HIGH PERFORMANCE SOLUTION PROCESSED TRANSPARENT ELECTRODES FOR OPTOELECTRONIC DEVICES

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Whitney Beth Gaynor

December 2010
© 2011 by Whitney Gaynor. All Rights Reserved.
Re-distributed by Stanford University under license with the author.

This work is licensed under a Creative Commons Attribution-Noncommercial 3.0 United States License.  
http://creativecommons.org/licenses/by-nc/3.0/us/

This dissertation is online at: http://purl.stanford.edu/rn236gp4284
I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Peter Peumans, Primary Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Michael McGehee, Co-Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Alberto Salleo

Approved for the Stanford University Committee on Graduate Studies.

Patricia J. Gumport, Vice Provost Graduate Education

This signature page was generated electronically upon submission of this dissertation in electronic format. An original signed hard copy of the signature page is on file in University Archives.
ABSTRACT

Many thin-film optoelectronic devices, including displays and photovoltaic cells, require transparent conducting films as part of their device architecture. Sputtered indium tin oxide (ITO) is the most commonly used material and has high performance but is expensive and has some performance limitations, especially on flexible substrates. This dissertation presents high-performance composite transparent conducting films comprised of silver nanowires and polymer films for use as a replacement for ITO in these devices. These composites have lower sheet resistance than ITO with comparable transmission on both glass and plastic substrates and are demonstrated in this work to be compatible with high-efficiency organic photovoltaic devices. They are also more mechanically robust to ITO and show nearly substrate-independent performance. These composites have the potential to enable both low-cost photovoltaics and flexible displays.
Acknowledgments

There are many people for me to thank, without whom my time at Stanford and consequently this work would not have been nearly as successful and fulfilling as it has been.

First, I would like to thank my advisor, Peter, for all the support and helpful discussions and direction that he has given me during my graduate career. I always know that I will learn something new whenever I sit down and discuss my work with him, and I hope someday to be as well-versed in half as many subjects as he is. I very much appreciate the freedom to pursue my research interests that he has given me, and I appreciate his attitude that if you give it enough thought and creativity, you can engineer your way around any research problem. I will take that view with me as I leave school and pursue my future career.

I would like to thank all of my colleagues in the Peumans research group for the camaraderie in the lab and for introducing me to new projects and ideas. I have worked most closely with Jung-Yong Lee, who did the initial work on Ag nanowire electrodes and was a collaborator on the device fabrication in Section 5 of this work, Seung Rim, who helped with the simulations presented in Section 5, and Greyson Christoforo, who helped build the spray-coater used to fabricate the samples described in Section 6.4. Nicholas Sergeant connected me with Southwall Technologies, which provided the high-quality plastic substrates for device fabrication in Section 2.

I have also collaborated extensively with Stanford students in other research groups, and I appreciate their efforts on my behalf. Lucas Berla and Professor W. D. Nix helped with the nanoindentation measurements presented in Section 3.1. Han Sun Kim in
Professor Yi Cui’s lab synthesized the nanowires used in these experiments. I was able to fabricate all of the polymer solar cells presented here using equipment in Professor Mike McGehee’s lab, and he and his group members have been extremely supportive and helpful throughout my time in his lab. In particular, I would like to thank George Burkhard for teaching me to make the best polymer PV cells possible using our materials and Brian Hardin for helpful discussions, introducing me to other collaborative opportunities, and for generally being a good friend and sounding board. I would also like to thank Mike for being my academic advisor and connection to the Materials Science and Engineering Department, and for the helpful advice and wisdom throughout my entire time at Stanford.

On a more personal note, I would like to thank the friends with whom I’m lucky enough to spend my time outside of the lab for all of their support during the ups and downs of grad school. The wonderful people I’ve met while at Stanford have been there both for the fun and for the complaints, and I am really lucky to have met and to have spent time with such great people. My amazing fiancée, Ted, is an endless source of love, humor, and strength, and I appreciate every day that we spend together.

The members of my family, including my parents, grandparents, my sister, and my extended family are truly the most important people in the world to me, and without them I would certainly have never finished this work nor would I be where I am today. Ever since I was a small child, Mimi, my grandmother, told me that I should go to Stanford, because it is the very best school there is. She would be so proud of me knowing that I am earning my Ph.D. from her favorite institution. My parents have always supported my every endeavor since the day I was born, and their help, wisdom, advice, love, and the
values that they have instilled in me have been the driving forces for every success that I have had in grad school and in life. I love and appreciate them very much, along with Darby, my sister, who has been and always will be my best friend. I hope that my family can be proud of the work that I produce, both here, academically, and in the future.
# Table of Contents

1. **Introduction**..................................................................................................................1

   1.1. *Organic Photovoltaic Devices* ..................................................................................2

   1.2. *Evaluating Solar Cell Efficiency* .................................................................................9

   1.3. *Indium Tin Oxide Transparent Electrodes* .................................................................12

2. **Polymer / Ag Nanowire Composites** ..............................................................................17

   2.1. *Solution-Processed ITO Replacements* .................................................................18

   2.2. *PEDOT / Ag Nanowire Composite Films: Morphology* ....................................20

   2.3. *PEDOT / Ag Nanowire Composite Films: Performance* ....................................24

   2.4. *PEDOT / Ag Nanowire Composite Films: OPV Cells* ........................................27

   2.5. *Section Conclusion* .................................................................................................30

3. **Mechanical, Optical, and Thermal Properties of Laminated PEDOT:PSS / Ag Nanowire Composites** ........................................................................................................32

   3.1. *Lamination Mechanics* ..........................................................................................33

   3.2. *Optical Properties of Laminated Composite Films* ............................................38

   3.3. *Thermal Properties and Limits of Laminated Composite Films* .....................40

   3.4. *Section Conclusion* .................................................................................................46

4. **Fully-Solution Processed OPV Cells on Metal Substrates with Composite Top Electrodes** .........................................................................................................................48
4.1. Previously Reported Work .................................................................49

4.2. Device Fabrication ............................................................................53

4.3. Composite Top Electrode Performance .................................................55

4.4. OPV Device Performance ..................................................................57

4.5. Section Conclusion .............................................................................60

5. Composite Electrodes in 3-Terminal Tandem OPV Cells .........................62

5.1. Device Structure and Fabrication ..........................................................66

5.2. Device Performance ............................................................................68

5.3. A Materials Combination for High-Efficiency 3-Terminal Tandems ..............74

5.4. Section Conclusion .............................................................................78

6. Composite Fabrication and Cost Structure ..............................................80

6.1. Lab-Scale Composite Fabrication Method ..............................................81

6.2. Large-Scale Composite Cost Analysis ....................................................82

6.3. Replacing PEDOT in the Composite Structure .......................................84

6.4. Spray-Coating Ag Nanowires onto PMMA ...........................................89

6.5. Section Conclusion .............................................................................95

7. Conclusion .............................................................................................96

8. References.............................................................................................97
List of Tables

Table 2.1. Figures of merit and OPV cell performance for various transparent conductors. ................................................................. 18

Table 6.1. Large-scale composite materials cost ......................................................... 83

Table 6.2. Effects of higher pressure on the sheet resistance of spray-deposited composite electrodes without heat treatment ......................................................... 91

Table 7.1. Transparent conductor performance, including data presented in this thesis. ............................................................................. 102
List of Figures

Figure 1.1. Record organic photovoltaic efficiencies reported from 2001 through 2010. .4

Figure 1.2. Schematic of organic photovoltaic device structure with energy diagram. .....5

Figure 1.3. Molecular structures of the materials used in this study.................................8

Figure 1.4. Example of solar cell current density vs. voltage (J-V) curve. .........................10

Figure 1.5. The price of indium metal in dollars per kilogram from 2002 until 2006. ....13

Figure 1.6. SEM images of crack formation in ITO as a result of substrate bending. .....15

Figure 2.1. Transparent electrode fabrication procedure and cross-section SEM images of
laminated silver nanowires..................................................................................................21

Figure 2.2. SEM images of composite electrodes using 125 nm of PEDOT:PSS ..........22

Figure 2.3. Tapping mode AFM scan of the PEDOT:PSS / Ag nanowire surface ........23

Figure 2.4. Transmission over the wavelengths 350 – 800 nm comparing ITO on glass
and plastic with PEDOT:PSS / Ag nanowire composites on glass and plastic...........26

Figure 2.5. Current density vs. voltage for P3HT:PCBM solar cells on ITO on glass and
plastic and on PEDOT:PSS / Ag nanowires on glass and plastic ...........................29

Figure 3.1. Schematic of nanowire being pressed into polymer film....................33

Figure 3.2. Hardness vs contact depth for nanoindentation of 125 nm PEDOT:PSS film
and 500 nm PEDOT:PSS film on glass. .................................................................36

Figure 3.3. SEM image of PEDOT:PSS / Ag nanowire composite surface ..........37

Figure 3.4. Total absorption of a bare Ag nanowire film not including substrate
reflections......................................................................................................................38

Figure 3.5. Optical reflection and scattering over the visible spectrum for a bare
nanowire film (purple) and a PEDOT / Ag nanowire composite film ...............39
Figure 3.6. SEM images of bare Ag nanowire films and PEDOT:PSS / Ag nanowire composite films as deposited and after heating at 280 °C for 20 minutes.........42

Figure 3.7. Plot of the effects of heat and surface diffusion with increasing time, showing instability formation and nanowire spheroidizing, from Nichols and Mullins.97 ......45

Figure 4.1. Schematic of gravure printing process..............................................................49

Figure 4.2. Device structure and lamination process with cross-sectional and top down SEM views of PEDOT:PSS / Ag nanowire top electrode ........................................53

Figure 4.3. Specular and total transmission over the range of visible wavelengths for the organic layers used in the device with and without the top Ag nanowire mesh. ......56

Figure 4.4. Current density-voltage (J-V) curves for non-optimized devices measured as-fabricated (red), following ms pulsing at -5 V (yellow), and at -10 V (red) in the dark (dashed lines) and under 80mW/cm² AM1.5G illumination (solid lines).......58

Figure 4.5. Current density vs. voltage characteristics for partially optimized organic PV cells with PEDOT:PSS / Ag nanowire top electrodes. .................................................59

Figure 5.1. Two terminal two-junction tandem PV cell and three-terminal two-junction tandem PV cell with intermediate electrode.142 .................................................................65

Figure 5.2. Schematics relevant to the three-terminal tandem OPV cells fabricated in this work. .......................................................................................................................67

Figure 5.3. Current density vs. voltage characteristics for front inverted semitransparent polymer cell and back evaporated small molecule cell .......................................70

Figure 5.4. First published OPV devices fabricated with and Ag nanowire mesh transparent anode.74 .............................................................................................................71
Figure 5.5. Absorption measured for the bare P3HT:PCBM blend (purple) and the bare CuPc:C₆₀ bilayer on glass with calculated % EQE for the polymer front cell and the small molecule back cell in the three-terminal tandem structure..........................73

Figure 5.6. High efficiency three terminal tandem OPV structure simulated in this work with previously published current density vs. voltage characteristics for a single junction PCDTBT:PC₇₀BM OPV cell.¹⁵ .................................................................75

Figure 5.7. Experimentally measured absorption for P3HT:PCBM and PCDTBT:PC₇₀BM blend films on glass with calculated EQE from optical simulations for a P3HT:PCBM front cell and a PCDTBT:PC₇₀BM back cell in the three terminal tandem structure.................................................................77

Figure 6.1. Scanning electron micrographs of PMMA / Ag nanowire composite films. .86

Figure 6.2. Current density vs. voltage for the device structure: PMMA:AgNW / PEDOT (50 nm) / P3HT:PCBM (200 nm) / Ca (7nm) / Al (150 nm)..........................87

Figure 6.3. SEM image of sprayed commercial 16 µm long Ag nanowires on 125 nm of PMMA. ..............................................................................................................................................90

Figure 6.4. Angled SEM images of sprayed Ag nanowire / PMMA composite films with embedded and fused wire-wire junctions.................................................................92

Figure 6.5. Transmission curves and sheet resistance values for Ag nanowire / PMMA composites deposited via spin-casting PMMA and spraying nanowires onto a glass substrate. ................................................................................................93
1. Introduction

Organic semiconductors and optoelectronic devices has been a growing field since the first controllably conducting polymers were reported in the late 1970s. These thin-film devices are attractive for several reasons, such as chemical tunability, ease of processing, and the potential for low cost. Organic light-emitting diodes (OLEDs) were the first devices realized. They have been studied extensively in academia, and have now reached the point of commercialization on a large scale for display purposes. OLEDs are high-brightness, low power, have viewing angles of 180°, and have the potential to be both low-cost and flexible. They can emit red, green, or blue light for pixels in a display, or white light for lighting applications. Organic photovoltaic (OPV) cells have followed OLEDs and, though beginning with low-efficiency devices, they have now reached efficiencies that have the potential to be competitive with their inorganic counterparts, and companies have begun to commercialize this technology as well. Organic PV cells have the potential to be very low-cost, as their active materials can be deposited via high-throughput roll-to-roll processes, which is critical for photovoltaics to become an economically viable energy source.

Organic optoelectronic devices, as well as many other thin-film inorganic optoelectronic devices, all require a transparent electrode to allow light to enter (in the case of photovoltaics) or leave (in the case of emissive devices) the device, while conducting charge across its surface. This film must be highly transparent, have a low sheet resistance, and be compatible with high-quality device production. The state of the art material, tin-doped indium oxide (ITO), has very high performance, but also has many
drawbacks, which will be described in detail in section 1.3. This thesis presents a replacement composite material for ITO comprised of silver nanowires and polymer films that solves many of the issues with inorganic transparent conductors while maintaining or exceeding the high performance standards set by ITO. The use of these films is demonstrated in organic photovoltaic devices fabricated by well-established methods and show performance equivalent to or better than those fabricated on ITO. In addition, these composite films are more versatile than ITO and can be used to fabricate new organic photovoltaic device architectures that are not possible using ITO films. This thesis will also discuss the mechanical, optical, and thermal properties of these composites along with their fabrication details and potential large scale cost structure.

1.1. Organic Photovoltaic Devices

Photovoltaic cells are a promising source of clean, renewable energy, as they do not consume fuel, create no emissions, have no moving parts, and can, in various installations, produce power on either a consumer or power plant production scale. However, when compared with the cost of energy from coal-fired power plants, by which over half of the energy used in the United States is produced,\textsuperscript{20} energy from photovoltaics is expensive.\textsuperscript{21} The most efficient photovoltaic cells are produced from single crystal materials such as gallium arsenide and silicon.\textsuperscript{16} The vast majority, 78-80\%, of solar cells produced and sold are silicon cells.\textsuperscript{22} However, single crystal inorganic materials are very expensive to produce, as they have to be very high purity to make efficient devices. More recently, thin film photovoltaic devices have been developed that use less material and
can be fabricated and processed much more economically than single crystal PV cells.\textsuperscript{23} On the economic metric of dollars per watt peak, by which various PV technologies can be compared, these thin film devices can be competitive with single crystal solar cells.\textsuperscript{24}

Organic solar cells are an attractive emerging thin-film technology due, in part, to their low-cost potential. Organic semiconductors can be deposited in thin films via roll-to-roll processes such as thermal evaporation or printing from solution, and the raw materials are abundant and can be synthesized chemically, thus new materials are always in development to drive efficiency upward. Figure 1.1 shows record cell efficiencies, along with their reporting institutions, for organic photovoltaic cells from 2001 through the present record, which stands at 8.3%. Through cell processing and architecture developments as well as new active materials synthesis, the record cell efficiencies have steadily climbed to the point where OPV can be competitive with other thin-film technologies such as amorphous silicon,\textsuperscript{16} and modules are projected to hit the consumer marketplace as early as 2012.\textsuperscript{19} The industry’s vision is for OPV cells to be cheap, flexible, lightweight, and easy to install. There are, however, remaining issues that need to be addressed. One is that organic materials have inherently poorer electronic properties than inorganic crystalline materials and thus the active layer films must be thin in order to collect charge from the cell. However, if the active layer is too thin, not enough light will be absorbed to produce high efficiencies. New materials\textsuperscript{14, 15} and architectures\textsuperscript{25} are being developed in which a larger portion of the solar spectrum is absorbed, and this is necessary to eventually increase the cells’ efficiencies beyond 10%. The lifetime of these cells are also in question, as inorganic PV cells have an operating lifetime of up to 25 years,\textsuperscript{22} whereas OPV will need effective encapsulation to protect the active materials.
from atmosphere and moisture.\textsuperscript{26-28} In addition, none of the record efficiency OPV cells have actually been fabricated using a roll-to-roll process on flexible substrates,\textsuperscript{14,15,29} and thus the projected cost and efficiency structure has not been proven. However, research is ongoing in these areas, and this thesis work will touch on some of issues, including the most flexible OPV cell reported to date.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Record organic photovoltaic efficiencies reported from 2001 through 2010. Reporting institution is noted.\textsuperscript{17,19,30}}
\end{figure}

Organic solar cells, like other thin film PV technologies and other organic optoelectronic devices, have a sandwich-type structure, with an optically and electrically active layer placed between two electrodes. A schematic of a typical device structure is shown in Figure 1.2. One of the electrodes must be transparent as well as conductive to allow light to enter the cell. The material most frequently used as a transparent electrode
for OPV cells is indium tin oxide (ITO). The other electrode is generally a reflective metal such as aluminum or silver, which, in reflecting light, allows any light not absorbed in the cell on the first pass to have a second pass back through the device. For optimal device performance, these electrodes must make contact with the active layer in such a way that there is no energy barrier to charge transfer.\textsuperscript{31} To this end, often times interface layers to transport charges from the active layer to the electrodes are used.\textsuperscript{32-34} The active layer is comprised of an electron donating organic semiconductor and an electron accepting organic semiconductor to form a heterojunction. In the most efficient devices, these materials are mixed on the nanoscale to form a bulk heterojunction.\textsuperscript{35,36}

\textbf{Figure 1.2.} Left: schematic of organic photovoltaic device structure. Right: energy diagram of OPV materials and operation with an incoming photon and exciton formation.

