Studies of Conjugated Polymer Semiconductor Electronics and Optoelectronics

Dissertation

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By

Woo-Jun Yoon, M.S.E.
Graduate Program in Electrical and Computer Engineering

The Ohio State University
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Dissertation Committee:
Dr. Paul R. Berger, Advisor
Dr. Steven A. Ringel
Dr. Malcolm H. Chisholm
Abstract

Conjugated polymer semiconductors with their solution processibility at room temperature make them a key component for light-weight, large-area, flexible electronics and optoelectronics. This dissertation focuses on a number of advanced polymer semiconductor electronic and optoelectronic devices.

Highly efficient polymer bulk heterojunction (BHJ) solar cells were demonstrated through process optimization including varying the thickness of the LiF cathode interlayer sandwiched between the photoactive layer and Al cathode along with changing the postproduction annealing temperature. While varying the thickness of the LiF interlayer between the photoactive layer and Al cathode and the postproduction annealing temperature, a power conversion efficiency ($\eta_{eff}$) up to 3.6% with a high fill factor (FF) of 66% and an open circuit voltage ($V_{oc}$) of $\sim$0.61V was obtained when the devices incorporated with a 0.6 nm thick LiF layer were postproduction annealed at 160 °C for 30 min with a fixed donor and acceptor weight ratio of 1.0:0.8.

Surface modifications to the anode were also investigated for enhanced efficiency of polymer solar cells. An improved $\eta_{eff}$ for polymer BHJ solar cells was demonstrated, mainly due to the enhanced $J_{sc}$ through the usage of a thin islanded plasma-modified Ag atop indium tin oxide (ITO) anodes. Under forward bias, an enhanced hole injection was
recorded due to the interfacial energy step created between the ITO and the photoactive layer. An increased internal electric field increases at the anode interface may be assisting the extraction of photogenerated holes, leading to the increased $J_{sc}$ without significant changes to $V_{oc}$, FF, and the $R_s$ in the solar cell with modified surface.

In order to improve the efficiency of organic solar cells, one approach could be to yield increased optical absorption and photocurrent generation in the photoactive layer over a broad range of visible wavelengths by inducing surface plasmons through careful control of metallic nanoparticle’s properties. Plasmon-enhanced polymer solar cells were demonstrated using unique self-assembled layers of silver nanoparticles. An enhanced optical absorption was observed that improved $J_{sc}$ for polymer BHJ solar cells, mainly due to the localized surface plasmon-enhanced photogeneration through the usage of plasmon-active Ag nanospheres between the anode interfacial layer and the photoactive layer. In spite of the increased $J_{sc}$, significant $V_{oc}$ and FF losses were observed because of the surface recombination at the interface between the anode interfacial layer and the photoactive layer.

Conjugated polymer semiconductors and associated materials are very sensitive to intrusion of air or moisture and necessitate hermetic seals. A laser sealing approach was also investigated for air-stable operation of flexible organic solar cells. This work also aims to significantly reduce encapsulation times through rapid sealing via tailored laser welding, making immediate commercialization of organic solar cell technology highly probable. This project successfully demonstrated the feasibility of using a diode laser source to seal flexible polymer solar cells with anodes and cathodes. Throughout the
study, moderate seal strengths were obtained for each electrode material combination. Active solar cells were encapsulated and their partial operation was verified.

Strong negative differential resistance (NDR) performance of polymer tunnel diodes exhibiting large and reproducible NDR with a peak-to-valley current as high as 53 at room temperature was demonstrated. Additionally, a basic logic circuit operation was demonstrated using a pair of these polymer tunnel diodes connected in series to form a monostable-bistable transition logic element latch. This result indicates that polymer tunnel diodes are potential candidates for many flexible, low-power logic and memory applications for organic devices by using low-cost and simple solution processing.

A major hurdle to progress foldable electronics is the development of new gate dielectrics for flexible all-polymer, high performance thin film transistors (TFT). Organic based flexible dielectric films with high-$k$ for low voltage operation are desirable for future applications of organic TFTs, such as smartcards and radio frequency identification (RFID) tags, concurrently with flexible or conformable form factors. Polymeric bipolar thin films were investigated for their potential application as the gate dielectric in TFTs. A multilayer stack of polymeric thin films composed of alternating amine and carboxylic acid functional groups was deposited by pulsed plasma polymerization produced a composite structure having a relatively high-$k$ and low leakage current density as obtained without postdeposition annealing. This high performance multilayer polymer film stack, deposited at ambient temperature was not subjected to further treatment of any kind, is very promising in terms of use as a flexible dielectric material.
Dedication

Dedicated to my family
Acknowledgements

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Vita

1999....................................................B.S. Metallurgical Engineering, Korea University

2001....................................................M.S. Metallurgical Engineering, Korea University

2006....................................................M.S. Electrical Engineering, Ohio State University

2006 to present.................................Graduate Research Associate, Ohio State University

Publications

Refereed Publications


5. Woo-Jun Yoon, Sung-Yong Chung, Paul R. Berger, and Sita M. Asar "Room temperature negative differential resistance in polymer tunnel diodes using a thin


Conference Proceedings and Meeting Abstracts


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Field of Study

Major Field: Electrical and Computer Engineering
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Chapter 1: Introduction

Conjugated polymer electronics and optoelectronics are of tremendous interest for their potential to augment silicon electronics and the opportunity for relatively low-cost production on flexible, large-area substrates with high-throughput.

For example, the most successful application for conjugated polymer-based optoelectronics is organic light-emitting diodes (OLED) technology currently used in commercial applications such as small display screens for mobile phones and portable digital audio players; OLED displays are slowly replacing traditional liquid crystal displays (LCDs). Comparatively, polymer solar cell technology opens an excellent opportunity for point-of-use energy harvesting due to its potential for low-cost, large-area, and high-throughput. In recent years significant effort has been made toward commercializing polymer solar cells (i.e., Konarka) mainly due to the promising technology of lower costs compared to existing technology and the potential of fabricating flexible large-area devices at low process temperatures on flexible substrates.

Besides the performances of organic and conjugated polymer based thin-film transistors (TFT) had tremendous progress in the last decade for their niche applications, such as radio-frequency technologies, pixel drivers and switching elements in an active-matrix display (e.g., Plastic Logic). In parallel with these developments, a variety of high-\(k\) gate dielectrics using inorganic, polymeric, and self-assembled monolayer or
multilayer gate dielectrics, has been successfully implemented in TFTs, greatly reducing TFTs’ operating voltage and exhibiting excellent device performances. Polymer tunnel diodes are potential candidates to augment existing polymer electronics for many flexible, low-power logic and memory applications by replacing circuit complexity, number of devices and circuit power consumption.

This dissertation will consist of 8 chapters. Generally each of the following chapters consists of two parts. The first part is a summarization of prior work and background required to develop the experiments presented in this dissertation. The second part outlines experimental procedures and results as part of this dissertation.

In Chapter 2, a comprehensive overview of polymer solar cells will be presented in terms of the organic polymeric materials commonly used, a typical device configuration and the photocurrent generation steps in the device. The efficiency limiting factors in polymer solar cell will also be discussed.

A literature survey concerning process optimization for efficient polymer solar cells is first reviewed in Chapter 3. In the second part of Chapter 3 highly efficient polymer solar cells will be presented through process optimization including varying the thickness of a LiF cathode interlayer sandwiched between the photoactive layer and Al cathode along with changing the postproduction annealing temperature.

Chapter 4 will describe examples of prior work of interface and surface modifications to electrode for improved efficiency of polymer solar cells. Experimental results will be reported in the remaining part of Ch. 4, including optical, physical, chemical and electrical characterization of plasma-modified anode and device characterization of solar cells incorporating plasma-modified anode.
In Chapter 5, plasmon-enhanced polymer solar cells will be discussed toward enhancing optical absorption and resulting photocurrent output. The first part will provide an overview of plasmonic solar cells, including characteristics of localized surface plasmons in metal nanoparticles, wavelength tunability and examples of applications using plasmonic materials for various solar cells. We will then present the findings of our experimental work on plasmon-enhanced polymer solar cell using unique self-assembled layer of silver nanoparticles.

In Chapter 6, hermetic seals for polymer solar cells for long-term stability will be discussed. First, the failure mechanism to long-term stability in organic solar cells will be reviewed and examples of certified organic solar cells for commercial application highlighted. Next, the preliminarily experimental results for a laser sealing approach for air-stable operating and flexible organic solar cell will be presented.

The experimental investigation of negative differential resistance (NDR) in organic thin-film devices will be briefly reviewed in the first part of Chapter 7. Strong NDR performance of polymer tunnel diodes exhibiting large and reproducible NDR with a peak-to-valley current as high as 53 at room temperature will be then presented. Furthermore, a basic logic circuit operation will be demonstrated using a pair of these polymer tunnel diodes connected in series to form a monostable-bistable transition logic element latch.

Finally, organic dielectric films suitable for TFTs and facilitating all-polymer TFTs by tailoring high-\(k\) polymer films will be discussed. The present study in Ch. 8
involves an innovative approach to synthesis of totally organic dielectric films based on multilayered bipolar films produced by plasma enhanced chemical vapor deposition (PECVD).
Chapter 2: Polymer bulk heterojunction photovoltaic devices

2.1 Motivation

The world annual global energy consumption is expected to expand from the present level of ~13 terawatt (TW) to 30–50 TW by 2050 [25]. In order to meet this huge future demand, the proportions between various energy sources must each consider their impact on global warming and future supplies, which is raising tremendous interest in green energy solutions. Among various renewable sources, such as hydro-electric, geothermal, wind, solar and biomass power, the overall potential of solar power with about $1.2 \times 10^5$ TW of solar power striking the earth may be the only renewable energy source with the capacity to meet such a large portion of future energy demands [25].

Although there are various approaches for utilizing solar power, such as solar thermal systems, this dissertation addresses photovoltaic (PV) electricity generation for renewable, clean and sustainable energy sources while minimizing detrimental effects on the environment by reducing atmospheric emissions. To fully harvest energy directly from sunlight using PV technology, the U.S. Department of Energy is heavily funding research and development efforts into PVs through the Advanced Energy Initiative and the President's 2007 Budget propose a new $148$ millionSolar America Initiative (SAI) to accelerate the development of advanced PV materials that convert sunlight directly to
electricity [26]. The purpose of the SAI is to make PV cost-competitive with other forms of renewable electricity by 2015 [26].

Among various types of solar cells, organic solar cells open an excellent opportunity for point-of-use energy harvesting. Organic solar cells have become a focus of research due to their potential for low-cost, large-area, and high-throughput. A key advantage of organic PV technology is that organic materials being investigated are inherently inexpensive; typically have very high optical absorption coefficients; are compatible with plastic substrates; and can be fabricated using high-throughput low temperature processes for low-cost roll-to-roll manufacturing. Because of the potential for high-throughput industrial manufacturing of organic solar cell modules, organic PV technology is viewed by industry as an emerging technology, requiring less capital investment than fabrication techniques for Si-based devices.

Since the first investigation of an organic solar cell was performed in 1959 [27], the majority of work on solar cells use a single absorbing layer of organic semiconductor, resulting in very low efficiency (less than 1%). In organic semiconductors, the absorption of light always produces a tightly bound electron-hole pair (a mobile excited state or a Frenkel exciton) rather than free electron-hole pair as in inorganic materials. This occurs because organic materials typically have a low dielectric constant (typically 2-4) and excitons are localized on the molecules by weak intermolecular forces [28]. This low efficiency in single organic layer PV devices is because excitation dissociation requires a higher energy than the room temperature thermal energy [29]. In addition, the exciton diffusion length typically shows a large fluctuation, ranging from 5 to 20 nm, much shorter than the photoactive layer thickness [30-32]. The major breakthrough in organic
solar cell performance came in 1986 when Tang reported about 1% power conversion efficiency from a device with an organic heterojunction consisting of an electron donor and an electron acceptor layer [33]. This heterojunction concept is the fundamental topology of current organic PV cells to overcome the intrinsic disadvantages of exciton generated solar cells, such as dye-sensitized solar cells [34] and planar heterojunction solar cells based on small molecular weight organic materials [35].

The significant breakthrough in organic solar cells was reported in 1992 by Heeger *et al.* introduced the bulk heterojunction (BHJ) as a promising opportunity by mixing together conjugated polymer materials as the donor and a fullerene (or its derivative) as the acceptor materials, creating so called polymer:fullerene BHJ solar cell [36, 37]. Since then, the performance of polymer:fullerene BHJ solar cells has improved rapidly from very low efficiencies to moderate efficiencies, such as *Konarka* at 5.2% (12/2006) and *Plextronics* at 5.4% (7/2007), where efficiencies were certified by the National Renewable Energy Laboratory (NREL) [38, 39]. Furthermore, Konarka’s flexible polymer-based BHJ solar cell demonstrated high lifetimes (>1000 hrs) under accelerated conditions tested by the Energy Research Centre of the Netherlands brings commercialization of this technology to the forefront [40].

However, the overall performance of polymer:fullerene BHJ solar cells is not yet high enough for commercial opportunities. A break-even point is anticipated if polymer solar cell efficiencies surpass 10%. Current disadvantages are the narrow absorption of the incoming solar spectrum in the photoactive layer as well as the low long-term stability of the devices. A number of key issues must be overcome in order to maximize the overall efficiency of the devices. In particular, the short-circuit current needs to be
increased either through photo absorption enhancement with infrared (IR) sensitive, low-bandgap organic material and active acceptor materials or by improving the charge mobility and thus charge collection efficiency [41]. For example, most semiconducting organic polymers have a bandgap larger than 1.9 eV, which covers only ~24% of the air mass 1.5 global (AM 1.5G) solar photon flux, while a bandgap of 1.1 eV can cover ~63% of the AM1.5G solar photon flux assuming ideal absorption of the solar photon flux by the materials. Another approach to improving the short-circuit current in polymer:fullerene BHJ PV devices is interface and surface engineering to the electrodes, such as surface plasmons at the anode surface [42] or efficient electron-blocking/hole-transporting anode interfacial layers [2]. Or the tandem cell architecture or multi-junction solar cell could be an effective approach to improve cell efficiency [43, 44]. Finally, device degradation should be addressed in terms of device design, materials engineering, and an improved encapsulation method [45].
2.2 Overview of polymer:fullerene derivatives bulk heterojunction photovoltaic devices

Figure 2.1 shows several examples of a few commonly used conjugated polymer organic materials and fullerene derivatives. In polymer:fullerene BHJ solar cells, the photoactive layer is based on a mixture of conjugated polymers with fullerene derivatives with the primary effect of an ultrafast photoinduced electron transfer between the conjugated polymer and the fullerene derivatives upon exposure to sun light [36].

![Chemical structure and abbreviations](image)

Figure 2.1 Chemical structure and abbreviations of a few commonly used conjugated polymer materials as electron-donating materials (p-type) and fullerene derivatives as electron-accepting materials (n-type): (a) Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (b) Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) (c) Poly(3-hexylthiophene-2,5-diy) (P3HT) (d) Phenyl-C61-Butyric-Acid-Methyl Ester ([60]PCBM), (e) Phenyl-C71-Butyric-Acid-Methyl Ester ([70]PCBM).

A typical polymer:fullerene derivatives BHJ solar cell consists of a photoactive layer sandwiched between two different electrodes, one of which should be transparent, such as indium tin oxide (ITO), in order to allow the incoming photons to reach the
photoactive layer. The schematic drawing of the device is shown in Fig. 2.2 [3]. Charge separation occurs at the interface between conjugated polymers as a donor and fullerene (or its derivative) as an acceptor. Electron transport occurs through the fullerene derivatives and hole transport is along the conjugated polymer. Figure 2.3 shows a transmission electron microscopy (TEM) image of the nanostructured interpenetrating network in P3HT:PCBM BHJ thin film [4].

Figure 2.2 The schematic drawing of a polymer:fullerene derivatives BHJ solar cells. (Adopted from Ref.[3])
Figure 2.3 TEM image of bi-continuous interpenetrating donor-acceptor networks of a P3HT:PCBM BHJ layer after thermal annealing. (Adopted from Ref.[4])
Upon light absorption, the charge carriers are generated inside the photoactive layer. And due to the presence of a built-in electric field provided by the asymmetrical work functions of the electrodes, these charges are transported and collected by the external circuit. In this way, an organic solar cell converts light directly into electricity.

In order to make an optimal interface between the organic layer and the electrodes, such as an Ohmic contact, an interfacial layer is often employed adjacent transparent conducting oxide (TCO) anode (e.g. ITO) and metal cathode (e.g. Ag, Au, Al). For the anode interfacial layer, to enhance photoinduced hole-extraction and to promote planarization of the ITO surface, a thin transparent conducting polymer poly(styrenesulfonate) doped poly (3, 4-ethylenedioxythiophene) (PEDOT:PSS), is typically introduced onto the ITO before the photoactive layer formation.

Generally the cathode interfacial layers are low-work function metals and very thin metal-halides. Widely used cathodic interfacial materials are Ca, Ba, Mg and LiF. Figure 2.4 shows a typical device structure and the TEM image of a cross section of the device with the atomic force microscope (AFM) and TEM image of a MDMO-PPV-PCBM BHJ thin film [5].
Figure 2.4 (a) Schematic of the device structure of a polymer:fullerene BHJ solar cell (b) TEM image of a cross section of the device [5] (c) AFM and TEM image of polymer:fullerene composite thin film. (Adopted from Ref.[5])

Figure 2.5 shows the schematic energy-level diagram of a polymer:fullerene BHJ solar cell under short-circuit condition with illumination. When absorption of sunlight occurs in a PV device, photons excite the donor. Together the photocurrent generation process follows the sequential steps [6]: (1) exciton generation, mostly in the conjugated polymer (donor) due to almost negligible absorption in the acceptor; (3) generated exciton diffuse within the donor phase; (4) dissociation of e-h pairs to free charge-carriers at the donor/acceptor interface; (5) transport of free charge carriers; (6) charge collection at the respective electrodes. Possible loss mechanisms are (2) exciton decay without
luminescence, if excitons are generated too far from the donor/acceptor interface, ground state recombination of e-h pairs, occurs or bimolecular recombination of the free e and h.

