Applications of Nanoimprinted Structures to Organic Photovoltaics

by

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Small-molecule organic photovoltaic cells (OPVs) have the potential to be a low-cost, flexible power conversion solution to many energy problems [1]. These OPVs take advantage of an extremely thin active layer which enables this flexibility and reduces material volume. However, it is this thin quality that calls for improved power conversion efficiency compared to traditional silicon solar cells. Thin films suffer from reduced optical path lengths, which hinder light absorption and hence, power conversion efficiency. Many designs have been proposed to improve light absorption [2],[3],[4],[5, 6]. A novel light-trapping substrate geometry for OPVs is presented which is based on a conformally-coated, subwavelength-textured substrate design which is intended to substantially increase optical path lengths. The subwavelength nature of these Nanocones/Nanowedges decouples the light propagation from the exciton diffusion path. This is an optimized situation for efficient charge transfer. Enhanced power absorption into the OPV active layer has been demonstrated via numerical computation methods, including COMSOL FEM and Lumerical FDTD. The challenge to fabricate a working device by using nanoimprinting to create the structures in a conductive polymer will be presented, where the nanoimprinting process is optimized to maintain good electrical properties of the patterned conductive film. We will also present an alternative approach that utilizes a conformal coating of the organic conductor PEDOT onto the pre-patterned nanostructures. Uniform and conformal PEDOT coverage over the nanoscale features was achieved using an all-dry deposition process [7].
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1.1 Organic Photovoltaic Cells

Organic photovoltaic cells (OPVs) absorb photon energy from the spectrum of visible and invisible light emitted from the sun which can be extracted as electricity. This excitonic transfer of energy is described in Figure 1, where the photon energy creates an exciton, or hole-electron pair, which travels to a heterojunction and separates into free-flowing charge, or current. Figure 2 shows a model of an actual OPV cell developed in the laboratory.
Using inexpensive organic dye photo-absorbent materials, these devices provide a number of advantages over silicon-based solar panels. OPVs are more suitable for devices with thin, flexible substrates due to their nanometer-sized exciton diffusion length. This property also leads to an extremely light weight platform, making OPVs more integrable opto-electronic devices. Because of their low-cost, low-profile, and low-weight characteristics, OPVs are well suited for roll-to-roll mass manufacturing, which would further reduce its cost and availability as an alternative energy generating solution.
1.2 Limitations of Organic Solar Cells

A paper solar array, such as the one pictured below in Figure 3, requires thin films of photovoltaic material to enable flexibility.

![Printed flexible solar cell](image)

Figure 3: Printed flexible solar cell

Thin films are also desirable for organic active materials to compensate for poor exciton mobility to the charge-splitting zone, or heterojunction [8]. Films with a thickness of or close to the exciton diffusion length, or the maximum distance the excitons can travel before being lost to recombination, increase the number of excitons that are split to form current. If the active layer is too thick, the exciton will recombine or otherwise diffuse before reaching the heterojunction, which prevents current flow. Figure 4 illustrates this exciton path through the active layer toward the heterojunction where “t” represents active layer thickness.

![Exciton path length compared to light path length](image)

Figure 4. Exciton path length compared to light path length
If we keep the active layer thin, the incident light will have a shorter path length than in the thicker film, resulting in less light being absorbed and thus, less current generated [9]. But, as we see in Figure 4, if we increase the active layer thickness to increase the light path, we lose more excitons and reduce photocurrent. It is this design trade-off that compels engineers to enhance light-trapping, or light-absorbing, structures that can maintain the thin film requirement.

1.3 Light-Trapping Concept and Previous Methods

To enhance light-trapping in OPVs, engineers have designed substrates to increase light reflections internal to the device. More reflections create longer optical path lengths and increase the probability that light will be absorbed and will induce exciton generation. Structures can be built externally, as in the case of micro-lenses and mirrors, which refract incoming light and reflect out-going light, trapping the light inside the device [10]. They can also be built internally, as in the case of diffraction gratings made of the active material itself [11]. Light is trapped within the active layer, further increasing the probability that light will be trapped and absorbed. Examples of both of these strategies are shown in Figure 5.

Figure 5. Internal gratings [11] (left) and External Micro-lenses [10] (right) increase light reflections in the active material
Other designs consist of “wrapping” the active layers of the device around a textured substrate. A common design is an array of pyramids or cones that act as an anti-reflection coating and a way to increase internal reflections. The anti-reflection mechanism is due to a more gradual change in refractive indexes between air and the device. Zhu et al. demonstrated near-perfect absorption with the “Nanodome” design (see Figure 6) and with a resulting 25% increase in cell power conversion efficiency [12]. There are many more design possibilities, including coherent light-trapping in photonic crystals, lambertian surface roughening, and plasmonic wave guiding via nanoparticles or gratings [13],[14],[3].

Figure 6. Light-trapping nanocones (left) and nanodomes [12] (right) on silicon substrate solar cells
1.4 Light-Trapping Design in this Work

The light-trapping design pursued in this work seeks to enhance light absorption by decoupling the optical and electrical pathways within the active layer of the device [15], as seen in Figure 7. Decoupling the optical and charge pathways enables a longer pathway for light absorption while maintaining a short pathway for charge separation.