This bulk heterojunction film morphology is tied directly to the operation principles of the OPV cell. First, light is absorbed in the bulk heterojunction active layer in the cell.
This photon transfers its energy to an electron sitting in the highest occupied molecular orbital (HOMO) level of one of the active materials (shown in Figure 1.2 in the poly-3-hexylthiophene donor polymer). This energetic electron is promoted to the lowest occupied molecular orbital (LUMO) energy level, leaving a positively charged hole in the HOMO where the electron once sat. The Coulombic binding energy between this electron and the created hole is significant enough such that the carriers do not become free, but are linked as a pair of charges called an exciton. This exciton must then be split so that charge can be extracted from the cell. Exciton splitting occurs at the interface between the donor and acceptor material, where the exciton will be split by the internal field, as it is energetically favorable for the electron to sit in the acceptor material and the hole in the donor. The exciton must diffuse to an interface for this to occur. The exciton has a short, finite lifetime, on the order of a few hundred picoseconds, before the electron will recombine with the hole. Thus, there is also a finite diffusion length over which the exciton can move, typically between 5 and 10 nm. If it does not find an interface over which it can split and transfer charge within this diffusion length, it recombines and the absorbed energy is lost. The bulk heterojunction design creates a large surface area between the donor and acceptor for the exciton to diffuse toward. It is also crucial that the nanoscale mixing of the donor and acceptor molecules in the bulk heterojunction is on the optimal length-scale, with domains on the order of twice the exciton diffusion length. Once the exciton is split, and charge is transferred, the electron must make its way through the acceptor to be collected at the cathode while the hole must travel through the donor to be collected at the anode. This necessitates that the phases of donor and acceptor in the bulk heterojunction morphology are continuous so that charge
extraction can occur, and that the respective materials have reasonable charge carrier mobilities for the charges they are transporting. For solution processed OPV cells, the bulk heterojunction morphology optimization can be controlled during active layer deposition by a careful choice of solvent, drying conditions, ratio of blend components, and heat treatments. Due to the relatively low charge mobility in organic materials and their limited thin-film light absorption, a fundamental trade-off in organic PV cell efficiency occurs: the OPV cell must be thick enough to absorb light, but not too thick such that the excitons cannot split and the charge cannot be extracted from the cell.

While organic photovoltaic cells can be fabricated from blends of both small organic molecules and polymers, one particular materials system was chosen for use and study in this work. The materials combination of the electron donating polymer regioregular poly-(3-hexylthiophene) (P3HT) and the electron accepting fullerene derivative C_{61} butyric acid methyl ester (PCBM) have been reported to produce OPV efficiencies over 4%. Schematics of the molecules can be seen in Figure 1.3. These materials are readily available and have been widely studied in the academic community. Due to the regioregularity of P3HT’s side-chains and the strong delocalization of the pi electron systems along the backbone allowing it to attain a high degree of crystallinity, it can reach charge mobilities as high as 0.1 cm^2/V•s. Fullerenes derivatives such as PCBM are the most commonly used and studied electron acceptors in polymer PV cells. This is because the fullerene molecule has a very high electron-affinity while the methyl ester tail allows the molecule to be soluble in the same organic solvents, such as chlorobenzene and ortho-dichlorobenzene, as the polymer. Thus, while it is
improbable that P3HT:PCBM photovoltaic cells will become a commercially competitive technology,\textsuperscript{51} they are a model bulk heterojunction OPV system, are well-understood by the scientific community,\textsuperscript{26, 29, 31, 33, 34, 38, 41, 43, 46, 51} and produce reasonably good efficiencies with which to evaluate the electrodes fabricated and presented in this study.

**Figure 1.3.** Molecular structures of the materials used in this study. From left, electron donating polymer poly-(3-hexylthiophene) (P3HT), electron accepting fullerene C\textsubscript{61} butyric acid methyl ester (PCBM) and conducting polymer suspension poly-(4,3-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS).

The other molecular schematic in Figure 1.3 is of the polymer blend poly-(4,3-ethylene dioxythiophenepoly(styrene-sulfonate) (PEDOT:PSS). It is intrinsically conducting, and is packaged in an aqueous suspension that can be cast into thin films.\textsuperscript{55} PEDOT:PSS is commonly used as an interface layer in optoelectronic devices between the conductive transparent anode and the active layer of OLEDs\textsuperscript{56-58} and OPV cells.\textsuperscript{14, 15, 26, 29, 49, 51} It is used to adjust the workfunction of the anode, promoting hole transport to the
A conductive electrode, while planarizing the anode surface.\textsuperscript{56-58} PEDOT:PSS is solution-processable, resistant to organic solvents, and can have low lateral conductivity to minimize cross-talk between devices.\textsuperscript{55} It is also transparent in very thin films.\textsuperscript{59} For these reasons PEDOT:PSS is used as a hole transport layer in high efficiency OPV cells, and in this work it figures prominently into the fabrication of composite electrodes.

\subsection{1.2. Evaluating Solar Cell Efficiency}

To measure how efficient a solar cell is, a voltage is applied across the electrodes and swept from negative to positive voltage, in the case of OPV cells, from -1 V to 1V in the dark and under illumination. An example of a typical current density vs. applied voltage (J-V) curve in the dark (grey) and light (green) is shown in Figure 1.4. The saturation photocurrent produced under illumination can be seen in the vertical distance between the dark and light curves in reverse bias. The cell produces power under illumination in forward bias, in the third quadrant of the plot shown.
**Figure 1.4.** Example of solar cell current density vs. voltage (J-V) curve in the dark (grey) and under illumination (green). Open circuit voltage (Voc), short circuit current density (Jsc), and fill factor (FF) are noted on the plot.

The power conversion efficiency (PCE) of a solar cell is defined as:

\[
PCE = \frac{\text{power generated}}{\text{illumination}} = \frac{P_{\text{MAX}}}{L}
\]

(1.1)

where \(L\) is the illumination power intensity per area in watts per square cm and \(P_{\text{MAX}}\) is the maximum power produced by the cell, which is defined as the maximum possible value of the electrical power produced in watts per area:

\[
P_{\text{MAX}} = J_{\text{MP}} \times V_{\text{MP}}
\]

(1.2)
where \( J_{\text{MP}} \) is the current density in amps per square cm at the maximum power point and \( V_{\text{MP}} \) is the voltage at the maximum power point. This product is also illustrated in Figure 1.4 by area inside the green square.

There are three characteristic device values that are measured when a solar cell is tested for efficiency. The first is the short circuit current density, \( J_{\text{sc}} \), which is the amount of photocurrent produced at zero applied voltage. The second is the open circuit voltage, \( V_{\text{oc}} \), which is the amount of voltage produced at zero current. The open circuit voltage in organic solar cells corresponds to the difference in energy between the HOMO of the donor material and the LUMO of the acceptor material, providing the electrodes make Ohmic contacts.\(^{31}\) The values of \( V_{\text{oc}} \) and \( J_{\text{sc}} \) are noted where they appear on the plot in Figure 1.4. The third characteristic device metric is the fill factor (FF), which is defined as:

\[
\text{FF} = \frac{V_{\text{MP}} \times J_{\text{MP}}}{V_{\text{oc}} \times J_{\text{sc}}} \quad (1.3)
\]

This can be visualized in Figure 1.4 as the area of the large grey box divided by the area of the green box, and represents the fraction of the possible power that is produced by the cell, given the voltage and current produced. The better the cell is, the closer to 1 this value will be. Looking closely at these characteristic values and their definitions, they can be related to overall power conversion efficiency by simply rearranging and combining equations 1.1, 1.2, and 1.3:

\[
\frac{\text{FF} \times V_{\text{oc}} \times J_{\text{sc}}}{L} = \frac{P_{\text{MAX}}}{L} = \text{PCE} \quad (1.4)
\]
If the device is tested with an L value of one sun, or 100 mW/cm², as is done in a standard testing environment, the power conversion efficiency is simply the product of Voc, Jsc, and FF. Thus these characteristics are important indications of the quality of the device, and maximizing them will maximize the power conversion efficiency.

1.3. Indium Tin Oxide Transparent Electrodes

All organic optoelectronic devices, including OLEDs and OPV cells, require a transparent electrode. Tin-doped indium oxide (ITO) is the highest-quality transparent conducting film used in optoelectronic devices today and therefore is the one most commonly used in organic photovoltaic cells as well as other technologies such as LCD and light-emitting displays. There are other transparent conducting oxides in use by industry such as fluorine-doped tin oxide and zinc oxide, but none of these other materials have the same low sheet resistance combined with high transparency as ITO. However, despite its high performance as thin films on glass substrates, the use of ITO and relying on this material for the production of flexible and low-cost devices has many drawbacks.

Cost is a primary issue both in raw material cost and in deposition methods. For optoelectronic device such as organic photovoltaics that are relying on low-cost to become competitive in the marketplace, this is critical. Indium is a rare metal. It is derived from the mining and refinement of zinc ores and as such there are no known pure indium sources in the earth’s crust. Approximately 70 percent of refined indium is used
for transparent conductive coatings for the display industry,\textsuperscript{61} and this has driven the cost upwards by an order of magnitude between 2002 and 2006, as shown in Figure 1.5.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure1.5.png}
\caption{The price of indium metal in dollars per kilogram from 2002 until 2006.}
\end{figure}

The sputtering process by which ITO is deposited onto a substrate is also expensive and time-consuming. Commercially-produced ITO is deposited by dc-magnetron sputtering,\textsuperscript{61} a vacuum system that can cost upwards of $15M depending on capacity. In addition, the materials usage efficiency of dc-magnetron sputtering is low, and frequently only 20-35\% of the target is utilized, causing long stretches of machine downtime. The extra target material can be recycled, but this is also an expensive process, and companies must carry the inventory expense into the cost of their produced films. Sputter rates vary from 0.1 nm per second to 10 nm per second based on the application of the film, but in general, for lower sheet resistances slower deposition rates must be used. Thus, the ITO production process is low-throughput and this, combined with equipment costs and raw
material price and usage, makes ITO a very expensive material to use. In fact, in cost studies of organic photovoltaic cells, ITO is shown to be the single most expensive layer, at $8 - $13 per square meter.\textsuperscript{62}

There are inherent performance limitations of indium tin oxide. ITO is a wide-bandgap semiconductor, doped to degeneracy, and the processing and deposition conditions have a profound effect on the properties of the film. Ideally, the polycrystalline film has few microstructural defects, a maximum number of activated Sn doping sites, and a sub-stoichiometry of oxygen.\textsuperscript{61} This is to maximize free carriers in the film while preventing electron scattering sites, and processing conditions such as oxygen partial pressure during deposition can affect these properties greatly. In addition to atmospheric conditions, the temperature of the substrate must be elevated to between 200 and 300 degrees Celsius in order to create the optimal polycrystalline microstructure and minimize those defects.\textsuperscript{61} Deposited on glass, ITO can have sheet resistances as low as 20 ohms per square with 90\% transmission. However, many industries, including organic PV and the display industry envision flexible, lightweight devices built on plastics.\textsuperscript{5,63-65} ITO can be sputtered in a roll-to-roll configuration onto webs of plastic up to 7 m wide, but the performance of ITO is limited on these substrates due to the heating requirement for the lowest sheet resistances. These films are typically deposited on optical quality poly(ethylene terephthalate) (PET), and the low temperatures and higher throughputs with plastic roll-to-roll deposition produce films with far more microstructural defects and far fewer activated dopants. This results in sheet resistances between 40 ohms per square and 400 ohms per square with comparable transmission to the films on glass.\textsuperscript{61} Another major performance limitation of ITO is also directly related to its deposition on plastic
substrates – ITO is inherently brittle. As a film is bent, microscopic cracks begin to form on the surface and a corresponding increase in sheet resistance occurs.\textsuperscript{66-68} Figure 1.6 shows scanning electron microscope (SEM) images of crack formation as a result of bending ITO.\textsuperscript{66} The images are of ITO on polymer substrates that has been bent and then flattened again for imaging. This is a significant disadvantage for applications in which the final device structure is supposed to be flexible, bendable, or foldable, as ITO places a limit on the minimum possible bending radius.

\textbf{Figure 1.6.} SEM images of crack formation in ITO as a result of substrate bending. Top: tension, bottom: compression.\textsuperscript{66}

Thus, for both cost and performance considerations, a replacement transparent conductor is needed. This material should have figures of merit of transparency and conductivity that meet or exceed the values of ITO while being more mechanically robust and not requiring expensive or high-temperature substrate processing. This material
should perform equally well on any type of substrate, cost less than ITO, and be compatible with high-quality optoelectronic devices. This thesis work presents a composite material system comprised of silver nanowires and polymer films that meet these criteria, fully characterizes these films, and demonstrates their use as a transparent conductor in various high-efficiency organic photovoltaics.
2. Polymer / Ag Nanowire Composites

Tin-doped indium oxide (ITO) is an essential component of many optoelectronic devices\textsuperscript{60, 69} including displays and thin-film photovoltaic (PV) cells. However, ITO has several shortcomings. The price of indium has increased by an order of magnitude over the past five years due to display industry demand, and the sputtering process by which ITO is deposited is expensive and slow.\textsuperscript{51} This is critical for thin-film PV cells as these technologies are aiming at a low cost per area.\textsuperscript{23} Both the display and PV industries have envisioned flexible devices, but to obtain the lowest ITO sheet resistance, the substrate must be treated at a temperature that is too high for plastics to withstand,\textsuperscript{61, 70} leading to decreased performance. Furthermore, ITO is brittle and cracks when bent.\textsuperscript{66, 68} Hence, there is a demand for a transparent conductor with substrate-independent performance equal to or better than ITO with a lower materials cost and improved robustness, deposited through a low-cost, low-temperature method.\textsuperscript{71} It is also essential that the transparent conductor can be used in high-quality optoelectronic devices. As in other reports, we use organic PV (OPV) cells to evaluate the performance of a transparent conductor.\textsuperscript{72-78} This is apt because the commercial success of OPV requires a very low cost per area and therefore hinges upon an ITO replacement, as ITO is the most expensive layer in these cells.\textsuperscript{62} In recent years, the efficiency of OPV has increased dramatically. The widely studied regioregular poly-(3-hexylthiophene) and C\textsubscript{61} butyric acid methyl ester (P3HT:PCBM) bulk heterojunction has produced solar cell efficiencies over 4%.\textsuperscript{29, 49, 50} Newer polymers with broader absorption have produced cells with efficiencies over 6%.\textsuperscript{14, 15}
2.1. Solution-Processed ITO Replacements

Many materials are emerging as solution-processed transparent electrodes, including carbon nanotubes,\textsuperscript{75} 79-83 reduced graphene oxide,\textsuperscript{76} 84-86 films using both carbon components,\textsuperscript{78} highly conductive poly-(4,3-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS),\textsuperscript{72, 73, 87} and Ag nanowire films.\textsuperscript{74, 77, 88} The figures of merit for these materials, including sheet resistance, transparency, and best reported OPV cell performance are listed in Table 1.\textsuperscript{73-76, 78, 89}

**Table 2.1. Figures of merit and OPV cell performance for various transparent conductors.**

<table>
<thead>
<tr>
<th>Transparent Conductor</th>
<th>Rs Ω/sq</th>
<th>% Transmission</th>
<th>Best OPV Cell Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO on glass</td>
<td>20</td>
<td>90</td>
<td>&gt; 4% (P3HT:PCBM)\textsuperscript{26, 29}</td>
</tr>
<tr>
<td>ITO on PET</td>
<td>42</td>
<td>91</td>
<td>3.66% (P3HT:PCBM)\textsuperscript{89}</td>
</tr>
<tr>
<td>PEDOT PH750 + 5% DMSO</td>
<td>102</td>
<td>84 (at 500 nm)</td>
<td>3.5% (P3HT:PCBM)\textsuperscript{73}</td>
</tr>
<tr>
<td>Carbon Nanotubes (CNT)</td>
<td>200</td>
<td>85</td>
<td>2.5% (P3HT:PCBM)\textsuperscript{75}</td>
</tr>
<tr>
<td>Graphene (solution)</td>
<td>5000</td>
<td>80</td>
<td>0.4% (CuPc:C60)\textsuperscript{76}</td>
</tr>
<tr>
<td>Graphene + CNT</td>
<td>240</td>
<td>86</td>
<td>0.85% (P3HT:PCBM)\textsuperscript{78}</td>
</tr>
<tr>
<td>Ag Nanowires</td>
<td>10</td>
<td>85</td>
<td>0.4% (CuPc:PTCB1)\textsuperscript{74}</td>
</tr>
<tr>
<td>PEDOT / Ag Nanowires on glass</td>
<td>12</td>
<td>86</td>
<td>4.2% (P3HT:PCBM)</td>
</tr>
<tr>
<td>PEDOT / Ag Nanowires on PET</td>
<td>17</td>
<td>83</td>
<td>3.8% (P3HT:PCBM)</td>
</tr>
</tbody>
</table>

Also in Table 2.1 are the figures of merit for ITO on glass and on polyethylene terapthalate (PET) plastic, measured in this work. It is reasonable to conclude that for the
carbon-based materials, the poor OPV performance with respect to ITO devices stems directly from the high sheet resistances of the anodes, and until the anode figures of merit improve, the device performance has reached its limit. However, this cannot be the case with Ag nanowires, as these films have both sheet resistance and transparency comparable to ITO, yet the best device efficiency reported is only 0.4%.\textsuperscript{74} Thus there must be another reason why these films cannot function as an ITO replacement.