Figure 2.5 Schematic energy-level diagram of (a) a bilayer device and (b) a BHJ device at short-circuit condition under illumination. The dot line shows the energy levels of the PCBM and the solid line indicates the energy level of the P3HT. (Adopted from Ref.[6])

Considering the photocurrent process steps, the internal quantum efficiency ($\eta_{IQE}$) can be written as

$$\eta_{IQE} = \eta_A \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC}$$  \hspace{1cm} (2-1)

where $\eta_A$ is the absorption efficiency of light within the photoactive layer, $\eta_{ED}$ is the exciton diffusion efficiency to a donor/acceptor interface site for later dissociation, $\eta_{CT}$ is the charge transfer efficiency, which is the efficiency for dissociation of an exciton into a
free e-h pair at the site, $\eta_{CC}$ is the charge collection efficiency [46]. For the reflectivity (R) of the substrate-air interface, the external quantum efficiency ($\eta_{EQE}$) is given by

$$\eta_{EQE} = (1 - R) \cdot \eta_{IQE} \quad (2-2)$$

The power conversion efficiency ($\eta_{eff}$) of the solar cell is given by

$$\eta_{eff} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_0} \quad (2-3)$$

where $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, FF is the fill factor, and $P_0$ is the incident power intensity.
2.3 Efficiency limiting factors in the photocurrent generation process of polymer:fullerene derivatives bulk heterojunction photovoltaic devices

2.3.1 Exciton generation

In polymer materials, efficient optical absorption can be obtained due to their high optical absorption coefficient (ca. $10^5 \text{ cm}^{-1}$) at the maximum of their absorption spectrum. As a result, only a few hundred nanometers of active layer thickness is required for absorption of the majority of light at the peak wavelength absorption, unlike Si-based solar cells. However, a relatively narrow absorption band for polymers limits the overall efficiency of these devices. In addition, absorption by the acceptor is non-existent (> ~300 nm) [47]. For example, Figure 2.6 shows the narrow absorption band of the photoactive layer of P3HT:PCBM bulk heterojunction.

Figure 2.6 Typical absorption spectrum of the photoactive layer (P3HT:PCBM blended film after annealing 160 °C for 30 minutes) with respect to the AM1.5G spectra.
Considering the spectral photon flux from the sun at the earth’s surface under the standardized AM1.5G with an intensity of 100 mW/cm$^2$, only ~19% of the total number of incident photons can be harvested due to the large bandgap of the absorber materials, greater than 2 eV (<650 nm). This produces an upper limit of $J_{sc}$ at 13.2 mA/cm$^2$. Most solution-processable semiconducting polymers have a bandgap larger than 1.9 eV. However, new synthetic chemistry on low bandgap polymer absorber could overcome limitations in current organic PV technology by expanding the optical absorption range [48]. For instance, extending the absorbance of polymers out to 900 nm (~1.4 eV) will allow for absorption of ~49% of the available photons providing a maximum $J_{sc}$ of 33.7 mA/cm$^2$ (Fig. 2.7).
Figure 2.7 Spectral irradiance of photon flux from the sun at the earth’s surface (1000W/m², AM1.5G) and the integral of the curve of the obtainable short circuit current density for an absorber material with a step function absorbance at that wavelength as a function of wavelength. This assumes step function absorbance at the wavelength indicated. The current densities are for nonconcentrated (one sun) sunlight. (Adopted from Ref. [7])
2.3.2 Exciton diffusion and dissociation

Although optical absorption can be enhanced by increasing the optical absorption path length ($1/\alpha$), there is an inevitable tradeoff between the optical absorption and the exciton diffusion length ($L_D$) because $L_D$, which characterizes the effective width of the active area of the polymer film (donor) at the acceptor interface, is typically much less than $1/\alpha$. It means that photogenerated excitons can not efficiently reach a donor/acceptor interface prior to dissociation into free charge carriers. For conjugated polymers, $L_D$ has been reported to be less than 20 nm [30-32]. For such a short $L_D$ in most of polymers, it indicates that a carefully controlled nanostructure is required for efficient exciton diffusion and dissociation in a BHJ layer. In a P3HT:PCBM BHJ solar cell, there are many parameters for controlling the nanostructure of a BHJ layer, such as regioregularity of P3HT [9], conjugation length and poly-dispersity of P3HT [49], vapor pressure of the solvent used [10], P3HT:PCBM weight ratio [11], and annealing conditions (temperature, time, ambient, time) [50]. If these conditions are controlled well, a self-assembled interpenetrating donor-acceptor junction can be effectively formed with nanoscale dimensionality [51]. And, given that phase-separation of the two-component system occurs at the nanoscale, it can lead to efficient diffusion and dissociation of photogenerated excitons at the distributed interfaces, furthermore providing continuous pathways for electron and hole transport and collection through percolation.
2.3.3 Transport of charge carriers

While increasing $1/\alpha$ can be limited by a short $L_D$ in polymers, the low charge carrier mobilities of most polymers can be another significant efficiency limiting factors in polymer:fullerene BHJ solar cells. In the thermally annealed P3HT:PCBM blend film (fast growth and 1:1 wt%), the electron and hole mobility have been reported to be only $\sim3\times10^{-7}$ and $\sim1.5\times10^{-8}$ m$^2$/V⋅s, respectively [52]. Due to the low electron and hole mobility, the thickness of the active layer is limited to just $\sim100$ nm, leading to a limited absorption of only $\sim60\%$ of the incident light at the absorption maximum. However, it has been reported that hole mobilities in the blend film can be improved up to $\sim5\times10^{-7}$ m$^2$/V⋅s by varying the solidification time of the P3HT:PCBM blend film using high boiling point solvent [53]. Typically P3HT films are mostly amorphous, but P3HT has a much higher degree of crystalline structure than other polymers due to self-organization of P3HT into a lamella structure with two-dimensional conjugated sheets formed by interchain $\pi-\pi$ stacking. Depending on processing conditions, the lamellae can adopt two different orientations (plane-on and edge-on orientation), the mobilities of which differ by more than a factor of 100 [54]. In a P3HT:PCBM blend film by the slow growth process, the efficient formation of self-organized ordered structure can contribute to an enhanced hole mobility [10]. Due to this increased hole mobility, a thicker photoactive layer can be fabricated up to $\sim300$ nm, leading to greater optical collection efficiency, which subsequently increases $J_{sc}$. 

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2.3.4 Charge collection at the cathode

Optimization of the electrodes is another important challenge to overcome efficiency-limiting factors for organic PV devices. Generally, a bilayer cathode consists of a low work function metal (Ca, Ba, Mg) or a thin cathode interfacial layer encapsulated with Al, such as, Ca/Al and LiF/Al. The low work function of the electrodes is mainly responsible for the built-in potential for optimal charge extraction and Ohmic contact to the photoactive layer [55]. However, the nature of the polymer/metal interface is very sensitive to the electrode material and deposition parameter. Defect states originating from chemical reactions and interdiffusion at the interface can create interfacial barriers or midgap states that can pin the Fermi level of the electrodes, leading to lowered open-circuit voltage ($V_{oc}$) and increased series resistances [56] Chemical reactions and interdiffusion between polymers and the cathode at the interfaces can also significantly affect the device stability.

2.3.5 Charge collection at the anode

For an anode contact, creating low optical loss with low sheet resistance is an important issue. Although an ITO/PEDOT:PSS anode is widely used in P3HT:PCBM BHJ solar cells due to a reasonable Ohmic contact to the photoactive layer and its high transparency, some issues should be addressed for high performance and long-term stability of the cell, such as the tradeoff between the transmittance and the sheet resistance or etching of the ITO due to the strong acidic nature of PEDOT:PSS [57].
Even though ITO is probably the most successful of the TCOs, another key drawback with the ITO materials as a TCO is that indium is a relatively scarce element, which can be obtained mainly as a by-product of zinc ore processing. The amount of indium consumed is mostly a function of worldwide liquid crystal display (LCD) production and its demand has increased quickly in recent years with the popularity of LCD computer monitors and televisions, which now account for 50% of indium consumption [58]. Based on content of indium in zinc ore stocks, the estimated reserves are only approximately 6000 tones of economically-viable indium, and there is only 13 years' supply of indium left at current consumption rates [58]. A successful commercialization pathway needs to implement an In-free solution.

In order to address the issues related to the anode, various interface and surface engineering techniques at the anode include alternative TCO anodes [14, 59], direct surface modification of the ITO anodes [60], alteration of the hole transporting layer (HTL) [61, 62], insertion of electron blocking layers [2] and creation of surface plasmons [42].
Chapter 3: Study on process optimization for efficient polymer:fullerene derivatives bulk heterojunction photovoltaic device

P3HT and PCBM BHJ solar cells are being actively studied as affordable large area solar cells that can be affixed conformally to surfaces or put into a flexible form factor. Prior work has identified blends as a promising opportunity, mixing conjugated polymer materials together as the donor and fullerene derivatives as the acceptor materials [37]. If process conditions are well controlled, a self-assembled interpenetrating donor-acceptor junction can be formed with nanoscale dimensionality. And, given that phase-separation of the two component system occurs at the nanoscale, it can lead to efficient dissociation and collection of photogenerated excitons at the distributed interfaces, providing continuous pathways for electron and hole transport and collection through percolation [10, 50].

In a P3HT:PCBM BHJ solar cell, there are many parameters for controlling the self-organizing properties of the nanostructure of a BHJ layer, including regioregularity of P3HT [9], molecular weight and poly-dispersity of P3HT [8, 49], vapor pressure of the solvent used [10, 63], P3HT:PCBM weight ratio [11], and annealing conditions (temperature, time, ambient, time) [50]. In addition, optimizing composite electrodes for electron extraction is another significant fabrication process [12, 55, 56]. Due to the process-sensitive performance of P3HT-PCBM based PV devices, great effort towards the fabrication process have been made to improve the power conversion efficiency ($\eta_{eff}$)
by an optimization of the short-circuit current density ($J_{sc}$), the open-circuit voltage ($V_{oc}$) and the fill factor (FF).

### 3.1 Parameters for process optimization for the fabrication

#### 3.1.1 Controlling self-organization properties of conjugated polymer as a donor in a photoactive film

##### 3.1.1.1 Effect of molecular weight of P3HT

In polymer BHJ solar cells, molecular weights (MW) of P3HT affect the device performance by altering the morphology of the photoactive layer [64, 65]. Ma et al. [8] investigated the morphology of the photoactive layer and device performance of P3HT:PCBM BHJ solar cell using different MWs of P3HT: low MW P3HT ($\overline{M}_n$=13000 g/mol, $\overline{M}_w$=26 200 g/mol, polydispersity index=2.01, a degree of polymerization (DP)=78; high MW P3HT ($\overline{M}_n$=62500 g /mol, $\overline{M}_w$=153800 g/mol, polydispersity index=2.46, DP=376; Medium MW P3HT ($\overline{M}_n$=55000 g/mol). $\overline{M}_w$ and $\overline{M}_n$ are a weight-average molecular weight and a number-average molecular weight, respectively.

The polydispersity, a measure of the distribution of molecular mass in a given polymer sample, is defined as $\overline{M}_w / \overline{M}_n$.

In this study, the devices fabricated using higher MW P3HT tend to exhibit higher performance due to the longer conjugation length of P3HT chain and better interconnections with the bicontinuous network with PCBM. However, due to the
solubility problem of the higher MW P3HT, the optimized performance of PV devices was obtained by using a mixture of high and low MW P3HT with high/low ratio of 1:4 (Figure 3.1).
3.1.1.2 Regioregularity effect in P3HT

The asymmetry of 3-substituted thiophenes results in three possible couplings when two monomers are linked between the 2- and the 5-positions. These couplings are 2, 5′ or head–tail (HT) coupling; 2, 2′ or head–head (HH) coupling; and 5, 5′ or tail–tail (TT) coupling. These three diads can be combined into four distinct triads: HT-HT, HH-TH, HH-TT, and TT-HT. The triads are distinguishable by nuclear magnetic resonance spectroscopy and the degree of regioregularity (RR) can be estimated by integration [66]. Kim et al. [9] studied the influence of polymer RR of P3HT on the molecular nanostructure, and on the resulting material properties and PV device performance.

In this study, it is found that there is a strong influence of RR of P3HT on solar-cell performance, which can be attributed to enhanced optical absorption and transport resulting from the organization of P3HT chains and domains. Each RR of P3HT in this work is 90.7%, 93%, and 95.2%, respectively.

The highest efficiency was obtained using the P3HT polymer with the highest RR (95.4%), combined with optimized process of the photoactive layer thickness of ~175 nm and the specific device annealing condition for 2 hrs at 140 °C (Figure 3.2). The enhanced performances of PV devices with the highest RR of P3HT can be explained by the increased interplane packing density of molecular structure of P3HT parallel to the substrate upon thermal annealing (Figure 3.3).
Figure 3.2 EQE spectra of the p3HT:PCBM solar cells with different RR of P3HT (black, red and blue colors indicate 95.2%, 93% and 90.7% RR, respectively, and solid and dashed lines show not-annealed and annealed (140 °C for 2 h) films, respectively) (Adopted from Ref.[9])
Figure 3.3 The molecular structure of P3HTs for 100% RR and 90% RR (Adopted from Ref.[9])
3.1.1.3 Effect of solvent evaporation rate

Li et al. [10, 63] reported controlling the morphology of the blend film of the P3HT and PCBM by changing the solvent evaporation time. The P3HT:PCBM blend solution (1:1) was made from 1,2-dichlorobenzene (DCB), which has a higher boiling point \( T_b \) of 180.5 °C than typical solvents, such as chlorobenzene \( (T_b=131 \degree C) \) and toluene \( (T_b=111 \degree C) \). Different spin-coating time was used to control the solvent evaporation time. In this report, the overall performance of the PV devices was optimized when the solvent evaporation time is greater than 1 min, which can be obtained when the spin-coat time is 50 s. For the spin-coat time less than 50 s, both the \( J_{sc} \) and the PCE are maximized. However, the \( J_{sc} \) and PCE values are significantly decreased for the spin-coat time between 50 s and 55 s (Figure 3.4). This work employed various characterization techniques such as photoluminescence spectroscopy, UV-vis absorption spectroscopy, atomic force microscopy, and grazing incidence X-ray diffraction measurements for the photoactive film controlled by various solvent-evaporation time, the results showed that the enhanced PV performance could be contributed to the promoted planar conformation and well-ordering of the P3HT chain during slow solvent evaporation. Controlling the solvent evaporation time of the photoactive layer results in an enhanced hole mobility and thus more balanced charge transport in the bulk heterojunction film [67].
Figure 3.4 $J-V$ characteristics under illumination for devices with different film growth rates by varying the solvent evaporation time. The solvent evaporation time for different films were 20 min (no. 1), 3 min (no. 5), 40 s (no. 6) and 20 s (no. 7). (Adopted from Ref. [10])
3.1.1.4 Thermal annealing effects of P3HT:PCBM blend film

Various studies have focused on the thermal annealing effect of the P3HT:PCBM blend film on the performance of PV devices [11, 50, 68, 69]. Figure 3.5 shows the photovoltaic device performance parameters as a function of annealing temperature [11].

Figure 3.5 Variation of performance of PV devices with P3HT:PCBM (1:1 by weight) blend film devices as a function of annealing time under AM1.5 (100 mW/cm²). (Adopted from Ref. [11])
Although each study employs different process conditions, such as RR, MW of P3HT, solvent, blending ratio, and metal cathode, the overall mechanism behind the improved performance of PV devices upon thermal annealing at higher temperature could be that the blend films efficiently develop a strong interpenetrating self-assembled donor-acceptor junction with nanoscale dimensionality. And, given that phase-separation of the two component system occurs at the nanoscale, it can lead to efficient dissociation and collection of photogenerated excitons at the distributed interfaces, providing continuous pathways for electron and hole transport and collection through percolation [4, 51]. Another explanation is that the hole mobility in the P3HT phase of the blend film has been significantly increased by more than three orders of magnitude, up to $2 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ after thermal annealing, compared with the hole mobility of $1 \times 10^{-11} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ in as-cast P3HT:PCBM blend film [52].
3.1.1.5 Composition of donor and acceptor blend

Composition of P3HT and PCBM in the blend film is another important parameter, affecting the performance of PV devices. Kim et al. [11] focused on blend solutions with various compositions, e.g., P3HT:PCBM=1:0, 1:0.1, 1:0.5, 1:1, 1:2, and 1:4 weight ratio in chlorobenzene. The highest efficiency was obtained for the 1:1 of P3HT:PCBM weight ratio composition (Figure 3.6). This result can be attributed to tighter intermolecular packing of P3HT molecular chains due to a homogeneous blend of P3HT with PCBM. For the 1:4 composition, the P3HT chains are well blended with PCBM molecules, causing suppressed intermolecular packing of the P3HT chains [11].

![Figure 3.6 EQE and the power conversion efficiency (PCE) for devices with P3HT:PCBM blend films as a function of PCBM weight ratio under illumination: filled square under 6.2 mW/cm² at 480 nm; open square under 0.03 mW/cm² at 480 nm); and PCE (filled triangle: under 6.2 mW/cm² at 480 nm). The inset shows the open circuit voltage and fill factor as a function of PCBM weight fraction under monochromatic light (480 nm) excitation with an intensity of 6.2 mW/cm². (Adopted from Ref. [11])](image-url)
3.1.2 Variation of metal cathode

The work function and interfacial chemistry of the cathode metal contact materials also play a crucial role to govern the BHJ PV devices performance. Reese et al. [12] reported a very systematic study by using a series of composite cathodes. Either a single layer or a bilayer metal contact was employed, e.g., Ag, Al, Mg:Ag/Ag, LiF/Al, Ca/Al, and Ba/Al. The results showed that Ba/Al and Ca/Al electrodes performed best, with similar open-circuit voltages of ~600 mV and power conversion efficiencies of ~3.7% (Figure 3.7).

Figure 3.7 Performance of P3HT:PCBM PV devices with variation of cathode layers. (Adopted from Ref.[12])
In addition, the PV devices with these two electrodes showed similar device stability with degradation of 11%~16% in net conversion efficiency after six weeks, compared with the PV devices with other electrodes (Figure 3.8). In this work, the incorporation of silver into the electrodes led to considerably more degradation than other electrode types due to silver oxidation. Typically low work function metals yield better performance of the PV devices, which can be attributed to lowering series resistance and corresponding FF.

Figure 3.8 Normalized efficiency as a function of time. (Adopted from Ref.[12])
3.2 Optimized fabrication process for efficient P3HT:PCBM (fixed 1:0.8 weight ratio) bulk heterojunction photovoltaic devices

Among a substantial body of work on highly efficient P3HT-PCBM based bulk heterojunction PV devices well summarized by Bundgaard et al. [48], Ma et al. was one of the few exceptions, who used a 1:0.8 weight ratio of P3HT-PCBM rather than the more common 1:1 weight ratio [50]. Ma et al. indicated that a 1:0.8 weight ratio of P3HT:PCBM effectively suppressed growth of large PCBM aggregates that could cause degradation of PV devices after thermal annealing. By raising the thermal budget, a more effective interpenetrating donor-acceptor junction with nanoscale dimensionality could be realized upon thermal annealing with higher temperatures. But, Ma et al. employed a simple Al-only cathode and no further process optimization was carried out.