![Diagram showing light path and exciton transport path](image)

*Figure 7. Exciton transport path is decoupled from light path*

This design can also be developed in various aspect ratios, where the pitch of the feature is small, on the order of 100nm, while the height can vary from 100nm to 300nm. A higher aspect ratio is hypothesized to increase the optical path length while maintaining a subwavelength, or $\lambda < 500nm$, pitch. The subwavelength dimension of the pitch of the features is important to reduce light loss due to diffraction and reflection, as shown in Figure 8. Assuming a normal incident wave, light will diffract in several orders, $m = 0, \pm 1, \pm 2 \ldots$. In Figure 8c, the diffraction equation is calculated assuming a normally incident light to find the limit of the pitch.
length, $\Lambda$, in relation to the wavelength of light coming in, $\lambda$. It is shown here that when $\Lambda < \lambda$, which is a subwavelength pitch dimension, the only order of $m$ that satisfies this relation is the $m = 0$ order. All other orders of diffraction are weak evanescent modes. The subwavelength feature size thus increases the percentage of light available to be absorbed by the active layer on top of these features.

**Figure 8.** Subwavelength pitch reduces diffraction of light down to the $m=0$ order [16]
2.1 Creating Nanotextured Masters

In the proposed design, the active layers are conformally coating an array of Nanocones or Nanowedges (see Figure 9). The substrate is made of a conductive form of acrylic (PANI/PMMA) and is the pattern is transferred by nanoimprinting, or stamping a silicon master onto the substrate in the presence of heat and pressure. The pattern on the Si master is created using interference lithography with a 157 nm source [17]. An etch mask is patterned in hydrogen silsesquioxane (HSQ). The pattern is then transferred to the silicon master via reactive ion etching, or RIE, using an oxygen plasma. The vertical etch rate of the Si is faster than the lateral etch rate which creates the tapered features.

Figure 9. SEM image of Nanowedges (left) and Nanocones (right)
2.2 Nanoimprint Process

The nanoimprinting process takes place in a custom chamber designed by Dr. Ted Bloomstein at MIT Lincoln Labs. Figure 10 details the main components of the nanoimprint tool. The steel chamber houses a sample platform or cell. Dry air is maintained at a constant pressure of 260 PSI within this cell. The heater block is located directly beneath the cell platform and has a feedback system with a contact probe thermocouple to maintain constant temperature.

![Nanoimprint tool diagram](image)

Figure 10. Nanoimprint tool

In Figure 11, it is shown how the Si master transfers the pattern of nanofeatures to the thermoplastic substrate, PMMA. The silicon master is first cleaned for 5 minutes under oxygen
plasma and then exposed to a fluorinating agent, tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane under vacuum for 1 hour, to prevent the PMMA from sticking to the master after imprinting. The PMMA substrate is fabricated by spin-coating 60uL of PMMA dissolved in anisole (Microchem, solids 4%) onto a Si or glass substrate, then heated on a hot plate at 150C for 10 minutes to remove the solvent. The master is then placed on top of the PMMA sample and the sample cell is tightly closed. In this specific nanoimprint process, the PMMA substrate sample is brought to the glass transition temperature ($T_g$) of 135C, as shown in Figure 12.

![Figure 12. Glass transition temperature for PMMA is 135C](image)

The sample is then placed under 260 PSI for 2 minutes. The temperature quickly reduces to 40C before the pressure is released to allow the features to cool and set, as the release of the master could potentially disturb the nanofeatures if they are still hot. Once the temperature of the sample cell reaches 40C, the sample cell is opened and the sample is removed. The master is released from the sample using a clean and sharp lab blade to wedge them apart. The master is then sonicated in acetone for 5 minutes to dissolve any PMMA that had adhered to the master.
2.3 Conductive Thermo-Plastic OPV Device Design

![Figure 13. a.) CIAIPc organic donor layer; b.) DBP organic donor layer](image)

Once the PMMA substrate is patterned, it is ready to be coated with the organic active layers. The electron-donor materials, or active layers, explored in this study will be Chloroaluminum phthalocyanine (CIAIPc) and tetraphenyldibenzoperiflanthene (DBP) as shown in Figure 13.

![Figure 14. CIAIPc photovoltaic property, EQE, of planar OPV with CIAIPc active layer](image)

CIAIPc is especially interesting because the recorded external quantum efficiency (EQE) is close to 30%, which means that there is a 3x room for improvement (see Figure 14). These
active materials will be tested and optimized for conformal coverage of the textured substrate, optical properties, and device performance. Planar OPVs using C1AlPc have achieved >3% power conversion efficiency [18]. Planar OPVs using DBP have achieved 3.6% PCE [19]. Thus, both active materials have been shown to be promising as donor materials and are both relatively new materials for OPVs, making them worthwhile to study.