In this work, we prove that Ag nanowire film roughness is why these electrodes are incompatible with efficient devices, and we solve this significant morphology issue, transforming the promise of Ag nanowire electrodes into a truly effective ITO replacement technology. We achieve this by creating an organic – inorganic composite, embedding Ag nanowires into the conducting polymer PEDOT:PSS. This results in smooth, solution-processed transparent conducting films that have sheet resistances and transmissivities comparable to ITO on glass and better than ITO on plastic. We produce high-efficiency P3HT:PCBM solar cells with PEDOT:PSS / Ag nanowire anodes that have the same performance metrics as those fabricated on ITO on glass, showing that PEDOT:PSS / Ag nanowire films are the first solution-processed ITO replacement meeting every performance requirement. By fabricating the composites and devices on flexible substrates, we also show that PEDOT:PSS / Ag nanowire films have superior mechanical and electrical properties to ITO, and we are able to demonstrate the highest-efficiency flexible P3HT:PCBM solar cell reported. The figures of merit for the composites are shown in Table 2.1 and match or exceed ITO, performing far above and beyond other solution-processed transparent conductors. This technology, combined with
the recent advances in efficiency,\textsuperscript{14, 15} could allow OPV to become commercially competitive, as well as enable flexible displays to become a reality.

\section*{2.2. PEDOT / Ag Nanowire Composite Films: Morphology}

Films of 50 - 100 nm-diameter Ag nanowires were drop-cast from suspension onto glass.\textsuperscript{74, 77} The nanowires were then laminated onto spin-cast PEDOT:PSS films of varying thickness at $2.4 \times 10^4$ psi in order to investigate the morphology of the composites. The fabrication process is illustrated in Fig. 2.1a. In all cases, the wires transferred completely to the polymer. Figures 2.1b – 2.1e show cross-sectional scanning electron micrographs (SEMs) of nanowires embedded into four different thicknesses of PEDOT:PSS: 25 nm (1b), 50 nm (1c), 75 nm (1d), and 100 nm (1e). There are no observable differences in the resulting films to the eye, nor are there apparent differences in top view SEMs. However, cross-sectional SEMs reveal that as the PEDOT:PSS thickness increases, the composite morphology changes dramatically. On 25 nm of PEDOT:PSS, the nanowires transfer to the PEDOT:PSS but do not sink into the polymer along their lengths, resulting in a forest-like structure. As the PEDOT:PSS layer increases to 50, 75 and 100 nm, the wires sink into the PEDOT:PSS and the meshes become flatter, the polymer filling the deep spaces between the wires. In order to create completely flat films for use as electrodes, the PEDOT:PSS needs to be thick enough to embed both single wires and the wire-wire junctions that are essential to conductivity.
Figure 2.1. 2.1a) Transparent electrode fabrication procedure. 2.1b-e) Cross-section SEM images of silver nanowires laminated under the same conditions onto varying thicknesses of PEDOT:PSS: 2.1b) 25 nm, 2.1c) 50 nm, 2.1d) 75 nm and 2.1e) 100 nm.

Figure 2.2 shows SEMs of Ag nanowires laminated into 125 nm of PEDOT:PSS, resulting in a transparent, conductive, composite film with a surface flat enough for use as an electrode. A top view SEM is shown (Figure 2.2a). Using image-processing
software, we determined that the Ag nanowires cover 29% of the film. Cross-sectional SEMs (Figure 2.2b, colorized for clarity) show that the nanowires are nearly completely embedded into the PEDOT:PSS. An off-angle cross-section (Figure 2.2c) shows that all wires are in the plane of the substrate and appear fully connected. Figure 2.2d (colorized for clarity) confirms that the wire-wire junctions are embedded into the PEDOT:PSS layer, allowing the upper wires to stay flush.

![SEM images of composite electrodes using 125 nm of PEDOT:PSS.](image)

**Figure 2.2.** SEM images of composite electrodes using 125 nm of PEDOT:PSS. (a) top view. (b) cross-section. (c) angled cross-section. (d) close-up angled surface showing junctions of nanowires embedded into the polymer.

Tapping mode AFM was used to further characterize the composite’s surface morphology. The AFM topographical image of the PEDOT:PSS / Ag nanowire film is shown in Figure 2.3. The RMS roughness was measured at 11.9 nm, with the nanowires
protruding between 20 and 30 nm above the PEDOT:PSS surface as shown in the line scan also in Figure 2.3. This is in contrast to bare Ag nanowires, in which top-to-bottom height can be as large as 200-300 nm, depending on the number of wires stacked in junctions. The wire used in the line scan is denoted by the dark blue box in the topographical image. We note that while the maximum and minimum heights are accurate, the bell-shape of the line scan does not reflect the actual topography (see Fig. 2), but is an artifact of the AFM scan. For comparison, the RMS roughness of ITO films was measured at <3 nm, substantially smaller than the value for our composites. However, as will be shown using OPV device data, this amount of roughness does not impair the preparation of high quality devices.

*Figure 2.3. Tapping mode AFM scan of the PEDOT:PSS / Ag nanowire surface (top),*
and AFM height line profile of a nanowire (bottom). The wire used in the line scan is indicated by the dark blue box in the topographical image.

2.3. PEDOT / Ag Nanowire Composite Films: Performance

Sheet resistance and optical transmission measurements were taken to compare the performance of the composite films to that of ITO. Samples were prepared on glass and on 5-mil PET. On glass, the ITO sheet resistance was 20 Ω/□, while the PEDOT:PSS / Ag nanowire composite from Fig. 2.2 was 12 Ω/□. On PET, there was a larger difference between the films, as the ITO sheet resistance was 42 Ω/□ whereas the PEDOT:PSS / Ag nanowire film was only 17 Ω/□. Because no high-temperature processing steps are required in the composite film fabrication, the sheet resistance is nearly substrate-independent, and the value for the composite on PET is lower than ITO on glass. Sheet resistance measurements of 125 nm of PEDOT:PSS result in values greater than 10 MΩ. This means that the PEDOT:PSS is not conducting over large scales, and the bulk of the composite conductivity occurs in the nanowires.

Transmission measurements were taken with the light incident through the substrate. An integrating sphere was used to collect direct and diffuse transmission, as it has been shown that 17-20% of the light transmitted through Ag nanowires is diffuse. The measurements do not include substrate reflections. The average transmission of ITO on glass (20 Ω/□) over wavelengths 350 – 800 nm is 90% (Fig. 2.4a, light blue solid). The PEDOT:PSS / Ag nanowire composite (12 Ω/□) on glass has an average transmission of 86% (Figure 2.4a, green solid). The inset photograph (Figure 2.4a) demonstrates the
transmission of PEDOT:PSS / Ag nanowires on plastic with the Stanford University seal visible behind the inner square where the film is located. On PET, the transmission spectrum of the ITO is very different, as ITO transmission varies with thickness and manufacturing process. The average transmission of ITO on plastic (Figure 2.4a, blue dashed) is 91%, although the standard deviation is much greater than on glass. The PEDOT:PSS / Ag nanowire film on plastic (Figure 2.4a, green dashed) shows a lower average transmission at 83%, although it is important to note that the spectral response of the composites is far more substrate-independent than that of ITO. The 3% lower transmission for this sample as compared to the one on glass can be attributed to variations in the nanowire suspension. The slightly lower transmission in the PEDOT:PSS / Ag nanowire composite as compared to ITO is in large part due to parasitic absorption in the PEDOT:PSS layer. The transmission spectrum of the PEDOT:PSS layer alone (Figure 2.4a, dark blue), has an average value of 95.5% over the spectral range. This accounts for the lower transmissivity obtained here compared to previous studies of Ag nanowires.\textsuperscript{74, 77, 88}
Figure 2.4. (a) Transmission over the wavelengths 350 – 800 nm for ITO on glass (light blue solid) and on plastic (light blue dashed), 125 nm PEDOT:PSS on glass (dark blue), and 125 nm PEDOT:PSS with nanowires on glass (green solid) and on plastic (green dashed). ITO and PEDOT:PSS / Ag nanowires sheet resistances on glass are noted. Inset (a) PEDOT:PSS / Ag nanowire film (inner square) on plastic in front of the Stanford University seal. (b) Sheet resistance vs. radius of curvature for ITO (blue) and PEDOT:PSS / Ag nanowires (green) on PET. Sheet resistance values for flat films are noted.

In addition to their lower cost, the composites are far more resilient to mechanical stress than ITO. To demonstrate this, films fabricated on flexible substrates were bent while the sheet resistance was measured. In Figure 2.4b, the sheet resistance of an ITO film on 5-mil PET (Sigma-Aldrich) is compared to that of a PEDOT:PSS / Ag nanowire composite prepared on 5-mil PET (Southwall Technologies) as a function of the substrate.
bending radius. The ITO sheet resistance increases significantly and irreversibly when a bending radius of 8.5 mm is reached, corresponding to a strain of 0.75%, in agreement with the literature. In contrast, the same experiment does not significantly alter the sheet resistance of the composite electrodes even at a bending radius of 1.2 mm (3.5% strain).

2.4. PEDOT / Ag Nanowire Composite Films: OPV Cells

Bulk-heterojunction photovoltaic cells using P3HT:PCBM were fabricated on ITO and on PEDOT:PSS / Ag nanowire films on both glass and plastic. For comparison, the same devices were also built on bare Ag nanowire films on glass. The transparent conductors served as anodes. In all cases, a 50 nm-thick PEDOT:PSS film was deposited by spin-coating, followed by a ~200 nm-thick photoactive layer. The vacuum-deposited cathode consisted of 7 nm of Ca followed by 200 nm of Al. All device areas were 7 mm². Current density vs. voltage for devices on glass / ITO (light blue lines), on bare Ag nanowires (dark blue lines), and on glass / PEDOT:PSS / Ag nanowires (green lines) in the dark (dashed lines) and under 100 mW/cm² AM 1.5G illumination (solid lines) are shown in Figure 2.5a. On glass / ITO, the open circuit voltage is 0.625 V, the short circuit current density is 10.4 mA/cm², the fill factor is 0.65, and the power conversion efficiency is 4.2%. On glass / Ag nanowires, the cell performance decreases substantially. The open circuit voltage is 0.415 V, the short circuit current density is 2.8 mA/cm², and the fill factor is 0.25, resulting in a 0.3% power conversion efficiency. This curve is representative of the performance of all P3HT:PCBM devices made on bare nanowires, with significant shunting and a poor fill factor. The optimal active layer morphology and
phase separation in bulk heterojunction OPV is critical to all points of operation.\textsuperscript{29, 43, 44}

The cell performance and controlled fabrication indicate that the morphology required for high efficiency cannot be achieved on rough Ag nanowires. This clearly demonstrates why Ag nanowire films are not a suitable ITO replacement despite having low sheet resistance and high optical transmission. This is not the case for the composite films. On glass / PEDOT:PSS / Ag nanowires, the open circuit voltage is 0.615 V, the short circuit current density is 10.4 mA/cm\textsuperscript{2}, the fill factor is 0.65, yielding the same power conversion efficiency, 4.2\%, as the device on ITO. There is no significant difference in device performance in any metric from the ITO device and these efficiencies, at above 4\%, are on par with the best cells reported using these materials.
**Figure 2.5.** Current density vs. voltage for P3HT:PCBM solar cells on ITO (light blue), on Ag nanowires (dark blue) and on PEDOT:PSS / Ag nanowires (green) in the dark (dashed) and under 100 mW/cm$^2$ of AM 1.5G illumination (solid) on glass (2.5a) and on plastic (2.5b). Inset 2.5b) P3HT:PCBM solar cell fabricated on plastic / PEDOT:PSS / Ag nanowires, viewed through the substrate.
Figure 2.5b shows current density vs. voltage for devices on plastic substrates on ITO (blue lines) and PEDOT:PSS / Ag nanowires (green lines) in the dark (dashed lines) and under 100 mW/cm² AM 1.5G illumination (solid lines). The inset shows flexible devices on PEDOT:PSS / Ag nanowires viewed through the substrate. In this case, the Voc for both devices is 0.605 V. Due to ITO transparency, that device has a higher Jsc, 10.8 mA/cm², versus 9.74 mA/cm² for the PEDOT:PSS / Ag nanowire device. However, because the composite sheet resistance is lower, the fill factor is raised from 0.52 on ITO to 0.64. This increases the efficiency from 3.4% on ITO to 3.8% on PEDOT:PSS / Ag nanowires on plastic, which is the highest efficiency flexible OPV cell fabricated using any transparent anode. Based on these results, we anticipate the use of these composites in other types of rigid and flexible thin-film solar cells and displays.

2.5. Section Conclusion

In this section, we have produced, presented, and characterized a truly effective ITO replacement by embedding Ag nanowires into conducting polymer. This raises the OPV performance with respect to rough Ag nanowire electrodes by an order of magnitude. The composites are low-cost, their performance is nearly substrate-independent, and they require no vacuum or high-temperature processing while being able to tolerate >5 times larger mechanical strain than ITO due to substrate bending. Based on the data in Table 2.1, our approach results in the best solution-processed transparent conducting film reported and the only one capable of replacing ITO in high-efficiency rigid and flexible
optoelectronic devices. This technology will help to enable applications such as flexible displays and low-cost photovoltaics.
3. Mechanical, Optical, and Thermal Properties of Laminated PEDOT:PSS / Ag Nanowire Composites

Polymer / silver nanowire composites have been shown in the previous section to be an effective replacement for indium-tin-oxide in organic photovoltaic cells, and show the potential to be used in other types of thin-film optoelectronic devices. These composites are compatible with high-efficiency devices because they have high transparency (86%), low sheet resistance (12 Ω/□), and low surface roughness (11.9 nm). They are fabricated by embedding a silver nanowire mesh film into a 125 nm spin cast film of the polymer poly-(4,3-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) via lamination at high pressure.

In this section we explore the mechanical and optical effects of this pressing process, in order to better understand the fabrication in detail, the optical effects of pressure on nanowire mesh films, and why these films are able to have the low roughness values that are compatible with high-efficiency OPV. We also explore the thermal stability of the composites relative to bare Ag nanowire films. We are able to understand the composite surface roughness in terms of the mechanical properties of the component materials as well as show that the composite films are more thermally stable than their bare Ag nanowire counterparts. These studies can help further an understanding on how to eventually improve the performance of these composite films.
3.1. Lamination Mechanics

Silver nanowires were synthesized using polyvinylpyrrolidone to direct the growth,\textsuperscript{90, 91} producing five-fold twinned structures\textsuperscript{92} with diameters between 50 and 100 nm.\textsuperscript{90-92} They were deposited from suspension in methanol onto glass, annealed, and pressed into a 125 nm thick PEDOT film following the procedure described in Section 2. The geometry of the pressing process for a single nanowire is illustrated in Figure 3.1.

![Figure 3.1. Schematic of nanowire being pressed into polymer film. Left, prior to pressing. Right, equilibrium force balance at the final pressing stage.](image)

Based on this geometry, there are two interfaces at which plastic deformation can occur: the interface between the PEDOT and the nanowire and the interface between the nanowire and the pressing surface. The indentation hardness of a material is defined as:

\[
\text{hardness, } H = \frac{\text{applied force, } F}{\text{indented area, } A}
\]  

(3.1)
Thus, for a single nanowire, two indentations are occurring, one at each interface. The nanowire indents the PEDOT and the press surface indents the nanowire. For a nanowire with length $L$, being pressed into the polymer using a force $F$, as illustrated in the force balance in Figure 1, at the PEDOT / nanowire interface:

$$W_1 \times L = \frac{F}{H_{\text{PEDOT}}} \quad (3.2)$$

where $H_{\text{PEDOT}}$ is the indentation hardness of the polymer and $W_1$ is the width of the indented area. At the press surface / nanowire interface:

$$W_2 \times L = \frac{F}{H_{\text{AgNW}}} \quad (3.3)$$

where $H_{\text{AgNW}}$ is the hardness of the nanowire and $W_2$ is the width of the indented area. Because the force and the length are the same, the two equations can be divided to produce a relationship between the two ratios:

$$\frac{W_2}{W_1} = \frac{H_{\text{PEDOT}}}{H_{\text{AgNW}}} \quad (3.4)$$

Thus the surface morphology of the composite can be modeled through this force balance and confirmed by finding the indentation properties of the individual components. This can be done via nanoindentation, which simulates the nanowire pressing into the polymer by lowering an indentation tip with a known hardness onto a surface using a specified force to cause plastic deformation of the surface. When the indenter is removed, it leaves behind a plastically deformed indentation area. This force
divided by the area indented is the indentation hardness of the surface, and this process was carried out on PEDOT:PSS films.