In these studies, a highly efficient P3HT:PCBM bulk heterojunction PV devices using a LiF/Al bilayer cathode and a fixed 1:0.8 weight ratio was studied. By varying the thickness of a LiF interlayer sandwiched between the photoactive layer and Al cathode, along with controlling the postproduction annealing temperature, the highest efficiency recorded was with a 0.6 nm thick LiF layer and a postproduction annealing temperature of 160 °C for 30 min. With these parameters, an $\eta_{\text{eff}}$ up to 3.6% with a very high FF of 66% under air mass 1.5 global (AM 1.5G) spectral illumination (100 mW/cm²) was measured in the optimized PV devices.
### 3.2.1 Experiment

ITO-coated glass substrates (Delta Technologies, LTD) were ultrasonicated in acetone and isopropyl alcohol, dried with nitrogen, and subsequently dried overnight before device fabrication. The sheet resistances of the substrates were ~12 Ω per square, confirmed using a 4-point probe measurement. The substrates were next spin-cast using highly conducting poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS) (Baytron® P, standard grade, HC Stark) after passing it through a 0.45 μm filter. The substrates were then annealed at 140 °C for 10 min in air with a resulting thickness of ~40 nm. Thicknesses were confirmed by ellipsometry using PEDOT:PSS/Si test samples and surface profiler (Dektak, Veeco Instruments Inc.) for PEDOT:PSS/ITO/glass with a variation was ±2 nm. Samples were then transferred into a nitrogen glove box environment with less than 1 ppm level of oxygen and moisture for spin-casting of the photoactive layer.

The mixed solution consisting of P3HT and PCBM in chlorobenzene (Sigma-aldrich) was then spin-cast on the top of the PEDOT:PSS layer. The mixed solution had a P3HT:PCBM weight ratio of a 1:0.8 with a concentration of 10 mg/ml (P3HT). The P3HT (Merck Chemicals, Ltd) with 94.5% regioregularity, and PCBM (Nano-C, Inc.) were used without further purification. The P3HT used here has a weight-average molecular weight ($M_w$) of 26200 g/mol, corresponding to a number-average molecular weight ($M_n$) of 13000 g/mol, and with a polydispersity ($M_w/M_n$) of 2.

After spin-casting the photoactive layer, the devices were pumped down immediately in a vacuum (~$10^{-7}$ Torr) and then the multilayer stack completed by
shadowmask evaporation of the LiF/Al cathodes. The LiF interlayer thicknesses deposited were varied (0.6~1.2 nm) to observe the dependence of the device performance on the thickness of LiF layer. The final device structure is ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al.

Next, the postproduction thermal annealing temperature was studied over a temperature range (110~160 °C), by directly placing the completed PV devices on a digitally controlled hotplate for 30 min. in the nitrogen glove-box. After annealing the devices, they were cooled down to room temperature prior to subsequent measurements or subsequent processing. The thickness of P3HT:PCBM blend film after annealing was estimated to be about 120 nm verified using surface profilometry.

The surface morphologies of P3HT:PCBM blend film after postproduction annealing at different temperatures were studied using an atomic force microscopy (AFM) (Dimension 3100, Veeco Instruments Inc.) in tapping mode. The absorption spectra of P3HT:PCBM blend film on quartz substrate after postproduction annealing was monitored using UV/visible/near infrared spectrometer (Lambda 900, PerkinElmer, Inc.). The actual device area was determined with a scanning electron microscope (XL30, Philips), instead of assuming the area defined by the shadow mask used for evaporating the LiF/Al cathodes in order to overcome shadow effects that could result in any errors in the calculated current-density values [8]. The active area (A) of the devices was 0.47 mm², which is slightly larger than the area (0.42 mm²) defined by the shadow mask.

Electrical measurements were performed with a semiconductor characterization system (SCS42000, Keithley Instruments, Inc.) at room temperature in air without any device encapsulation under the spectral output from the Xenon lamp in a 150W solar
simulator (Newport) using an AM 1.5G filter (Newport) with an intensity of 100 mW/cm$^2$. No significant change in the PV device’s efficiency due to degradation was recorded over the time scale needed to collect the data. In order to minimize possible errors in extracting the PV device’s efficiency, the light intensity was first calibrated to a standard inorganic solar cell that had been previously calibrated by the National Renewable Energy Laboratory. However, the spectral-mismatch factor can not be close to unity between simulated light-source and the AM1.5G standard solar spectrum through this type of calibration because the spectral response of the calibration cell is not properly matched with that of the actual test solar cell, as described by Shrotriya et al. [70]. Therefore, the spectral mismatch factor of ~1.35 was used to correct the PV device performance [70].
3.2.2 Optimization of cathodic interfacial layer

Figure 3.9 shows the effect of varying the LiF interlayer thickness on the current density-voltage ($J-V$) characteristics of the devices annealed at a fixed temperature of 150 °C for 30 min and illuminated under AM 1.5G filtered spectral light (100 mW/cm$^2$). The highest $\eta_{\text{eff}}$ of 2.8% with a FF of 62%, $V_{\text{oc}}$ of 0.60 V, and the $J_{\text{sc}}$ of 7.6 mA/cm$^2$ is obtained in the PV device incorporating a 0.6 nm thick LiF layer.

![Figure 3.9 J-V characteristics of the devices (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) annealed at fixed temperature of 150 °C for 30 min with varying the LiF thickness under AM 1.5G filtered spectral illumination (100 mW/cm$^2$).](image-url)
From the $J$-$V$ curve, the series resistance ($R_S$), defined by the slope of the $J$-$V$ curve at $J=0$ mA/cm$^2$, was estimated to be $\sim 7.4 \ \Omega\cdot$cm$^2$. As expected, $V_{oc}$ remains almost the same within $\sim 50$ mV, or less, for the devices since the fabrication conditions for both the P3HT:PCBM blend film, cathode deposition, postproduction annealing were held constant. With thicker LiF layers, a small decrease of $\sim 7\%$ in $J_{sc}$ is observed but thicker LiF layers significantly decreased the FF of devices to as low as 46\% due to the increased $R_S$ in agreement with a previous report [71]. For the device with the LiF thickness of 0.9 nm and 1.2 nm, $R_S$ was estimated to be $\sim 14 \ \Omega\cdot$cm$^2$ and $\sim 37 \ \Omega\cdot$cm$^2$, respectively (Figure 3.10). It is not clearly understood why the insertion of the LiF interlayer would significantly improve the $\eta_{eff}$ of the device under illumination. However, it has been suggested in the literature that the LiF could form a dipole moment across the junction as well as it could modify the P3HT:PCBM blend film itself, such as diffusion and doping [3].
Figure 3.10 Effect of varying the LiF thickness on the specific series resistance ($R_s \cdot A$) and FF of the device (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) annealed at fixed temperature of 150 °C for 30 min under AM 1.5G filtered spectral illumination (100 mW/cm²).
3.2.3 Controlling the nanostructure of a bulk heterojunction layer through post-production annealing

Figure 3.11 shows the effect of postproduction annealing temperature on the $J-V$ characteristics of the devices with a fixed LiF layer thickness of 0.6 nm under AM 1.5G filtered spectral illumination (100 mW/cm$^2$). The devices annealed at 160 °C exhibited the best performance with the highest $\eta_{eff}$ of 3.6% with a FF of 66%, the $V_{oc}$ of 0.61 V, and the $J_{sc}$ of 9.0 mA/cm$^2$. The $\eta_{eff}$ for the PV devices annealed at 150 °C and 110 °C was ~2.8% and ~2.2%, respectively.

Figure 3.11 $J-V$ characteristics of the devices (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) incorporated with a fixed LiF layer thickness of 0.6 nm with varying postproduction annealing temperature under AM 1.5G filtered spectral illumination (100 mW/cm$^2$).
The improved $J_{sc}$ and $FF$ upon high temperature annealing can be ascribed to the decreased $R_s$ of the devices from $\sim 8.8 \ \Omega \cdot \text{cm}^2$ after annealing at 110 °C to 6.5 $\Omega \cdot \text{cm}^2$ after annealing at 160 °C (Figure 3.12). In P3HT:PCBM based PV devices, the enhanced $\eta_{eff}$ upon high temperature postproduction annealing can be due to a well-developed interpenetrating donor-acceptor junction with phase-separation of the two component system at the nanoscale, leading to efficient dissociation of photogenerated excitons at the distributed interfaces, thus providing continuous pathways for electron and hole transport and collection through percolation.

![Figure 3.12](image)

Figure 3.12 Effect of varying annealing temperature on the specific series resistance ($R_s \cdot A$) and FF of the device (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) with a fixed LiF layer thickness of a 0.6 nm with varying postproduction annealing temperature under AM 1.5G filtered spectral illumination (100 mW/cm$^2$).
Figure 3.13 shows the AFM tapping-mode height images (5 μm × 5 μm area) for each of the P3HT:PCBM (in 1:0.8 weight ratio) blend films on PEDOT:PSS/ITO substrates. The raw AFM data was analyzed using the WSxM program (Nanotec Electronica S.L., Spain).

A control sample shows the surface roughness without postproduction annealing and then the evolution of the surface structures with increasing annealing temperatures. Regardless of postproduction annealing, P3HT:PCBM blend films reveal a coarse surface morphology. The root-mean-square (rms) roughness of unannealed P3HT:PCBM blend films was ~8.3 nm, while the rms roughness of each film annealed at 110 °C, 150 °C, and 160 °C was ~8.2 nm, 8.6 nm, and ~7.9 nm, respectively. The RMS roughness of each of the P3HT:PCBM blend films did not show any trend with increasing temperatures. However, more delicate hill-like features were developed in the blend films annealed at higher temperature. For the correlation between the device performance and the surface morphology of the blend film, the highest $\eta_{eff}$ was obtained from the devices annealed at a higher temperature, and it can be attributed to improved charge collection efficiency by increasing contact areas at the interface between the blend film and the cathode.
Figure 3.13 AFM tapping mode height images (5 μm × 5 μm) for P3HT:PCBM (1:0.8) blend film (a) without postproduction annealing in the image Z range (Z) of 70.2 nm and with postproduction annealing for 30 min at (b) 110 °C (Z=61.6 nm), (c) 150 °C (Z=57.0 nm), and (d) 160 °C (Z=59.8 nm).
3.2.4 Characterization of the device performance under optimized condition

In these experiments, the $\eta_{\text{eff}}$ of the PV device was optimized with a 0.6 nm thick LiF interlayer postproduction annealed at 160 °C for 30 min using a P3HT:PCBM weight ratio of a 1:0.8 and a solution concentration of 10 mg/ml (P3HT). Figure 3.14 shows $J$-$V$ characteristics of 5 representative devices from 5 different substrates under dark and under AM 1.5G filtered spectral illumination (100 mW/cm²). The optimized PV device exhibited an $\eta_{\text{eff}}$ of 3.6±0.2% with a very high FF of 64±2%. The $V_{oc}$ and the $J_{sc}$ of the devices were 0.61±0.01 V and 8.8±0.3 mA/cm², respectively. The $R_s\cdot A$, was estimated to be about ~6.5±0.4 Ω-cm².

![Figure 3.14](image)

Figure 3.14 $J$-$V$ characteristics of 5 representative devices incorporated with a LiF layer thickness of a 0.6 nm (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) from different substrates after postproduction annealing at 160°C for 30 min under AM 1.5G filtered spectral illumination (100 mW/cm²).
Under darkness, the devices exhibit high current rectification ratio of \(-7.5 \times 10^3\) at ±2 V, exhibiting an ideality factor (~1.6) in the +0.5V exponential region as determined from the \(J-V\) slope.

The Figure 3.15 shows the absorption spectra of annealed P3HT:PCBM (1:0.8) blend films on quartz used in this study showing the red shoulder (at 602 nm), often attributed to interplane interactions, indicating self-organization of the regioregular P3HT is still effective in these P3HT:PCBM blend films specifically with a fixed P3HT:PCBM weight ratio of 1:0.8. The high \(\eta_{eff}\) obtained here can be attributed to efficient charge separation and transport in the photoactive layer by controlling the donor-acceptor interpenetrating nanoscale structure with high temperature annealing and additionally enabling efficient charge collection by the cathode with the insertion of a metal-halide interlayer.

Figure 3.15 The absorption spectra of the P3HT:PCBM (1:0.8) blend film on quartz after annealing at 160 °C for 30 min. The absorbance is baseline corrected with a background of quartz substrate.
For the optimized device, the device performances ($J_{sc}$, $V_{oc}$, FF, and $\eta_{eff}$) were measured with different incident light intensities ($P_0$) from 0 to 100 mW/cm$^2$ (Figure 3.16). The linear dependence of $J_{sc}$ on $P_0$ was observed, and the $V_{oc}$ gradually decreased as the $P_0$ decreased. The small variation of the FF was observed within ±2% from 100 mW/cm$^2$ to 50 mW/cm$^2$.

Figure 3.16 Effect of varying light intensity on (a) $J_{sc}$ and $V_{oc}$, (b) FF and $\eta_{eff}$ of the device (ITO/PEDOT:PSS/P3HT:PCBM/0.6 nm LiF/Al) after postproduction annealing at 160°C for 30 min under AM 1.5G filtered spectral illumination (100 mW/cm$^2$).
3.2.5 Conclusion

Highly efficient poly(3-hexylthiophene) and [6,6]-phenyl C$_{61}$ butyric acid methyl ester bulk heterojunction photovoltaic devices have been demonstrated under AM 1.5G spectral illumination (100 mW/cm$^2$). While varying the thickness of the LiF interlayer between the photoactive layer and Al cathode and the postproduction annealing temperature, an $\eta_{\text{eff}}$ up to 3.6% with a high fill factor of ~66% was obtained when the devices incorporated with a 0.6 nm thick LiF layer were postproduction annealed at 160 $^\circ$C for 30 min with a fixed P3HT:PCBM weight ratio of 1.0:0.8.
Chapter 4: Tailored modification to electrode for improved efficiency of organic photovoltaic devices

In the first part of this chapter, various electrode modifications for organic PV devices are reviewed. Furthermore, suggested mechanisms beyond improved device performance with modified electrodes will be discussed. In the second part of this chapter, an improved efficiency device using surface modifications to ITO anodes through oxygen plasma treated silver will be shown. In order to understand the overall physical mechanisms behind this improvement, the physical, chemical and optical properties of this modified ITO anode will be discussed using various surface characterization techniques. This will include a detailed analysis of the oxygen plasma treated silver/ITO interface via the Kelvin-prove (KP) technique and x-ray photoelectron spectroscopy (XPS).
4.1 Various surface modification techniques

Among recent advances towards improving the $\eta_{\text{eff}}$ in organic PV devices, various interface and surface engineering techniques to the ITO anode have demonstrated improved efficiencies for organic PV devices by an optimization of the $J_{\text{sc}}$, $V_{\text{oc}}$, and FF. Various surface modification techniques include alternative transparent conducting oxide (TCO) anodes [13, 14], direct surface modification of the ITO anodes [1, 15, 72], modification of the anode with an interfacial layer [60, 61], alteration of the hole transporting layer (HTL) [2, 16] or insertion of exciton blocking layers [73].

4.1.1 Alternative transparent conducting oxides (TCO) anodes

Among the many transparent conducting oxides, such as In$_2$O$_3$, SnO$_2$, and ZnO (doped and undoped), ITO (typically 9~10 mol % tin oxide in indium oxide) has been most widely used as an anode in OLEDs due to its high transparency and good conductivity properties [74, 75] as well as its common availability. However, alternative TCOs, such as ZnO or doped SnO$_2$, have been employed in organic PV technologies because the scarcity of In has resulted in a soaring price of ITO-coated glass substrates [76]. Organic PV devices, with photoactive layers typically < 100 nm thick, can readily be short circuited due to the significantly rough surface of these TCOs, which can protrude through thin organic layer connecting anode with cathode directly. On the other hand, organic PV devices incorporating with these alternative TCOs have been reported.
Aluminum doped zinc oxide (ZAO) Schulze et al. [13] employed three kinds of aluminum doped zinc oxide (ZAO) deposited by direct current (dc) magnetron sputtering (ZAO1) using a ZnO target with 2 wt % Al₂O₃ and radio frequency magnetron sputtering (ZAO2 and ZAO3) using a ZnO target with 1 wt % Al₂O₃ for small molecule PV devices based on an oligothiophene derivative as donor and fullerene C₆₀ as acceptor molecule. For light trapping with an textured anode electrode, the ZAO3 is chemically surface-etched. In this work, all substrates show a high transmission of over 80% in the visible spectral region, and the surface roughness of these substrates is about 1~2 nm for ITO, ZAO1, and ZAO2 and about 38.5 nm for the etched surface of ZAO3. The sheet resistances of the substrates were ITO: 42 Ω/sq, ZAO1: 34 Ω/sq, ZAO2: 8 Ω/sq, and ZAO3: 27 Ω/sq. The work function was estimated to be -4.5 eV for ZAO1 film and slightly less than -4.5 eV for ZAO2 and ZAO3 due to a lower doping ratio of Al₂O₃ in ZnO compared to that of the ZAO1. The results showed that the PV devices fabricated using ITO and ZAO anodes have almost identical performance (Figure 4.1). The ηeff of the PV devices with different TCO anodes is in the range between 2.3% and 2.9% with a high FF of ~40%. The V_{oc}, and the J_{sc} of the devices were ~1.01 V and ~8.4 mA/cm².
Figure 4.1 $J-V$ characteristic of PV devices (under 1–1.2 sun) using ITO (cell A, solid line), ZAO1 (cell B, dotted line), ZAO2 (cell C, line with open circles), and ZAO3 (cell D, dashed line) as anode material. The PV devices showed the same $V_{oc}$ and similar FF. The lower current density in cell D is due to the thick $p$-doped hole transport layer, which absorbs a small amount of the incoming light. (Adopted from Ref. [13]).

**F-doped SnO$_2$** Yang et al. [14] reported small molecule organic PV devices with F-doped SnO$_2$ anode electrode. The thickness of F-doped SnO$_2$ was about 750 nm thick, and it showed 70–80% transmittance in the visible range, which is approximately 10% less than that for 150 nm thick ITO anodes (Figure 4.2). The F-doped SnO$_2$ anode electrode also exhibited very rough surface with the root-mean-square (RMS) roughness of ~39 nm, compared with that of ITO anodes with the RMS roughness of ~2.8 nm (Figure 4.2). The sheet resistance of F-doped SnO$_2$ anode was less than 12 $\Omega$/sq. Under the specific fabrication condition, the PV devices with F-doped SnO$_2$ anodes showed the $\eta_{eff}$ of 2.5% under 1 sun illumination.
Figure 4.2 (a) Optical transmittance of F-doped SnO2 and ITO anode with respect to air mass AM 1.5 solar radiation spectra (b) The surface topography of F-doped SnO2 anode (c) The surface topography of ITO-coated glass substrates measured using atomic force microscopy (AFM). (Adopted from Ref.[14])
4.1.2 Direct surface modification of the ITO anodes

Surface modification of ITO anodes through the use of self-assembled monolayers (SAMs) Khodabakhsh et al. [15] investigated the performance of an organic solar cell through surface modifications of ITO anode using self-assembled monolayers (SAM) of molecules with permanent dipole moments, which enhanced $J_{sc}$ without any significant change to $V_{oc}$ in organic PV devices based on a copper phthalocyanine (CuPc):C$_{60}$ heterojunction (Figure 4.3). These SAMs on ITO anodes did not alter the roughness of the surface but created the interfacial energy steps between ITO and organic layer. In this work, the physical mechanisms behind the enhanced performance of PV devices under illumination are not clearly understood. However, this improvement could be attributed primarily to an enhanced interfacial charge transfer rate at the anode, due to both a decrease in the interfacial energy step between the anode work function and the highest occupied molecular orbital (HOMO) level of the organic layer, and a better compatibility of the SAM-modified electrodes with the initial CuPc layers, which leads to a higher density of active sites for charge transfer. In addition, calculations of the electric potential distribution for the device structures indicated that increasing electric field at the heterojunction improved the exciton-dissociation efficiency.
Figure 4.3 (a) Chemical structures of the SAMs used in this study: i) 4-chlorobenzoylchloride (CBC), ii) 4-chlorobenzenesulfonyl chloride (CBS), and iii) 4-chlorophenyldichlorophosphate (CBP). (b) $J-V$ characteristics of the five devices as under simulated AM1.5 irradiance (100 mW/cm²). (Adopted from Ref.[15])
Plasma treatment on ITO anodes Hong et al. [1] investigated the PV performances with ITO anodes treated by different gas plasma, e.g., CF4, O2, Ar, H2 or ultra-violet (UV) ozone. Although the surface energy of ITO was significantly changed by varying the plasma treatment condition, leading to different morphologies of organic layers atop the ITO, the main parameters of performance of PV devices were almost unaffected. Parameters for the PV devices are summarized in Table 4.1. The series and shunt resistances of the PV devices were also not significantly changed with different treatments. They concluded no significant impact of substrate plasma treatment on hole collection, although hole injection under forward bias showed strong dependence on these treatment methods.