![Figure 15. Schematic of active layers on textured OPV](image)

These organic active layers are deposited onto the Nanofeatures via thermal evaporation at a rate of 0.5 Å/s. Each layer is deposited directly onto the previous layer under a vacuum of $3 \times 10^{-6}$ torr. In Figure 15, the conformal coverage of the features by the active layers is illustrated. This conformal coverage was tested and observed for C1AlPc on the Nanowedge features. A coating thickness of 17nm was measured on the side wall of the feature, as shown in the SEM photo in Figure 16c. Coverage is also observed for Nanocones in Figure 16a.
Figure 16. a.) Active layer on PMMA Nanocones; b.) Diagram of a.; c.) Active layer on PMMA Nanowedges; d.) Diagram of c.)
3.1 Optical Properties of Organic Active Layers

To better understand the optical properties of the organic active layers CIA1Pc and DBP, optical measurements were taken to determine reflection, transmission, absorption, and dielectric properties. The absorption peak of CIA1Pc is at $\lambda = 700\text{nm}$. For DBP, there are two absorption peaks, one at about $\lambda = 560\text{nm}$ and one at about $\lambda = 620\text{nm}$. The active layers were thermally evaporated in different thicknesses onto transparent glass substrates. Absorption was then derived from measured transmission and reflection data. This data, shown in Figure 17a and Figure 17c, was taken by a Cary UV-Vis spectrometer. Because the exciton diffusion length of CIA1Pc is 20nm, a 20nm thick layer was deposited onto a glass substrate, a nanocone-textured PMMA on glass substrate, and a nanowedge-textured PMMA on a glass substrate. These three samples were compared to determine if the features increased the absorption of light into the active layer. The absorption actually decreases on the nano-textured samples (see Figure 17b and Figure 17d) for both DBP and CIA1Pc, which is the opposite of the expected result, that the features would increase absorption into the active layer.
This unexpected result led us back to the transmission data, which showed the same phenomenon (see Figure 18) where the sample the transmits the least (absorbed the most) was the sample that had a planar film of 20nm of CIAIPc or DBP on a glass substrate.
In reviewing the absorption data versus thickness of the active layer, it suggests that the 20nm planar layer was optically thicker than the 20nm deposited onto the nano-features. This makes sense since the nano-features have a higher surface area than the planar footprint they sit on. While the organic material is deposited onto these nanofeatures, the same volume of material is covering more surface area, leading to a thinner coating than the planar sample. To correct for this thinning effect, a correction factor was calculated that accounted for the extra surface area from the Nanowedge and the Nanocone. As shown in Figure 19a-c, correction factors were calculated to increase the amount deposited onto the features to achieve a sidewall thickness of 20nm. This sidewall thickness is the exciton diffusion length and must be kept as thin as possible.
Another interesting optical property is the dielectric constants, n and k. These constants are not typically found in the literature like more common organic materials and must be measured. This data can then be imported into modeling software to more accurately represent the active layer in those models. The data shown in Figure 20 is the k, or extinction coefficient, taken by spectroscopic ellipsometry, and fitted using a Cauchy model of best fit. These samples were prepared by thermally evaporating the active layers onto a planar glass substrate in different thicknesses. We notice a red-shift in the k peak for CIAlPc with increasing thickness. No such red-shift is observed with DBP.
3.2 Predicting Power Enhancement through Finite Element Models

In order to predict the power absorption enhancement provided by the subwavelength nano-scale periodic features, a finite element model of the active layer was created. These models are essential to understand how the fields interact with these nanofeatures. This software is also a valuable tool for experimentation because the OPV architecture can be designed and optimized before being implemented in the lab. In this work, COMSOL Multiphysics package is used. Specifically, we used RF as the main tool kit.

![Comparing Beer's Law to COMSOL Power Absorption Results](image)

Figure 21. Comparing COMSOL calculation to Analytical Beer's law

To begin the modeling process, a quick reality-check is good practice to ensure that the software is in agreement with analytical laws. In Figure 21, the COMSOL calculation of the power absorbed into a 20nm thick planar active layer of n=2 and k=1 matches closely to the Beer’s law calculation of a planar material of the same dimension and optical properties. Checking the COMSOL results against analytical laws is good practice whenever possible. In the case of solving Maxwell’s equations, this is not so simple. This is why we are using software to approximate the solution to Maxwell’s equations in the first place.
\[
\vec{P} = \vec{E} \times \text{conj}(\vec{H})
\]

\[
\text{Power} = \frac{1}{2} \int_{\text{surface}} \text{real}(\vec{P}) \cdot ds
\]

\[
\text{Power}_{\text{normalized}} = \frac{\text{Power}}{\text{Source Power}}
\]

Figure 22. Power absorption calculation is a poynting vector integration

To calculate the power absorbed by a material in these models, the pointing vector is integrated over the surface, as shown in Figure 22.

