their thickness.
To obtain atomic scale resolution the probe needs to be controlled with an accuracy of 1 pm\[33\], so piezoelectric actuators are used. Taking advantage of their anisotropic character piezoelectric materials are manipulated to change their shape when an electric field is applied. Typically high voltages are required but this polarization may be lost after prolonged use or if the material is overheated above its Curie temperature\[33\]. The ceramic materials such as PZT (lead zirconium titanate) are fashioned into a four –part piezo tube. As the piezo tube bends, movement of the tip in three dimensions is made possible. The bending process is nonlinear and thus adds errors.

According to the authors, positioning performance of the Piezo tube scanner is limited by several problems; first the nonlinearity of the tube as mentioned above, second the hysteresis of the scanning movement, third the creep in the ceramic, and noise and drift in the high voltage supply, and finally thermal drift of the whole mechanical system. These aberrations affect the sensitivity and response of the system and periodic calibration is an imperative for every range of interest. At small ranges the piezoelectric effect is insignificant but for large topographic images approaching 100 microns the negative ramifications of the piezoelectric effect increases. Commercially available grids are needed to calibrate the instrument to accommodate the various dimensions associated to the features of interest.

In AFM, rectangular images are produced by raster scan. The (x-y) location positioning numbers of the scanning tip is recorded line by line, using software. The position numbers are converted into amplified voltages which control the probe movement. The topography is due to the z- position governed by a closed loop feedback system.
Since vibrational and acoustic noise are major sources of error in SPM analysis it is critical that the tip holder, sample holder and actuators are as sturdy as possible. A rigid construction will increase the mechanical eigenfrequency of the instrument. This eigenfrequency limits the feedback control speed. In addition to acoustic noise, isolation from building vibrations is important and so an air table in combination with an acoustic chamber dramatically reduces the impact of these ambient noise sources.

Although many techniques exist to detect the tiny bends in the cantilever in tip sample interactions, most use the beam-bounce method. Typically, a laser beam is deflected on the backside of a cantilever. The deflection is monitored by a four-quadrant, position sensitive photodiode which allows for the detection of the normal bending and the torsional distortion as well. The torsional changes are consequential in measuring the lateral forces impacting the probe which is used for phase analysis.

5.2 Tapping Mode Microscopy

The intermittent contact of the surface by the oscillating tip as opposed to the permanent touching of the surface in contact mode is called tapping. Pioneered by Martin et al. and perfected by Zhong et al., tapping mode AFM exploits the tip-oscillation. The tip is made to oscillate near its resonant frequency and the root mean square value of the deflection detector is used to control the tip-sample separation distance.
The shape of the force-distance curve[35] defines the interaction forces measured at various distances between the approaching tip and the sample. The tip is initially far away at a force of zero. On close approach the tip is pulled toward the surface by attractive van der Waals forces and snaps onto the surface. This force causes the cantilever to bend down. Upon contact the repulsive regime begins, forcing the cantilever to bend upwards. This repulsion eventually reaches its peak force threshold and the tip is retracted and brought back to the zero-force reference baseline. The tip may stubbornly stick to the surface during retraction because of the powerful attractive VDW forces until it finally snaps off. The process continues as the tip is moved to the next location and the process repeats. The unique hysteresis behavior of the material surface with the tip, at each location, is captured in the force distance curve.

In AFM analysis, the computer controls the signals for scanning, then collects, stores and displays the data. The two-dimensional data is typically rendered in false color for each (x, y) value. The measured pixel is usually color coded to show the highest elevation as white and the lowest valley as darkest. The image is processed to remove artifacts and optimize contrast. Image tilt, bowing and other distortions due to instability in the instrument and creep in the piezoelectric actuators can be removed by filtering and smoothing software. Plane fitting algorithms and Fourier analysis can be used to correct image distortions. For measurement of feature dimensions such as a step height, a histogram of the recorded data or line sections through the step is extracted[33].
The thickness and morphology of the active layers of these BHJ, OPV devices are important data needed in the creation of optimized organic solar devices. The use of Atomic force microscopy is an important tool to reach this goal. We have studied these phenomena using a Bruker Innova AFM (figure 0.1) and have found that the thickness can be measured but there are three important things to consider to obtain accurate and precise thickness data.

5.3 AFM instrument calibration

To certify that the AFM instrument is functioning properly we needed to calibrate it. We used a NIST traceable MEMS fabricated grid having features with a nominal 10nm pitch and square troughs each 182nm deep, Figure 5.2. After imaging we can use post processing software tools to determine the actual pitch and step heights of the features. The calibration process will adjust the instrument parameters so that the voltage settings employed in the feedback loops are optimized. This optimization will ensure that the imaging of unknown samples is believable and that the surface feature dimensions are accurate.
Figure 5.2 Top view of 50-µm² image of grid showing regular pattern of Mems fabricated square holes.
Using Nanoscope software we determined that the pitch is 10.1 µm Figure 5.3, and the step height is 197nm having a standard error of 8%.

Figure 5.4 histogram of relative height distributions. The nominal depth 182 nm. The observed depth = 197nm and Error = 8%.
5.4 Edge creation in thin films

One of the most important steps in thickness analysis is the removal of coated material above the substrate.

a) Sloped edge requires more real estate  

b) Idealized step across edge

c) Worst case scenario: rough surface with uneven floor. No real floor detectable.