<table>
<thead>
<tr>
<th>Treatment methods</th>
<th>Surface energy (N/m)</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (A/cm²)</th>
<th>FF</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ plasma</td>
<td>74.2</td>
<td>0.468</td>
<td>0.002 45</td>
<td>0.58</td>
<td>~16</td>
<td>~2500</td>
<td>1.9</td>
</tr>
<tr>
<td>CF₄ plasma</td>
<td>70.3</td>
<td>0.459</td>
<td>0.002 39</td>
<td>0.57</td>
<td>~18</td>
<td>~2500</td>
<td>1.8</td>
</tr>
<tr>
<td>Ar plasma</td>
<td>73.0</td>
<td>0.476</td>
<td>0.002 40</td>
<td>0.57</td>
<td>~17</td>
<td>~2500</td>
<td>1.9</td>
</tr>
<tr>
<td>UV ozone</td>
<td>72.0</td>
<td>0.463</td>
<td>0.002 41</td>
<td>0.59</td>
<td>~15</td>
<td>~2500</td>
<td>1.9</td>
</tr>
<tr>
<td>H₂ plasma</td>
<td>55.3</td>
<td>0.504</td>
<td>0.002 39</td>
<td>0.56</td>
<td>~19</td>
<td>~2000</td>
<td>1.9</td>
</tr>
<tr>
<td>No treatment</td>
<td>56.4</td>
<td>0.504</td>
<td>0.002 42</td>
<td>0.54</td>
<td>~21</td>
<td>~2000</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 4.1 Parameters for PV devices with ITO anodes treated by different gas plasma, e.g. CF4, O₂, Ar, H₂ or ultra-violet (UV) ozone under a halogen lamp illumination at an incident intensity of 35 mW/cm². (Adopted from Ref.[1])
4.1.3 Modification of anodic interfacial layer

Zhang et al. [60] investigated the influence of different anode buffer layers on the performance of PV devices. In this work, different PEDOT:PSS as the anodic interfacial layer was employed; special PEDOT:PSS for OLED application (Baytron® P VP AI4083, resistivity=500~5000 ohm-cm, PEDOT:PSS ration=1:6 by weight, H. C, Starck), standard PEDOT:PSS (Baytron® P, resistivity=1~100 ohm-cm, PEDOT:PSS ration=1:2.5 by weight, H. C. Starck) and sorbitol-doped standard PEDOT:PSS. The differences between these buffer layers are their conductivity and their chemical composition. In this work, the conductivity of the annealed buffer layer increased in the order: Special PEDOT:PSS, standard PEDOT:PSS, and sorbitol-doped PEDOT:PSS. Using doped buffer layers, an enhanced hole injection under dark was observed, possibly attributed to the small reorganization of the insulating layer PSS on top of PEDOT which altered the charge injection at the interface between anode and photoactive layer. The PV devices with the high conductivity buffer layer showed higher $J_{sc}$ and lower $V_{oc}$ and FF than the PV devices with other buffer layers. The increased $J_{sc}$ could be due to that the condition for high hole injection by the doped buffer layer changed the internal field distribution.
Thin metal oxides as alternative anode buffer layers \(\text{PEDOT:PSS}\) layers have been very widely used in organic electronic devices as anodic buffer layers, providing a variety of functions: (1) planarization of rough ITO surfaces to reduce probability for the electrical shorts; and (2) lowering of hole injection barrier \([77-79]\). Although PEDOT:PSS layers have been successfully implemented to organic PV devices \([80]\), it has been reported that the PEDOT:PSS layer could adversely affect the overall device performance because (1) aqueous PEDOT:PSS dispersion with strong acid properties of (pH=\(\sim\)1) can be corrosive to the ITO anodes, affecting the long-term stability of the devices \([81]\); (2) The PEDOT:PSS layer typically deposited by spin-coating shows inconsistent surface morphology, resulting in electrical inhomogeneity \([82]\); and (3) In PLED structures, the PEDOT:PSS layer is inefficient to block the electron, reducing current efficiency due to electron leakage current to the anode \([81]\). Thus, great effort has been made to replace the PEDOT:PSS layer with more robust and stable materials for PV applications.

Transition metal oxides as the buffer layer Shrotriya \textit{et al.} \([16]\) reported PV devices incorporating with a transition metal oxide layer between the ITO anode and the photoactive layer. In this report, two different transition metal oxides, such as vanadium oxide \(\text{V}_2\text{O}_5\) and molybdenum oxide \(\text{MoO}_3\), were prepared by thermal evaporation with the variation of the thickness from \(1\) nm to \(10\) nm. The work functions of these materials were \(\sim\)4.7 eV for \(\text{V}_2\text{O}_5\) and \(\sim\)5.3 eV for \(\text{MoO}_3\), respectively. Their AFM images showed that the random islands were formed on the ITO surface with the RMS roughness of less than \(10\) nm (Figure 4.4).
Figure 4.4 AFM images (1 µm×1 µm) of transition metal oxides thermally evaporated on top of the ITO surface: (a) 3 nm V2O5, (b) 10 nm V2O5, (c) 3 nm MoO3, and (d) 10 nm MoO3. (Adopted from Ref. [16])

In their work, the control device (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) exhibited an \( \eta_{eff} \) of 3.18 % with a FF of 59.6 %. The \( V_{oc} \) and the \( J_{sc} \) of the control devices were 0.59 V and 8.95 mA/cm², respectively. Specifically for the experimental device incorporating a 5 nm thick MoO3 layer between the ITO and PEDOT:PSS (ITO/MoO3(5 nm)/P3HT:PCBM/Ca/Al), respectively, an \( \eta_{eff} \) of 3.33% with \( V_{oc}=0.60 \) V, \( J_{sc}=8.94 \) mA/cm², and FF=61.9 % were measured. The PV devices with a 3 nm thick V2O5 (ITO/ V2O5 (3 nm)/P3HT:PCBM/Ca/Al) also showed an \( \eta_{eff} \) of 3.18% (Figure 4.5). This work
successfully demonstrated thin transition metal oxide layers as alternative anode interfacial layers, effectively replacing PEDOT:PSS layers in polymer PV devices.

![Figure 4.5 J-V characteristics of PV devices under simulated AM1.5G illumination of 100 mW/cm² for a device with different types of anode interfacial layers: ITO only, ITO with PEDOT:PSS (25 nm), ITO with V₂O₅ (3 nm), and ITO with MoO₃ (5 nm). (Adopted from Ref.[16])](image)

**A p-type semiconducting nickel oxide as an alternative anode interfacial layer** More recently an encouraging report described a polymer PV device structure that employ a p-type semiconducting nickel oxide (NiO) as an anode interfacial layer [2]. NiO films were grown by pulsed-laser deposition (PLD) in an ambient O₂ atmosphere at a pressure between 2×10⁻² and 2×10⁻⁵ torr with various thickness from 5 nm to 77 nm. The valence band, conduction band, and the Fermi energy level were found to be 5.4 eV, 1.8 eV and 5.0 eV, which are adapted from the previously published work. It indicates that a band structure of NiO is very suitable for P3HT:PCBM BHJ devices because it provides an
ohmic contact to the P3HT and has a sufficiently large conduction band minimum to play a role as an electron-blocking layer. Another advantage using $p$-NiO is that the NiO deposition process significantly planarized the rough ITO surface, typically an RMS roughness of 4~5 nm, to 1 nm ~1.5 nm for NiO deposited ITO substrates. In addition, the optical transmittance was found to be very high for the visible range, up to a 10 nm thick NiO film, starting decreasing for a 20 nm thick NiO film.
Figure 4.6 (a) Optical transmission spectra of various-thickness NiO films grown on ITO/glass (b) AFM images (0.5 µm×0.5 µm) of NiO on ITO and bare ITO (Adopted from Ref.[2])
By increasing the thickness of the NiO, a reduction of the FF and $J_{sc}$ was observed due to the increased series resistance and the decreased optical absorption (Figure 4.7). The optimized performance was obtained from the PV devices with an insertion of the NiO layer (10 nm thick), showing an increased $\eta_{eff}$ as high as 5.2% with a very high FF of 69% and a $V_{oc}$ up to 638 mV versus the control PV devices (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al). Parameters for the performance for the PV devices are summarized in Table 4.2.

Figure 4.7 $J–V$ characteristics of the PV devices under simulated AM1.5G irradiance (100 mW/cm$^2$). (Adopted from Ref.[2])
<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$, V</th>
<th>$J_{sc}$, mA/cm²</th>
<th>$FF$, %</th>
<th>Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-nm PEDOT:PSS</td>
<td>0.624</td>
<td>9.54</td>
<td>40.4</td>
<td>2.40</td>
</tr>
<tr>
<td>Control</td>
<td>0.515</td>
<td>10.7</td>
<td>50.7</td>
<td>2.87</td>
</tr>
<tr>
<td>5-nm NiO</td>
<td>0.634</td>
<td>11.5</td>
<td>63.3</td>
<td>4.75</td>
</tr>
<tr>
<td>10-nm NiO</td>
<td>0.638</td>
<td>11.3</td>
<td>69.3</td>
<td>5.16</td>
</tr>
<tr>
<td>20-nm NiO</td>
<td>0.591</td>
<td>8.83</td>
<td>55.2</td>
<td>2.96</td>
</tr>
<tr>
<td>43-nm NiO</td>
<td>0.586</td>
<td>8.09</td>
<td>52.4</td>
<td>2.55</td>
</tr>
<tr>
<td>77-nm NiO</td>
<td>0.581</td>
<td>7.49</td>
<td>49.8</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Table 4.2 Parameters for PV devices with modified ITO anodes by pulsed-laser deposited NiO under simulated AM1.5G irradiance (100 mW/cm²). (Adopted from Ref.[2])
4.2 Surface modification to anode through oxygen plasma treated silver

In this dissertation, we demonstrated an improved efficiency, up to 3.9 % with a high fill factor of ~63% under AM 1.5G spectral illumination and 100 mW/cm² intensity for P3HT:PCBM bulk heterojunction PV devices with a 1:0.8 (P3HT:PCBM) weight ratio using surface modifications to ITO anodes through oxygen plasma treated silver. Here an enhanced short-circuit current density was achieved without significant loss in the open-circuit voltage (> 0.6V) nor the fill factor (> 63%), leading to an efficiency jump from 3.6% in the control devices to 3.9% with the surface modified ITO anode. In order to understand the overall physical mechanisms behind this improvement, we studied the physical, chemical and optical properties of this modified ITO anode using various surface characterization techniques. This will include a detailed analysis of the oxygen plasma treated silver/ITO interface via the Kelvin-prove technique and x-ray photoelectron spectroscopy.
4.2.1 Motivation

Although direct surface modifications to the ITO anode have been successfully implemented for organic light emitting diodes (OLED) to improve their device performance by creating an interface energy step between the ITO and the HTL, thereby enhancing hole injection by effectively lowering the hole injection barrier, this approach has not been fully explored for organic PV yet. For an OLED, carriers are inserted over the energy step, whereas for PV devices, the carriers are extracted down this energy barrier, which means the carriers are not inhibited from extraction from the active layer by the injection barrier [55].

Recently it has been reported that the creation of interface energy step could improve the charge collection efficiency in organic PV devices, leading to an increase of the $\eta_{\text{eff}}$ by improving the $J_{\text{sc}}$ without any significant change to $V_{\text{oc}}$ and FF [15]. In this part of the chapter, it will be presented efficient PV devices through tailored modifications to electrode surfaces. Then it will be discussed the related overall physical mechanisms behind this improvement.
4.2.2 Experiment

The ITO-coated glass substrates (Delta Technologies, LTD) were ultrasonicated in acetone and isopropyl alcohol, dried with nitrogen, and subsequently dried in overnight before device fabrication. A nominally 1 nm thick film of oxygen plasma treated Ag was then added atop the ITO-coated glass substrate by the following two steps. First, a 1 nm thick Ag metal was electron beam evaporated at a low pressure range (~10\(^{-7}\) Torr) atop the ITO. Next, the Ag metal was treated using an inductively coupled plasma reactive ion etching (ICP-RIE) system with an oxygen plasma at an RF power of 100 W for 1 minute at room temperature.

The substrates were next spin-cast using highly conducting PEDOT:PSS (Baytron\(^{\text{®}}\) P, standard grade, HC Stark) after passing through a 0.45 \(\mu\)m filter. The substrates were then annealed at 140 °C for 10 min in air with a resulting thickness of ~40 nm and then transferred into an inert glove box environment with \(\leq 1\) ppm level of oxygen and moisture for spin-casting of the photoactive layer.

The mixed solution consisting of P3HT and PCBM in chlorobenzene was then spin-cast on the top of the PEDOT:PSS layer. The mixed solution had a P3HT:PCBM weight ratio of a 1:0.8 with a concentration of 10 mg/ml (P3HT). The P3HT (Merck) with 94.5 % regioregularity and PCBM (Nano-C) were used without further purification. After spin-casting the photoactive layer, the devices were pumped down in vacuum (~10\(^{-7}\) Torr) and then the multilayer stack completed by the shadowmask evaporation of a LiF/Al cathode. The final composite device structure is ITO/O\(_2\) plasma treated Ag/PEDOT:PSS/ P3HT:PCBM/LiF/Al. Post-production thermal annealing was then
performed by directly placing the completed device on a digitally controlled hotplate at 160 °C for 30 min in an inert glove-box. After annealing the devices were cooled down to room temperature prior to subsequent measurements.

In our experiments, control devices (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) were also fabricated and tested without any surface modification of ITO anodes. In order to minimize variation in the results that might arise due to different processing condition, such as spin-casting the PEDOT:PSS layer, spin-casting the photoactive layer, depositing the LiF/Al cathode metal contact and post-production annealing, both sets of PV devices (control and experiment) with different anode structures were fabricated during the same batch processing.

The actual device area determined with an XL30 Environmental Scanning Electron Microscope (ESEM) (Philips) was 0.47 mm². The $J-V$ measurements were performed with a semiconductor characterization system (SCS42000, Keithley Instruments, Inc.) at room temperature in air without any device encapsulation under the spectral output from a Xenon lamp from a 150W solar simulator (Newport) using an AM 1.5G filter (Newport) with an intensity of 100 mW/cm². No significant change in the PV device’s efficiency due to degradation was recorded over the time scale needed to collect the data.

In order to minimize possible errors in extracting the PV device’s efficiency, the light intensity was first calibrated to a standard inorganic solar cell that had been previously calibrated by the National Renewable Energy Laboratory. However, the spectral-mismatch factor can not be close to unity between the simulated light-source and the AM1.5G standard solar spectrum through this type of the calibration because a
spectral response of the calibration cell is not matched with that of the actual test solar cell, as described by Shrotriya et al. [70]. Therefore, the spectral mismatch factor of \( \sim 1.35 \) was used to correct the PV device performance [70].

We studied the physical, chemical and optical properties of the anode electrodes before and after oxygen plasma treatment using various surface characterization techniques. With these substrate preparations described previously, four different sets of substrates were systematically compared: bare ITO, as-deposited Ag/ITO, oxygen plasma treated ITO and oxygen plasma treated Ag/ITO.

The surface morphologies of the substrate’s anodes were studied using a Dimension 3100 atomic force microscopy (AFM) (Veeco) in tapping mode and with a Sirion scanning electron microscope (SEM). The optical transmittances of the substrates were monitored using a Lambda 900 UV/vis/NIR spectrometer (PerkinElmer). For the AFM and optical transmittance measurement, the substrates with the HTL were also monitored. The HTL was applied onto the substrates using highly conducting PEDOT:PSS after passing through a 0.45 \( \mu \)m filter. The substrates were then annealed at 140 °C for 10 min in air with a resulting thickness of \( \sim 40 \) nm. In order to elucidate the role of oxygen plasma treated Ag in the chemical bonding interfacial morphology, X-ray photoelectron spectroscopy (XPS) was employed. Finally, the work functions of the substrates were investigated using Kelvin probe (KP) method. The experiments are conducted using a commercial AFM (NanoScope® IV Dimension 3100™ with Extender™ Electronics Module, Veeco). The AFM probes are coated with
platinum-iridium (SCM-PIT™, Veeco). In this method, the work functions of the various anode configurations are calculated from the measurement of the KP contact potential difference with respect to a gold reference electrode.
4.2.3 Optical, physical, and chemical characterization of oxygen plasma modified ITO anode

Figure 4.8 shows the optical transmittance of the anodes over the visible range (300–800 nm). For this range, the averaged transmittance of the oxygen plasma modified Ag (1 nm)/ITO coated glass substrate remains almost identical to a bare ITO-glass substrate, about 84%. The plasma surface modifications did not measurably affect the overall transmittance, specifically at the absorption peak (~555 nm) of an annealed P3HT:PCBM blend film (weight ratio of 1:0.8 with a concentration of 10 mg/ml of P3HT in chlorobenzene). After PEDOT:PSS spin coating, an insignificant change in transmittance for PEDOT:PSS/ITO and PEDOT:PSS/oxygen plasma modified Ag/ITO was measured. The transmittances at 555 nm of the substrates are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Transmittance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare ITO</td>
<td>84.3</td>
</tr>
<tr>
<td>PEDOT:PSS/ITO</td>
<td>80.9</td>
</tr>
<tr>
<td>Modified Ag/ITO</td>
<td>84.1</td>
</tr>
<tr>
<td>PEDOT:PSS/Modified Ag/ITO</td>
<td>81.1</td>
</tr>
</tbody>
</table>

Table 4.3 The transmittances at 555 nm (absorption peak of the photoactive layer) of the substrates
Figure 4.8 Optical transmittance of the ITO, PEDOT:PSS/ITO, modified Ag (1 nm)/ITO and PEDOT: PSS/modified Ag/ITO.