Starting with the basic Nanowedge design, shown in Figure 23, the power absorption in this active layer was calculated and compared to the power absorbed in the planar active layer. This active layer is sandwiched between two layers of glass with \(n=1.5\) and the active layer itself is a test material of \(n=2\) and \(k=1\) for simplicity. The dimension of the Nanowedge is 100nm in height, 100nm in width, with a sidewall thickness of 20nm, for a total surface area of 4500nm \(^2\). This sidewall thickness is measured perpendicular to the charge-splitting region, or heterojunction. This represents the exciton diffusion length of ClAlPc. The planar active layer also has a 100nm width and a thickness of 20nm perpendicular to the charge collection region, for a total surface area of 2000nm \(^2\). The active layer on the textured surface has a total surface area that is more than 2x the surface area of the planar control to which we are comparing the power absorption. The total amount of material is not held constant, but the exciton diffusion length is. As shown in the graph of Figure 23, there is a calculated 81% increase in power absorption is from the planar control of \(S_A = 2000nm^2\) at 40.2% absorption to the textured active layer of \(S_A = 4500nm^2\) at 72.8% using an incident light of \(\lambda = 500nm\). This design essentially says for the same exciton diffusion length, over the same footprint of substrate area, more material can be deposited in such a way as to increase the power absorbed into this layer.
To observe the reduction of diffraction orders due to the subwavelength effect, a parametric model was created to observe the power flow through the active layers. The power flow is defined as the pointing vector, from Figure 22, and is represented by white arrows in Figure 24. In Figure 24a, the Nanowedge features are designed with a pitch of 1\(\mu\)m, which is larger than the incident light of 500nm. Notice the diffracting Poynting vectors of the micron-scaled feature as compared to the subwavelength-scaled feature in Figure 24b. The Poynting vectors of Figure 24b are much straighter with minor deviance from the \(m = 0\) order, as described in Figure 8.

Figure 23. Power absorbed of textured active layer compared with planar active layer varies according to surface area of active layer
Different feature geometries were explored to get a sense of the best architecture to use for the OPV nano-textured substrate. In Figure 25, Nanowedges were designed with a constant base width of 100nm and increasing height from planar or 0nm to 200nm. This study increased the aspect ratio of the feature, as defined by the height to width ratio. At a height of 200nm, for the same exciton diffusion length, the power absorbed into the active layer is 92.3% of the incident source power of $\lambda = 500nm$. The COMSOL FEM approximations were compared to the Rigorous Coupled Wave Analysis (RCWA) analytical solutions as further corroboration.
In addition to normally incident light, non-normally incident light was used as the source power. The angle of the incident light was varied from 0 to 90 degrees, or from normal to parallel to the surface of the substrate. These power absorption results shown in Figure 26 from COMSOL and RCWA in the angled study closely match, but slight dimension differences in the geometry of the feature created could account for the small discrepancies. Maximum power absorption occurs at a normal incidence and decreases as the angle approaches parallel to the substrate for the Nanowedge sample of height 100nm (shown in Figure 26a). Maximum power absorption peaks about 43° from the normal and decreases as the angle approaches parallel to the substrate for the planar sample (shown in Figure 26b). This study is important due to the angled light coming from the sun as it moves across the sky. If no solar-tracking technique is used, most of the sunlight will hit the OPV at an angle off the normal.
Another geometry explored was Nanowedges with different pitches of increasing width, from 100nm to 10um. Each active layer was designed to maintain a constant 20nm exciton diffusion layer and maintain a 3:1 aspect ratio. These designs are shown in Figure 27.

![Figure 27. Illustration of Nanowedge active layer with increasing pitch and constant 3:1 aspect ratio](image)

The power absorption was calculated for each of these features and is shown in Figure 28. As the feature pitch increases, the power absorption decrease as a result of the feature becoming less subwavelength to orders of magnitude larger than the incident light. In the table of Figure 28, the surface area of each of the features is listed. In this case, despite the increase in
the available material to absorb photon energy, the percentage of power actually being absorbed decreases. This may indicate an increase in reflection and diffraction away from the substrate.

![Graph comparing pitch vs. power absorbed at freq=500nm]

### Table: Power absorption decreases with increase in pitch. Aspect ratio is held constant 3:1

<table>
<thead>
<tr>
<th>Pitch (um)</th>
<th>Area of Active Layer</th>
<th>Glass height above point (nm)</th>
<th>Power absorbed at 500nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>12160.0 nm²</td>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>0.25</td>
<td>30400.0 nm²</td>
<td>100</td>
<td>0.88</td>
</tr>
<tr>
<td>0.5</td>
<td>60800.0 nm²</td>
<td>100</td>
<td>0.80</td>
</tr>
<tr>
<td>1</td>
<td>1.216 um²</td>
<td>100</td>
<td>0.82</td>
</tr>
<tr>
<td>5</td>
<td>0.608 um²</td>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>10</td>
<td>1.216 um²</td>
<td>100</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 28. Power absorption decreases with increase in pitch. Aspect ratio is held constant 3:1.
3.3 Demonstrating absorption enhancement on textured surfaces

To demonstrate the enhanced absorption for non-planar vs. planar architectures, PMMA substrates were imprinted with the patterns listed in Table 1.

<table>
<thead>
<tr>
<th>Pattern ID</th>
<th>Groove depth</th>
<th>Period/pitch</th>
<th>Line width</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G50</td>
<td>50 nm</td>
<td>139 nm</td>
<td>69.5 nm</td>
<td>square trenches</td>
</tr>
<tr>
<td>G200</td>
<td>200 nm</td>
<td>833.3 nm</td>
<td>416 nm</td>
<td>square trenches</td>
</tr>
<tr>
<td>G350</td>
<td>350 nm</td>
<td>700 nm</td>
<td>375 nm</td>
<td>triangular trenches</td>
</tr>
<tr>
<td>Nanowedges</td>
<td>70-100 nm</td>
<td>100 nm</td>
<td></td>
<td>2D array of cones</td>
</tr>
<tr>
<td>Nanocones</td>
<td>70-100 nm</td>
<td>100 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the square trench patterns, a significant increase in absorption is seen in comparison to the unpatterned sample, as shown in Figure 29a. The absorption increases with increasing groove depth. The enhancement is likely a combination of increased optical path-length and reflective light bounces.