Figure 5.5 Sketches of a) sloped b) ideal edges and c) edges corrupted by pileup and residual material on substrate after scrape off.

First, one needs to be able to create good quality steps with edges that approach ninety degrees. This allows the probe tip to traverse the edge with enough real estate to go over edge-to bottom of edge –then to substrate. The complete cycle
should take no more than 40 microns. This will allow the scanner to traverse no more than 40% of its axial limit. If the scanner is scanned repeatedly at 100 microns, the piezo scanner can become defective and suffer from dynamic hysteresis.

The Innova AFM can operate in both open and closed loop modes. Open loop works well for dimensions less than 1 micron but for larger dimensions closed loop is preferred. Closed loop mode ensures positioning accuracy.

![Figure 5.6 AFM images of calibration grid showing loss of signal function due to piezo malfunction.](image)

This produces a phase lag in probe response which appears to exacerbate with time. If the piezo scanner is in operation for a long period at these extreme dimensions, the calibration can become compromised and the instrument range of operation can be reduced.
If a good step is had (Figure 5.5 Sketches of a) sloped b) ideal edges and c) edges corrupted by pileup and residual material on substrate after scrape off., then navigation of the edge by the probe is easy. If the edges are defective, with edge pile-ups, or substrates still contain residual materials from the removed thin film (Figure 5.5c), then more real estate is needed to record these phenomena. Indeed, as one seeks to accommodate these defects within the 100micron scan range, even more of the range is utilized. For example, if an edge is sloped (Figure 5.5a), much more of the available scan length is needed to recover a reasonable baseline.

5.5 Thin film edge creation challenges

The hardest challenge in this study was the creation of a good step. We tried long and hard to get a process that worked. First we tried the usual tape approach. First, Kapton tape was affixed to an edge of the substrate before spin coating. The tape is removed after coating the solution. This approach was quickly abandoned due to the wicking effects of the solvent under the tape (Figure 5.7a). The solvent would imperfectly dissolve away material creating a wrinkled edge. The use of a dampened cotton swab and chloroform dampened microscope-lens-cleaning tissue was ineffective as well. (Figure 5.7b and 5c). The tissue was neatly folded to create a “sharp” edge, damped with chloroform then rapidly swiped across film. Although this process created a macroscopically pleasing edge, the defects observed on the nanoscale made this approach unsuitable for good height analysis. We had some success with a sharp blade and the thin scratches of a forceps’ point (Figure 5.7d). The sharp blade often created both problems with pileup on the film’s cut edge and stubborn residue on the substrate. The benefit of a forceps’ tip is the finely grooved line produced (Figure 5.7d). This grooved line in cross-section is shaped like a “V”.
Figure 5.7 micrographs of select edges showing taped and wiped edges compared to regions undisturbed by solvent.

The outstanding problem with this approach was the inability to unambiguously identify the substrate floor. Indeed, we could not ascertain from our profiles whether the substrate itself had been breached. Table 1 summarizes the challenge of edge creation for this work until we introduced the water submersion technique.
Table 5.1 List of film edge creation approaches attempted and results.

<table>
<thead>
<tr>
<th>Edge produced by</th>
<th>Edge quality</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform dipped cotton swab</td>
<td>very poor</td>
<td>not useful</td>
</tr>
<tr>
<td>Kapton tape edge</td>
<td>poor</td>
<td>Ugly edge with evidence of wicking</td>
</tr>
<tr>
<td>Wet blade</td>
<td>poor</td>
<td>-volatile solvent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Blotches when wet</td>
</tr>
<tr>
<td>Blade</td>
<td>okay,</td>
<td>Some smearing with SQ,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>error &gt;10%</td>
</tr>
<tr>
<td>Fine tipped forceps</td>
<td>decent,</td>
<td>ideal in some locations error ~10%</td>
</tr>
<tr>
<td>Water submersion</td>
<td>Excellent</td>
<td>improved data precision error ~5%</td>
</tr>
</tbody>
</table>
Figure 5.8 AFM height image of dig region when forceps scratch is used.

Figure 5.9 height image a) above three-(RGB) 2D profile sections b) across edge showing how pileup problems and baseline roughness complicates step height analysis.
5.6 Water submerged samples

The film sample was dipped for approximately 1-minute in distilled water. Incompatible surface tension and capillary forces would cause the film to flake off from the glass substrate.

![Image](image_url)

**Figure 5.10** Top and side view images of water treated edge obtained from DHSQ(OH)$_2$:PCBM film. The edges have no significant pileup and the floor is uniform and flat.

Qualitatively it appeared that this was a good way to make step edges, Figure 5.10, so we embarked on a rigorous test using our own AFM. Unfortunately, after only a few sample sets our instrument failed. Nevertheless, we generated enough data to give some confidence that we had stumbled upon an excellent approach to making sharp, well-defined edges for thickness analysis of our SQ:PCBM films.
Figure 5.11 Top and side view images of water treated edge obtained from a squaraine: PCBM film. The edges have no significant pileup and the floor is uniform and flat. Consequently, easily identifiable and interpretable step heights can be determined.
Table 5.2 Data of select water treated 8mg/mL DHSQ(OH)2: PCBM film samples, showing relatively low standard deviations indicating good data precision for the thickness determinations.