Figure 4.9 shows the AFM tapping mode images (5 μm × 5 μm) for ITO and oxygen plasma modified Ag/ITO substrates. The RMS roughness of a bare ITO surface was ~2.86 nm with the image Z range of ~23.64 nm. After oxygen plasma treated Ag on ITO, the RMS roughness of the ITO surface was slightly decreased to ~2.74 nm with the image Z range of ~21.03 nm recorded. Oxygen plasma treatment did not roughen the modified ITO anode surface measurably. After PEDOT:PSS spin-casting, substrates with and without modification have similar RMS roughness of ~1 nm with the image Z range of ~15 nm showing the surface modification has a negligible effect on the morphology of PEDOT:PSS layer.
The surface morphology of bare ITO, oxygen plasma treated ITO, Ag/ITO and oxygen plasma modified Ag/ITO coated glass substrate is inspected by SEM, as shown in Figure 4.10. Before oxygen plasma treatment of the Ag/ITO substrate, it is shown that discontinuous and small islands of Ag with non-uniform diameters are distributed on the ITO anode. After oxygen plasma treatment, irregularly shaped and non-uniform sized islands of oxygen plasma treated Ag are formed on the ITO surface.

(a)                                     (b)

Figure 4.9 AFM tapping mode images (5 μm × 5 μm) for (a) bare ITO and (b) Modified Ag (1 nm)/ITO. The RMS roughness of a bare ITO surface was ~2.86 nm with the image Z range of ~23.64 nm. After oxygen plasma treated Ag on ITO, the RMS roughness of the ITO surface was slightly decreased to ~2.74 nm with the image Z range of ~21.03 nm recorded.
Figure 4.10 SEM images of (a) bare ITO, (b) oxygen plasma treated ITO, (c) e-beam deposited Ag (1 nm)/ITO, and (d) oxygen plasma modified Ag (1 nm)/ITO.
Figure 4.11 shows the XPS wide scan survey spectrum of the substrates. For bare ITO and oxygen plasma treated ITO, strong In 3d, Sn 3d and O 1s peaks were observed as expected. With the exception of a reduced C 1s peak (not shown here), the oxygen plasma treatment did not significantly change the surface chemistry. After the evaporation of 1 nm of Ag, strong Ag 3d and Ag 3s peaks appeared, indicating Ag elements are distributed on the ITO surface. After the oxygen plasma treatment, the Ag 3d and Ag 3s peaks are still present although their intensities are slightly reduced, indicating that the oxygen plasma did not remove the Ag material in any significant manner.

Figure 4.11 The XPS wide scan survey spectrum of the substrates.
Figure 4.12 shows the XPS spectra of the Ag 3d and O 1s core level regions for as-deposited Ag/ITO and oxygen plasma treated Ag/ITO. After an oxygen plasma treatment, it is observed that the binding energy of the Ag 3d$_{5/2}$ peak shifted from 368.1 eV to 367.8 eV, clearly indicating that the Ag is oxidized into an AgO$_x$ state by the oxygen plasma. For the O 1s peak after oxygen plasma, it was located at 529.4 eV in Figure 4.12(b). From the deconvolution of the XPS Ag 3d$_{5/2}$ peak, the full width at half maximum of the Ag 3d peak broadens, indicating that the oxygen plasma treated Ag does not completely oxidize Ag and that some metallic Ag still coexists.
Figure 4.12 XPS spectra of (a) the Ag 3d and (b) O 1s core level regions for bare ITO, oxygen plasma treated ITO, as-deposited Ag/ITO and oxygen plasma treated Ag/ITO.
Previously it was reported that modified silver oxide, either Ag$_2$O or AgO$_x$ between an anode and the HTL in OLEDs resulted in enhanced hole injection by creating an interfacial energy step [83-85]. Choi et al. [84] reported that the AgO$_x$ layer between an Ag anode and the HTL in OLED could increase the work function of Ag by 0.4 eV, leading to the potential barrier lowering for the hole injection from Ag to the HTL. Similarly, Moon et al. [85] employed ~1 nm thick Ag$_2$O nanodots between the ITO and the HTL in OLED, leading to the enhanced current density and the lowered turn-on voltage in OLEDs. Generally it is known that silver oxide are p-type semiconductors with their work function ranging from 4.8 to 5.1 eV, depending on the processing condition [86]. For plasma treated ITO, oxygen plasma treated Ag on glass, PEDOT:PSS on glass, the absolute value of the work function for KP measurements has been calculated by assuming a value of the work function of the gold probe of -5.1 eV and measuring the contact potential difference between the probe and the substrate [87]:

$$V_c = \phi_1 + (W_p - W_1)/e$$  \hspace{1cm} (4-1)

where the contact potential difference is $V_c$, the work functions of the probe $W_p$ (eV) and sample $W_1$ (eV), and the surface potential of the sample $\phi_1$ (V). Given that the coverage of oxygen plasma treated Ag (1 nm) on ITO is very low, a 20 nm thick film of oxygen plasma treated Ag on a glass substrate was used for KP measurements. For plasma treated ITO, plasma treated Ag on glass, PEDOT:PSS on glass, the $V_c$ was measured to be -0.22V, -0.4V and +0.16V, respectively (Figure 4.13). As a result, the work function
of plasma treated ITO, plasma treated Ag on glass, PEDOT:PSS on glass was estimated to be -4.88 eV, -5.06 eV and -5.26 eV, respectively, confirming that the interfacial energy step between the ITO and PEDOT:PSS is created.
Figure 4.13 The contact potential difference, $V_c$ (V) of (a) plasma treated ITO ($V_c=-0.22$V), (b) plasma treated Ag on glass ($V_c=-0.40$V) and (c) PEDOT:PSS on glass ($V_c=+0.16$V).
4.2.4 Device characterization of P3HT:PCBM BHJ PV devices with oxygen plasma modified ITO anode

The sheet resistances of substrates were monitored using 4-point probe measurement. After the oxygen plasma treated Ag film was formed on the ITO-coated glass substrate, the sheet resistance was slightly increased from 11.9±0.4 Ω/sq to 12.4±0.6 Ω/sq.

Figure 4.14(a) shows the $J$-$V$ characteristics under AM 1.5G filtered illuminations for a calibrated solar simulator with an overall intensity of 100 mW/cm$^2$. The control device (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) exhibited an $\eta_{eff}$ of 3.6±0.2 % with a very high FF of 64.4±1.8%. The $V_{oc}$ and the $J_{sc}$ of the control devices were 0.61±0.01 V and 8.8±0.3 mA/cm$^2$, respectively. For the experimental devices incorporating a modified Ag (1 nm) between the ITO and PEDOT:PSS, an $\eta_{eff}$ of 3.9±0.3% with $V_{oc}$=0.60±0.01 V, $J_{sc}$=10.3±0.3 mA/cm$^2$, and FF=62.8±0.7% were measured. For each set of control and experimental devices, the $R_s \cdot A$, defined by the slope of the $J$-$V$ curve at $J$=0 mA/cm$^2$ was estimated to be about ~6.9±0.1 Ω-cm$^2$ and ~7.3±0.2 Ω-cm$^2$. Despite similar series resistances, the FF in the devices with modified anodes slightly decreased to 63% compared with 66% for the control devices because of an elevated shunt resistance, indicated by the higher slope for the $J$-$V$ curves near 0 V while under illumination.

As expected, $V_{oc}$ remains almost the same within ~100 mV, or less, for both devices since the fabrication conditions for both the P3HT:PCBM blend film and cathode deposition were held constant [88]. The sole differential was the plasma treated Ag, which possibly enhances $J_{sc}$, where $J_{sc}$ increased from 8.8 mA/cm$^2$ for the bare ITO to
10.3 mA/cm² for the plasma modified Ag/ITO anodes. As a result, the $\eta_{\text{eff}}$ of the devices with surface modified anodes was increased from 3.6% for the control devices, up to 3.9%.

Figure 4.14(b) shows the $J-V$ characteristics for both devices under darkness. Under darkness, both devices exhibit high current rectification ratios of $\sim 4.6 \times 10^3$ for the devices with modified anode and $\sim 7.5 \times 10^3$ for the control devices at $\pm 2$ V, indicating that the surface modifications on the ITO anodes did not significantly short the electrical junction between the anode and the cathode. The elevated reverse saturation current and forward biased current for the experiment samples, while exhibiting similar ideality factors ($\sim 1.6$) in the $+0.5$V region, determined from the slope of exponential part of the $J-V$ characteristics to the control sample suggest that the energy barrier between the ITO and polymer has been lowered, while not introducing recombination centers. Indeed, a pronounced higher level of injected current is measured for the oxygen plasma treated sample for modest forward biases, below $+0.4$ V, where a reduced potential energy barrier between the anode and the polymer should more dramatically enhance injected hole diffusion current. The higher leakage current density in the devices with the modified ITO anode ($V < 0.5$ V) results in the slightly decreased FF measured.

For the devices with the modified ITO anodes, the presence of an interfacial energy step between the ITO and PEDOT:PSS is indicated from the forward bias $J-V$ characteristics under darkness, as shown in the inst of Figure 4.14(b), where current injection is dramatically enhanced. It is observed that the dark current density was increased at a given voltage upon insertion of modified Ag between ITO and
PEDOT:PSS layer in agreement with the results of KP measurement. Parameters for the control and experimental PV devices under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm² are summarized in Table 4.4.
Figure 4.14 (a) $J$-$V$ characteristics of the control and experimental PV devices under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm$^2$. (b) The corresponding $J$-$V$ characteristics in darkness. The inset is the linear scale of forward biased $J$-$V$ characteristics of both PV cells under darkness.
<table>
<thead>
<tr>
<th></th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$\eta_{eff}$ (%)</th>
<th>$R_s\cdot A$ (ohm-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>64.4(1.8)</td>
<td>8.8(0.3)</td>
<td>0.61(0.01)</td>
<td>3.6(0.2)</td>
<td>6.9(0.1)</td>
</tr>
<tr>
<td>Experimental</td>
<td>62.8(0.7)</td>
<td>10.3(0.3)</td>
<td>0.60(0.01)</td>
<td>3.9(0.3)</td>
<td>7.3(0.2)</td>
</tr>
</tbody>
</table>

Table 4.4 Parameters for the control and experimental PV devices under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm$^2$.

The optical transmittance for both anodes was the same at the visible range as well as at the absorption peak of the active blend film (Figure 4.8), indicating almost no loss of incident light delivered to the active region when under illumination. As a result, their identical absorption spectra of the photoactive layers were observed from both devices. Nevertheless, an enhanced $J_{sc}$ by a factor of 17% was measured for the devices with the modified ITO anodes versus the control devices, leading to that the overall $\eta_{eff}$ of the devices with surface modified anodes was increased by an overall factor of ~10%.

Given that the coverage of modified Ag (1 nm) on ITO is very low with small island formation as observed previously in the AFM and the SEM images, the difference of optical-field distribution in the photoactive layers for both devices could not explain the measured $J_{sc}$ differences [89].

Furthermore, the modified ITO anodes were not observed as more compatible with the P3HT:PCBM layers because substrates with and without modification have similar RMS roughness of ~1 nm after PEDOT:PSS spin-casting, leading to a negligible effect on the morphology of P3HT:PCBM layer.
The overall physical mechanisms behind this improvement are not clearly understood. However, considering the enhanced hole injection from their $J-V$ curves under darkness with modified ITO surface as well as the KP measurement, surface modification to the anode significantly changes conditions for charge injection and extraction. Since the hole mobility of P3HT phase in the P3HT:PCBM blend film without the thermal annealing has previously reported to be $10^{-11} - 10^{-12}$ m$^2$/V·s [52], whereas it has been reported the electron mobility is $\sim 10^{-8}$ m$^2$/V·s [90], the charge transport in a P3HT:PCBM blend film is highly unbalanced. Due to such unbalanced charge transport properties, the accumulation of holes near the anodes is typically larger in the PV devices than that of electrons, causing the space-charge-limited (SCL) photocurrent [91]. As a result, the internal electric field can increase close to the anode by assisting the extraction of photogenerated holes [91], leading to an increased $J_{sc}$ without significant changes to $V_{oc}$, FF, and the $R_s$ in the PV devices with modified surface.

4.2.5 Conclusions

In conclusion, we have shown an improved $\eta_{eff}$ for polymer-fullerene bulk heterojunction PV devices, mainly due to the enhanced $J_{sc}$, through the usage of a thin islanded plasma-modified Ag atop ITO anodes. Considering the enhanced hole injection due to the created interface energy step between the anode and the photoactive layer, the internal electric field increases close to the anode by assisting the extraction of photogenerated holes, leading to the increased $J_{sc}$ without significant changes to $V_{oc}$, FF, and the $R_s$ in the PV devices with modified surface.
Chapter 5: Surface plasmon enhanced organic photovoltaic devices toward improved optical absorption and photocurrent

Key advantages of organic photovoltaic (PV) technology are that organic based PV versus traditional inorganic semiconductors (a) are inherently inexpensive; (b) typically have very high optical absorption coefficients (≥10⁵ cm⁻¹); (c) are compatible with plastic substrates; and (d) can be fabricated using high-throughput low temperature processes for low-cost roll-to-roll manufacturing [92]. Although organic solar cells have improved rapidly from very low efficiencies to moderate efficiencies of ~3−5% [9, 10, 93], the overall performance of organic solar cells is not yet high enough for commercial opportunities.

In order to improve the efficiency of organic solar cells, one approach, addressed in this chapter, is to yield increased optical absorption and photocurrent generation in the photoactive layer over a broad range of visible wavelengths by inducing surface plasmons through careful control of metallic nanoparticle’s properties. It is well known that the optical absorption spectra of metal nanoparticles are dominated by localized surface plasmons [94]. With incident light, the surface charges of metallic nanoparticles interact with the electromagnetic field, leading to an electric field enhancement that can then be coupled to the photoactive absorption region. It has been extensively studied that surface plasmon resonance can be tuned by changing the size, shape, particle material, and substrates and the dielectric properties of the metal particles [95-97].
5.1 Motivation

The application of plasmonic materials to various PV devices has been widely utilized for improving the PV device performance [17, 98-109]. Recently Morfa et al. [103] reported an improved $\eta_{\text{eff}}$ from $\sim1.3\%$ to $\sim2.2\%$ using surface plasmon-active Ag nanoparticle layers on ITO anode in P3HT:PCBM bulk heterojunction solar cell (ITO/PEDOT:PSS/P3HT:PCBM/Ba/Al). In their study, an enhanced $J_{\text{sc}}$ is reported due to the increased optical absorption from surface plasmons. However, these Ag nanoparticles were actually random shapes formed during the early stages of electron-beam evaporation, forming a discontinuous Ag film of small islands with non-uniform diameters distributed on the ITO anode. As a result, their particle size and shape varied over a wide distribution which could distort the plasmonic effects by broadening their spectral enhancement [110].

Figure 5.1 shows the absorption spectra of Ag nanoparticles (1 nm) deposited by electron-beam deposition, showing a broadening and a decrease of the height of the plasmon absorption band. Sundararajan et al. [111] also showed that nanoparticles aggregates on the active area of the silicon diode can lead to suppression of photocurrent.
Table 5.1 summarizes the examples of the application of plasmonic materials to various optoelectronic devices including various types of solar cells and photodectors using different deposition techniques and plasmonic materials. With a few exceptions [112, 113], a majority of work employs an evaporation technique to deposit the plasmonic materials. However, it is difficult to control the size, shape, and distribution of deposited plasmonic materials, as summarized in Table 5.1.

Recently various approaches to implementing a controlled surface plasmon-active Ag film onto organic solar cells have been introduced as random Ag nanohole films or periodic Ag nanocavity array [104, 114]. However, it is still a challenge to achieve
controllable dimensions of nanoparticles (holes) size with a correspondingly tight
distribution.

In this work, a unique colloidal Ag nanoparticle solution with the presence of
suitable organic capping groups that stabilize the nanoparticles and inhibit their
propensity to agglomerate is applied to organic bulk heterojunction PV devices [115]. An
improved optical absorption and photocurrent for PV devices is demonstrated due to the
increased electric field in the photoactive layer by excited localized surface plasmons of
Ag nanospheres.
<table>
<thead>
<tr>
<th>Type</th>
<th>Materials</th>
<th>Deposition</th>
<th>Size, shape, and distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOI photodector [116]</td>
<td>Ag</td>
<td>Thermal evaporation</td>
<td>40/66/108 nm, random &amp; random</td>
</tr>
<tr>
<td>Si pn cell [113]</td>
<td>Au</td>
<td>Self-assembled (Colloidal solution)</td>
<td>50, 80, 100 nm, sphere &amp; random</td>
</tr>
<tr>
<td>a-Si:H p-i-n cell [112]</td>
<td>Au</td>
<td>Self-assembled (Colloidal solution)</td>
<td>100 nm, sphere &amp; random</td>
</tr>
<tr>
<td>SOI cell [102]</td>
<td>Ag</td>
<td>Thermal evaporation</td>
<td>10~27 nm, random &amp; random</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Thermal evaporation</td>
<td>4~10 nm, random &amp; random</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Thermal evaporation</td>
<td>1 nm, random &amp; random</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Thermal evaporation</td>
<td>11.6 nm (2 nm), random &amp; random</td>
</tr>
<tr>
<td>n-CdSe/p-Si cell [107]</td>
<td>Au</td>
<td>Pulsed laser deposition</td>
<td>10/20 nm, sphere &amp; random</td>
</tr>
<tr>
<td>Dye sensitized cell  [118]</td>
<td>Au</td>
<td>E-beam lithography</td>
<td>Elliptical (200/120 nm), uniform</td>
</tr>
</tbody>
</table>

Table 5.1 Examples of prior works in the area of plasmon-enhanced optoelectronic
5.2 Overview of surface plasmon in metal nanoparticles

5.2.1 Characteristic of localized surface plasmons in metal nanoparticles

Localized surface plasmons (LSP) are charge density oscillations confined to metal nanoparticles. Movement of the conduction electrons upon excitation with incident light leads to a buildup of polarization charges on the particle surface. This acts as a restoring force, allowing a resonance to occur at a particular frequency, which is termed the dipole surface plasmon resonance frequency. At the wavelength near the surface plasmon resonance, excitation of LSPs by light results in strong light scattering in the appearance of intense surface plasmon absorption bands and an enhancement of the local electromagnetic fields.