For the smaller features, SEM images were taken to compare the thickness of the active layer in comparison to the measured thickness on planar substrates. Due to the directional nature of thermal evaporation, when evaporating 20 nm of DBP, only the top and bottoms of the features end up with a 20 nm layer thickness while the side wall coverage is approximately half as thick (~10 nm), Figure 29b. The same trend is seen for a 40 nm DBP layer where the base layer is 40 and the side walls are half as thick (~20 nm), Figure 29c.

Some of these coverage issues could be overcome by tilting the stage during evaporation or evaporating small amounts at different angles to increase line of sight coverage. In Figure 29d the absorption of DBP and PEDOT on a planar substrate is compared to DBP and PEDOT deposited on the nanowedges pattern both with a base 20 nm DBP layer (thinner side wall
coverage) and with a thicker DBP layer that gives a 20 nm sidewall coverage. The same was done in Figure 29e for the nanocones pattern.
Figure 29. (a) Absorbance of DBP (20nm) on PEDOT (15nm) on square trench imprinted PMMA vs. planar PMMA (b) SEM image of DBP (20nm) on nanowedges pattern (c) SEM image of DBP (40nm) on nanowedges pattern (d) absorbance of DBP (20nm base thickness and wall thickness) on nanocones pattern vs. planar PMMA
For all the samples there was an increase in the absorption even at a base of 20 nm DBP thickness and with the sidewalls having a <20 nm DBP thickness. With these dimensions applied to a photovoltaic cell, in comparison to a planar cell with a 20 nm active layer, the thinner sidewall thickness, would lead to less charge recombination. For the nanowedges pattern, the absorption peaks at 560 nm and 610 nm respectively increased by 16% and 14% for the 20nm base layer and by 51% and 45% for the 20nm side wall layer. For the nanocones pattern, the absorption peaks at 560 nm and 610 nm respectively increased by 17% and 17% for the 20nm base layer and by 55% and 47% for the 20nm side wall layer. In a full device, the absorption enhancement may improve even further with the inclusion of the reflective metal back electrode [20].
CHAPTER 4
DEVICE RESULTS
AND
CHALLENGES

4.1 Planar Device Performance using Conductive Thermo-Plastic

One of the main objectives of this work is to imprint a conductive PMMA substrate that acts as the electron transport layer that connects to an ITO electrode. A conductive textured substrate allows the organic active layer to be electrically in contact with the bottom electrode. This eliminates the need to coat the textured substrate with the bottom electrode which would add more layers that must fit within the small space between the features. A high-k, reflective, textured bottom electrode may also reduce the light-trapping effect by disturbing the fields in between the features and absorbing most of the light due to its high k nature. The conductive plastic used in this study is a PMMA with 20k polyaniline (PANI) (see Figure 30a) in a 20% concentration, which has been demonstrated to as an imprintable conductive polymer [21]. Several different types of conductive dopants were used such as dodecyl benzene sulfonic acid (DBSA) (see Figure 30b), camphor sulfonic acid (CSA), and Bis(2-ethylhexyl) phosphate (DEHHP).
The control device structure is described in Figure 31. The bottom electrode is a transparent, conductive oxide made of indium tin oxide, or ITO. A hole-blocking electron transport layer, MoO3, is next, followed by the organic electron donor C1AlPc, the electron acceptor, C60, and the hole-transport layer BCP. The top electrode is Ag.

The planar experimental OPV device structure is shown in Figure 32 has a 300nm thick PMMA-PANI layer as the electron transport layer instead of the MoO3. This PMMA-PANI mixture is dissolved in M-Krezol and spun coat onto the ITO substrate at a rate of 2k RPM. The sample is then placed on a hot plate at 150C for 10min to release the solvent. Several types of PMMA-PANI were tested. The only mixture that performed repeatedly and similarly to the
control is the PMMA-PANI-DBSA polymer, shown in Figure 30. Another mixture performed similarly to control, the PMMA-PANI-DEHHP polymer, but only if the device structure were inverted, as shown in Figure 33.

![Inverted device structure and resulting IV curve as compared to control](image-url)
4.2 Challenges to Device Performance

Many of the planar OPVs using the various PMMA-PANI polymers did not perform as well as the control, such as the blue curve in Figure 32b. A leakage pathway from the PMMA-PANI layer and the Ag top electrode was suspected to be a cause. Because the lateral conductivity of PANI is much higher than the vertical conductivity, the contact between the PANI layer and the metal contacts resulted in a leakage pathway, or short circuit as shown as show in Figure 34. To remove this leakage pathway, the PANI layer was masked by a .5cm x .5cm Si square centered on the substrate and then placed in a plasma oven for 1 minute to remove the exposed PANI.