It is known that when performing nanoindentation of soft thin films on hard substrates that the substrate can affect the measurement\textsuperscript{93}, so two different film thicknesses of PEDOT:PSS were used: 125 nm as used in the composites, and 500 nm in order to obtain a hardness value for the PEDOT:PSS independent of the glass substrate. Figure 2 shows the hardness vs. contact depth profiles for the two different PEDOT thicknesses. The hardness of PEDOT:PSS independent of the glass substrate can be determined by the flat portion of the plot of the 500 nm thick film between contact depths of 45 nm and 100 nm. This value is 150 MPa. However, as the indenter moves deeper into the sample, the hard glass substrate begins to play a role and the effective hardness is now a combination of the film and substrate properties. This causes the upward slope that is present in these data. This effect is even more pronounced for the 125 nm thick film, as the substrate effects can be seen as early as 25 nm into the indentation. Thus, even though PEDOT:PSS is a soft material, the 100 nm diameter nanowire, as it is pressed into a 125 nm thick film, feels an effective hardness that is much higher than 150 MPa at the equilibrium force balance point. In section 2, AFM studies of these composites show that once pressed, the nanowires protrude ~25 nm above the PEDOT surface. This means that for a 100 nm diameter wire the maximum depth it would reach is ~75 nm below the surface, where the effective hardness of the PEDOT film is around 420 MPa, or 2.8 times higher than the hardness of PEDOT:PSS.
Figure 3.2. Hardness vs contact depth for nanoindentation of 125 nm PEDOT:PSS film on glass (top) and 500 nm PEDOT:PSS film on glass.

Measuring the indentation hardness of Ag nanowires is a less trivial issue. At the time of this writing, we have not successfully been able to isolate and directly measure the indentation hardness of a single nanowire as used in these composites. However, another group used an AFM tip to both image and indent a silver nanowire to determine its indentation hardness along with other mechanical properties. The first nanoindentation
measurements of single Ag nanowires were done on 45 nm diameter wires, and the hardness was found to be 870 MPa. We are using this value in our model, and from our results, it seems to be close to the value for the Ag nanowires used in our experiments.

An SEM micrograph of the surface of the composite is shown in Figure 3.3. This SEM shows the flattening of the wires as well as the widths of the nanowires indented into the polymer. From this image, we see that the ratio of the indentation width of the wire indented area to the polymer indented area is 0.51. The hardness values measured by nanoindentation confirm this ratio to be 0.48, and thus the model and the image match very closely.

**Figure 3.3.** SEM image of PEDOT:PSS / Ag nanowire composite surface showing flattening of nanowires as well as indentation lengths of the polymer and nanowire.
3.2. Optical Properties of Laminated Composite Films

This nanowire pressing and flattening has an effect upon the optical properties of the composites that is plainly visible to the naked eye. Optical absorption, transmission, scattering, and reflection measurements were taken illuminating the sample from both the front (film) and back (glass) sides. Absolute absorption was taken by placing the sample in the center of an integrating sphere using a bare glass reference. The integrating sphere has a reflective interior that is completely closed except for a small aperture into which the incident illumination passes. There is a reflective baffle in front of the photodiode to ensure that the light is evenly reflected within the sphere. Total absorption of a bare nanowire film is shown in Figure 3.4. Over the visible spectrum, from 400 – 800 nm, the average absorption is only 2.9%.

![Absorption vs Wavelength](image)

**Figure 3.4.** Total absorption of a bare Ag nanowire film not including substrate reflections. Average absorption over the visible spectrum is 2.9%.
Total transmission was measured by placing the sample in front of the integrating sphere, and scattering was measured by subtracting a specular transmission measurement (without the sphere) from the total transmission. Reflection was calculated by subtracting the total transmission from the total absorption. As the lamination occurs, the wires flatten out on top, but are still in their original shape on the underside and the inherent roughness in the film caused by the wire-wire junctions is pushed downward into the polymer. This is apparent in the differences in light scattering and reflection that is measured when the sample is illuminated from each side. The percentage of light that is scattered from the front and back as well as the reflection from each side is shown in Figure 4b. These data show that the wires, as they flatten out, scatter less and reflect more over the entire spectrum, and that the rough underside of the composite behaves much more like a bare nanowire film than does the smoothed composite surface.

![Graphs showing optical reflection and scattering](image)

**Figure 3.5.** Optical reflection (left) and scattering (right) over the visible spectrum for a bare nanowire film (purple) and a PEDOT / Ag nanowire composite film taken from the rough (glass) side (blue) and the smooth (film) side (green).
This is further optical confirmation that this lamination technique is successful in lowering the top surface roughness by embedding the wire-wire junctions away from a device to be built on top. However, there are some applications for which having more scattering is advantageous and surface roughness is not as critical. For these, different processing could be employed to retain some roughness or to create a balance between roughness and scattering tailored to the application at hand.

3.3. Thermal Properties and Limits of Laminated Composite Films

To determine the range of applications for which these composite electrodes could be useful, it is important to determine their maximum operating temperature. In addition, it is important to determine what, if any, effect the lamination and embedding into the polymer film has upon the thermal behavior of Ag nanowires. Bare and composite films were heated to 210, 220, 230, 260, 270, and 280 °C for 20 minutes and the results were examined under the scanning electron microscope in order to detect any morphology changes.

For temperatures up to 230 °C, a 20 minute anneal did not significantly change the morphology of either the bare Ag nanowires or the composite films. However, as the temperature increased to 260 °C and beyond, the nanowires began to coalesce, with the silver aggregating into droplets at the wire-wire junctions and along the lengths of the nanowires. This phenomenon was visible in both the bare and embedded samples, but was more significant in the bare samples. At 280 °C, the bare nanowires were completely coalesced, whereas the composites still had long wires along with visible wire to wire
connections. Figure 3.6 shows SEM images of as prepared bare nanowire (a) and composite films (b). The initial sheet resistance of bare nanowire sample was 11.1 $\Omega/\square$, while the initial sheet resistance of the composite was 10.5 $\Omega/\square$. The next four images are of the same samples after heating at 280 °C for 20 minutes, bare nanowires in images c and e, and the composite in d and f. It is clear from the completely coalesced nanowires in images c and e, and confirmed by a sheet resistance measurement, that the bare nanowire film no longer has any connected pathways or lateral conductivity. However, due to the only partial change in the film morphology from heating, the composite has a measurable sheet resistance of 82.2 $\Omega/\square$ after the 280 °C, 20 minute anneal. This is significant, because it shows that embedding the wires slows down the thermal processes that degrade these films’ performance as conductors.
Figure 3.6. SEM images of bare Ag nanowire films (a, c, e) and PEDOT:PSS / Ag nanowire composite films (b, d, f) as deposited (a, b) and after heating at 280 °C for 20 minutes (c – f).
To explain the nanowire coalescence, the possibility of the nanowires melting was considered. It has been found for particles on the nanoscale that the melting point drops below the bulk melting point of the material.\textsuperscript{96} However, putting the physical parameters of these Ag nanowires into the Gibbs-Thomson equation for melting point depression:

\[ T_M = T_{MB} \left[ 1 - \frac{4\sigma_{SL}}{H_f\rho_s d^{3/2}} \right] \]  \hspace{1cm} (3.5)

where \( T_M \) is the melting point as a function of particle diameter \( d \) (100 nm), \( T_{MB} \) is the bulk melting temperature, \( \sigma_{SL} \) is the solid-liquid interface energy, \( H_f \) is the enthalpy of fusion, \( \rho_s \) is the density of the solid, and \( 3/2 \) is the shape factor for a nanowire,\textsuperscript{96} a melting point of 926 °C is the result. Thus, the wires are not reaching the liquid state in these heating experiments, and another mechanism must be at work.

The motion of atoms via thermally activated surface diffusion was then considered, as this can happen at relatively low temperatures. By approximating the nanowire as cylindrical with hemispherical end-caps, which is close to the actual structure of the wire as shown in SEM images (Figures 2.2, 3.3), a model can be derived. Surface diffusion is driven by the system’s tendency to reduce surface energy when atoms become mobile, which is significant in nanostructures, as a larger fraction of the system’s overall free energy is on the surface. The chemical potential, \( \mu \), of an atom on a surface of a nanostructure is directly related to the curvature of the surface, defined as \( 1/r \), where \( r \) is the radius of curvature of the surface. For a hemispherical end-cap, as there is curvature in two dimensions, this can be written as:
\[ \mu = V_A \frac{2\gamma}{r} \quad (3.6) \]

Where \( V_A \) is the volume of an atom, and \( \gamma \) is the surface energy of the material. For the cylindrical surface of the nanowires, because it only has curvature in one dimension along the outer diameter, the chemical potential for an atom on the surface there is:

\[ \mu = V_A \frac{\gamma}{r} \quad (3.7) \]

This means that there is a difference in chemical potential between the atoms on the ends of the wire and those along its length, which becomes the driving force for diffusion, \( F \), via the reduction in surface energy.

\[ F = -\Delta \mu = \frac{\gamma}{r} \quad (3.8) \]

The plot in Figure 3.7 shows the shape evolution over time of the tip of a cylindrical rod coalescing by surface diffusion, as calculated by Nichols and Mullins, using a finite difference method to solve the partial differential diffusion equations.\cite{Nichols1968} As the atoms from the spherical end-caps diffuse onto the cylindrical surface, they do not coat the surface evenly, but stay within a short distance from the tip, creating an enlarged bulb. This bulb then increases over time and a neck begins to form, which eventually becomes unstable and leaves the egg-shaped bulb separated from the rest of the wire. This process then occurs over and over until the entire wire becomes a series of droplets lying in the direction of the length of the original wire. It is apparent from images c – f in Figure 3.6 that this model fits the experimental images very closely. In attributing the nanowire coalescence to surface diffusion, this means that this process is dependent upon the
surface energy between the silver atoms in the nanowire and whatever other surface it touches. This concept explains why embedded wires are slower to coalesce – the surface energy between the silver and the solid polymer film is higher than that between silver and air. In addition, this also explains why there are thin lines of silver along the lengths of the coalesced wires in the images of the bare wire films. A poly-L-lysine monolayer film was used to disperse and adhere the nanowires to the surface, creating a thin strip of tightly bound, high surface energy atoms. These are left behind as the unbound atoms that are free to diffuse coalesce into droplets.

![Diagram](image)

**Figure 3.7.** Plot of the effects of heat and surface diffusion with increasing time, showing instability formation and nanowire spheroidizing, from Nichols and Mullins.97

Thus, it can be concluded that the surface energy interaction between the polymer and the Ag nanowire plays a dominant role on thermal stability of these composites, and tuning this energy may be a way to increase the maximum operating temperature for applications requiring higher temperatures for longer timescales.
3.4. Section Conclusion

This section presented the mechanics of the lamination procedure that leads to the composites’ low surface roughness, as well as the optical and thermal effects of embedding the nanowires into a polymer film. It was found that the pressing process can be modeled as an equilibrium force balance that takes into account the hardness of the polymer and the nanowires. The hardness of PEDOT:PSS was examined with nanoindentation, and it was found that the pressing mechanics for the composite were influenced by the hard glass substrate under the 125 nm thick film. Taking this into account, the model predicts that the nanowire flattened surface is 48% as wide as the PEDOT:PSS indentation, which agrees with the experimental value of 51% very closely.

The optical properties of the composite films were measured from both the front (smooth) and back (rough) sides, and compared with the optical reflection and scattering of a bare Ag nanowire film. These data showed further confirmation that the inherent roughness is directed away from the top surface, as the bottom surface behaved very similar to the bare film, while the top surface showed reduced scattering and increased reflection, characteristic of flatter films.

Finally, the thermal properties of both the composites and bare Ag nanowire films were examined. It was found that after a 20 minute, 280 C anneal, bare Ag nanowire films were completely coalesced, whereas many wires that were embedded in the composite kept their original shape. After 20 minutes at 280 C, the bare nanowire film with an initial sheet resistance of 11.1 \( \Omega/\square \) showed no remaining conductive pathways, whereas the composite film with an initial sheet resistance of 10.5 \( \Omega/\square \) showed an
increase in sheet resistance to $82.2 \ \Omega/\square$. This coalescence can be attributed to thermally activated surface diffusion, which explains the slowing degradation of the composites compared to their bare Ag nanowire counterparts, as the surface energies between the nanowires and air and the nanowires and polymer are different.

By understanding these properties and the science behind them, we not only can explain mechanical, optical, and thermal behavior, but we can use this knowledge as a way to characterize a class of composite materials, utilizing different polymers with various mechanical, optical, and surface properties. In this way, the composite properties such as surface roughness, light scattering, and thermal stability become controllable, and opportunities to fabricate even better transparent electrodes could arise from this work.
4. Fully-Solution Processed OPV Cells on Metal Substrates with Composite Top Electrodes

Solution-processed polymer / Ag nanowire composite transparent electrodes can be used in a variety of ways that ITO cannot. Because they are substrate-independent, solution-processed, and do not require high substrate temperatures to obtain low sheet resistances, device architectures that are not possible using ITO can be fabricated using PEDOT / Ag nanowire devices. In this section we report a polymer photovoltaic cell architecture in which every layer is deposited from solution, with the composite electrode deposited as the last step.

Polymer photovoltaic cells are attractive as low-cost alternative to inorganic photovoltaics largely due to their deposition methods. Roll-to-roll high-throughput manufacturing is the focus of OPV companies that are commercializing both small molecule and polymer photovoltaics. For small molecule OPV, device architectures fabricated from start to finish, including the electrodes, through thermal evaporation have been demonstrated. For this process, the cost would be further lowered by the use of only one large roll-to-roll system capable of fabricating all layers in the cell. However, for polymer OPV cells in which the active layer is deposited from solution, this is not the case. In a standard device configuration, neither electrode is deposited from solution: the ITO anode is sputtered and the metal cathode is thermally evaporated. In general, there is also at least one interface layer that is evaporated as well. This means that, unlike a fully evaporated cell, the polymer OPV cell in the standard configuration cannot be continually processed using one piece of equipment, making this fabrication more costly. It has been demonstrated that active polymer layers can be deposited through methods such as
gravure printing, a diagram of which is shown in Figure 4.1. Gravure printing is very high-throughput and is used for applications such as currency, laminates, wallpapers, and magazines. However, for organic photovoltaics, this would become most cost effective if every layer in the cell could be deposited via the same process.

Figure 4.1. Schematic of gravure printing process.

4.1. Previously Reported Work

Organic bulk heterojunction PV cells fabricated from both polymers and small molecules show promise as an alternative to their inorganic counterparts with a potentially lower module cost per peak Watt. Much of this cost reduction relies on the ability to use high-throughput processing techniques such as roll-to-roll coating on low-cost substrates. Both vacuum and solution-based roll-to-roll coating can be cost-effective, and the lowest costs will be achieved when all coating steps are performed either from
solution or in vacuum as this prevents the need to switch between tools. Metal foil substrates and plastic foils with opaque metal coatings are particularly attractive because they are low-cost and, unlike transparent plastic foil substrates, have excellent barrier properties against the permeation of O$_2$ and H$_2$O which would otherwise lead to device degradation. However, no high-performance polymer devices whose active layer is deposited from solution onto metal foil without the use of vacuum-deposition for some of the layers have been reported. The goal of this work is three-fold: (1) to develop a device that can be processed onto a substrate using only solution processes, (2) to eliminate the costly metal oxide transparent electrode and replace it with an equivalent that is solution-processed and equally conductive and transparent, and (3) invert the devices optically such that light is not incident from the substrate side to allow for the use of opaque substrates.