The extinction of the metal nanoparticles consists of the sum of the scattering and absorption. For metal nanoparticles with a diameter much smaller than the wavelength of incident light, the scattering and absorption cross sections are shown by

\[
C_{\text{scattering}} = \frac{1}{6\pi} \left( \frac{2\pi}{\lambda} \right)^4 |\alpha|^2 \tag{5-1}
\]

\[
C_{\text{absorption}} = \frac{2\pi}{\lambda} \text{Im}[\alpha] \tag{5-2}
\]

where \(\lambda\) is the incident wavelength (corresponding to a frequency \(\omega\)) and \(\alpha\) is the polarizability of the particle.
The polarizability ($\alpha$) of the particle is given by

$$\alpha = 3V \left[ \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \right]$$

(5-3)

where $\varepsilon(\omega)$ is the complex relative permittivity of the metal, expressed as $\varepsilon_1(\omega) + i\varepsilon_2(\omega)$, $\varepsilon_m$ is the dielectric function of the surrounding mediums, and $V$ is the volume of the particle. From Eq. (5-3), the particle polarizability will be very large when $\varepsilon(\omega) = -2\varepsilon_m$, which is defined as dipole surface plasmon resonance. The wavelength of this plasma resonance is therefore given by the wavelength dependence of $\varepsilon_1(\omega)$ when $\varepsilon_2(\omega)$ is small or does not change significantly around the plasma resonance. Around the surface plasmon resonance, the scattering cross section can be larger than the geometric cross section due to very large polarizability of the metal nanoparticles. The scattering efficiency ($Q_{\text{scattering}}$) is given by

$$Q_{\text{scattering}} = \frac{C_{\text{scattering}}}{C_{\text{scattering}} + C_{\text{absorption}}}$$

(5-4)

For metal, the complex relative permittivity of the metal particle can be described by the Drude model, which is the equation of motion due to restoring force on the electrons in the metal to an applied electromagnetic field of angular frequency ($\omega$):

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}$$

(5-5)
where $\varepsilon_0$ is the contribution due to interband transitions ($\varepsilon_0 = 5$ for silver), $\omega_p$ is the bulk plasma frequency ($\omega_p = 9$ eV for silver), and $\Gamma$ is the relaxation constant ($\Gamma = 0.02$ eV for silver) [119]. The bulk plasmon frequency $\omega_p$ is given by

$$\omega_p = \sqrt{\frac{Ne^2}{me_0}}$$

(5-6)

where $N$ is the density of free electrons, $e$ is the electronic charge, $m$ is the effective mass of an electron and $\varepsilon_0$ is the free-space dielectric constant. By inserting Eq. (5-5) into Eq. (5-3) the polarizability of the metal sphere, $\alpha$ in free space ($\varepsilon_m=1$) can be expressed as

$$\alpha = 4\pi r \left[ \frac{\omega_p}{\omega_p^2 - 3\omega^2 - i\Gamma\omega} \right]$$

(5-7)

From the real part of Eq. (5-7), the surface plasmon resonance frequency in free space occurs at

$$\omega_{sp} = \sqrt{3}\omega_p$$

(5-8)

Surface plasmon resonance can be tuned by changing the size, shape, particle material, substrates and overcoating of the metal particles [96, 102, 109, 120-122]. The surface plasmon resonance frequency in free space occurs at $\omega_{sp} = \sqrt{3}\omega_p$ and the bulk plasmon resonance frequency, $\omega_p$ is predominantly dependent on the density of free
electrons from the Eq. (5-8). For Al and Ag, the density of free electrons is higher than that of Cu and Au, resulting in the surface plasmon resonance in Al and Ag occurring at the near UV and visible ranges of the optical spectrum. Ag can be efficient due to its lower absorption and low cost, compared with Au or Cu [109]. By increasing the particle size, the surface plasmon resonance is red-shifted due to dynamic depolarization and significantly broadens [102]. The resonance frequency also becomes red-shifted when the dielectric functions of the surrounding medium increase [121].
5.2.2 Examples of surface plasmon-enhanced photovoltaic devices

Westphalen et al. [17] investigated the influence of silver metal clusters in the depletion layer of a Schottky contact formed between ITO and zinc phthalocyanine (ZnPc) on its optical and photovoltaic properties (ITO/Ag/ZnPc/Ag). The thicknesses of the silver island layers formed by thermal evaporation varied from 4 nm to 10 nm. Figure 5.2 shows the TEM images of the thermal evaporated silver cluster (4 nm) on a carbon TEM grid before and after thermal annealing. Densely packed broad islands with sizes ranging between 10 nm and 20 nm were observed. After annealing the islands coalesced and the size of the particles became larger with a mean diameter of around 36 nm.

Figure 5.2 TEM images of the thermal evaporated silver cluster (4 nm) on a carbon TEM grid (a) before and (b) after thermal annealing. (Adopted from Ref. [17])
They demonstrated that the incorporated metal clusters lead to an increase of the $J_{sc}$ in a spectral region where the Ag cluster absorbs but the ZnPc layer does not due to a plasmon-enhanced excitation of an electron of the metal cluster (Figure 5.3).

Figure 5.3 Variation of $J_{sc}$ and optical extinction as the function of the wavelength in the PV devices without and with silver cluster. The spectra (1) and (2) were obtained at two samples prepared under slightly different annealing conditions. (Adopted from Ref.[17])
Recently, Morfa et al. reported an improved $\eta_{\text{eff}}$ from $\sim1.3\%$ to $\sim2.2\%$ using surface plasmon-active silver nanoparticle layers on ITO anode in P3HT:PCBM BHJ solar cell (ITO/PEDOT:PSS/P3HT:PCBM/BaAl) [18]. The device structure and SEM image of a silver film (2 nm) on ITO are shown in Figure 5.4.

![Figure 5.4](image)

Figure 5.4 (a) The device structure of a P3HT:PCBM BHJ solar cell (ITO/Ag/PEDOT:PSS/P3HT:PCBM/Ba/Al) and (b) SEM image of a silver film (2 nm) on ITO. (Adopted from Ref.[18])

This enhancement is due to the increased optical absorption by surface plasmons. The highest $J_{\text{sc}}$ was obtained for devices incorporating a 2 nm nominal thickness of Ag on ITO. As a result, the device with Ag showed improved $\eta_{\text{eff}}$ of $\sim2.2\%$ with respect to the reference devices (measured using NREL’s XT-10 simulator). The incident photon to current efficiency (IPCE) spectra clearly showed the origin of the increased $J_{\text{sc}}$ and thus the overall efficiency (measured using NREL’s IPCE user facility using a calibrated
photodiode as a reference). At a longer wavelength than 500 nm, a strong enhancement in IPCE is observed for all devices with Ag metal on ITO except the device with 4 nm of Ag metal (Figure 5.5).

Figure 5.5 (a) variation of $J_{sc}$ as varying the thickness of Ag metal (b) IPCE spectra of devices incorporated with 1 nm, 2 nm, 3 nm and 4 nm of Ag metal. (Adopted from Ref.[18])
5.3 Plasmon-enhanced polymer:fullerene derivatives bulk heterojunction photovoltaic devices using self-assembled layer of silver nanoparticles

5.3.1 Experiment

The ITO-coated glass substrates were ultrasonicated in acetone and isopropyl alcohol, dried with nitrogen, and subsequently dried overnight in air before device fabrication. The substrates were next spin-cast using PEDOT:PSS) (Baytron® P, standard grade, HC Stark after passing through a 0.45 \( \mu \)m filter. The substrates were then annealed at 140 °C for 10 min in air with a resulting thickness of ~40 nm.

The Ag colloidal solution was then spin-cast atop the ITO-coated glass substrate. The substrates were then annealed at 140 °C for 10 min in air and then transferred into an inert glove box environment with \( \leq 1 \) ppm level of oxygen and moisture for spin-casting of the photoactive layer.

The mixed solution consisting of P3HT and PCBM in 1,2-dichlorobenzene was then spin-cast at 1000 rpm on the top of the self-assembled layer of Ag nanoparticles (AgNP), as described by Li et al.[10]. The mixed solution had a P3HT:PCBM weight ratio of a 1:1 with a concentration of 20 mg/ml (P3HT). The P3HT (Merck) with 94.5 % regioregularity and PCBM (Nano-C) were used without further purification. The P3HT used here has a weight-average molecular weight \((M_w)\) of 26200 g/mol, corresponding to a number-average molecular weight \((M_n)\) of 13000 g/mol, and with a polydispersity \((M_w/M_n)\) of ~2.

After spin-casting the photoactive layer, thermal annealing was then performed by directly placing the device on a digitally controlled hotplate at 110 °C for 10 min in an
inert glove-box. The thickness of the photoactive film was ~160 nm. The devices were pumped down in vacuum (~10^{-7} Torr) and then the multilayer stack completed by the shadowmask evaporation of a Ca (25 nm)/Al (80 nm) cathode. The final composite device structure is ITO/PEDOT:PSS/AgNP/P3HT:PCBM/Ca/Al. In our experiments, control devices (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) were also fabricated and tested without the self-assembled layer of Ag nanoparticles. Both sets of PV devices (control and experiment) were fabricated during the same batch processing. The active device area \( (A) \) was 0.01 cm\(^2\).

The current density-voltage \((J-V)\) measurements were performed with a semiconductor characterization system (Keithley 4200) at room temperature in air without any device encapsulation under the spectral output from a 150 W solar simulator (Newport) using an AM 1.5G filter. The light intensity was precisely calibrated to a KG5 color filtered silicon diode (Hamamatsu S1133) that had been recently calibrated by the National Renewable Energy Laboratory (NREL), as described by Shrotriya \textit{et al.} [123].

The induced photo-current efficiency (IPCE) was measured using a current preamplifier under short-circuit conditions after illuminating the devices with monochromatic light from a quartz-halogen lamp passing through a monochromator.
5.3.2 Optical, physical and chemical characterization of colloidal silver nanoparticles and self-assembled layers

For the colloidal Ag nanoparticle in toluene with a concentration of 0.5 wt% (Metamateria Partner), an average diameter of Ag nanoparticles was ~3.65 nm with a very high uniformly sized distribution profile of ~81%, determined by dynamic light scattering (Fig. 5.6a). The UV-Vis spectrum of Ag nanoparticles solution shows a plasmon resonance peak at 412 nm with the full width at half maximum (FWHM) of ~61 nm, indicating the characteristics of Ag particles with a plasmon absorption band (Fig. 5.6b).

Transmission electron microscopy images (TEM) indicate the self-assembled layer of Ag nanospheres with an average diameter of ~4 nm with uniform particle-to-particle spacing (Fig. 5.7a). The UV-Vis spectrum of self-assembled layer of Ag nanoparticles shows the localized surface plasmon resonance peak at 465 nm with a FWHM of ~95 nm (Fig. 5.7b) [115].
Figure 5.6 (a) Particle size distribution of colloidal Ag nanoparticle with the concentration of 0.5 wt%. The average diameter of particles is ~3.65 nm with very high uniform size distribution profile of ~81%. The inset is the real image of the colloidal solution. (b) UV-Vis absorption spectra of the diluted Ag colloidal solution showing a plasmon resonance at 412 nm with the FWHM of ~61 nm (The absorbance is baseline corrected with a background of toluene).
Figure 5.7 (a) TEM image of the self assembled Ag nanospheres layer with an average diameter of ~ 4 nm and with periodic particle-to-particle spacing (b) UV-Vis absorption spectra of the self assembled layer of Ag nanoparticles (The absorbance is baseline corrected with a background of quartz substrate).
In the X-ray photoelectron spectra, the Ag 3d_{5/2} peak is observed at 368.2 eV with a very narrow FWHM of 0.68 eV (Figure 5.8), which compares with elemental Ag (368.27 eV). This indicates a portion of the Ag nanoparticles remains elemental.

Figure 5.8 XPS spectra of the Ag 3d from the self-assembled layer of Ag nanoparticles
Figure 5.9 shows the AFM tapping-mode height images (5 μm × 5 μm area) for the self-assembled layer of Ag nanospheres studied, indicating very smooth surface with RMS roughness of 1.86 nm in the image Z range (Z) of 14.9 nm.

Figure 5.9 The AFM tapping-mode height images (5 μm × 5 μm area) for the self-assembled layer of Ag nanospheres studied
5.3.3 Device characterization of polymer:fullerene derivatives bulk heterojunction photovoltaic devices with self-assembled layer of silver nanoparticles

Figure 5.10 shows the optical density of P3HT:PCBM blend films with and without a self-assembled layer of Ag nanoparticles, both with the red shoulder (at 602 nm), indicating effective self-organization of the regioregular P3HT regardless of self-assembled layer [9]. In the spectral range of 350 nm to 650 nm where the P3HT:PCBM blend film is absorbing, the enhanced optical absorption was observed due to the increased electric field in the active photoactive layer by excited localized surface plasmons around the Ag nanospheres. This result corresponds to a ~16% increase of the total optical absorption of the devices in the spectral range of 350 nm to 650 nm.

Figure 5.10 The optical absorption spectra of the P3HT:PCBM bulk heterojunction with and without self-assembled layer of Ag nanoparticles (The absorbance is baseline corrected with a background of PEDOT:PSS/quartz substrate).
The IPCE measurements for the control and experimental devices are shown in Fig. 5.11. Prior to the IPCE measurement, the spectral response of the color-filtered silicon solar cell (Hamamatsu S1133) was measured and normalized to the NREL calibration result shown in the inset of Fig. 5.11. The IPCE of the control devices follows primarily the optical density of the P3HT:PCBM layer and the maximum IPCE was \(~45.7\%\) at 480 nm. With the presence of Ag nanoparticles in contact with the photoactive layer, the maximum IPCE was increased to \(~51.6\%\) at 500 nm. By integrating the product of this IPCE and the global reference solar spectrum, the calculated \(J_{sc}\) was \(~6.8\) mA/cm\(^2\), whereas it was \(~6.1\) mA/cm\(^2\) for the reference devices. With the presence of Ag nanoparticles in contact with the photoactive layer, an additional local photocurrent was created due to the enhancement of the photogeneration of excitons associated with enhanced electric field intensity from the localized surface plasmon resonance.
Figure 5.11 IPCE measurement of the control device (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) and the experimental device (ITO/PEDOT:PSS/Ag nanoparticles (AgNPs)/P3HT:PCBM/Ca/Al). The inset is the spectral response of the color-filtered silicon solar cell (Hamamatsu S1133) measured in the lab and then normalized to the NREL calibration data.
Figure 5.12(a) shows $J-V$ characteristics of both devices under darkness. The control PV device exhibited a high current rectification ratio of $\sim 1 \times 10^5$ at $\pm 1$ V, whereas it was only $\sim 26$ at $\pm 1$ V for the experimental devices, indicating that the presence of the self-assembled Ag nanoparticles on the PEDOT:PSS layer significantly shorted the electrical junction between the anode and the cathode. The highly elevated reverse saturation current for the experiment samples suggests that the Ag nanoparticles significantly introduced surface recombination centers, leading to a higher leakage current density in the experimental devices for $V < 0.5$ V. This position of the silver nanoparticle layer directly in contact with the active light absorbing polymer was probably a source of recombination.

Under AM 1.5G filtered illuminations for a calibrated solar simulator with an overall intensity of 100 mW/cm², the control device (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) exhibited an $\eta_{eff}$ of $\sim 2.2\%$ with a high fill factor (FF) of $\sim 64\%$. The open-circuit voltage ($V_{oc}$) and the $J_{sc}$ of the control devices were $\sim 0.56$ V and $\sim 6.2$ mA/cm², respectively (Figure 5.12b). For the experimental devices incorporating the self-assembled Ag nanoparticle layer between the PEDOT:PSS and P3HT:PCBM, an $\eta_{eff}$ of 1.2 % with $V_{oc}=0.42$ V, $J_{sc} \sim 7.0$ mA/cm², and FF $\sim 35\%$ were measured. For experimental devices, the increased $J_{sc}$ was observed due to the enhancement of the photogeneration of excitons near the plasmon resonance and into the red, as shown in Fig. 5.11. The measured $J_{sc}$ here also matches closely the $J_{sc}$ calculated from the IPCE measurement ($J_{sc} \sim 6.9$ mA/cm²). However, the specific series resistance ($R_s\cdot A$), defined by the slope of the $J-V$ curve at $J=0$ mA/cm² is estimated to be about $\sim 48.1 \Omega \cdot \text{cm}^2$ (for experimental
devices), increased by more than a factor of three compared with the control devices (~13.3 Ω-cm²). Due to the combination of elevated series resistance and lowered shunt resistance, the FF in the experimental devices significantly decreased to ~35 %. Although the fabrication conditions for both the P3HT:PCBM blend film and cathode deposition were held constant in this work, $V_{oc}$ decreased in the experimental devices. This lowered $V_{oc}$ could be due to the higher surface recombination at the interface between the self-assembled layer of Ag nanoparticles and the P3HT:PCBM film.
Figure 5.12 (a) $J-V$ characteristics of the control device (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) and the experimental device (ITO/PEDOT:PSS/Ag nanoparticles (AgNPs)/P3HT:PCBM/Ca/Al) in darkness. (b) The corresponding $J-V$ characteristics under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm$^2$. 
<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta_{eff}$ (%)</th>
<th>$R_{sh}$ (kΩ)</th>
<th>$R_s \cdot A$ (Ω⋅cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6.2 ±0.13</td>
<td>0.56±0.01</td>
<td>64±1.8</td>
<td>2.2±0.23</td>
<td>98±39</td>
<td>13.3±1.8</td>
</tr>
<tr>
<td>Experimental</td>
<td>7.0±0.15</td>
<td>0.42±0.03</td>
<td>35±1.4</td>
<td>1.2±0.07</td>
<td>24±5</td>
<td>48.1±5.9</td>
</tr>
</tbody>
</table>

Table 5.2 Parameters for the control and experimental PV devices under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm$^2$.

When the Ag nanoparticles are formed instead between the ITO and PEDOT:PSS (ITO/Ag nanoparticles/PEDOT:PSS/P3HT:PCBM/Ca/Al), the photocurrent enhancement was not observed while recorded $V_{oc}$ and FF are ~0.56 V and ~41 %, respectively. This could be attributed to the exponential decay of the electrical field by excited surface plasmons of Ag nanoparticles in the PEDOT:PSS layer. The surface recombination at the Ag nanoparticle layer could, however, be significantly reduced by placing the Ag nanoparticles under the PEDOT:PSS layer. Further optimization of the plasmon-enhanced organic bulk heterojunction is underway.

Further optimization of the plasmon-enhanced organic bulk heterojunction can be achieved by tailoring geometrical parameters such as the size and shape of nanoparticles. This optimization is currently in progress by extending the finite-difference time-domain method [124] to Drude dispersion models [125, 126] and the periodic boundary condition.
5.3.4 Conclusions

In conclusion, an enhanced optical absorption and improved $J_{sc}$ for polymer-fullerene bulk heterojunction PV devices were demonstrated, mainly due to the localized surface plasmon-enhanced photogeneration of excitons through the usage of plasmon-active Ag nanospheres between the PEDOT:PSS and the photoactive layer. Although the measured $J_{sc}$ was increased, significant $V_{oc}$ and FF losses were observed. Considering the enhanced saturation current from their $J$-$V$ curves under darkness, the Ag nanoparticles considerably increased the surface recombination at the interface between PEDOT:PSS and P3HT:PCBM.
Chapter 6: Hermetic seals for organic photovoltaic devices for long-term stability

6.1 Introduction

Organic solar cells are of tremendous interest for their potential societal benefits and the opportunity for relatively low-cost production on flexible substrates [127, 128]. Organic semiconductors and associated materials are, however, very sensitive to intrusion of air or moisture and require hermetic seals [45]. Because the chemical electronic materials involved are specific to their end use, custom joining technology plays a role in developing good seals with long life. These devices are multi-layered and require specific substrates. The sealing materials cannot leach pollutants into the organic system or failure may result; therefore, highly specific joining/sealing techniques are required.