<table>
<thead>
<tr>
<th>Water treated thickness study-1</th>
<th>9/16/16</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHSQ(OH)2:PCBM</td>
<td>Thickness in nanometers</td>
</tr>
<tr>
<td>film 1</td>
<td>an</td>
</tr>
<tr>
<td>film 2</td>
<td>70</td>
</tr>
<tr>
<td>film 3</td>
<td>89</td>
</tr>
<tr>
<td>film 4</td>
<td>86</td>
</tr>
<tr>
<td>avg</td>
<td>83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water treated thickness study-2</th>
<th>9/20/16</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHSQ(OH)2:PCBM</td>
<td>Thickness in nanometers</td>
</tr>
<tr>
<td>film 1</td>
<td>108</td>
</tr>
<tr>
<td>film 2</td>
<td>108</td>
</tr>
<tr>
<td>film 3</td>
<td>108</td>
</tr>
<tr>
<td>film 4</td>
<td>98</td>
</tr>
<tr>
<td>avg</td>
<td>105</td>
</tr>
</tbody>
</table>

The edges produced in this process were generally clean and useful for analysis by AFM. The data obtained, Table 5.2, using the water treatment method produced standard deviations that were approximately 5%. This was a remarkable improvement over profilometry and the other edge creating approaches we tried. Double digit errors were not uncommon before the water treated approach.

The quality of the thickness data generated by AFM is a function of the AFM’s ability to properly navigate the edge-cliff and reliably employ a flat substrate or film surface for its baseline. The substrates used were thoroughly cleaned.
microscope glass slides to permit easy removal. Film thickness measurement is a relative determination and for each determination, a consistently flat baseline is indispensable.

Prior to utilizing the water treatment approach, the combined challenges of obtaining high quality edges and obtaining precise data forced us to consider an alternative approach to measuring thickness. One popular alternative is the use of ellipsometry. Ellipsometry measures changes in light polarization to determine the sample material’s properties of interest, such as film thickness and optical constants[36]. If the refractive indices of substrate and thin film layers are known, models can be constructed to extract the thickness of the layer. Employing Fresnel’s equations each material’s thickness and optical constants can be calculated. We could not obtain the requisite modelling equations so Confocal microscopy was attempted instead.
Chapter 6  Confocal Microscopy

6.1 Confocal microscope technique

To verify our thickness measurements, we explored 3D optical profilometry using the Nanovea PS50 profiler[37]. This profiler uses the Chromatic Confocal technique which measures a physical wavelength directly related to a specific height without using any complex algorithms or need for modeling as in ellipsometry. This ensures accurate results for all surface conditions. There is no influence from the sample's reflectivity, no need for frequent calibrations and no effects due to changes in measurement parameters. Utilizing a raster scan, the Profilometer can measure in 2D and 3D at standard speeds with an Optical Pen, or 200 times faster with a Line Sensor[38]. The data yields 1) precise surface topography measurement on any surface, 2) accurate shape measurement of small parts and features and 3) superior ability to accurately measure and analyze surface form.

The Chromatic Confocal technique employs a white light source (LED) that passes through a series of lenses, called an optical pen, which has a high degree of chromatic aberration. The refractive index of the lenses will vary the focal distance of each wavelength of the white light. In effect, each separate wavelength of the white light will focus at a different distance from the optical pen, creating the measurement range. When a surface of interest is within the measurement range a single wavelength of the white light will be in focus while all others will be out of focus. The white light is then reflected through the optical pen; it then passes through a pinhole filter that allows only the focused wavelength to pass through to a CCD.
spectrometer. The CCD will indicate the wavelength in focus, which corresponds to a specific distance for a single point. The physical wavelength measured uses no algorithms, thus providing the highest accuracy independent of form, roughness level, illumination and measurement speed. There is no special leveling procedure required.

The technique measures a direct physical wavelength linked to a specific height which ensures accuracy of the data. Nearly any material surface can be measured, even with high surface angles. Moreover, because the testing parameters has no effect on results, the data is easy to compare from sample to sample and from one instrument to another.

6.2 Confocal data analysis

To confirm height accuracy, a 12mg/mL DHSQ(OH)$_2$:PCBM film sample from a set, which yielded data that ranged from approximately 98-210nm in height, was analyzed by confocal microscopy. This sample’s edge was obtained by wiping with a chloroform dampened lens tissue. The sample was then raster scanned to generate a topographical map (Figure 1.2). Next, using instrument-associated software, two-dimensional line profiles were drawn through representative portions of the acquired image. The four lines drawn across the edge (Figure 6.2) to determine the step height were statistically analyzed to yield some sense of comparative accuracy and precision.
Figure 6.1 Four line profiles through coated and uncoated regions of SQ film, showing analysis locations for step height analysis.

Average step height: 0.145 μm, std dev

Figure 6.2 a) Location 1 step height: 0.159 μm, b) Location 2 step height: 0.145 μm, c) Location 3 step height: 0.159 μm, d) Location 4 step height: 0.116 μm
The four line profiles of step height analysis also show the line fit and regions used for calculation. We notice rougher regions on substrate. This relatively large substrate floor perturbations, due to unremoved residue, hurt precision and accuracy.

The average step height obtained by this method is consistent with the ~ (120-150 nm) observations using AFM for our thicker SQ:PCBM blends.

Confocal microscopy data confirmed our observations using AFM. Nevertheless, the high standard deviation even for this cursory look was troubling by again highlighting the challenge of creating a well-defined substrate floor for our analysis. Scraping and shearing of the coated film from the surface (figure 6.2) with a sharp blade and using a chloroform dampened lens tissue has been shown to be ineffective in creating a pristine floor. The measurement of thickness is a relative technique so each plane (or at least one) needs to be consistent and flat to be used as a reliable baseline. The longer-range averaging over 350µm helps to neutralize the local baseline aberrations.