![Device Structure with leakage pathway](image)

**Figure 34. a.) Device Structure with leakage pathway; b.) Conductivity values for conductive plastic substrate dopants**

<table>
<thead>
<tr>
<th>PANI dopant</th>
<th>Lateral Conductivity</th>
<th>Vertical Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA20</td>
<td>2.12</td>
<td>0.000067</td>
</tr>
<tr>
<td>DBSA20</td>
<td>2.66</td>
<td>0.0000067</td>
</tr>
<tr>
<td>DEHHP20</td>
<td>0.01</td>
<td>0.000177</td>
</tr>
</tbody>
</table>

This masking process is shown in Figure 35a. The resulting PMMA-PANI layer is restricted to just above the ITO contact, so that the organic layers can create a barrier between the PMMA-PANI layer and the Ag top electrode. The completed device structure is shown in Figure 36a.
Figure 35. Leakage pathway is removed with masked plasma etch

However, after using this etch process, the device performance only improved marginally as far as increasing the Jsc for the PMMA-PANI-CSA polymer, as shown in Figure 36. The only polymer mix that performed as well as control repeatedly is the PMMA-PANI-DBSA layer. We decided to carry out the next experiments using the PMMA-PANI-DBSA polymer only.

Figure 36. Device performance only marginally improved by plasma etch for CSA dopants

The low conductivity shown by the low Jsc in Figure 36 for the PMMA-PANI-CSA device was addressed by etching the top layer with a Xylene (Aldrich, 98.5%) etch process. The PMMA-PANI-CSA was first spun coat onto the ITO/glass substrate and heated on the hot plate at 150°C for 10 min to remove the solvent. The sample was then dipped into the Xylene etchant.
for varying times to see the effect of etching this first layer. The hypothesis was that the top most layer may be oxidized or contain more PMMA than PANI, creating a resistive interface. This top layer would be etched away revealing more of the PANI and thus making the interface more conductive. However, the performance did not improve as expected, as shown in Figure 37. For most devices, the Jsc did not increase significantly, but the shunt resistance seemed to be decreasing, meaning that leakage pathways were created. This can be seen in the increasing slope of the test devices in the third quadrant of the graph in Figure 37.

![Figure 37. Device performance as a result of treating surface with Xylene etch](image)

The effect of the Xylene etch on the surface of the PMMA-PANI-CSA layer was studied via Atomic Force Microscopy (AFM). As shown in Figure 38, as the etching time increases from 0 seconds to 3 minutes, the surface roughness increases from less than 25nm to 400nm. The particulates in the 3 minute etch are obvious from the 3D rendered image on the right.
These particulates, more clearly illustrated in Figure 39, likely create a leakage pathway from the top electrode to the PMMA-PANI-CSA layer. Xylene treatments were then abandoned since they only further reduced the performance of the OPV.

After abandoning the PMMA-PANI-CSA conductive plastic and focusing on the PMMA-PANI-DBSA conductive plastic for making the OPVs, planar imprinting tests were implemented to study the degradation effect of heating the plastic to 160°C, the glass transition temperature. Planar imprints consist of imprinting the PMMA-PANI-DBSA on ITO using a planar Si master with no features at three temperatures: 140°C, 150°C, 160°C. Devices were made from these planar
imprinted substrates and the Jsc was measured. As shown in Figure 40, the imprinted devices all have a Jsc that is lower than the control. The slope in the third quadrant is also steeper, meaning there is more leakage current and the shape of the curve in the fourth quadrant suggests the fill factor (FF), is also much lower than control. Clearly, the imprint process itself leads to degradation of the conductive plastic which prohibits any possible observation of enhancement from the light-trapping features.

![Device performance for planar imprinted devices using PANI-DBSA-PMMA at various temperatures](image)

**Figure 40.** Device performance for planar imprinted devices using PANI-DBSA-PMMA at various temperatures

Imprints were then implemented at lower temperatures to mitigate this loss in performance as much as possible. Imprinted Nanowedge features in a 300nm layer of PMMA-PANI-DBSA on Si substrates are shown in Figure 42. The imprints were carried out at 140C, 150C, and 160C. Imprinting quality, measured by the height of the features, increases with increasing temperature.
Figure 41. Glass transition temperature $T_g$ of PMMA-PANI-DBSA is 160°C.