A current state-of-the-art approach to hermetic sealing of organic PV is to apply an epoxy resin to effectively glue a transparent cover [21, 45]. However, this epoxy must be cured either by time, temperature, ultraviolet exposure, or a combination of the above. Sealing in this manner can takes hours or a full day, which is contrary to the high-throughput manufacturing envisioned.

This experiment aims to reduce encapsulation times through rapid sealing via tailored laser welding, making immediate commercialization of organic PV technology highly probable in the collaboration with Edison Welding Institute (Columbus, OH).
6.2 Examples of encapsulated organic solar cells for commercial application

In 2008, IMEC (Leuven, Belgium) reported the method to stabilize the morphology of P3HT:PCBM PV devices at the nanoscale, leading to an improved lifetime at least a factor 10 [19]. It has been known that the overall efficiency and operation of organic solar cells strongly depends on the morphology of the photoactive layer [4, 51]. Although prior work has identified blends as a promising opportunity, mixing conjugated polymer materials together as the donor and fullerene derivatives as the acceptor materials, phase-separation of the two component system at the nanoscale can be deteriorated due to the segregation of the mixture, which can prevent efficient dissociation and collection of photogenerated excitons at the distributed interfaces. Previously IMEC has reported that this phase segregation affects the mobility of the organic polymer and that fixation of the nanomorphology of the polymers could result in a prolonged operational lifetime [129].

The key technology of this report was a new fabrication method and new conjugated polymers to stabilize the nanomorphology of the active layer, leading to more robust phase segregation and prolonged operation. They demonstrated that the bulk heterojunction organic solar cells based on this new material showed no degradation of the efficiency after more than 100 hours, whereas reference cells with a commercial P3HT degraded already after a few hours (Figure 6.1). They showed the TEM images of a stable morphology of the photoactive layers using the novel conjugated polymer after degradation at 100°C for 2 h, while a P3HT/PCBM BHJ layers with a commercial P3HT showed significant phase segregation (Figure 6.2).

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Figure 6.1 Efficiency comparison of P3HT/PCBM (1:1) BHJ solar cells (cell A) and a novel conjugated polymer:PCBM solar cell (cell B). (Adopted from Ref. [19])

Figure 6.2 TEM images of the photoactive layers after degradation at 100°C for 2 h from P3HT/PCBM (1:1) blend (left) and a novel conjugated polymer:PCBM blend (right). (Adopted from Ref.[19])
Hauch et al. [20] conducted accelerated lifetime testing on flexible P3HT:PCBM BHJ solar cells. The devices were encapsulated with food package quality barrier coated plastic films with a water vapor transmission rate of 0.2 g/(m² day) at 65 °C/85% relative humidity (rh). A lifetime test was performed under three different climate conditions: 65 °C (high temperature), 65 °C under 1 sun (sun soak), and 65 °C at 85% rh (damp heat). While the PV devices were kept open during storage at 65 °C and 65 °C at 85% rh, respectively, the devices were stored at short circuit condition at 65 °C under 1 sun.

At 65°C under 1 sun (sun soak) condition, the $V_{oc}$ and FF decreases by ~5% from the initial normalized value over 1250 h. For the same test condition, the $J_{sc}$ decreases by ~20% in the 1500 h, eventually failed after 1500 h. Overall efficiency decreased by ~25% over 1500 h (Figure 6.3).
Figure 6.3 Lifetime test performed under three different climate conditions: 65 °C (high $T$ storage), 65 °C/1 sun (sun soak), and 65 °C/85% rh (damp heat). (Adopted from Ref. [20])
Hauch et al. [21] also performed lifetime measurement on flexible P3HT:PCBM BHJ solar cells under outdoor conditions at the Konarka rooftop testing setup in Lowell, MA. It was demonstrated here that flexible solar cell modules survived over 1 year of outdoor exposure without significant performance losses.

The schematic cross-section of an encapsulated flexible solar cell is shown in Figure 6.4. The modules consist of the cells with active areas $>1$ cm$^2$ per cell and efficiencies $>1\%$ under AM1.5 illumination. The modules were encapsulated using transparent barrier films with a water vapor transmission rate of 0.03 g/(m$^2$ day) at 38 °C/100%rh. After 14 months outdoor test, the total efficiency of the module increased by 3.3% due to a relative increase in FF of 10.8%, with a decrease in $V_{oc}$ by 6.8% (Figure 6.5). No significant change in $J_{sc}$ was observed before and after, indicating no major photo bleaching of the active layer.

Figure 6.4 Schematic cross-section of an encapsulated flexible solar cell. (Adopted from Ref.[21])
Figure 6.5 Relative variation of the performance parameters extracted from the $J-V$ characteristics of the module, before and after 14 months outdoor degradation. (Adopted from Ref.[21])
6.3 A Laser sealing approach for air-stable operating and flexible polymer:fullerene derivatives bulk heterojunction photovoltaic devices

6.3.1 Experiment

For our preliminary encapsulation experiment, ITO coated on glass (Delta technologies, LTD) was used as a test substrate. The thickness of ITO was ~120 nm and the sheet resistance was ~10 Ω per square. Patterning the ITO coatings was performed to define a pattern of five parallel strips-shaped transparent anodes (21 mm × 1 mm) using conventional photolithography and HCl-based wet etching. Five additional strips of Al cathode material (21 mm × 1 mm) were also formed on the patterned ITO/glass substrate perpendicular to each other. The strips of Al cathode were evaporated thermally at pressures below 10⁻⁶ Torr with thicknesses nominally 100 nm using shadowmask.

For the encapsulation of PV devices, a multilayer sputtered In₂O₃/Au/Ag on optical grade polyethylene terephthalate (PET) substrate (Delta Technologies, LTD) was used as a flexible substrate coated with a transparent conducting oxide (TCO) as an anode. This substrate was chosen because it exhibits high transmittance over the visible range and low resistance characteristics similar of those of the ITO coated on glass substrates. It is also known that they are capable of being subjected to a radius of curvature of 10 mm without damaging to the conductive anode.

The sheet resistance of In₂O₃/Au/Ag on PET was about 12 Ω per square using a 4-point probe measurement. The optical transmittances of the substrates were monitored over the visible range (300–800 nm) using a Lambda 900 UV/vis/NIR spectrometer.
(PerkinElmer), as shown in Figure 6.6. Specifically for at the absorption peak (~555 nm) of an annealed P3HT:PCBM blend film, the nominal transmittance of the In$_2$O$_3$/Au/Ag on optical grade PET and ITO on glass were ~80.4% and ~89.3%, respectively. The strips of Al and In$_2$O$_3$/Au/Ag coating were formed under the same condition used for the preliminary test.

![Graph showing optical transmittance](image)

**Figure 6.6** Optical transmittance of the In$_2$O$_3$/Au/Ag on optical grade PET substrate and ITO on glass substrate.

To create a hermetic seal, a 1-mil-thick Teonex® Q51 polyethylene naphthenate (PEN) film was used. The key features of this film are (1) high stiffness and mechanical strength; (2) low thermal shrinkage; (3) greater hydrolysis resistance compared to PET;
(4) low moisture absorption; (5) excellent solvent resistance. In this work, the PEN film was used as the covering packaging material for final devices due to high seal quality obtained between PEN and PET.

To meet the objectives of this study, a laser sealing approach was selected to determine the feasibility of encapsulating photovoltaic devices with PEN film due to precise control of the melt area with minimal damage to the anode and cathode. A thin coating of infrared absorber (Gentex Clearweld® LD140B) was applied to the PEN film using an acid brush. It absorbs infrared energy and converts it to heat to create a seal at the interface.

For preliminary experiments, a 100-W JDSU Industrial Diode Laser with a 915 nm wavelength was used to evaluate the feasibility of sealing PEN to glass having strips of both ITO and Al coatings. During experiments to seal PEN to PET substrate, both a 5-W Miyachi Unitek YAG laser system and a JDSU Industrial Diode Laser, operating at 915 nm (100 W) were tested.

The fixture shown in Figure 6.7 was designed to weld assemblies with a 17 mm × 17 mm seal around the perimeter to use on the final active photovoltaic cells. Figure 6.8 show enclosures with perimeter seals with rounded and 90-degree corners. Initially, rounded corners were used to avoid hesitation by the laser motion system, but it was later found that at slow travel speeds it was not necessary.
Figure 6.7 Fixture used to weld final assemblies with a 17 mm × 17 mm seal around the perimeter to use on the final active photovoltaic cells.
Figure 6.8 (a) Photo images of sealed enclosure (rounded corners) with PEN and PET with In$_2$O$_3$/Au/Ag anode (b) Magnified image of sealed enclosure (90-degree corners) with PEN and PET with In$_2$O$_3$/Au/Ag anode
The fabrication of PV devices was performed under the same condition described in Chapter 3 on this dissertation. The active area of the devices (1 mm$^2$) is defined as the overlap of TCO anodes and Al strips.
6.3.2 Result and discussion

There was success sealing PEN to glass with moderate peel strengths. However, identifying process conditions that resulted in moderate seals with PEN to glass, ITO coating, and Al coating was problematic. Damage to the Al coating occurred at conditions that yielded moderate seal strengths between the PEN film and glass substrate. Micrographs of seals between PEN and glass substrate with Al strips are included in Figure 6.9. Damage to the Al strips can be seen in the center of the seal region.

When a 5-W Miyachi Unitek YAG laser system was used to seal PEN to the PET substrate with Al strips and In$_2$O$_3$/Au/Ag coating, sealed samples with strong peel resistance were created with all combinations including (1) PEN to PET substrate; (2) PEN to Al coating on PET substrate; (3) PEN to In$_2$O$_3$/Au/Ag coating on the PET substrate.

However, these seals resulted in laser-induced damage to the In$_2$O$_3$/Au/Ag coating. As shown in Figure 6.10, when exposed to high peak pulses of laser energy, the In$_2$O$_3$/Au/Ag coating were completely damaged and were removed from the seal area. This prevented electrical continuity for seals created with overlapping pulses. A high resistance could be measured when the spots were not completely overlapped (Figure 6.10). These overlaps were controlled by pulse frequency and travel speed. The seal strengths suffered and the damage to the In$_2$O$_3$/Au/Ag coating was still evident.
Figure 6.9 (a) Photograph of PEN coated with IR absorber sealed to glass substrate with Al strips using a 5-W Miyachi Unitek YAG laser system (b) Optical microscope image of damaged Al strips after laser exposure.
Figure 6.10 (a) Micrograph of initial trials included reducing the pulse overlap using a 5-W Miyachi Unitek YAG laser system (b) Close-up of above region.
Indium oxides are known to absorb infrared energy [130]. The degradation observed at the strips indicated that the In$_2$O$_3$/Au/Ag coating suffered from thermal shock. By making single laser passes on the In$_2$O$_3$/Au/Ag coating coated PET without infrared (IR) absorber, evidence of heating was observed. The added absorption of the In$_2$O$_3$ coating promoted excessive heating with high energy pulses. The absorption characteristics of the In$_2$O$_3$/Au/Ag coating posed a significant obstacle when trying to identify laser sealing parameters. This limited the maximum energy density for the other critical sealing combination (PEN to Al). The YAG laser was abandoned in favor of a system with a more controlled heat input.

When using a JDSU Industrial Diode Laser operating at 915 nm (100 W), PEN coated with IR absorber was sealed to PET with In$_2$O$_3$ coating on the entire sample for the initial experiments. Sealing conditions were found that provided moderate peel strengths but maintained some degree of electrical conductivity through the seal. Figure 6.11 shows an example of a successful laser seal between these materials.
For enclosing PEN with PET having patterned In$_2$O$_3$ strips, parameters were screened including power level, travel speed, and spot size. Different sealing parameters were required from those used with PET substrates entirely coated with In$_2$O$_3$. During these trials, linear laser passes were made across the five In$_2$O$_3$ strips as shown in Figure 6.12. In this micrograph, it can be seen that the seal region expands at the In$_2$O$_3$ strips due to increased absorption.
Enclosure samples were tested for seal strength and electrical continuity through the seal region. Both of these requirements were equally important. Sealing conditions that yielded moderate strengths with minimal damage to the In$_2$O$_3$ or Al strips were difficult to identify. Compromise was made by focusing more on the continuity of the In$_2$O$_3$ strips than seal strength. For the In$_2$O$_3$ strips, there were only a few conditions that resulted in a measurable resistance, which is still too high for PV application.

The structure of encapsulated PV devices is PET/(In$_2$O$_3$/Au/Ag)/PEDOT:PSS/P3HT:PCBM/LiF/Al. In Figure 6.13, the laser seal can be seen overlapping the photoactive layer. The seal is more apparent at the In$_2$O$_3$ crossovers due to the additional absorption. At the Al crossovers, there is no apparent damage. By observing the In$_2$O$_3$
crossovers at higher magnification, the photoactive layer can be observed in the sealing region and the appearance of the In$_2$O$_3$ is altered.

Figure 6.13 (a) Seal around perimeter of the PV devices (b) Seal of the PV devices at In$_2$O$_3$ crossovers

For the PV devices before laser sealing, an $\eta_{\text{eff}}$ of 0.32% with $V_{\text{oc}}=0.40$ V, $J_{\text{sc}}=3.8$ mA/cm$^2$, and FF=21% were measured. Compared with the PV devices using ITO/glass substrates, the overall performance of the PV devices with a flexible In$_2$O$_3$/Au/Ag on PET substrate is very low because the fabrication process was not optimized. Immediately after sealing, the $V_{\text{oc}}$ and $J_{\text{sc}}$ were measured for the enclosed active PV devices. The $V_{\text{oc}}$ of the enclosed active PV devices was similar with that of the unsealed PV devices. However, the measured $J_{\text{sc}}$ was very low.

The total resistance of electrodes $R_t=V/I$, was measured by passing a current $I$ through the bar strips electrodes and measuring the voltage $V$ across the two contact
separated from each other by spacing (~20 mm). The $R_t$ of the In$_2$O$_3$/Au/Ag anode before laser sealing was about ~155 Ohm. After laser sealing, the $R_t$ were estimated $>10^6$ Ohm indicating the electrical discontinuity, while the $R_t$ of Al cathode did not significantly change before and after sealing (Figure 6.14).

![Figure 6.14](image)

(a) Measured total resistance of (a) In$_2$O$_3$/Au/Ag strip and (b) Al strip after sealing

Overall, it appears different sealing parameters will be needed for different sections of the device. This could be achieved using existing parameter controls for welding; however, project time did not permit that type of optimization. The objective of this project was to evaluate the feasibility of laser sealing of dissimilar material layers for flexible organic PV devices. Unenclosed, exposed active cells last in the air ambient approximately 1 hour before failure. While the welds to the Al strips may have been
weak, the cause for electrical failure was the performance degradation imparted to the In$_2$O$_3$/Au/Ag strips. Using optical microscopy, the seal area over the In$_2$O$_3$/Au/Ag strips was examined. At low magnification (50×), small cracks in the In$_2$O$_3$/Au/Ag coating can be observed throughout the entire sealed area (Figures 6.15). The sealed region expands at the In$_2$O$_3$/Au/Ag strip from additional heat generation. At higher magnification, greater detail of the linear cracks can be observed. The thermal stress cracking directly results in increased resistance and low electrical conductivity.
Figure 6.15 (a) Micrograph of seal region at an In$_2$O$_3$/Au/Ag bar crossover (b) Magnified micrograph of (a).
6.3.3 Conclusions and future work

This project successfully demonstrated the feasibility of using a diode laser source to seal flexible organic photovoltaic devices with anodes and cathodes, such as Al and In$_2$O$_3$/Au/Ag. Throughout the study, moderate seal strengths were obtained for each material combination. Active photovoltaic cells were encapsulated, and their partial operation was verified. Although the photoactive layer showed signs of deterioration after a few days after sealing, this was well beyond the expected lifetime outside of a glovebox environment without encapsulation. Future work should include the followings:

1. Extend laser sealing to other substrate and anode/cathode materials.
2. Optimize the process for each material combination.
3. Consider masking In$_2$O$_3$ crossovers to minimize damage.
4. Minimize damage/cracking of In$_2$O$_3$. 
Chapter 7: Room temperature negative differential resistance in polymer tunnel diodes and demonstration of threshold logic

7.1 Introduction

Negative differential resistance (NDR) devices, in general, have tremendous potential for low power memory [131] and logic [132], but successful demonstrations of room temperature NDR suitable for circuit applications have been restricted to rigid inorganic semiconductors. Smartcard technology, in particular, for banking and medical information, would be advanced by flexible low-power memory. The advantage of quantum functional circuits is illustrated by the N-shaped electrical characteristics of two serially connected NDR devices which can be exploited to form two stable latching points. When this pair is fashioned into a one-transistor tunneling diode static random access memory (1T TSRAM) cell utilizing NDR devices with extremely low valley current densities, the number of devices needed and the standby power consumption are greatly decreased from traditional six transistor SRAM memory [131]. The requirement of an NDR device for these circuit topologies is room temperature NDR operation with a reasonably high peak-to-valley current ratio (PVCR) [$\geq 3$]. The creation of a suitable organic-based NDR device could enable new opportunities in molecular and organic based memory and logic circuits [133, 134].
Since the first report of NDR using molecules as the active material [135], electronic devices using single (or multiple) molecules that exhibit NDR have intrigued researchers for their potential in low power electronics [133], but, to date, these demonstrations have limited yield, repeatability and often a non-optimal current-voltage shape for proper latching behavior [136-138]. A prime motivator is the wide versatility in chemical and molecular structures that allows for a large ability to tune the diode behavior.

Comparatively much thicker layered organic devices, similar to polymer light emitting diodes (PLED) [139], which also exhibited NDR, would have a considerable advantage over molecular junctions, such as low fabrication costs and flexible substrates. During the past ten years, attempts have been made to investigate NDR behavior in organic thin film devices that have similar configurations with molecular junctions but it has not been demonstrated successfully yet [22, 140-142]. In addition, most organic thin film devices were operated under positive bias, and not explored in the negative bias regime. Recent reports of polymer thin film memory devices are based on bistable conductance states, not NDR behavior [143, 144].