### 6.3 Thickness analysis Summary

In summary, Atomic Force microscopy shows real promise but it is a difficult analysis due to possible AFM instrument piezo fatigue at longer scan lengths. Analysts will need to be judicious in evaluating the sample edge. The un-optimized edge can lead to significant loss of precision and high standard deviations. Submerging the sample in water for a few minutes has been our best edge creation
approach yielding much improved single digit standard error. Confocal microscopy works as well but it is very time consuming and suffers from the negative effects of uneven substrates. In the literature, TEM, optical profilometry and stylus profilometry among others have been used to measure thickness of OPV layers. Our access to AFM and profilometry instruments was crucial to our choice of technique.

Although the success of the water-submerging flake-off approach shows promise, experimental improvements are still needed to fulfil the potential of the water treatment edge creation approach. For our 19mm x 19mm film sample only a tiny fraction of the sample gets removed and often the flaked off material gets stuck on the sides of the film-removed areas, such that the edge becomes ruined by layering. We hand held the sample submerging only a third into the water. Complete submersion, possibly using a lab jack, may allow for more sample to be exposed and removed. The layer thickness analysis should be representative of the entire sample and so the sampled locations analyzed must be more representative of the entire surface. The analysis of the entire surface is not practical and, so, ideally four locations at the corners and one in the middle make sense Figure 6.3.

![Figure 6.3 Five idealized locations per film to obtain representative thickness.](image)

5
However, what usually determines the locations chosen is the quality of the coating and the avoidance of defects.

Our analysis of four spin cast films, prepared from the same 8mg/mL stock solution, and measured using AFM, show that we can make uniform films, Figure 6.4. The average thickness of the set was 113nm with a 10% standard deviation and calibration yielded a standard error of approximately 8%. These errors compare well to the errors associated with the overall system. To determine if systematic errors exist, frequent calibration is necessary to monitor the accuracy of the thickness measurement.

![DHSQ(OH)2 films thickness (nm)](image)

**Figure 6.4 Film thickness for 8mg/mL DHSQ(OH)2 at 700rpm**

Problems with dynamic hysteresis in the xy scanner forced us to monitor the calibration more frequently. Nevertheless, we recognized that the thickness is a relative measure in the vertical dimension so even though the horizontal axes may be compromised, we were in some instances still able to extract accurate film thickness results.
Chapter 7  Morphology

Morphology describes the form of a thing and, in materials science specifically, how molecules are arranged and ordered in condensed matter. In his work on conjugated polymers with BHJ architectures, Schwartz[39] discussed how processing history (e.g., the choice of solvent in the casting solution or thermal annealing) can lead to differences in film morphology[39]. In addition, Single-molecule experiments by Huser et al. [24], have shown that changing the processing conditions can alter the emission properties of individual MEH-PPV chains. Similar processing-history-dependent variations in the Photoluminescence (PL) spectra of conjugated polymers also occur in bulk film samples. Polymer and small molecules morphology evolves in similar ways so we expect these studies to indicate that the morphology of our small molecule BHJ design can be optimized if we use similar processing parameters as control knobs. In this study, we used thermal annealing to explore morphology effects.

7.1 Phase analysis using AFM

In addition to step height analysis of our films for thickness, we wanted to explore the composition of the domains using phase mode imaging. Although we knew any domain distinctions were essentially superficial, we theorized that the surface property may provide at least hints as to what may be happening in the bulk. Garcia et al. [40] have studied the phase mode analysis extensively and observed that the sensitivity of phase shifts to material and topographic properties has made phase
images an unavoidable tool in many applications and opened another way to 
investigate material properties with nanometer resolution. Mapping topography and 
composition simultaneously has been a nagging hurdle for microscopists. Moreover, 
the challenge of quantitative characterization of material properties, i.e. spectroscopy 
capabilities, is still limited due to the lack of enough selectivity to isolate the specific 
sample property responsible for the phase shift changes. Our attempt to characterize 
the film composition by phase analysis was generally ineffective when using our 
Innova AFM, so we teamed up with another research group (chapter 10) with the 
requisite resources to try to at least improve our odds. Phase is one indicator of 
morphology and XRD is usually the technique of choice when bulk morphology is the 
analytical goal. Our access to a copper sourced beamline allowed us to examine the 
morphology of our samples using XRD.
Chapter 8  X-ray diffraction

The benefit of OPV technology is tied to the ability to create relatively cheap and easily processed materials[41] with high PCE’s. Knowledge of the morphology and its impact on device performance will be critical in the creation of next generation devices. This change in morphology by thermal annealing is well documented to enhance blend microstructure and consequently the PCE of OPV devices. Although the precise mechanism is debatable, Brabec et al.[42] offer that increased absorption of sunlight occurs with annealing and the mobility of the charge carriers is enhanced. In the Squaraine:PCBM matrix, the fullerene is thought of as being squeezed out of the squaraine matrix to reunite with a growing PCBM phase.