The organic bulk heterojunction system used here consists of the donor material regioregular poly-(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM). This system has produced single-junction cell efficiencies over 4%. The most common device of this type is fabricated using the superstrate cell structure: glass/Indium Tin Oxide (ITO)/poly-(4,3-ethylene dioxythiophene) (PEDOT):poly(styrene-sulfonate) (PSS)/P3HT:PCBM/Al. Often, a thin evaporated layer of LiF or another alkali metal-containing salt is added between the polymer and Al cathode to lower the barrier to electron transport at that interface. More recently, polymer bulk heterojunction devices have been reported that are electrically inverted. The ITO-coated glass is still the superstrate, but in these devices, the ITO functions as the cathode. To change the work function of the ITO, various strategies have
been used, such as treatment with Cs$_2$CO$_3$ using vacuum-deposition$^{108}$ and solution-processing,$^{110}$ solution-processed amorphous TiO$_x$$^{107, 109, 110}$ and ZnO$^{111}$, and self-assembled monolayers.$^{106}$ These devices have reached power conversion efficiencies over 4%.$^{108}$

However, there remain problems with this approach. Indium is an expensive metal and ITO is deposited in a time-consuming sputtering process, which would damage the underlying organic if used as a top electrode.$^{112}$ In addition, the brittle nature of ITO makes it unattractive for use in flexible organic solar cells.$^{68}$ Various solution-processable alternatives to ITO have been proposed and used in solar cells, including carbon nanotubes$^{75, 113, 114}$ and graphene sheets,$^{76, 84, 86, 115}$ and more recently combinations thereof.$^{78}$ Even though reasonable device efficiencies have been obtained in organic PV cells in which ITO was replaced with CNTs in the standard device configuration,$^{75}$ the properties of CNT films do not compare favorably to ITO. The sheet resistances are around 200 $\Omega$/ at the 85-90% transmissivity required for efficient device performance.$^{75, 113}$ The only polymer bulk heterojunction device reported in which a CNT film was used as a top electrode in an inverted organic PV cell on ITO yielded a poor power conversion efficiency of 0.3%.$^{114}$ Graphene sheets show similar performance to CNT films and in addition require very high temperature annealing steps to obtain conductivities that are still too high for efficient devices to be fabricated.$^{76, 84, 86, 115}$ Combining the two carbon nanostructures into one electrode still does not result in sheet resistivities and transmissivities comparable to ITO.$^{78}$ Ag nanowire films remain the only solution-deposited ITO alternative that meets the performance requirements for photovoltaics, at
10 Ω/ with 85% transmissivity over the wavelength from 400 nm to 800 nm,24 and in this paper we demonstrate their use as a top electrode.

A few previous organic solar cell device architectures that are ITO-free have been reported, with the layers deposited in a substrate configuration onto metal. One structure showed poor device performance using monochromatic light.116 Another utilizes e-beam evaporated Ti as the cathode and a shadow-masked evaporated Ag grid for the anode, which shades part of the device area, lowering device performance.117 Semitransparent metal films have been used as transparent top electrode in vacuum-deposited small-molecule devices on metal substrates.118-120 No device has been reported in which every layer is deposited from solution onto a low-cost substrate with good barrier properties to yield promising device efficiencies. Here, we fabricate an efficient P3HT:PBCM bulk heterojunction organic solar cell on a metal substrate with the active layer, workfunction adjustment layers, and transparent electrode are all deposited from solution.
4.2. Device Fabrication

![Device structure and lamination process](image1)

**Figure 4.2.** (a) Device structure and lamination process. (b) Cross-sectional scanning-electron micrograph (SEM) in which the Ag film, the organic layers, and the top Ag nanowire mesh electrode are visible. (c) A top-view SEM of the devices in which the nanowire mesh is shown to be a continuous network.

The PV cells are built on an opaque 150 nm-thick vacuum-deposited Ag film on glass. The glass substrate is not essential but provides a convenient way to handle the substrates during the subsequent spin-coating steps. Figure 2a shows the device structure and a diagram of the lamination process used to obtain the top electrode. Cs₂CO₃ in 0.2 wt. % 2-ethoxy-ethanol solution is spun onto the Ag film and then annealed for 20 minutes at 150 °C to reduce the cathode workfunction, as described by Liao, et al.¹⁰⁸ This is
followed by spinning of a 2.5 wt. % 1:1 P3HT:PCBM blend from ortho-dichlorobenzene at 600 rpm for 45 seconds. The films are allowed to dry in a covered Petri dish, and are then annealed at 110 °C for 10 minutes to evaporate remaining solvent. PEDOT:PSS (Clevios CPP 105D) is then spun on top of the bulk heterojunction layer. Prior to spinning, the PEDOT:PSS is sonicated for 15 minutes and then heated at 90 °C for 25 minutes. This approach improves wetting of the hydrophobic P3HT:PCBM by the hydrophilic PEDOT:PSS. The device is then annealed at 130 °C for 25 minutes, which smoothes the PEDOT:PSS surface and evaporates water left in the film.

The top electrode (anode) is fabricated from an Ag nanowire mesh. The Ag nanowire mesh is prepared on a separate pre-cleaned glass substrate by drop casting a suspension of Ag nanowires and allowing them to dry while agitated on a shaker, as described in Ref. 25. The glass is dipped in an aqueous poly-l-lysine solution (0.1% w/v, Ted Pella) for 5 minutes prior to coating to increase its affinity for the nanowires. The mesh films are then annealed at 180 C for one hour to lower the sheet resistance. Ag nanowire electrodes have been shown to have a transparency similar to ITO at a sheet resistance of ~10 Ω/ , appropriate for use in thin-film photovoltaics. The as-prepared Ag nanowire films are pressed with a clean glass substrate at 5.9x10^3 psi for 30 seconds to flatten the nanowire mesh and remove features that may otherwise punch through the active layer. The pressed films are then laminated on top of the PEDOT:PSS surface of the solar cell structures under the same pressure for one minute, as shown in Figure 1a. In a manufacturing process, this step could serve to both complete the devices and package them, leaving them between two low-cost, highly protective barrier layers, glass and metal. This would eliminate the need for additional packaging steps and materials,
driving down manufacturing cost. In this case, for laboratory devices, the glass donor substrate is removed to leave the nanowires transferred to the PEDOT:PSS as the top electrode. The nanowires sink into the soft polymer layer and adhere. However, as shown in the cross-sectional scanning electron micrograph (SEM) in Figure 2b, some portions of the nanowires also lift up as the glass is removed. An SEM of the top surface of the finished devices is shown in Figure 2c. The Ag nanowires form a continuous mesh through which current can be conducted laterally. For current density-voltage (J-V) measurements, the bottom Ag anode is exposed by dissolving the nanowires and polymer layers with acetone, while the nanowire electrode is contacted on top with a soft probe consisting of a fine (100 μm diameter) Au wire.

### 4.3. Composite Top Electrode Performance

Figure 2 shows specular optical transmission data over visible wavelengths for a device structure without the Ag/Cs₂CO₃ cathode, deposited on quartz both with (green) and without (red) a nanowire anode. Also shown is total optical transmission data collected using an integrating sphere (yellow) for same structure with the anode. The specular transmittance through the device decreases when the nanowires are present due to both optical absorption in the nanowires and due to scattering. The total transmission curve includes the light scattered through the device by the nanowires. By comparing the total and specular curves for the structures with nanowires and averaging over the visible spectrum, it is shown that 83% of the transmission through the Ag nanowire mesh is specular and the remaining 17% is diffuse. This plot also shows that in the wavelength
region from 450 nm to 650 nm, where the absorption of the active layer is the strongest, the decrease in total transmission due to the nanowires averages only 11.8%. Over the entire visible spectrum, this loss is 16.2%. Both of these numbers are consistent with previous reports for the solar transmittance of Ag nanowire meshes with conductivities useful for photovoltaics.\textsuperscript{74}

\textbf{Figure 4.3.} Specular transmission over the range of visible wavelengths for the organic layers used in the device with (green) and without (red) the top Ag nanowire mesh electrode. Total (specular plus diffuse) transmission over the range of visible wavelengths for the organic layers with the top Ag nanowire mesh electrode (yellow).
4.4. **OPV Device Performance**

In measuring the J-V curves for these devices in the dark and under illumination, large dark leakage currents were observed. Figure 4.4 shows non-optimized J-V device data for these devices as fabricated (red) in the dark (dashed line) and under 80 mW/cm$^2$ of AM 1.5G illumination (solid line). The large dark currents are attributed to the roughness of the nanowire electrode, which results in some nanowires extending further into the active layer and creating locally thinned device regions. These preferential current pathways can be eliminated by applying ms-long voltage pulses in forward bias to burn out local shorts. Figure 4.4 also shows J-V curves in the dark (dashed lines) and under illumination (solid lines) following an applied pulse of -5 V (yellow) and -10 V (green).

![Figure 4.4. Current density-voltage (J-V) curves for non-optimized devices measured as-](image-url)
fabricated (red), following ms pulsing at -5 V (yellow), and at -10 V (red) in the dark (dashed lines) and under 80mW/cm² AM1.5G illumination (solid lines).

J-V curves in the dark (green dashed line) and under 100 mW/cm² AM 1.5G illumination (green solid line) are shown in Figure 4.5. For the device structure described above, with a device area of 2 mm², the open circuit voltage is $V_{oc} = 0.51$ V, the short circuit current density is $J_{sc} = 10.59$ mA/cm², and the fill factor is 0.46. This yields a power conversion efficiency of $\eta = 2.5\%$. We note that no spectral correction factor was used to correct $J_{sc}$ and $V_{oc}$. These devices retain some conduction through a shunt, as seen in the dark J-V characteristics. This is attributed to the remaining roughness of the nanowire electrode and the resulting locally thinned device regions, which produce a shunt resistance of 1 kΩ/cm². The $V_{oc}$ of these devices is around 10 mV lower than the best devices made in the standard configuration.\textsuperscript{104, 105, 122} This may be partially due to the lack of chemical or structural modifications that occur when the metal cathode is evaporated onto the polymer in superstrate devices.\textsuperscript{123} This alters the barrier to charge transport at this interface, and could play a role in lowering the $V_{oc}$. 
Figure 4.5. Current density-voltage (J-V) characteristics for the partially optimized organic PV cells in the dark (dashed lines) and under 100 mW/cm² AM1.5G illumination (solid lines). The green curves are for a device with the structure Ag/Cs₂CO₃/P3HT:PCBM/PEDOT/Ag nanowire mesh. The red curves are for the same device structure, omitting the Cs₂CO₃ interface layer.

Also shown in Figure 4.5 are the J-V characteristics of a device without the Cs₂CO₃ treatment of the Ag cathode in the dark (dashed gray line) and under illumination (solid gray line). $V_{oc}$ is reduced to 0.19 V, $J_{sc}$ to 7.8 mA/cm², and the fill factor to 0.32, resulting in a power conversion efficiency of $\eta = 0.6\%$. The increase in leakage current
originates from the use of a thicker, non-optimized nanowire electrode in this device. These results show that the Cs$_2$CO$_3$ layer enhances charge collection and transport between the Ag substrate and the organic layers. This is consistent with reported findings for both solution-processed and evaporated Cs$_2$CO$_3$ interface layers, which have been found to lower the Ag workfunction to 3.45 eV (spin-cast Cs$_2$CO$_3$), 3.06 eV (spin-cast Cs$_2$CO$_3$ after annealing)$^9$, and 2.2 eV (vacuum-deposited Cs$_2$CO$_3$)$^8$.

4.5. Section Conclusion

In this section, we reported fully solution-processed organic photovoltaic cells that are electrically and optically inverted, on opaque Ag cathodes. This device structure is made possible through the use of composite PEDOT:PSS / Ag nanowire films as the top transparent conducting electrode. These electrodes are currently the only solution processed ITO alternative that have a performance comparable to sputtered transparent conducting oxides, and in this work we demonstrate their transfer and use as top electrodes. The fabricated PV cells reach a power conversion efficiency of 2.5% under 100 mW/cm$^2$ of AM 1.5G illumination, and because they are deposited onto metal they have unique advantages. Metals are exceptional barriers to moisture and oxygen$^{101}$ and they can be textured or shaped into different form factors to enhance light trapping.$^{124, 125}$ Hermetic cell packaging can be achieved by laminating these cells to glass. Such an approach retains the throughput advantages of roll-to-roll deposition, but uses glass substrates as a barrier and convenient form factor for panel installation. These cells are also potentially useful as components in tandem cells that are not constrained by current-
matching. Because they are ITO-free and fully processed from solution, their cost is potentially very low.
5. Composite Electrodes in 3-Terminal Tandem OPV Cells

In 1961, Schockley and Queisser calculated the ultimate efficiency limit of a single p-n junction solar cell with an optimal bandgap of 1.1 eV to be 30%. This means that to achieve efficiencies above 30%, different device architectures that are capable of harvesting more of the solar spectrum must be employed. Tandem PV cells, in which cells with different bandgaps are stacked to split and therefore absorb more of the solar spectrum, have a much higher fundamental efficiency limit. The most efficient photovoltaic cells ever reported are inorganic crystalline tandem cells with three junctions, which, under concentrated sunlight, exhibit efficiencies as high as 42.4%. However, producing cells that yield efficiencies in this range is slow, difficult, and costly. This is partly because the materials must be very pure, but it also has to do with the fabrication process. The sequential semiconductors must be lattice-matched as they are grown epitaxially, and to do this, a very slow, precise, and expensive technique such as organometallic chemical vapor deposition or molecular beam epitaxy must be employed. So while they are highly efficient, they are not suitable for economically viable energy generation.

Organic thin films, because they are amorphous, are not subject to lattice matching as is the case with crystalline tandem PV cells, which means that it may still be possible to fabricate tandem OPV cells in a low-cost, high-throughput manner. In addition, tandem devices have the chance to combat two fundamental issues regarding OPV. The first is absorption. All organic materials have absorption spectra that are made up of peaks at certain wavelengths, and as such there is currently not a single organic material that
absorbs strongly across the entire solar spectrum. With more than one absorbing layer, complimentary absorbers can be designed and the absorption peaks tuned such that each cell absorbs strongly over a narrow wavelength range, so in tandem a larger portion of solar irradiation is used. The second issue is that of film thickness versus charge transport. Because another cell is behind the first and can absorb light that the first cell does not, each cell can be thinner so the charge transport requirements for each material are relaxed. Thus, while OPV tandem cells may never reach the efficiencies that inorganic crystalline tandem cells obtain, they do have the potential to be more efficient than single-junction cells, and currently, the OPV device with the highest efficiency reported, at 8.3%, is a two-cell tandem stack.

The most widely reported tandem organic PV architecture is comprised of two or more organic PV cells, either all evaporated small molecule cells, all solution-processed polymer cells, or some of each type, stacked on top of each other, connected electrically in series, and separated by a thin recombination layer. These recombination layers are generally made using nanoscale metal structures or a thin metal oxide layer, and the best ones are efficient enough such that there is nearly no loss in voltage produced – the tandem open circuit voltage is approximately equal to the sum of the individual cells’ open circuit voltages. In addition to designing an appropriate recombination layer as to minimize loss of voltage, these tandem cells must be carefully optimized so that the current produced in each cell is equal. This is because, when cells are connected in series, the sub-cell that produces the least amount of current limits the total current value. Thus, when designing series-connected tandem cells, the thickness of each sub-cell must be optimized to match the current production in each
sub-cell. A drawback in this is that the optimal thickness for current matching may not be the optimal thickness for charge transport for that cell, nor will it yield the highest cell efficiency possible from that material. This results in considerable challenges when designing materials for tandem cells, in that these series connected tandems must be optimized both optically and electrically.

If a transparent electrode were placed between the sub-cells of a tandem structure, this would allow independent electrical access of each cell. A schematic of this is shown in Figure 5.1. In this way, the currents from each cell can be extracted separately, allowing each cell to produce a different photocurrent without being limited by the other cells. The result is that the overall efficiency of the stack becomes simply the sum of the efficiencies of the sub-cells as measured in the stack. Besides each cell being able to produce different photocurrents and no loss of current, this multi-terminal device architecture has very significant design advantages. Because current matching is no longer a requirement, the stack and materials used therein need only to be optimized optically to produce the highest efficiency from each sub-cell and therefore from the whole stack. The multi-terminal architecture, to be realized, demands a transparent conductor that can be placed between sub-cells in a tandem stack. This transparent conductor needs to have both high transparency such that the back cell receives illumination, and low sheet resistance to ensure efficient charge collection from both cells. It also needs to be able to be deposited in a way that does not damage the cell beneath it while maintaining good performance. Sputtered ITO is not a practical solution, as it damages the underlying organic and needs to be heated during deposition for optimal performance. This multi-terminal device architecture has been demonstrated
recently using both carbon nanotube meshes\textsuperscript{114}, but the device characteristics clearly imply that the efficiency of the stack is limited by the poor conductivity of the intermediate electrode. Only Ag nanowire meshes and these composite polymer / Ag nanowire electrodes have been shown to be a solution-processed alternative to ITO with the same transparency and conductivity,\textsuperscript{74} and as such, they are an appropriate choice for intermediate electrodes in multi-terminal tandem OPV cells.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Two terminal two-junction tandem PV cell. (b) Three-terminal two-junction tandem PV cell with intermediate electrode.\textsuperscript{142}}
\end{figure}

This section presents our work on three-terminal tandem OPV cells, both theoretical and experimental, using PEDOT:PSS / Ag nanowire composite electrodes, and shows that this device architecture is a promising way to realize high efficiency devices.
5.1. Device Structure and Fabrication

Figure 5.2 shows a schematic of the experimentally realized layered device structure, with front and back cells, and the intermediate composite electrode shown. A semitransparent P3HT:PCBM bulk heterojunction PV cell was fabricated as the front device. Indium tin oxide (ITO) on glass was used as the substrate. The ITO was etched into stripes ~2 mm in width using HCl vapor at 60 °C in order to separate and define the devices. A schematic of the device layout on the substrate is also shown in Figure 5.2. The patterned substrate was cleaned in detergent, de-ionized (DI) water, acetone, and boiling isopropanol before being subjected to uv-ozone treatment for 15 minutes. Cesium carbonate, dissolved in a 0.2 wt.% solution in 2-ethoxyethanol, was spun onto the ITO at 1000 rpm to modify the workfunction and create an electron-sensitive contact. This layer was annealed at 150 °C for 20 minutes before the active layer, a 2.5% 1:1 ratio blend of P3HT:PCBM in ortho-dichlorobenzene was spun at 800 rpm to create a film thickness of ~200 nm. After a 10 minute anneal at 110 °C to remove the solvent, the PEDOT:PSS (Clevios CPP 105D) was spun following the procedure described in Section 4.74,77 Following the 25 minute, 130 °C anneal of the PEDOT:PSS layer, a mesh film of Ag nanowires was transferred to the polymer on top of the inverted cell to create the composite electrode. The Ag nanowire donor substrate was prepared by drop-casting, as described in Sections 2, 4, and 674,77 and was annealed at 180 °C and pre-pressed at 1 x 10^4 psi prior to lamination to increase conductivity and reduce initial roughness respectively. It was also patterned into a stripe ~2 mm in width that was laminated perpendicularly to the stripes of ITO in order to define three device areas per substrate (Figure 5.2). After lamination, the entire structure was re-pressed at ~1 x 10^4 psi with a
clean glass substrate to further flatten the composite electrode. A bilayer small molecule OPV cell was evaporated on top of the inverted semitransparent polymer cell in a chamber at a pressure under $7 \times 10^{-7}$ torr. Copper phthalocyanine (CuPc), 25 nm, was evaporated first as the donor film, followed by 50 nm of the fullerene $C_{60}$ as the acceptor. Chemical diagrams of these components are shown in Figure 5.2. A 10 nm exciton blocking layer of bathocuprene (BCP) was evaporated, followed by 100 nm of Ag as for the cathode. The chamber was vented and a mask inserted prior to the Ag evaporation to define the electrodes (Figure 5.2).