This is because 160°C is the material’s glass transition temperature ($T_g$), as shown in Figure 41. Imprinting at this temperature or above will soften the material enough to transfer a full feature from the master. Imprinting at temperatures below the $T_g$ will result in partial transfer of the features, which makes a feature with a smaller aspect ratio and thus a smaller potential light-trapping effect. This trade-off is one of the major challenges of this work. Higher temperatures lead to better features, but lower conductivity. This is a major disadvantage of imprinting part of the device as opposed to imprinting a non-conductive substrate to act as the support for the device and building the entire device, including the bottom electrode, off of this textured base.
The next step was to create an OPV from the imprinted PMMA-PANI-DBSA substrate. Another major obstacle was imprinting this layer after it was spun-coat on the ITO. The conductive plastic had extremely poor adhesion to the ITO substrate. When the Si master was released from the ITO substrate, the PMMA-PANI-DBSA layer would rip off of the ITO and stick to the Si master, as shown in Figure 43. This occurred repeatedly, despite several re-flourinations of the Si master. Because of these many challenges to imprinting a textured substrate in PMMA-PANI-DBSA and maintaining good conductivity after imprinting at high temperatures, this device design was placed on hold. During this time, new device designs were designed that would not suffer from these aforementioned disadvantages to device fabrication and performance.
oCVD PEDOT is a new way of making the commonly used organic conductive polymer. It is created in an all-dry, high vacuum environment within a special chamber. The monomer is oxidized using a catalyst, in this case FeCl, and polymerizes into a polymer directly onto a substrate placed in the chamber [7]. The chemical formula for oCVD PEDOT is shown in Figure 44a and the chamber system is illustrated in Figure 44b.
The oCVD PEDOT deposition method has advantages over the traditional solution-process deposition of PEDOT:PSS, or spin-coating. This spin-coating process is illustrated in Figure 45b, where the conductor is deposited using a pipette syringe onto the substrate and spun at a high speed or RPM for 60s. The solvent is then removed when the substrate is placed on a hot plate at 150°C for 10 minutes. oCVD deposition is an all-dry process, eliminating the need for solution processing, solvent removal, or contacting the sample with H2O or solvent. The oCVD process is also an ideal choice for creating conformal layers of PEDOT on various types of surfaces. In this work, we are interested in conformally coating nanoscale features. Coverage of micro-scale features is also studied to demonstrate the versatility of oCVD pedot and the limits of spun-coat PEDOT: PSS.
5.2 oCVD PEDOT Conformality on Nano- and Micro-features

The defects of spin-coating PEDOT:PSS on nano and micro-features are illustrated in Figure 46. These defects include non-uniform or non-conformal coating meaning a welling in between features resulting in a thick layer in between features while leaving a very thin layer on top of the features. Another defect is the PEDOT:PSS not reaching in between the features at all, resulting in blanketing. Lastly, air gaps can occur if both of blanketing and welling occurred simultaneously.

The ideal conformal coating would occur as illustrated in Figure 47. The polymer needs to coat with uniform thickness the trough in between the features, the sidewall of the features, and the tops of the features. The nano-features shown here are Nanosquares (LightSmyth).
These features were studied because it was easy to purchase the masters off the shelf whereas the Nanowedge and Nanocone masters needed to be custom fabricated. The geometry was not crucial, only the size of the features in this case. The sharp edges of these Nanosquare features are an advantage because they are a challenge to coat evenly and can further demonstrate how adept oCVD PEDOT can be at conformal coating and how limited PEDOT:PSS can be at conformally coating small features.
The results of this conformality study are presented in Figure 48. In the left column, Figure 48a,c,e are all cross-sectional SEM images of PEDOT:PSS spun-coat onto the features while Figure 48b,d,f show images of oCVD PEDOT on the same feature. Figure 48a demonstrates the air-gap defect of PEDOT:PSS on nanowedges. Figure 48b shows nanofeatures of the same scale coated with oCVD PEDOT and cleanly fill in all features with no air gaps. Figure 48c shows the non-uniform thickness of PEDOT:PSS, with thicker PEDOT on the bottom.
of the nanowedge and thinner PEDOT on the top. Figure 48d shows oCVD PEDOT uniformly coating the edges of the nanowedge. Figure 48e shows non-uniform thickness occurring in micron-scale squares with PEDOT:PSS. Figure 48f shows uniform thickness on the bottom, sidewall and top layers of the micro-squares. These results show how versatile oCVD PEDOT is as a conformally depositing organic polymer electrode. oCVD PEDOT can work with a variety of substrates, surfaces and textures. This method of electrode deposition is also well suited for roll-to-roll manufacturing, making it easier to fabricate OPVs on a large scale and further reduce costs.
5.3 Establishing planar performance for oCVD PEDOT OPV

a.) Front view

b.) Side view

Figure 49. Planar device structure with PEDOT as the bottom conductor

Devices were fabricated using a planar layer of oCVD PEDOT to establish a performance level for the control, or non-textured, device, as shown in Figure 49. The bottom PMMA layer in the control is planar, but the future test devices will be textured.

Figure 50. Planar devices using the oCVD PEDOT layer are not functional despite using various rinsing methods

The oCVD PEDOT layer in these planar control devices did not perform as well as the non-pedot control, as shown by the pink curve in Figure 50. All devices shorted. One possible cause is that the FeCl catalyst particles remained in the PEDOT, creating a non-uniform surface with large particulates that create leakage pathways from the bottom electrode (PEDOT) to the
top (Ag), as shown in Figure 50. Despite a myriad of rinsing techniques, shorting remained a problem. Further work will be done to establish a base level performance for the oCVD PEDOT planar control device.

5.4 Imprinting oCVD PEDOT

![Diagram](image)

Figure 51. a.) Diagram of imprint process for oCVD PEDOT b.) SEM of imprinted oCVD PEDOT

Instead of imprinting a charge-transport layer, the electrode itself can be imprinted, as shown in Figure 51. Imprinting oCVD PEDOT is difficult since this polymer does not have a clearly defined glass transition temperature, as shown in Figure 52. This technique has been demonstrated using PEDOT:PSS by Yang et al., [22] in which dehydrated PEDOT:PSS, deposited on ITO, is imprinted using a silicon mold with < 100nm feature sizes. Larger, 600 nm, gratings were created in PEDOT:PSS using a PDMS mold by Chou et al. [23] Researchers have also demonstrated similar imprinting techniques to pattern the active layers before evaporating the back metal electrode [24, 25]. To imprint the oCVD PEDOT, the imprinting time was increased to 10 minutes based on Yang’s process to transfer the pattern shown in Figure 51.
Simple texturing of the PEDOT electrode could be used to enhance both charge transport between the PEDOT and the active layers by creating a high surface area interface and light absorption by creating a non-planar framework on which to deposit the active layers.