X-rays are electromagnetic waves with wavelengths in the region of an Angstrom. X-rays interact with the surface of a material by the photoelectric effect postulated by Einstein in the early 20th century. The wavelength of x-rays is similar in size to the bond lengths in molecules, so when a group of light waves change direction and intensifies after passing through an aperture or passing by an obstacle (such as electrons), diffraction occurs. These electrons interact with the oscillating electric field of the light waves producing the diffraction.

When a group of monochromatic wavelengths impinges on a crystal lattice, the wavelets scattered by a sheet of theses atoms combine to form a reflective wave. If the path difference reflected by successive sheets is an integer, then the interference is constructive and a strong signal is created. The directions of the diffracted rays

52
depend upon the d-spacings of the unit cells. The Bragg formulation is the most popular approach to interpret crystalline diffraction. Using Braggs law for reflection given by below, the d-spacings can be determined.

\[ n\lambda = 2dsin\theta \]

Equation 8.1 Braggs law of reflectivity

Max Von Laue[43] discovered in 1912 that the orderly array of atoms in a crystal can scatter x-rays. Conversely, x-rays of known wavelength can be used to determine the atomic structure of crystals. The crystal structure is determined from the intensities and directions of the diffracted x-ray beams. Each crystal is comprised of countless repeat unit cells which stack in three dimensions. This periodic array of atoms make up the crystal lattice. Each lattice point is an atom attached to a regular pattern of others that are uniquely oriented in space. This group of atoms is called a basis which, when repeated in space, forms the lattice.

Light waves of one frequency that come from the same source at nearly the same time are coherent. This means that they have the same phase or have a predictable phase difference. When coherent waves coincide, they interfere with each other and their amplitudes add giving constructive or destructive interference. The resulting peaks and troughs can double (for maximum constructive interference) or plateau (annihilated) for destructive or can be in between (Phase shifted).

In X-ray diffraction, the diffraction pattern produced by these plane waves is monitored and analyzed to yield structural information of the material. Substances can
have varying degrees of order and symmetry in their molecular arrangements. These arrangements cause reflections to occur producing constructive interference at certain angles and coherent interference in spots. For a material, a unique series of reflections with different intensities is produced where the intensities are determined by the packing of the molecules in the crystal lattice.

Previous XRD powdered diffraction studies on single crystal DHSQ(OH)$_2$ (shows that the main diffraction peak occurs at angle 5.38). If we see a response for our films at this reflection angle then we can be confident that the material is DHSQ(OH)$_2$.

![Figure 8.1 XRD powder diffraction pattern of DHSQ(OH)$_2$ showing the main lattice spacing in single crystal at 5.38 (2-theta angle).](image)

The analysis of Squaraine thin films by XRD was done in PMMA. The analysis in PMMA was done to examine the effect of self-aggregation by the Squaraine molecules. The PMMA molecules are amorphous even at high temperatures and do not form crystals. This allows for the unambiguous study of the Squaraine aggregation only. From our previous work, we know that in PMMA films there is hardly any phase separation, so the assumption is that only squaraine monomers exist. Phase separation results from subsequent annealing which can allow us to control the degree of phase separation and thus domain size.
15% DHSQ(OH)₂ in 20mg/mL PMMA sample solutions were prepared by spin-casting onto cleaned glass slides at 1500rpm. The blended solution was first heated on a hotplate for 10 minutes at 40°C to ensure complete solubility. After coating with film, three samples were placed on a hot plate for 1, 4 and 10 minutes. The anneal time was monitored using a stopwatch. The annealed samples were then stored in microscope slide holders, and placed in light-tight boxes to prevent deterioration.

XRD analysis was performed on a copper sourced beam line equipped with collimator slits to restrict spherical and chromatic aberrations. A voltage of 40 kilovolts and 25 milliamps was employed for the diffraction.

Figure 8.2 Overlaid XRD profiles of 16 mg/mL DHSQ(OH)₂: PMMA films on glass showing the effect of annealing time as function of peak intensity. The degree of aggregation order appears to increase with annealing time at 155°C.

The data show that the peak intensity increases from approximately 530 counts in the unannealed state to over 2200 counts after 10 minutes of annealing. This
increase is synonymous with an increase in crystallinity and suggests that the Squaraine molecules arrange themselves into a more crystalline organization as the time allowed for molecular packing increases.

![Counts vs Angle](image)

**Figure 8.3** Overlaid processed XRD profiles of 16 mg/mL DHSQ(OH)2: PMMA films on glass showing the effect of annealing time as function of peak intensity. The degree of aggregation order appears to increase with annealing time at 155°C.

The un-annealed curve in shows a shift which can indicate an increase in the lattice dimensions or a systemic aberration in the XRD beamline. We noticed on several occasions that if the sample was not positioned in a consistent way, the peak position would shift. Nevertheless, our data seem to correspond to other work in which the Bragg angle decreases slightly with increased annealing time. The Bragg angle is inversely proportional to the d-spacing so when the angle decreases the lattice
spacing increases. This may be a consequence of relaxation of the aggregated matrix or a filling in of the many vacancies existing therein.
Chapter 9  UV-Vis spectroscopy

9.1 Squaraine solid state aggregation

Our group has studied spin cast Squaraine:PMMA films with UV-Vis spectroscopy extensively. Our DHSQ(OH)$_2$:PMMA films were annealed to compare the effect of incremental annealing on material property. In un-annealed films the squaraine molecules are thought to exist as monomers. When annealed at temperatures approaching 155$^\circ$C, aggregation occurs and a noticeable change in the degree of molecular order may be detected. One technique which can be used to yield information regarding the change in morphology is UV-Vis spectroscopy. Although limited for chemical identification, UV-Vis shines in its ability to quantify species[44] even in complicated matrices. If the Beer-Lambert law (Equation 9.1) is applied, the concentration of species may be calculated.

\[
A = \varepsilon b c
\]

Equation 9.1 Beer-Lambert law

Where \( A \) is absorbance, \( \varepsilon \) is the molar extinction coefficient, \( b \) the path length and \( c \) the concentration of the species under investigation. This shows the linear relationship between absorbance and concentration[45].