**Figure 5.2.** Schematics relevant to the three-terminal tandem OPV cells fabricated in this work. **Left:** device structure including inverted semitransparent polymer front cell, PEDOT / Ag nanowire intermediate electrode, and evaporated small molecule back cell. **Top Right:** small molecule structures used in evaporated cell; copper phthalocyanine (CuPc) as the donor and the fullerene $C_{60}$ as the acceptor. **Bottom Right:** substrate patterning used in order to access both cells for characterization using probes.
5.2. Device Performance

A probe station was used to test the resulting three-terminal tandem devices. Due to the layout of the three electrodes, each device can be probed individually within the tandem using one hard probe and one soft probe consisting of a 100 micron diameter gold wire: the inverted cell by probing between the ITO and the composite electrode, and the small molecule cell by probing between the composite electrode and the evaporated Ag pad. The cells were tested in the dark and under 100 mW/cm$^2$ AM 1.5G solar simulated illumination. Current density vs. voltage (J-V) of the both the front P3HT:PCBM cell (purple) and the CuPc:C$_{60}$ back cell (blue) are shown under illumination in Figure 5.3. For the front cell, the open circuit voltage (Voc) is 0.54 V, the short circuit current density (Jsc) is 10.1 mA/cm$^2$, and the fill factor (FF) is 0.46. This yields a power conversion efficiency for this cell of 2.5%. For the back cell, the Voc is 0.42 V, the Jsc is 1.89 mA/cm$^2$, the FF is 0.50, and the power conversion efficiency is 0.41%. Because each cell can be measured individually, the total efficiency for the stack of two cells is simply the two individual efficiencies summed together, 3.0%. While the back cell only adds 0.41% to the total stack efficiency, this is significant because although the current through this cell is low, it can be extracted due to the three-terminal architecture without reducing the current extracted from the front cell.

However, this stack is still not as efficient as the best single junction cells reported,$^{14,15}$ nor are they even as efficient as the best P3HT:PCBM single junction cells reported.$^{29,104}$ The losses in the front cell primarily come from the Voc and FF. The low Voc points to
charge collection issues at the Cs₂CO₃ interface, as the contact at that point may not be Ohmic. The losses in the fill factor arise from the roughness of the Ag nanowire mesh as it is pressed into the PEDOT:PSS to form the composite. It is clear from the J-V curves that the front cell (Figure 5.3, purple) shows far more shunting behavior than the back cell (Figure 5.3, blue). This is because the nanowires in the composite protrude down into the PEDOT:PSS when pressed. As was previously shown in Section 2, the junctions between the nanowires become embedded in the polymer, and in this process, the surface roughness from the nanowire mesh is directed toward the front cell. The optical effects of this process were shown in Section 3, and the effect on an underlying device was shown first in Section 4 and is shown again here. Pulsing the cell and higher voltages prior to measurement can help to burn out local shorts, but cannot completely correct the fill factor or eliminate shunting. By contrast, the opposite surface of the composite upon which the small molecule OPV cell is built is very smooth with flat wire-wire junctions, and that is reflected in the higher fill factor and the shape of the J-V curve of that cell.
Figure 5.3. **Current density vs. voltage characteristics for front inverted semitransparent polymer cell (purple) and back evaporated small molecule cell (blue) illuminated with 100 mW/cm² of AM 1.5G solar simulated light. The total efficiency of this tandem structure is the sum of the two efficiencies of the individual cells: 3.0%.**

The effect of the composite electrode becomes very clear when compared to the first device ever fabricated on Ag nanowire mesh films. Shown in Figure 5.4 is the current density vs. voltage characteristics for a small molecule bilayer OPV device using CuPc as the donor and PTCBI, as the small molecule acceptor (molecular and device structures shown in Figure 5.4). This device structure is identical to the top cell in our tandems except for the acceptor material, yet the shape of the curve is very different. Compared to the control device on ITO, the device on Ag nanowires shows very significant shunting both in the dark and under 65 mW/cm² of solar simulated AM 1.5G illumination. This is due to the roughness of the wires and more significantly the large top-to-bottom height.
difference at the wire-wire stacked junctions that protrude towards the cell. This results in a very low fill factor for this cell and consequently a lower power conversion efficiency (0.38%) than the device fabricated on ITO (0.42%). In the J-V curve of the small molecule cell on the smooth composite electrode (Figure 5.3), this shunting is not present.

![Graph showing J-V characteristics for ITO control device (red) and Ag nanowire experimental device (black) in the dark (closed symbols) and under 65 mW/cm² solar simulated illumination (open symbols).](image)

**Figure 5.4.** First published OPV devices fabricated with and Ag nanowire mesh transparent anode.⁷⁴ Left, J-V characteristics for ITO control device (red) and Ag nanowire experimental device (black) in the dark (closed symbols) and under 65 mW/cm² solar simulated illumination (open symbols). Top right: chemical structure of PTCBI, acceptor molecule. Bottom right: device structure.

In addition to performance issues with the individual cells, there are optical factors that provide an upper limit to the efficiency that can be obtained using the three-terminal device architecture with these materials. Figure 5.5 shows the absorption over the visible spectrum for the active layers of the cells used in this device demonstration:
P3HT:PCBM bulk heterojunction (purple) and CuPc:C_{60} bilayer (blue). The overall absorption in the P3HT:PCBM is much greater than that in the CuPc:C_{60}, purely based on thicknesses, as the P3HT:PCBM is ~200 nm thick while the CuPc:C_{60} is only ~75 nm thick. This means that because the P3HT:PCBM cell is in front, much of the incident light never reaches the back cell. In addition, there is significant overlap between the absorption spectra below 600 nm. These two factors combine to lower the possible power output from the back cell. Optical simulations were carried out using the transfer matrix formalism in Matlab to calculate the maximum power conversion efficiencies expected from this material system. To this end, the external quantum efficiency (EQE) for the wavelengths over the visible spectrum of each subcell was calculated. External quantum efficiency is defined as the percentage of charges converted per incident photons by the cell. This value is dependent upon the absorption spectrum of the active material, how efficient it is in producing and splitting excitons, as well as allowing charge to be collected from the cell. The integration of each of these EQE curves gives the photocurrent produced by the respective cells. The experimental fill factors and open circuit voltages for each cell plus the real and imaginary parts of the refractive index over the visible spectrum of the materials were used as input for the model. For P3HT:PCBM, the optical properties were approximated by holding the real part of the refractive index, n, at n = 1.8 and calculating the imaginary part, κ, from the measured absorption spectrum and the Beer-Lambert law:

\[ I = I_0 e^{-\alpha x} \]  

\[ (5.1) \]
Where $I$ is transmitted light intensity, $I_0$ is initial light intensity, $x$ is the film thickness, and $\alpha$ is the absorption coefficient, which is related to the imaginary part of the index of refraction, $\kappa$, by the equation:

$$\alpha = \frac{4\pi \kappa}{\lambda_0}$$ (5.2)

Where $\lambda_0$ is the wavelength of light in free space, related to the wavelength of light in the medium by the real part of the index of refraction, $n$:

$$n = \frac{\lambda_0}{\lambda}$$ (5.3)

Where $\lambda$ is the wavelength of light in the medium. While these approximations, particularly that of the real part of the refractive indices holding constant, are not exact, they are good enough to get an idea of how the OPV cells will perform.

**Figure 5.5.** Left: absorption measured for the bare P3HT:PCBM blend (purple) and the bare CuPc:C$_{60}$ bilayer on glass. Right: calculated % EQE for the polymer front cell (purple) and the small molecule back cell (blue) in the three-terminal tandem structure.
The theoretical efficiencies and short circuit current densities are noted.

The plot in Figure 5.5 confirms that the short circuit current densities for the two sub-cells will be very different. It also shows that the efficiency from these two sub-cells, using the experimental Voc and FF values in this configuration is expected to be 2.67% for the P3HT:PCBM front cell and 0.78% for the back CuPc:C_{60} cell. This yields an overall efficiency of 3.45%, which is higher by only 0.45% than the value obtained experimentally. This is positive, in that the experimental values and the calculation match closely, which gives validation to the modeling method, but it also shows that the expected efficiency of this materials combination is relatively low.

5.3. A Materials Combination for High-Efficiency 3-Terminal Tandems

The next step in this process is to look at materials combinations for the front and back cells that have a higher efficiency potential. In 2009, Park et al reported an organic PV cell that reached 6.1% efficiency using the donor polymer poly[N-90 0 -hepta-decanyl-2,7-carbazole-alt-5,5-(40 ,70 -di-2-thienyl-20 ,10 ,30 -benzothiadiazole) (PCDTBT) blended with the acceptor [6,6]-phenyl C_{70} -butyric acid methyl ester (PC_{70}BM). The structure of the polymer’s monomer repeat unit is shown in Figure 5.6, as well as the current density vs. voltage and device characteristics for a cell made using PCDTBT and PC_{70}BM. Most prominently, the open circuit voltage for these devices is much larger that that of the P3HT-based PV cells: 0.88 V for PCDTBT vs. 0.62 V for P3HT. The objective is to replace the CuPc:C_{60} cell in the previous three-terminal architecture such
that the back cell can contribute more significantly to the overall efficiency of the structure, and to simulate this device architecture to determine the maximum achievable efficiency. The device structure that was simulated is shown in Figure 5.6.

The modeled device structure uses ITO as a first transparent electrode, upon which an inverted P3HT:PCBM cell is built, following the same procedure and having the same optical properties as in the previous three-terminal tandem device. The PEDOT / Ag nanowire composite is again used as the intermediate electrode, with the front cell contacted between the ITO and the PEDOT / Ag nanowires. The second cell is built on
top of the composite in the standard configuration: PEDOT (50 nm), PCDTBT:PC$_{70}$BM (80 nm), and a Ca / Al cathode (100 nm). The top cell is contacted between the composite and the metal cathode. The optical properties of the PCDTBT:PC$_{70}$BM layer were determined in a similar way to those of the P3HT:PCBM layer. The real part of the refractive index was estimated to be a constant 1.8 over the spectrum, while the imaginary part was derived from absorption measurements taken of an 80 nm thick film spun at 1400 rpm onto glass from 5 mg/mL PCDTBT in a 1:4 ratio with PC$_{70}$BM ortho-dichlorobenzene solution. This is the same thickness and solution concentration that is used to make highly efficient PV cells.

The absorption measurement results for the PCDTBT:PC$_{70}$BM blend are shown in the left side of Figure 5.7 along with the P3HT:PCBM absorption. While there is significant overlap in the absorption spectra, the PCDTBT absorbs more strongly on both the blue and red ends of the spectrum, and putting this cell behind a P3HT:PCBM cell would allow it to absorb any light in the middle portion of the spectrum as well that was not absorbed during the first pass through the front cell.

The simulated EQEs for each cell in the modeled 3-terminal tandem cell are shown in the right side of Figure 5.7. This simulation assumes the IQE of the P3HT:PCBM cell is 80%,$^{145}$ the fill factor of that cell is 0.69 and the Voc is 0.63 V,$^{25}$ the IQE of the PCDTBT:PC$_{70}$BM cell is 90%, the Voc is 0.88 V, and the fill factor is 0.66.$^{15}$ The simulation then calculates short circuit current densities of J$_{sc} = 8.68$ mA/cm$^2$ for the front P3HT:PCBM cell and J$_{sc} = 6.78$ mA/cm$^2$ for the back PCDTBT:PC$_{70}$BM cell, resulting in power conversion efficiencies of 3.77% and 3.94% respectively. This gives an overall efficiency of 7.71% for the entire 3-terminal structure. Because the back
electrode reflects the light back through the structure, the light gets a second pass and a second chance to be absorbed by both cells. In addition, constructive interference occurs due to this reflection. This accounts for the significant EQE photocurrent observed in the PCDTBT:PC$_{70}$BM cell between 650 nm and 725 nm.

Figure 5.7. Left: experimentally measured absorption for P3HT:PCBM (purple) and PCDTBT:PC$_{70}$BM (blue) blend films on glass. Right: calculated EQE from optical simulations for a P3HT:PCBM front cell (purple) and a PCDTBT:PC$_{70}$BM back cell (blue) in the three terminal tandem structure. Cell efficiencies and short circuit current densities are noted, with a total tandem efficiency of 7.71%.

While these simulations using real material data and absorption are promising in realizing high efficiency tandem OPV cells, the reality is that unless these cells are able to reach at least 10% efficiency they will not be able to compete with other thin film PV
technologies. However, as our group has shown in simulations, this device architecture has the potential to produce optimized two-cell, three-terminal tandem OPV stacks that reach theoretical efficiencies of 12.3%\textsuperscript{142}. This optimization, though, would require further materials development to tailor the absorption spectra of the individual active layers to the device structure, such that they are perfectly complimentary absorbers, while maintaining good photovoltaic characteristics. This is a significant challenge, but knowing that these efficiencies could be attainable through the three-terminal tandem architecture and the use of composite Ag nanowire / polymer electrodes is a promising step forward in OPV research.

5.4. Section Conclusion

In this section, PEDOT / Ag nanowire composite electrodes were demonstrated as effective intermediate electrodes for tandem organic photovoltaic cells that have three-terminals and are not constrained by current-matching. This device architecture allows each cell in a stacked tandem structure to be independently electrically accessed such that each cell can produce a different amount of photocurrent that still contributes to the overall power generated by the stack, as the efficiency of the total stack is simply the sum of the efficiencies of the component cells. This device architecture, made possible by the composite electrodes, allows for greater freedom in stack design, as the tandem cells only need to be optimized optically.

Both theoretical and experimental device data was presented. 3-terminal tandem cells using a solution-processed P3HT:PCBM front cell and a CuPc:C\textsubscript{60} thermally evaporated
back cell. The experimental data matched closely with the model in predicting cell efficiency. This model was then used to simulate a high-efficiency tandem structure that combines materials shown to produce high-efficiency single-junction OPV cells. The simulated result was that 7.7% power conversion efficiency could theoretically be achieved with that materials combination. A fully optimized 3-terminal tandem cell with perfectly complimentary absorbers has been shown to have a maximum efficiency of 12.3%, which shows that this is a very promising device architecture for producing very high efficiency OPV cells.
6. Composite Fabrication and Cost Structure

We have demonstrated in the work presented in the previous sections that PEDOT / Ag nanowire laminated composite films have low sheet resistance, high transparency, low surface roughness, and can be used as an ITO replacement in polymer OPV cells. This is important work because the cost of OPV cells is limited currently by the cost of the ITO transparent conductor.\textsuperscript{62} In addition, on plastic substrates with a roll-to-roll high throughput process, the performance of ITO is poor, bringing down the efficiencies of devices fabricated on it.\textsuperscript{89} It is well established that a high-throughput printing method is one of the lowest-cost methods of depositing a thin film, and thus a high-performance transparent conductor has a price advantage if it can be deposited from solution in a roll-to-roll fashion, which we have demonstrated here. However, we must also perform a cost analysis on the materials to confirm that fabricating these films is indeed more economical than ITO.