A textured electrode may also reduce the risk of slightly inconsistent thicknesses of coating the electrode on large area textured surfaces. Texturing the electrode itself may also eliminate an entire fabrication stage of imprinting a substrate that may require optimization for imprint quality and to make sure the substrate material is compatible with the electrode.

Texturing a conformally-coating electrode opens up new ways of device fabrication. PEDOT electrodes can be coated onto non-planar untexturable surfaces and then textured, opening up a larger range of potential substrates and applications. For example, PEDOT can be conformally coated onto flexible substrates, then textured after deposition to enhance light absorption.

Devices will be fabricated using this textured oCVD PEDOT electrode and documented as part of a future work.
CONCLUSIONS

This work has explored a light-trapping design for OPVs consisting of nanoscale, subwavelength, high-aspect ratio features imprinted into conductive polymers. This design was predicted to enhance light absorption into the active layer by 81% when comparing a planar at 40.2% absorption to a textured design of Nanowedges 100nm in width and 100nm in height at 72.8% absorption. Absorption is predicted to increase with increasing height for the same width. Measured light absorption enhancement from active-layer-only coated features was less than this predicted enhancement. For the nanowedges pattern, the absorption peaks at 560 nm and 610 nm respectively increased by 16% and 14% for the 20nm base layer and by 51% and 45% for the 20nm side wall layer. For the nanocones pattern, the absorption peaks at 560 nm and 610 nm respectively increased by 17% and 17% for the 20nm base layer and by 55% and 47% for the 20nm side wall layer. In a full device, the absorption enhancement may improve even further with the inclusion of the reflective metal back electrode. Devices were fabricated first to establish a planar control performance and a planar imprinted control performance, but device performance suffered from the degradation effects of the imprinting process. High heat led to reduced conductivity of the conductive polymer PMMA-PANI-DBSA. Textured devices faced further challenges in fabrication such as lack of imprinted PMMA-PANI-DBSA adherence to the ITO substrate. Imprinting a conductive polymer at high heat that shares an interface with the active layers may not be the most robust device design. However, successful imprints occur at the glass transition temperature, 160°C, which is a high heat. This design trade-off is another disadvantage of imprinting a conducting polymer that is part of the active device.
A new device was designed for an imprinted, light-trapping OPV substrates where the bottom electrode, oCVD PEDOT, was coated onto the imprinted features made of non-conductive PMMA. These features would not be part of the active device, but simply a substrate underneath the full device. Devices built using oCVD PEDOT to establish a planar control device only shorted despite various rinsing techniques. Imprinted devices with an oCVD PEDOT coating will be part of a feature work after the planar control device performance is established. During the creation of this device, the conformal coating of oCVD PEDOT was demonstrated to be superior to using the spun-coat PEDOT:PSS. PEDOT:PSS left defects such as air-gaps and non-uniform thicknesses around both nano- and micro-scale features. oCVD PEDOT was shown to conformally coat nano- and micro-scale features. The versatility of oCVD PEDOT suggests that it has the potential to coat many types of surfaces, which is a huge advantage for thin and flexible OPVs.

The imprinting of oCVD was then explored as yet another imprinted device design where the bottom electrode is imprinted and the full device is created on top of it. Imprinting oCVD was demonstrated in this work. Texturing of the PEDOT electrode could be used to enhance both charge transport between the PEDOT and the active layers by creating a high surface area interface in addition to trapping more light. Imprinting a conformally coating organic polymer electrode makes it possible to build enhanced OPV devices on unimprintable surfaces like glass, fabric or paper.
FUTURE WORK

The thermal mechanical properties of oCVD PEDOT such as Tg are not currently understood. Further thermal characterization of oCVD PEDOT is needed to completely understand if the PEDOT film becomes rubbery at the imprinting temperature. Preliminary measurements, shown in this work, of Tg for oCVD PEDOT showed no clearly defined lass transition temperature. These properties will be more fully documented and published in a future work.

Further analysis is necessary to fully characterize the oCVD PEDOT film after the imprinting process to determine if any degradation had occurred. This analysis along with thermal properties of oCVD PEDOT will be measured and documented in a future work. We are building on previous work, such as that by Yang et al. [22], who demonstrated imprinting of PEDOT:PSS. This works aims to document that imprinting oCVD PEDOT is indeed possible, if not currently understood, using imprinting methods (time and temperature) previously demonstrated [23].

To further the study of conformally coating oCVD PEDOT for OPVs, the challenges to fabricating a planar control device must be met, such as rinsing and creating a PEDOT layer with low surface roughness. Full, imprinted and coated devices will then be fabricated and tested to evaluate an enhancement of power conversion efficiency.

To complete this study of imprinted oCVD PEDOT for OPVs, devices will be fabricated using this textured oCVD PEDOT electrode and documented as part of a future work.
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