Incremental annealing can help us monitor this effect and possibly find ways to identify this optimized morphology for each squaraine moiety under consideration.
Squaraine solid state film absorption spectra differ significantly from the absorption spectra in solution. The absorption spectrum for DHSQ(OH)$_2$ in the solid state, (blue line) is broadened giving rise to two peaks, one at 550 nm and the other at 650 nm. In solution (red line), the spectrum has a sharp and narrow absorption peak at 645 nm with a shoulder at 600 nm. This aggregation is due to self-organization of the squaraine molecules due to the intermolecular forces between the molecules.

![Normalized absorption spectra of DHSQ(OH)$_2$ squaraine in solution (no aggregation) (red line) and in solid state (with aggregation) (blue line)](image)

These SQ dyes can give rise to two different types of aggregation: - one which is blue shifted, compared to the monomer band of the solution spectra known as the H – aggregate and the other which is red shifted compared to the monomer band of the solution spectra known as the J – aggregate. This can be explained by the molecular exciton coupling theory, which describes the coupling of the transition dipole moments when two monomer molecules are brought together.
UV-Vis absorption spectra are an excellent indicator of transition dipole moment coupling processes and the associated energy level splitting in SQ films. This split is very different when in solution. Dimer models show that as the tilt angle approaches 90° the hypsochromic “blue” shift occurs as the H-aggregate is formed. The bathochromic “red” shift occurs with J-aggregates having smaller angles. In the SQ samples studied we do not see a simple peak shift. Instead, a broad range of angles are represented by our spectra.

Using a single monochromator UV-2600 Shimadzu spectrophotometer, the films were analyzed to determine how light is moderated after interaction with the specimen. In UV-vis spectroscopy ultra violet and visible light is radiated unto a sample and the wavelengths absorbed and transmitted is recorded. Similarly, the wavelengths reflected from the surface may also be the signal source. Deuterium and tungsten lamps are used to cover both UV and visible ranges respectively. The absorption spectra often contain peaks, plateaus and valley regions which create characteristic profiles which can be used to identify a chemical in solution or semi-transparent film.

9.2 Annealing of UV –Vis samples

Experimentally 15% DHSQ(OH)2 in 20mg/mL PMMA sample solutions were prepared by spin-casting onto cleaned glass slides at 1500rpm. The blended solution was first heated on a hotplate for 10 minutes at 40°C to ensure complete solubility. After coating with film the samples were placed on a hot plate for 0.5, 4 and 10 minutes, while held at 155°C. Another anneal temperature and time condition was
chosen at 145\(^{\circ}\)C for three minutes to get a sense of the direction of the time vs. temperature impact. The anneal time was monitored using a stopwatch. The annealed samples were then stored in microscope slide holders and placed in light-tight boxes to prevent deterioration. Next using a range of 300nm to 900nm, the absorbance spectra on the films were taken.

The data in figure 4 show that after 30 seconds of annealing, there is a significant drop in the 650-nm peak and a marked increase in the absorption at 560nm. In addition, the peak at 560nm increases with annealing time. This indicates a buildup in the squaraine H-aggregate orientation[46] or a blue shift. Our group’s previous work using a DBSQ:PMMA matrix identified an isosbestic point at 590nm which indicated conversion of one species into another. In similar fashion, we see at 590nm the same phenomenon. The un-annealed spectrum, which is considered to

![Figure 9.2 Absorption spectra of DHSQ(OH)\(_2\) in PMMA solid solution at various annealing times and temperatures (145 and 155°C) showing film absorption as a function of wavelength. Blue shift increases with annealing time.](image)
contain no aggregation, has a peak at 650nm. This corresponded very well to the
second peak observed in the annealed films. The presence of both peaks indicates the
presence of both monomer and H-aggregated species in the solid matrix. This study
confirms that for the DHSQ(OH)2:PMMA blend, the aggregation order is increasing
with annealing time. This is similar to that observed for previously studied squaraine
moieties such as DBSQ(OH)2. Therefore, the morphological transformation of the
active material and device performance impact may be predicted. Moreover,
annealing may be used as an effective control knob to optimize the BHJ morphology.
Chapter 10  Morphology using enhanced AFM module

10.1 film analysis using QNM peakforce

We recognized that despite our limited successes with UV-VIS and XRD, we wanted to explore domain size morphology using the AFM tool we had in house. One way to determine morphology is to use phase mode domain maps. Phase mode takes advantage of the phase lags and shifts experienced by the oscillating tip during image capture in AFM. Stickier materials, for example, would introduce a larger phase shift than smoother, less adhesive surfaces. These maps could identify the materials that were different. Our phase images obtained by AFM were inadequate due to poor contrast with our tips and nagging instrument problems involving piezo fatigue and xy-scanner failure.