In this section, we detail the fabrication of PEDOT / Ag nanowire composite electrodes on the lab scale, examine their cost structure, and explore opportunities for changing the procedure to possibly further lower the cost. We investigate replacing the PEDOT with another polymer, poly(methyl methacrylate) (PMMA), as well as replacing the transfer method by spraying Ag nanowires from solution, which is a more scalable process. These changes in process and materials also represent opportunities for improving the composite performance while implementing processing that could potentially be commercialized on a large scale.
6.1. Lab-Scale Composite Fabrication Method

Silver nanowires are grown in solution for use in the composite films, following the procedure published by Y. Sun and Y. Xia. 25 mg AgCl and 330 mg polyvinylpyrrolidone (PVP) are dissolved in 20 mL of ethylene glycol and heated to 170°C while vigorously stirred. The ethylene glycol acts as a reducing agent to produce Ag nanoparticle seeds from the AgCl. 110 mg of AgNO₃ dissolved in ethylene glycol are then added to the solution drop wise over 10 minutes. The PVP provides shape control, while the AgNO₃ provides the silver for the slow nanowire growth promoted by the drop wise addition. A centrifuge is then used to separate the nanowires from the ethylene glycol and the wires are re-suspended in methanol for deposition.

Donor nanowire films are fabricated through drop-casting. Coverslip glass #2, 1.8 cm by 1.8 cm, is pre-cleaned with detergent, de-ionized (DI) water, acetone, and boiling isopropanol. The substrates are then treated with poly-L-lysine 0.1 % (Ted Pella) in a 1:2 dilution with DI water for 3 minutes before being rinsed with more DI water and isopropanol then dried with compressed nitrogen. They are placed in a plastic Petri dish on an agitator plate. 25 microliters of Ag nanowire suspension in methanol is dropped onto the center of each substrate and is allowed to dry. Once the substrates are dry they are placed into a glass Petri dish and annealed at 180 °C for one hour.

The polymer film substrates are cleaned in the same manner as the nanowire donor substrates but instead of poly-L-lysine treatment they are treated with UV-ozone for 25 minutes. The cleaning method for both the glass and PET plastic substrates is the same, but before the polymer is deposited the PET is adhered to glass with kapton tape for
stability. PEDOT:PSS is spun-cast at 700 rpms to produce a 125 nm thick film and is annealed at 150 °C for 20 minutes. The donor films are then pressed into the polymer substrate using a manual hydraulic shop press (Torin Big Red Jack) at $2.4 \times 10^4$ psi between two steel plates then rotated 90 degrees and pressed once more. The nanowires sink into and are transferred to the polymer, and the donor glass can be removed. The composite is then pressed with a clean glass substrate for further flattening at $1.2 \times 10^4$ psi. Following this procedure, the film can be patterned using acetone on an applicator for use in devices.

### 6.2. Large-Scale Composite Cost Analysis

Based on this fabrication procedure, a materials cost analysis can be done to determine whether this materials system could, on a large scale, compete commercially with ITO. This cost analysis is based on a yield of 75% for 20 mL of synthesis, which, for a successful synthesis process is a good estimation. Bulk pricing for the chemicals used in the synthesis, AgCl, AgNO$_3$, ethylene glycol, polyvinylpyrrolidone (PVP), and the methanol for deposition were obtained from GFS Chemicals (AgCl, AgNO$_3$, ethylene glycol), Sigma Aldrich (PVP), and Duda Diesel (methanol). The prices and quantities are listed in Table 6.1, as well as the synthesis cost for 20 mL, and the cost, based on the area coverage used in the fabrication procedure, of coating one square meter of substrate.
Table 6.1. Bulk pricing for chemicals used in 20 mL of solution of Ag nanowire synthesis (assuming 75% yield) and cost for coating one square meter of donor substrate for large-scale composite manufacture. Total cost for all materials in composite is $2.74 per square meter.

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Bulk Price</th>
<th>Synthesis Cost</th>
<th>$ / m²</th>
<th>Cost %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>1 kg</td>
<td>$800.64</td>
<td>$0.02</td>
<td>$0.08</td>
<td>3.01%</td>
</tr>
<tr>
<td>Polyvinylpyrrolidone</td>
<td>1 kg</td>
<td>$65.00</td>
<td>$0.03</td>
<td>$0.12</td>
<td>4.21%</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>1 kg</td>
<td>$599.00</td>
<td>$0.07</td>
<td>$0.27</td>
<td>9.77%</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>1 L</td>
<td>$5.06</td>
<td>$0.10</td>
<td>$0.41</td>
<td>15.03%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1 L</td>
<td>$0.70</td>
<td>$0.01</td>
<td>$0.04</td>
<td>1.50%</td>
</tr>
<tr>
<td>PEDOT:PSS AI 4083</td>
<td>1 kg</td>
<td>$400.00</td>
<td>N/A</td>
<td>$1.82</td>
<td>66.48%</td>
</tr>
</tbody>
</table>

As shown in the table, bulk pricing for electronic grade PEDOT:PSS, Clevios AI 4083, manufactured by H. C. Starck, Inc. as used in this work, is $400 per kilogram in bulk. Based on the solids content of the suspension and the density of the molecules, and assuming a coating system without waste such as printing or doctor-blading, it would cost $1.82 to coat one square meter with a 125 nm thick film. From the cost percentage calculation in the table, it is clear that the polymer contributes most heavily to the total cost of the film at 66.5% of the total cost of $2.74 per square meter. However, this cost is already well below $8 - $13 per square meter for ITO. This analysis does not include manufacturing costs, but printing and lamination equipment cost far less than sputtering chambers, and over the life of the machinery they should contribute less to the film cost than the materials themselves.
6.3. **Replacing PEDOT in the Composite Structure**

If the electronic grade PEDOT:PSS were to be replaced with either a different grade of PEDOT:PSS (e.g. Clevios P) or a different polymer altogether (e.g. poly(methyl methacrylate), PMMA) this could bring the cost down significantly. Clevios P costs $95 per kilogram in bulk, resulting in a total composite cost of $1.35 per square meter, while PMMA costs only $2.13 per kilogram in bulk,\textsuperscript{146} and would thus be a negligible contributor to the cost of the composite at far less than one cent per square meter, resulting in a total composite cost of under $1 per square meter. In addition to cost, there are other reasons that replacing the PEDOT:PSS in these composites could be advantageous. As shown in Section 2, the 125 nm PEDOT:PSS film has 3 – 5% parasitic absorption in the visible spectrum, and replacing this layer with a more transparent polymer should increase the optical transmission of the composites as a whole. In addition, PEDOT:PSS is acidic and hygroscopic, and studies have shown that the acidity and water uptake in this material can reduce the lifetime of devices built with it.\textsuperscript{27, 28} PEDOT films also have a hydrophilic surface, and consequently it can be difficult to spin additional PEDOT in the device layers on top of the composite without dissolving it. Hence, replacing the PEDOT:PSS with a different polymer should increase the composite’s stability, shelf-life, and the lifetime of organic solar cells fabricated using composite anodes.

PMMA was chosen as the first replacement polymer for PEDOT:PSS in our experimental procedure. PMMA dissolved in anisole (MicroChem Corp.) is used as a
resist for electron beam lithography. It can be spin-cast onto a variety of substrates with precise thickness control, and is transparent and crosslinkable. For PMMA / Ag nanowire composites, all substrates were prepared the same way as with the PEDOT:PSS / Ag nanowire composites, except that PMMA dissolved in anisole with molecular weight 950,000 g/mol was spun onto glass at 1325 rpm to produce a 125 nm thick, highly transparent film. There is almost no absorption in a 125 nm thick PMMA film over the visible spectrum, and it acts as an anti-reflection coating on the back surface of a glass substrate, as its index of refraction is 1.492 compared to the 1.5 index of glass. This is an improvement of 3-5% in total transmission over the same thickness PEDOT film, and should result in more transparent composite films.

The standard device fabrication procedure for P3HT:PCBM OPV cells was followed in order to make PV cells to evaluate how effective these electrodes are. First, PEDOT:PSS (Clevios AI 4083) was spun onto the substrate at 3000 rpm. This is a difficult process because PMMA is hydrophobic, and PEDOT:PSS is in aqueous solution, and the film formed is not as smooth or continuous as those spun on either ITO / glass or PEDOT / NW composites. The PEDOT:PSS layer is annealed at 150 °C for 20 mins before the substrate is transferred to the glove box and the active layer of 2.5 wt % P3HT:PCBM in ortho-dichlorobenzene is spun at 800 rpm and is allowed to slowly dry overnight in a covered Petri dish. Following drying, the active layer is annealed at 110 °C for 10 mins to evaporate any remaining solvent, and then a 7nm Ca plus 150 nm Al electrode is evaporated.
Figure 6.1. Scanning electron micrographs of PMMA / Ag nanowire composite films. 6.2.a, top-down view showing wire mesh network. 6.2.b, angled surface view showing all nanowires lying flat. 6.2.c, close-up angled view showing embedded junctions as well as feature protruding ~100 nm above polymer surface as shown with the arrow.

SEM images of the composite electrodes post-nanowire transfer were taken to examine the surface morphology. Shown in Figure 6.1 is a top-down, flat image showing the percolating network (a), an angled cross-section showing the nanowires lying in the plane of the substrate (b), and a close-up angled cross-section in which a junction between two wires can be seen (c). Images a and b appear very similar to those composites fabricated using PEDOT:PSS (Figure 2.2). The nanowires form a network through which current can be conducted laterally, and they all lie flat in the plane, as is
consistent with a 125 nm thick polymer film. Image c shows an embedded junction, as expected for a 125 nm thick polymer film, but it also shows portions of the nanowire film that protrude further above the surface than the junction. This feature, indicated by the arrow, also has a round cross-section that is approximately 100 nm high. This indicates that the composites fabricated using PMMA may have a larger top-to-bottom roughness than those fabricated with PEDOT:PSS, and will have an effect on the devices built using them. In addition, the wires appear flatter than those embedded into PEDOT. This is an indication, based on the mechanics study in Section 3, that the PMMA produces a harder 125 nm thick film than does PEDOT. These differences in morphology could possibly be remedied by using higher pressures to transfer the nanowires.

**Figure 6.2.** Current density vs. applied voltage in the dark (dashed) and under 100 mW/cm² of solar simulated illumination for the device structure: PMMA:AgNW / PEDOT
(50 nm) / P3HT:PCBM (200 nm) / Ca (7nm) / Al (150 nm). Device power conversion efficiency is 3.0%.

Figure 6.2 shows the current density vs. applied voltage curve in the dark (dashed) and under 100 mW/cm² of solar simulated illumination (solid) for this standard P3HT:PCBM OPV cell on a PMMA / Ag nanowire electrode on glass. The power conversion efficiency of this cell is 3.0%, with the Voc = 0.62 V, the Jsc = 9.3 mA/cm², and the FF = 0.52. However, this cell performance is not as good compared to the P3HT:PCBM cell performance on ITO and on PEDOT / Ag nanowires largely due to the drop in fill factor from 0.65 with PEDOT to 0.52 with PMMA. The loss in fill factor is directly related to the shape of this JV curve, which shows a lower shunt resistance than for the devices on PEDOT with better fill factors. This shunting is most likely due to the higher degree of roughness in the electrode as compared to those fabricated with PEDOT:PSS as the base polymer. This stems from the two polymers having different mechanical properties. If PMMA is harder and more resistant to embedding, the wires will protrude further from the surface. In addition, the first PEDOT:PSS layer in the device fabrication process is used to planarize the surface. If the underlying surface is rougher or too hydrophobic, this may not be happening to the necessary degree, especially if the PEDOT:PSS isn’t wetting the PMMA surface as well as it wets the hydrophilic PEDOT / Ag nanowire composite.
6.4. Spray-Coating Ag Nanowires onto PMMA

In addition to replacing PEDOT with PMMA, a spray-deposition process to put down a layer of nanowires on top of spin-cast PMMA was developed. The nanowire laminated transfer process, while processed from solution, is still a batch process because each substrate must be laminated individually. Spray deposition is far more scalable than nanowire transfer and can be used to fabricate much larger-area films. The isopropanol nanowire suspension is pushed using a syringe through a line and through an atomizing nozzle. The substrates sit on a heated stage at 80 ºC that moves back and forth and allows for large area nanowire coverage. Spraying is done under laminar nitrogen flow and the density of nanowires deposited is controlled by the dilution of the suspension. The PMMA is spin-cast in the same manner as for the transferred composite films, but rather than fabricate Ag nanowire meshes on donor substrates, the wires are sprayed directly onto the PMMA and embedded using a mechanical press. The wires used in this process are commercially produced (Seashell Technologies, Inc) for the sake of the larger volume needed for spraying. Two lengths of Ag nanowires were purchased from Seashell, one 16 microns and the other 31 microns.

Due to the differences in the deposition process and in the mechanics of the commercially produced Ag nanowires, the post-fabrication processing of these films is different from the transferred composites. Pressure is used to embed the wires into the polymer. However, it was found that using the same amount of pressure as was needed to transfer the lab-grown wires into the PEDOT or PMMA was not sufficient to embed the commercial wires into PMMA. An SEM image is of the junctions between the wires is shown in Figure 6.3. This sample was pressed at $1.6 \times 10^4$ psi, and contains 0.3 mg of 16-
micron long Ag nanowires. As deposited, the sheet resistance was 4.5 MΩ/□. After pressing, this sheet resistance decreased to 8.5 Ω/□ with no heat treatment. However, despite the pressure and the inference from the drastic drop in sheet resistance that the junctions between the wires are making intimate contact, those junctions, as is clear from the SEM image, are not embedded into the polymer but rather lie above its surface, creating significant roughness that was not present in the transferred composite films made with lab-grown wires. This roughness is not compatible with efficient OPV devices, so different processing steps must be taken.

**Figure 6.3.** SEM image of sprayed commercial 16 µm long Ag nanowires on 125 nm of PMMA. Wire-wire junctions are shown (one of which is indicated by the arrow) and are not fully embedded into the polymer. Sample has a sheet resistance of 8.5 Ω/□.

Using only pressure, very reproducible low sheet resistance values could be attained with no heat treatment at all. Some samples were annealed after spraying using a laser to lower the initial sheet resistance and fuse the junctions, but after pressing, the laser anneal
didn’t make much of a difference in the final sheet resistance values, all of which were under 6 Ω/□. The effect of higher pressures on sprayed wires and the corresponding sheet resistance drops can be seen in Table 6.2. However, this is not necessarily an indication of embedded junctions, rather only that the wire-wire junctions are making intimate contact.

Table 6.2. Effects of higher pressure on the sheet resistance of spray-deposited composite electrodes without heat treatment.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Laser Anneal</th>
<th>Initial Rs</th>
<th>Pressure (psi)</th>
<th>Rs Post-Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass / PEDOT / Ag NW</td>
<td>yes</td>
<td>6.98 Ω/sq</td>
<td>3.2 x 10^4</td>
<td>5.5 Ω/sq</td>
</tr>
<tr>
<td>Glass / PEDOT / Ag NW</td>
<td>no</td>
<td>2.8 kΩ/sq</td>
<td>3.2 x 10^4</td>
<td>4.6 Ω/sq</td>
</tr>
<tr>
<td>Glass / PMMA / Ag NW</td>
<td>yes</td>
<td>4.68 Ω/sq</td>
<td>3.2 x 10^4</td>
<td>4.3 Ω/sq</td>
</tr>
<tr>
<td>Glass / PMMA / Ag NW</td>
<td>no</td>
<td>4.8 MΩ/sq</td>
<td>3.6 x 10^4</td>
<td>6.4 Ω/sq</td>
</tr>
<tr>
<td>PET / PEDOT / Ag NW</td>
<td>no</td>
<td>800 Ω/sq</td>
<td>3.2 x 10^4</td>
<td>6 Ω/sq</td>
</tr>
<tr>
<td>PET / PEDOT / Ag NW</td>
<td>no</td>
<td>369 Ω/sq</td>
<td>3.6 x 10^4</td>
<td>6 Ω/sq</td>
</tr>
<tr>
<td>PET / PMMA / Ag NW</td>
<td>no</td>
<td>1.8 MΩ/sq</td>
<td>3.2 x 10^4</td>
<td>6 Ω/sq</td>
</tr>
<tr>
<td>PET / PMMA / Ag NW</td>
<td>no</td>
<td>20 MΩ/sq</td>
<td>3.6 x 10^4</td>
<td>5.2 Ω/sq</td>
</tr>
</tbody>
</table>

Based on the mechanics of indentation described in Section 3, for the nanowires to indent the polymer and become embedded, they have to be harder than the polymer and not too soft such that they flatten before sinking into the polymer film. From the SEM images, it is clear that the mechanics of these commercial wires and how they interact
with the PMMA are different from the lab-grown wires. This is most likely due to the wire growth method, which Seashell Technologies will not share with its customers. However, the commercial growth method is certainly different from the method by which the lab wires are grown, and as a result, these wires most likely have different crystal defect structures, which affects their deformation mechanics. Because the junctions are sitting above the polymer, the conclusion can be drawn that the polymer is too hard relative to the wires, which likely means that the commercial wires are softer than the lab-grown ones. Because we cannot change the defect mechanics of the wires themselves, this issue must be tackled by adjusting the polymer layer. The polymer hardness can be adjusted in two ways. The first is to use a slightly thicker polymer layer. According to the plots in Figure 3.2, the thinner the polymer film is, the higher effective hardness the wire will feel at a shallower contact depth due to the hard glass substrate. Thus, a thicker film on glass will feel softer to the nanowire. In addition, a polymer film heated above its glass transition temperature will soften, as the polymer chains are freer to flow. This should also allow the nanowires and the wire-wire junctions to sink into a softened film.