Using our knowledge of annealing we hoped to use it as a tool to manipulate BHJ morphology in SQ based OPV’s. This process, manipulating annealing temperature and time, can help us identify an idealized morphology with maximum current output. In addition, if the area percent of the squaraine domains could be quantified, then one may be able to identify the surface morphology that corresponds to some optimal device performance.

In this effort, we made a series of films by varying both the annealing temperatures and times. The neat and blended films made were from 16mg/mL concentrations spin coated at 1500rpm. A subset of the samples studied is listed in Table 10.1.

Error! Reference source not found.
The poor phase data showed that our AFM system cannot perform the advanced contrast determinations to yield nanomechanical information about our samples. This allowed us to take advantage of a collaborative effort with another surface science group in Appalachian state university. They can employ the Bruker invented, QNM peak force module[47] attached to the more sophisticated Icon Atomic force microscope. This module purports to identify material variations unambiguously and at high resolution across a topographical image.

The fundamental basis of QNM peakforce mapping is its ability to acquire and analyze the force curves from each tap. To that end a force sensor is used that has a significantly larger bandwidth than the frequency of the intermittent tip-sample interactions. This allows for the instantaneous force on the tip to be measured rather than an averaged signal. This ability to separate the various signal contributions instantaneously and independently allows for the direct measurement of adhesion, dissipation, deformation and modulus contributions to the force. In practice, force curves are converted to a force vs. separation plot which is manipulated to extract the mechanical properties.

In QNM peakforce tapping analysis, the actual force exerted on the sample is used as the AFM feedback parameter during imaging[48]. A variant of tapping mode, where the tip is oscillated near its resonant frequency, peak force tapping offers direct control of the normal force while eliminating damaging lateral forces. The two principal differences[35] between tapping mode and peakforce are the much lower working frequencies and that in peakforce, the peak load force is constant.
With this technique, in addition to topology, other nanomechanical properties such as adhesion, deformation, and modulus are monitored. To obtain the Young’s Modulus, (or DmtModulus) the retract curve is fit using the Derjaguin–Muller–Toporov (DMT) mathematical model[49], [50].

Moreover, unlike tapping where the probe amplitude is kept constant by the feedback loop, Peakforce tapping controls the maximum force on the tip. This protects the tip and sample and enhances resolution during each tip sample interaction.

Along with topographical data that is generated simultaneously, contrast maps with high spatial resolution are produced. The number of grey levels or colors available to digitize the signal intensity at each pixel is the image, bit depth. For a digital image, it defines a pixel’s color or greyscale values in combination with other bits. In an 8-bit image (2^8) grey scale, for example, one of 256 shades is assigned to each pixel. Brightness is assigned to each pixel and the lighter shades are closer to 256 while the darkest approach zero. Several samples were evaluated. A list in Table 10.1 List of SQ films analyzed by QNM peakforce analysis. DH = DHSQ(OH)2below shows the variety of sample preparations involved. Two samples were prepared at the relatively extreme temperature of 200°C for 5 minutes, and then annealed at 200°C for four hours. With these extreme conditions, we hoped to record the fate of the blended materials. We expect to see a binary state with well-defined hard and soft regions.
Table 10.1 List of SQ films analyzed by QNM peakforce analysis. DH = DHSQ(OH)

<table>
<thead>
<tr>
<th>Films</th>
<th>Peak force analysis of log modulus data</th>
<th>Annealing condition</th>
<th>QNM analysis summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>16mg/mL at 1500rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>neat DH Unannealed</td>
<td>Unannealed</td>
<td>Unannealed</td>
<td>(Poor image) not very clear</td>
</tr>
<tr>
<td>neat PCBM Unannealed</td>
<td></td>
<td></td>
<td>homogenous matrix</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>Unannealed</td>
<td></td>
<td>large swath of harder regions</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>80°C for 1 min</td>
<td></td>
<td>Large well defined hard/soft</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>materials</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>100°C for 1 min</td>
<td></td>
<td>large hard and soft regions</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>120°C for 1 min</td>
<td></td>
<td>fine network of soft and hard</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>regions</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>150°C for 1 min</td>
<td></td>
<td>patched network of hard and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>soft regions</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>200°C for 5 mins</td>
<td></td>
<td>typical network of soft and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hard regions</td>
</tr>
<tr>
<td>1:1 DH:PCBM blend</td>
<td>200°C for 4 hrs.</td>
<td></td>
<td>crystallized surface</td>
</tr>
</tbody>
</table>

10.2 DMT-Modulus images using QNM peakforce module

The mechanical property maps were based on an image contrast protocol where the degree and extent of the material property was based on a color scale. To generate the data, special tips were required that were compatible with the range at which the sample signal was optimized.
Figure 10.1 Height and modulus images of DHSQ(OH)$_2$: PCBM blended film annealed at 80°C for 5 minutes. Shows nondescript height data compared to the impressive domains observed for hardness.

Compared to the nondescriptive homogenous-looking height image (a), the analysis of the SQ blend show significant contrast (b) which tempts us to assign these domains as PCBM and Squaraine domains. To make accurate assignments, one needs to be able to tell which species is harder. Moreover, it would be premature to say that these domains are pure, so the domains are thought of as SQ-rich or PCBM-rich.

These domains were assigned by measuring the hardness of neat species. Since we can now distinguish between the species, we thought we could use the contrast differences to track the growth of domain size as a function of annealing condition (Table 4.2). This was attempted, accompanied by varying degrees of success. Our study varied the annealing conditions while we kept the sample composition and concentration constant to ensure that any change was due to the morphological changes through annealing.
We expected to see a steady increase in domain size as the temperature changed, or similar domain growth with longer annealing times. This increase should plateau and decrease as the domain size enters the state of diminishing returns. This would occur as the domain size approaches its optimum and then ultimately exceed the exciton diffusion length. These losses would inevitably decrease device PCE.

The trend expected in Figure 10.2 with increasing annealing temperatures did not pan out. We expected larger and larger domain sizes.
The image data obtained was at best confusing. Even though we saw excellent contrast in the 80°C sample, we could not distinguish between the un-annealed case and 100°C. Moreover, one could argue that at 200°C for 5 minutes, the domain size of the harder material is somewhat depleted compared to the un-annealed state. Admittedly this study was a cursory look into the technique, and more data would need to be taken before hard conclusions are made. One clear indicator however, was the general trend in hardness range for the images. Apart from the 650MPa hardness for the 80°C sample, the hardness range of the samples trended upwards with annealing condition. The last two films in the above series (Figure 10.2) were scanned using a TAP525A probe. This tip was compatible with the harder surfaces generated at extreme annealing conditions. After 4 hours of annealing at 200°C the entire surface became decidedly crystalline (Figure 10.3).

![Figure 10.3](image)

**Figure 10.3** 10 micron images of DHSQ(OH)$_2$:PCBM blends at 200°C for 4 hrs showing crystalline features in the DMT modulus image and pockets of relatively softer material in the deformation image.

### 10.3 Quantitative analysis of surface morphology

If the right probe is selected and calibrated, PeakForce QNM can provide quantitative modulus results over the range of 700kPa to 70GPa.[47]. Indeed, Bruker notes that the key feature of the QNM application is the access to a wide range of
probes from low spring constants in the piconewtons (0.3 N/m to 300N/m) to micronewtons. This permits the analysis of softer hydrogels to metals and semiconductors. Our samples appear to be less than 1GPa hard when operated at device friendly annealing conditions.

If the area percent of the squaraine domains can be quantified, then one may be able to identify the surface morphology that corresponds to the optimal device performance. Tools that can do this are image processing software packages such as image J. Image J software was developed by the national Institute of Health (NIH) as a public domain java-based program. This software can read, edit, analyze and process 8, 16 and 32-bit floating point images. Image J can calculate area and pixel value statistics to determine the area percent of a domain in the image. In addition, contrast manipulation is possible to allow image segmentation, so that domains are grain boundaries are accurately delineated. Now that we can identify the domains in the sample we can quantify the area percent as an indicator of surface morphology.

![Figure 10.4, QNM peakforce analysis for nanomechanical properties: DMT Modulus(left) showing lighter regions are the harder PCBM interspersed with the softer squaraine. Enhanced image J image (right)segmented image into binary scale for area quantification.](image)

a) DMTMODULUS  
b) Image-J
Researchers have many techniques for investigating thickness and morphology of the active BHJ layer in OPV devices. Our work shows that AFM and profilometry are worthwhile choices for thickness. Creating a pristine edge using the water submersion approach will yield edges that resemble a step function. If such well-defined edges are developed, then AFM can easily navigate the edge. Images or profiles of such steps avoid long scan ranges which can lead to hysteresis (piezo fatigue) in the xy scanner. AFM is preferred to profilometry because AFM operational range is ideally suited for the ultra-thin samples. The sweet spot for profilometry approaches micron dimensions, which are significantly above the 200-50nm for our OPV devices. Confocal microscopy and others may be used but cost and other drawbacks make them unattractive for nanoscale determinations. If concentration is known, film thickness may be predicted using the modified Torkelson model.

\[
\text{Thickness}(\text{nm}) = 161061276600.0 \times \text{Concentration mg/ml}^{0.33}
\]

If the volatile solvent chloroform is used then a $+10\%$ correction is needed. Our analysis indicated that we can produce uniformly thick films with a standard error approaching 10\% which is on par with the error associated with the system. When we encountered the piezo fatigue problems we could certify our process by comparing our calibration data to expectations. Any concerns regarding systematic errors was checked using our calibration grid.

Morphology can be determined by XRD and TEM. We used XRD to show how the morphology of the squaraine changes with annealing. One technique that has
potential to greatly advance understanding of morphology in Squaraine based OPV is QNM peakforce analysis. This technique has the potential when coupled with image analysis to be able to quantify the domains generated in bulk heterojunction films.

Another technique with tremendous potential to yield morphology information is small angle X-ray spectroscopy (SAXS). SAXS is a contrast method that depends on the square of the difference in electron density between the molecules and the background matrix or the solvent (if doing solvent analysis). Most SAXS data are generated in synchrotrons. Synchrotrons are particle accelerators where charged particles (typically electrons) are accelerated to nearly the speed of light. As a byproduct of this acceleration X-rays are produced, these are further filtered to produce monochromatic radiation. The generated x-rays are focused through a sample and every particle inside of the beam will send out its signal. This captured spectrum is recorded and thus the average structure of all illuminated particles in the bulk can be measured.

Grazing incidence Small angle x-ray scattering (GISAXS) and wide angle X ray scattering (GIWAXS) are two powerful corollary techniques based on SAXS. These approaches also use X rays to probe matter yielding information of atomic structure and material composition. These techniques have become very popular in the analysis of the morphology of Organic photovoltaics.
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