Figure 6.4 shows SEM images of the wire-wire junctions in which the wires were pressed at a temperature of 100 °C at 6.0 x 10^4 psi, at the glass transition temperature of PMMA^{149}, into a 125 nm-thick film (Figure 6.5 a-b) and at 100 °C at 6.0 x 10^4 psi into 145 nm of PMMA (Figure 6.5 c-d). Both of these methods are effective in embedding the junctions between the wires away from any devices built on top of them and therefore in reducing the surface roughness. Both samples were fabricated using 31 micron long wires, with the sample on 125 nm thick PMMA having a sheet resistance of 3.9 Ω/□. 
visible transmission ~80% and the sample on 145 nm thick PMMA having a sheet resistance of 5.8 Ω/□ with visible transmission ~84%.

Figure 6.4. Angled SEM images of sprayed Ag nanowire / PMMA composite films with embedded and fused wire-wire junctions. Top (a-b): 125 nm of PMMA with wires embedded by pressing at 6.0 x 10^4 psi at 100 ºC. Sample uses 31 micron long wires and has a sheet resistance of 3.87 Ω/□. Bottom (c-d): 145 nm of PMMA with wires embedded by pressing at 6.0 x 10^4 psi at 100 ºC. Sample also uses 31 micron long wires and has a sheet resistance of 5.8 Ω/□.
The performance of the commercial wires embedded into PMMA in terms of transparency and sheet resistance surpasses that of the transferred composites using PEDOT:PSS. This is for two reasons. PMMA is more transparent at the embedding thickness than is PEDOT (Figure 2.4), and the longer commercial wires with flattened junctions via pressing result in higher conductivities and lower sheet resistances. Figure 6.5 shows the transmission curves for two example films using 31-micron long commercial sprayed Ag nanowires pressed at 6.0 x 10^4 psi into spin-cast 145 nm thick PMMA films at 100 °C. These two composite films have sheet resistances of 5.8 Ω/□ and 7.3 Ω/□ with average transmission in the visible wavelengths of 84% and 87% respectively not including the glass substrate. This performance is improved over the 12 Ω/□ and 86% transmission reported in Section 2.

![Graph](image)

**Figure 6.5.** Transmission curves (not including glass substrate reflections) and sheet
resistance values for Ag nanowire / PMMA composites deposited via spin-casting PMMA and spraying nanowires onto a glass substrate. The composites were then pressed at $6.0 \times 10^4$ psi at 100 °C to reduce surface roughness and sheet resistance.

In conclusion, this section has detailed both the fabrication method of lab-scale transferred polymer / Ag nanowire composites and also a scalable version of these composites deposited by spray-coating. OPV data has been shown for transferred composites using PMMA, and while the same device performance as reported in Section 2, using PEDOT, was not achieved, the devices are promising. The large-scale cost structure for these components has been outlined, showing that the composites, even using expensive electrical grade PEDOT Al 4083, are much less costly than ITO. Replacing PEDOT with a cheaper, more abundant polymer such as PMMA can reduce this cost, as the polymer is the single most expensive component of the composite, at 66.48% of the cost. Using PMMA as the polymer component of the composite results in a total composite cost of under $1 per square meter. Spray coating was demonstrated as an alternative to transferring nanowires for large-scale manufacturing. And lastly, the performance metrics of high transparency and low sheet resistance can be improved through the use of longer, spray-coated Ag nanowires, with heated pressing but no further high temperature anneal, and using PMMA, as it is a high-transparency polymer. Sheet resistances as low as 7.3 $\Omega/\square$ with 87% transmission over the visible spectrum are reported in this section, both values of which are better than those reported in Section 2 using PEDOT.
6.5. Section Conclusion

In this section the details of the PEDOT / Ag nanowire fabrication process were presented, along with the large-scale cost structure of the composites as presented and fabricated. The materials cost of the composite films as fabricated is $2.74 per square meter, compared with $8 – 13 for ITO\textsuperscript{62} which is very favorable. Strategies to reduce the cost of the composite films while potentially improving their performance and allowing for scalability in manufacturing were discussed. This included replacing the PEDOT:PSS with PMMA, which is more transparent, but also changes the mechanics of the process, as it appears to be a harder thin film. However, replacing PEDOT Al 4083 with PMMA would reduce the composite cost to under $1 per square meter.

A spray-coating technique was explored as a way to fabricate these composites on a larger scale by spraying the nanowires directly onto the polymer films rather than using transfer lamination from donor substrates. The post-spray processing of these films had to changed from the lamination process, as the mechanics of the commercial wires were different from the lab-grown wires. However, superior performance to PEDOT:PSS composites were seen in the spray-coated PMMA / commercial Ag nanowire composites, due to both the better transparency of PMMA as compared to PEDOT:PSS and to the lower sheet resistance brought about through using longer nanowires. By pressing the wires into the PMMA film while heating to the glass transition temperature of PMMA, smooth films with fused wire-wire junctions that have sheet resistances as low as 7.3 $\Omega/\square$ with 87% transmission were fabricated.
7. Conclusion

This thesis presented and characterized a composite transparent conductive thin film materials system, comprised of silver nanowires and polymer films, that demonstrates superior performance to all other solution-processed transparent conductors and comparable or improved performance when compared to indium tin oxide, the high-quality industry standard for optoelectronic applications.

Section two of this thesis presented the initial work using the conducting polymer poly-(4,3-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) and laminated Ag nanowire mesh films from donor substrates. It was found that by varying the thickness of the underlying polymer layer, the resulting morphology of the laminated composite could be controlled on the nanoscale. This is very critical, as the morphology of the surface of a transparent conductor will affect the quality of the device that can be built on it. By using 125 nm of PEDOT:PSS on a glass or PET substrate, very smooth composite films, with an RMS roughness value of under 12 nm were created. From SEM images, it is clear that embedding the nanowires into the polymer allows the rough wire-wire junctions between wires to protrude away from the top surface, creating a surface appropriate for fabricating high-quality optoelectronic devices. Transparent conductive films with sheet resistances as low as 12 Ω/□ with 86% transparency were fabricated on glass. On PET, films with sheet resistances as low as 17 Ω/□ with 83% transparency were fabricated. This sheet resistance value on PET is particularly significant, as the best quality ITO on PET only has sheet resistances around 40 Ω/□. These films were also shown to be far more robust to mechanical strain than ITO on flexible PET substrates.
They were bent in tension to a bending radius of 1.4 mm, corresponding to 3.5% strain, without any significant change in sheet resistance in the film. This is far better performance than ITO on PET, in which the sheet resistance increases irreversibly by a factor of 5 at a bending radius of 8.5 mm, corresponding to 0.75% strain.

Organic bulk heterojunction photovoltaic cells based on the P3HT:PCBM materials system were fabricated using these PEDOT:PSS / Ag nanowire composites on both glass and PET substrates. On glass, the high performance cells of ITO on glass were exactly reproduced on the PEDOT:PSS / Ag nanowire composites, and at 4.2%, these are on par with the most efficient OPV cells reported for this materials system. On PET, due to the superior conductivity of the composites as compared to ITO on PET, the efficiency of the OPV cells improved from 3.4% on ITO on PET to 3.8% on PEDOT:PSS / Ag nanowires on PET, making these the most efficient flexible OPV cells ever reported.

Section three of this work examined the PEDOT:PSS / Ag nanowire composites more closely and presented the results of an investigation into the mechanical lamination process, the optical effects of pressure during lamination, and the thermal stability of the composites as compared to bare Ag nanowire mesh films. Nanoindentation was used to determine the hardness of PEDOT:PSS films, which gives insight into the surface morphology of the composite films, as the nanowires flatten during the pressing process. It was found that the ratio of the hardnesses of the nanowires and the polymer can accurately describe the surface roughness and morphology visible via SEM. The optical effects of this lamination procedure were studied by measuring the scattering and reflection from each side of the composite – through the glass and on the surface – and comparing those values to those of a bare drop-cast Ag nanowire mesh film. These
results clearly showed that as the surface flattens, the optical scattering decreases, and the side of the composite visible through the glass is far rougher than the surface, as it behaves in both reflection and scattering much more similarly to the bare Ag nanowires than the pressed composite surface. Samples of both bare Ag nanowire films and PEDOT:PSS composite were heated for 20 minutes at temperatures up to 280 °C to determine the thermal stability of these materials. It was clear from the SEM images of the films post-heating that embedding the nanowires into the polymer slows the coalescence of the wires that occurs at elevated temperatures, and by matching these SEM images to a model, it was determined that thermally activated surface diffusion is responsible for the nanowire spheroidizing at temperatures under 300 °C.

In Sections four and five, applications for PEDOT:PSS / Ag nanowire electrodes were explored in which these composites were used in ways that ITO cannot be used. Section four presented fully solution-processed OPV cells based on the P3HT:PCBM system fabricated on metal substrates using the composite as the top transparent electrode. These devices reached efficiencies of 2.5%, and due to the lamination process via which the electrode is completed, could potentially be encapsulated during the fabrication process, further driving down the potential production cost of this type of fully solution-processed device architecture. However, the overall efficiency of this cell was limited by the roughness of the composite electrode’s underside directed towards the cell, as it was demonstrated in section three that the underside of the composite is far rougher than the surface. This issue would need to be solved for the efficiency of these devices to improve.
Section five demonstrated a three-terminal tandem OPV cell device structure in which a PEDOT:PSS / Ag nanowire composite was used as an intermediate electrode between two stacked OPV cells. This device architecture allows for the independent electrical access of each cell such that the tandem structure is not limited by the requirement of current matching in the top and bottom cells. This simplifies the evaluation of the tandem stack, as the overall efficiency becomes simply the sum of the efficiencies of the top and bottom cells. Experimentally, a three-terminal tandem stack was fabricated using a front solution-processed P3HT:PCBM polymer cell and a back evaporated small molecule CuPc:C₆₀ bilayer cell. The short circuit current densities produced from each cell were very different: 10.1 mA/cm² from the front cell, and 1.89 mA/cm² from the back cell, and yet because of the intermediate electrode, both cells still contribute to the overall efficiency of the tandem. The resulting tandem efficiency was 3.0%, with a 2.6% contribution from the front cell and a 0.4% contribution from the back cell. A model employing transfer matrix formalism was used to model the cell structure and predict the attainable efficiency from this stack, and the model results matched very closely with the experimental structure. However, due to spectral overlap in these two cells and the low efficiency of CuPc:C₆₀ bilayer cells, the efficiency potential of this stack is limited.

The model was then used to evaluate a materials combination with higher efficiency potential in the three-terminal tandem structure. P3HT:PCBM was modeled as the front cell, and the recently reported materials combination of PCDTBT:PC₇₀BM was modeled as the back cell. It was found that this materials combination has the potential to produce three terminal tandem OPV cells with efficiencies as high as 7.7%. With perfectly
complimentary absorbers this two-junction three-terminal tandem architecture has the potential to produce efficiencies over 12%. This is important, as with this architecture materials can be designed for their optical properties with relaxed electronic requirements, and using PEDOT:PSS / Ag nanowire composite electrodes, the three-terminal tandem stack can be realized.

The details of the lab-scale composite fabrication process as well as a large-scale cost structure of composite manufacture were described in Section six. It was found that the total cost of the materials for coating one square meter of substrate with a composite electrode is $2.74, assuming 75% yield from the Ag nanowire synthesis and loss-less coating of the polymer. However, it was also found that the PEDOT:PSS AI 4083, at $400 / kg comprised 66.5% of the total cost of the electrodes. It was also noted in Section two that the conductivity of the PEDOT:PSS AI 4080 contributed minimally, if at all, to the overall conductivity of the composites while showing some parasitic absorption over the visible spectrum. Thus, replacing the PEDOT:PSS with another polymer could not only lower the cost of these composites but could also improve their performance.

PMMA was chosen as the replacement polymer for use in the composite structure. Ag nanowires were laminated into 125 nm of PMMA to form a composite film, and a P3HT:PCBM OPV cell was built on top. This cell had an efficiency of 3.0% with a reduced fill factor when compared to those composites fabricated using PEDOT:PSS. This is due to the different indentation hardness of PMMA as compared to PEDOT:PSS, and the resulting increased roughness of the electrode.
Because lamination limits the fabrication procedure to batch-processing, other composite manufacturing procedures must be employed for larger scales. To this end, spray-coating was used to deposit Ag nanowires onto PMMA films. Commercial Ag nanowires suspended in isopropanol were used and the spray-coating parameters controlled such that the combination of low sheet resistance and high transparency could be obtained. By applying pressure only, the sheet resistances for these sprayed composites dropped from several $\Omega/\square$ to under 10 $\Omega/\square$ without any heat treatments necessary. However, high pressure in combination with heating to the glass transition temperature of PMMA (100 °C) ensured that the wire-wire junctions in the wire mesh were fused and embedded into the PMMA, creating, again, a smooth surface. These electrodes attain sheet resistances as low as 7.3 $\Omega/\square$ at 87% transparency, confirming that replacing PEDOT:PSS with PMMA can indeed improve composite performance.

**Table 7.1.** Transparent conductor performance, including data presented in this thesis.

<table>
<thead>
<tr>
<th>Transparent Conductor</th>
<th>Rs $\Omega$/sq</th>
<th>% Transmission</th>
<th>Best OPV Cell Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO on glass</td>
<td>20</td>
<td>90</td>
<td>&gt; 4% (P3HT:PCBM)&lt;sup&gt;26-29&lt;/sup&gt;</td>
</tr>
<tr>
<td>ITO on PET</td>
<td>42</td>
<td>91</td>
<td>3.66% (P3HT:PCBM)&lt;sup&gt;89&lt;/sup&gt;</td>
</tr>
<tr>
<td>PEDOT PH750 + 5% DMSO</td>
<td>102</td>
<td>84 (at 500 nm)</td>
<td>3.5% (P3HT:PCBM)&lt;sup&gt;73&lt;/sup&gt;</td>
</tr>
<tr>
<td>Carbon Nanotubes (CNT)</td>
<td>200</td>
<td>85</td>
<td>2.5% (P3HT:PCBM)&lt;sup&gt;75&lt;/sup&gt;</td>
</tr>
<tr>
<td>Graphene (solution)</td>
<td>5000</td>
<td>80</td>
<td>0.4% (CuPc:C60)&lt;sup&gt;76&lt;/sup&gt;</td>
</tr>
<tr>
<td>Graphene + CNT</td>
<td>240</td>
<td>86</td>
<td>0.85% (P3HT:PCBM)&lt;sup&gt;78&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ag Nanowires</td>
<td>10</td>
<td>85</td>
<td>0.4% (CuPc:PTCBI)&lt;sup&gt;74&lt;/sup&gt;</td>
</tr>
<tr>
<td>PEDOT / Ag Nanowires</td>
<td>12</td>
<td>86</td>
<td>4.2% (P3HT:PCBM)</td>
</tr>
<tr>
<td>PEDOT / Ag Nanowires</td>
<td>17</td>
<td>83</td>
<td>3.8% (P3HT:PCBM)</td>
</tr>
<tr>
<td>PMMA / Ag Nanowires</td>
<td>7.3</td>
<td>87</td>
<td>3.0% (P3HT:PCBM)</td>
</tr>
</tbody>
</table>
In conclusion, this thesis work represents a significant step forward in transparent conducting thin films research. The composite materials system of Ag nanowires embedded onto the surface of a polymer film shows performance comparable to or better than indium tin oxide on glass and far better than indium tin oxide on plastic substrates. The composites are low-cost, solution-processable, scalable through the use of spray-deposition, show nearly substrate-independent performance, are compatible with high-efficiency organic photovoltaic devices, and show the potential to be used in other high-quality optoelectronic devices. They can also be used to enable device architectures that are not accessible through the use of ITO. Table 7.1 summarizes the performance of various transparent conductors and compares the results presented here with ITO and other solution-processed transparent conductors, and it is clear that the results presented here are far superior to other reported materials systems.
References


5. Sony's New Flexible OLED is Thinner Than a Strand of Hair. 


32. Kim, Y.; Cook, S.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C., Organic Photovoltaic Devices Based on Blends of Regioregular Poly(3-


55. Kirchmeyer; Stephan; Reuter; Knud, Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene). 2005, 15, (21), 12.


64. Konarka Technologies, I. Konarka Opens World’s Largest Roll-to-Roll Thin Film Solar Manufacturing Facility with One Gigawatt Nameplate Capacity.
http://www.konarka.com/index.php/site/pressreleasedetail/konarka_opens_worlds_largest_roll_to_roll_thin_film_solar_manufacturing_fac


150. Zaller, I.; Frost, J. E. F.; Chabasseur-Molyneux, V.; B., F. C. J.; Pepper, M., Crosslinked PMMA as a high-resolution negative resist for electron beam lithography and applications for physics of low-dimensional structures. Semiconductor Science and Technology 1996, 11, 1235-1238.