It will be presented here strong room temperature NDR for polymer tunnel diodes using a thin tunneling layer sandwiched between the polymer and the anode. A key advantage is the pronounced NDR using a thick polymer layer with a large active area, circumnavigating the need for molecularly sized junctions. Current-voltage measurements show large and reproducible NDR with a PVCR as high as 53 at room temperature. It will be also shown basic logic circuit operation using a pair of these polymer tunnel diodes connected in series to form a monostable-bistable transition logic
element latch. Overall results indicate that polymer tunnel diodes are potential candidates for many flexible, low-power logic and memory applications for organic devices by using low-cost and simple solution processing.
7.2 Overview of negative differential resistance in organic thin film devices

NDR has been extensively investigated in molecular electronic junctions, based on covalent and Langmuir-Blodgett (LB) bonding of single molecules or molecular monolayer to conducting substrate, as characterized by scanning probe microscopy, or microelectronic techniques [145-148]. Although many results of NDR reported in molecular electronic junction are not yet fully clarified and understood, theses results has been utilized to investigate several fundamental aspects of molecule electronic junction behavior, still far from implementing to memory and logic applications, except a few studies of bistable conductance of molecular junction [133, 134].

Organic thin film devices, which also exhibited NDR, are similar to molecule electronic junctions, but relatively much thicker layered than molecular dimension. NDR in organic thin film devices has a considerable advantage over molecular junctions, such as low fabrication costs and flexible substrates. During the past ten years, attempts have been made to investigate NDR behavior in organic thin film devices but it has not been demonstrated successfully yet [22, 140-142, 149]. In addition, most of NDR behaviors have been considered only as an ‘anomalous current’, still very far from useful applications. Some recent reports organic thin film devices have been demonstrated for non-volatile memory application, based on bistable conductance states, not NDR behavior [150-154].

This review focuses on the NDR in two terminal organic thin film devices. It does not cover organic thin film devices showing bistable conductance for memory applications. Three-terminal organic electronic devices are also excluded in this review.
In 1995, the non-linear relationship between the current-voltage, somehow ‘current anomaly’ rather than NDR, was first reported by Bröms et al. [155] in PLEDs, which consist of single cyano-substituted poly(p-phenylene vinylene) (CN-PPV) thin layer between ITO anodes and Ca cathode (ITO/CN-PPV/Ca). However, NDR in this study was often only observed only during the first current-voltage scan.

Cimrov and Neher [141] reported both NDR behavior and bistable conductance in PLEDs consisting of single poly (p-phenylene vinylene) (PPV) thin layer between anodes and cathode (ITO/PPV/Al, Au/PPV/Al). In this paper it was reported that the current-voltage characteristics of the device (Au/PPV/Al) showed NDR in PLEDs measured only in vacuum, not in air.

Anomalous behavior of $J$-$V$ characteristics in PLED (ITO/PPV/Al) was also reported by Manca et al. [149] $J$-$V$ characteristics of PLED showed a typical Shockley-like diode curve in oxygen-rich atmosphere. However anomalies were observed in PLEDs operating in vacuum, He, Ar, and N$_2$ atmospheres.

Berleb et al. [22] investigated in detail the NDR behaviors in a variety of OLEDs comprised of conjugated (PPV) and non-conjugated polymer poly-N-vinylcarbazole (PVK), small molecular mass organic materials, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TPD) and tris(8-hydroxyquinolinato)aluminium (Alq3), and partially doped with fluorescent dyes (Figure 7.1). In this paper, the authors ruled out the dependence on the organic materials, irreversible burn-out of current pathway, and tunneling effect as the dominant mechanism of NDR, based upon their experimental results. The authors suggested that the mechanism of NDR is due to the current flow through localized current pathways.
Figure 7.1 $I-V$ characteristics of (a) a dye doped TPD/Alq3/OLED on semilogarithm scale, (b) a dye doped PVK OLED, and (c) a dye doped PVK OLED showing spatially localized emission at low voltages. (Adopted from Ref. [22])
Xu et al. [156] reported NDR in OLED using different PPV derivatives with modified side-chain. Regardless of modified side-chain of PPV derivatives, NDR behaviors are observed from the devices. However, the NDR behavior could not be reproduced quantitatively in this study.

Liu et al. [157] reported anomalous current-voltage characteristics of PLED incorporating copolymer containing triphenylamine and pheylene units (TPA-PPV). They found that the control device without TPA-PPV layer did not show any current anomaly. They proposed that the current-anomaly is dependent upon TPA-PPV characteristics and is possible due to photocarrier generation by re-absorption of electroluminescence light. However, extended experiments are necessary to fully clarify these results.

In 2003, Kolesnikov et al. [23] suggested that the space charge blocking of emissive centers arising from electron trapping near various inhomogeneties and metal spikes at a polymer (organic)/metal interface can also be a possible mechanism for NDR. Although this study was limited to OLEDs using aromatic polyimide, PVK, and dye doped PVK, the suggested mechanism can be a meaningful explanation for anomalous current-voltage characteristics including NDR behavior reported previously in single layer PLEDs, such as ITO/polymer/metal cathode (Figure 7.2).
Figure 7.2 (a) Current–voltage characteristics of the one (A) and another (B) OLEDs ITO/PVK/Al. (b) Current–voltage (1) and brightness–voltage (2) characteristics of the OLED Au/PI/Al: 20 nm thick Au layer was vacuum evaporated on ITO/glass substrate. (c) Current–voltage and brightness–voltage characteristics of the OLED ITO/PVK + DMABI/Ca/Al. (Adopted from Ref. [23])
Tang et al. [158] reported NDR in anode/organic thin film/cathode sandwich structure. Either ITO or Au was employed as an anode. As organic thin films, small molecule organic materials (e.g., Alq3 or N, N'-di(naphth-2-yl)-N,N'-diphenyl-benzidine) and polymeric materials (e.g., polystyrene) were used here. As cathode materials, Al, Ag, or Au were deposited through a shadow mask. The current-voltage characteristics showed NDR behavior and also memory effect. The authors concluded that NDR behavior can be caused by 2-dimensional single-electron tunneling through nanometer-sized metal islands inside crevice, formed unexpectedly by nucleation and growth of a thermally evaporated metal thin-film electrode. The observed phenomenon seems to be due to uncontrolled experiential condition, and not enough work was performed to fully explain the origin of the NDR behavior.
7.3 Room temperature negative differential resistance in polymer tunnel diodes and demonstration of threshold logic

7.3.1 Experiment

ITO coated glass substrates were used with a sheet resistance ($R_s$) of ~10 $\Omega$-cm. TiO$_2$ layers were then added atop the ITO anodes by the following two steps. First, a thin layer of Ti metal was electron beam evaporated in a low pressure range (~10$^{-7}$ Torr). Varying Ti layer thicknesses (2-20 nm) were deposited on a number of ITO-glass substrates to observe the dependence of NDR behavior on the thickness of the TiO$_2$ layer. Next, the Ti metal was oxidized using an inductively coupled plasma reactive ion etching (ICP-RIE) system with oxygen plasma at an RF power of 80 Watts and the substrate held at room temperature [159]. The duration of the plasma oxidation varied as a function of the Ti layer thickness in order to completely convert the metal layer to TiO$_2$. The TiO$_2$ layers were monitored using AFM and ellipsometry. AFM data indicate that the as-deposited metallic Ti layer with a grain structure converted to a smoother surface after oxygen plasma oxidation (Root mean square roughness ~ 1 nm). The refractive index of the thinner TiO$_2$ layers was ~2.2 as measured by ellipsometry, which clearly indicates the complete oxidation of the titanium films. For thicknesses $\geq$ 8 nm, the refractive index of the Ti/TiO$_2$ layer indicates an incomplete oxidation and $J-V$ characteristics also suggest the presence of metallic Ti below the TiO$_2$ along with a visual inspection of the layer transparency.

Thin films of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (Figure 7.3a) were then spin coated atop the TiO$_2$ layer from a 0.5% MEH-
PPV solution in 80% toluene and 20% tetrahydrofuran. This solution was warmed at 60 °C for 24 hours to control the local polymer morphology. The conjugated polymers used here were purchased without any chemical modification or purification. The spin-coated films were nominally 25 nm thick. The polymer tunnel diodes were completed by shadowmask evaporation (~10⁻⁶ Torr) of an Al cathode, about 100 nm thick, directly onto the MEH-PPV. All fabrication steps were performed in an inert glove box environment with less than 1 ppm level of oxygen and water. Electrical measurements were performed with a semiconductor characterization system (Keithley 4200) at room temperature under darkness. The ITO coated glass substrates of a control device (ITO/PEDOT:PSS/MEH-PPV/Al) was covered by PEDOT:PSS (Baytron® P) and they were then annealed at 110°C with a resulting thickness of ~60 nm, which should fully planarize any possible spikes protruding from the ITO surface. The resulting band diagram of the ITO/TiO₂/MEH-PPV/Al tunnel diodes is shown in Figure 7.3(b) and a schematic shown in Figure 7.3(c).
Figure 7.3 Polymer material and device structure with its associated energy band diagram used in this study to demonstrate robust, bulk and large area polymer tunnel diodes. (a) The structure of MEH-PPV. (b) The flat band energy level diagram for the polymer tunnel diode. (c) The ITO/TiO₂/MEH-PPV/Al device structure consists of a polymer thin film ~250 nm thick between an aluminum cathode and a transparent conducting anode, ITO coated with a thin TiO₂ layer (2~20 nm). The active area of all the devices studied was 0.19 cm².
7.3.2 Results and discussion

Typical $J-V$ characteristics of five different polymer tunnel diodes (a 2 nm thick TiO$_2$ layer) are shown in Figure 7.4(a). Large and reproducible NDR is observed for all devices in a bias ranging from -10 V to 0 V. The measured peak current density for these devices was 0.13 A/cm$^2$, with a valley current density of $\sim$0.004 A/cm$^2$, corresponding to a peak-to-valley current ratio (PVCR) of 35:1. The valley current density was generally two orders of magnitude lower than the peak current density for most of measured TiO$_2$-polymer tunnel diodes [$\leq 5.0 \times 10^{-3}$ A/cm$^2$], which is ideally suited for low power organic-based memory. A small variation ($\pm$ 0.001 A/cm$^2$ in the peak current density and $\pm$ 0.08 V in the peak current density position) was observed for successive sweeps. It should be noted that $J-V$ characteristics for all the devices measured in this study were repeatable. After testing, the devices were stored in an inert glove box for 30 days with little variation in their peak current density and peak current position. Some device-to-device variations were observed in the peak current density ($\pm$ 0.004 A/cm$^2$) and in the peak current position ($\pm$ 0.57 V). These device-to-device variations can be attributed to small variations in the thickness of TiO$_2$ layer and polymer films across each sample.

The effect of varying the thickness of TiO$_2$ to determine its influence on $J-V$ characteristics is shown in Figure 7.4(b)−(d). The device with a 4 nm thick TiO$_2$ layer has a maximum peak current density of 0.29 A/cm$^2$ with a PVCR of 53:1 (Figure 7.4b). The inset in Figure 7.4b is a forward and backward $J-V$ sweep of the same device showing some hysteresis. A shift of about 0.6 volts is observed. Some hysteresis is observed in all devices (up to an 8 nm TiO$_2$ layer) and is repeatable. As the TiO$_2$ layer thickness reaches
6 nm, the peak current density decreases (Figure 7.4c). However, the device with an 8 nm thick TiO₂ layer shows a large leakage current with its maximum peak current density of 0.23 A/cm² (Figure 7.4d). It was observed that the NDR behavior persists around -5 V with increasing TiO₂ layer thickness (up to 8 nm). However, due to a large leakage current in a bias range of -10 V and 0 V, the peak current density can not be measured quantitatively for devices with thicker TiO₂ layers. The large leakage current in thicker barrier samples can be ascribed to a localized current pathway through the remaining metallic Ti which was not completely oxidized and converted to TiO₂ during the plasma oxidation process. Table 7.1 summarizes the $J$-$V$ characteristics of the devices illustrating the peak current density, peak voltage, valley current density, valley voltage, and PVCR.

<table>
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<th>Tunneling barrier (nm)</th>
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<th>$V_{\text{peak}}$ (V)</th>
<th>$J_{\text{valley}}$ (A/cm²)</th>
<th>$V_{\text{valley}}$ (V)</th>
<th>PVCR</th>
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Table 7.1 The peak current density ($J_{\text{peak}}$), peak voltage ($V_{\text{peak}}$), valley current density ($J_{\text{valley}}$), valley voltage ($V_{\text{valley}}$), and PVCR are calculated from the $J$-$V$ curve of ITO/TiO₂/MEH-PPV/Al polymer tunnel diodes. Results from the best performed devices are presented.

Control devices, one without a TiO₂ layer (ITO/MEH-PPV/Al) and another inserting PEDOT:PSS between the ITO and MEH-PPV films (ITO/PEDOT:PSS/MEH-
PPV/Al) did not exhibit NDR in the bias range of -10 V and 0 V, which indicates that the observed NDR behavior is not induced by electron trapping in the ITO or metal spikes at the anode/polymer interface [23].
Figure 7.4 $J-V$ characteristics of 5 representative ITO/TiO$_2$/MEH-PPV/Al polymer tunnel diodes from the same sample which exhibit NDR under reverse bias with four different titanium layer thicknesses. (a) 2 nm; (b) 4 nm; (c) 6 nm; and (d) 8 nm. The inset of Fig.7.4b in the upper left corner shows an $J-V$ characteristic of polymer tunnel diode with hysteresis. The thickness of the as-deposited titanium layers before the plasma process is referred to as the thickness of the final TiO$_2$ layers.
For voltage sweeps in different directions, changes in the NDR were observed, shown in the Figure 7.5. In the first forward voltage sweep, the position of the peak current and valley current are in good agreement with the previous $J-V$ curves. When a second voltage sweep was applied in the reverse direction, the $J-V$ curve showed some hysteresis, as shown in the inset of Fig. 7.4b. The following third reverse voltage sweep, however, produced a decreased peak current by one order of magnitude. Then, the initial peak current reappears during the fourth voltage sweep in a positive direction. This switching effect might be due to different conduction pathways through disordered polymer regions over the TiO$_2$ surface or charging and charge removal in traps within the TiO$_2$ layer.
Figure 7.5 $J-V$ characteristics of a ITO/TiO$_2$/MEH-PPV/Al polymer tunnel diode (2 nm of a TiO$_2$ layer) which exhibits some switching effects. Curves 1, 2, 3, and 4 were the first, second, third, and fourth voltage sweeps, respectively.
The observed reverse-biased NDR behavior does not seem to occur via tunneling across the thin TiO$_2$ layer acting as a traditional tunneling barrier based upon the measured $J-V$ characteristics and observed switching effects. This is evidenced by the lack of the measured peak current density to exponentially decrease with increasing TiO$_2$ layer thickness (Table I).

Our results suggest that the NDR behavior observed occurs instead as a result of tunneling through localized defect sites [160] within the thin TiO$_2$ layers induced during the plasma oxidation that are confined to a small range of energies within the TiO$_2$ bandgap near the TiO$_2$ conduction band [161]. The mechanism for NDR under reverse bias in these ITO/TiO$_2$/MEH-PPV/Al tunnel diodes is speculated to occur via electrons emitted from the n-type ITO, tunneling through defect states in the TiO$_2$, which are then collected by the lowest unoccupied molecular orbital (LUMO) level in the MEH-PPV (Figure 7.3b). This hypothesis is reinforced by the diminished NDR observed in a control sample where the TiO$_2$ layer was plasma-oxidized at ~400 °C, which is known to lead to better crystalline [162] and therefore provides fewer defect states available for tunneling.

In a positive bias range 0 V and +10 V, NDR behavior was also observed in some devices. The peak and valley current varied from one $J-V$ measurement to the next, but by the same order of magnitude for the same device. The position of the peak and valley voltage also varied between $J-V$ measurements. Correspondingly, a rapid current drop to nearly zero at ~6 V was also sometimes observed.

To demonstrate useful quantum functional circuit operation using the polymer tunnel diodes, a MOBILE latch operation employing the monostable-bistable transition [132, 163, 164] was used. First, two polymer tunnel diodes with a 2 nm thick TiO$_2$ layer
were serially connected, and the bias \( V_{DD} \) was swept (the inset, Figure 7.6a). Figure 7.6a shows the two successive NDR regions. Next the MOBILE logic function was realized by incorporating a commercial junction field effect transistor (JFET) connected to the central storage node of the pair of serially connected polymer tunnel diodes, as shown in the inset of Figure 7.6b. In order for the polymer tunnel diode pair to latch, charging or discharging was provided by the JFET input current. With a JFET gate bias \( V_G \) of 1.5 V and drain-to-source bias \( V_D \) of 1 V, the input current was 20 mA. For an applied clock voltage \( V_{CLK} \) the output voltage at the sense node \( V_{SN} \) was measured when the JFET is in the off state (i.e. \( V_G = -3 \)) and on-state (i.e. \( V_G = 1.5 \) V) as shown in Figure 7.6b. The MOBILE circuit forms two stable latching points at the sense node, demonstrating bistable latching operation. For an applied \( V_{CLK} \) of -8 V, the voltages of the logic high \( (V_H) \) and low \( (V_L) \) are -1.95 V and -6.01 V, respectively. The percentage of voltage swing, which is ratio between \( V_H \) and \( V_L \) for applied \( V_{CLK} \), was 51%. Thus, stable latching and quantum functional circuit operation is demonstrated.
Figure 7.6 Bistable latching operation is demonstrated using two polymer tunnel diodes. (a) \( J \cdot V \) characteristics of two ITO/TiO\(_2\)/MEH-PPV/Al polymer tunnel diodes (a 2 nm thick TiO\(_2\) layer) connected in series in a bias range of \(-16\) V and \(0\) V. (b) Voltage at the sense node as a function of clock voltage of JFET-polymer tunnel diodes MOBILE latch with a 51% voltage swing of the applied \( V_{\text{CLK}} \) at \(-8\) V.
7.3.3 Conclusions

In conclusion, strong room temperature NDR for polymer tunnel diodes was demonstrated using a thin TiO$_2$ tunneling layer (~2-8 nm) sandwiched between the active layer and the indium tin oxide anode. Current-voltage measurements show large and reproducible NDR with a PVCR as high as 53 at room temperature. In addition, this type of NDR device showed logic circuit operation using a pair of these polymer tunnel diodes connected in series to form a monostable-bistable transition logic element latch. This result indicates that polymer tunnel diodes are potential candidates for many flexible, low-power logic and memory applications for organic devices by using low-cost and simple solution processing.
Chapter 8: Plasma polymerized multistacked organic bipolar films: A new approach to flexible high-$k$ dielectrics

Organic based flexible dielectric films with high permittivity ($\varepsilon$) are desirable for future applications of organic thin film transistors, such as smartcards and radio frequency identification (RFID) tags, that concurrently desire flexible or conformable substrates. Advances in the development of all-polymer field-effect transistors (PFETs) have been particularly significant for their potential in a flexible form. Major improvements have been reported for both the semiconductor and the dielectric components of the PFETs [165]. For example, with respect to semiconductor considerations, noteworthy gains have been achieved in increasing carrier mobility and in identifying lower-cost production technology; however, PFET operational voltages tend to be too high for the intended portable applications. But the voltages could be significantly lowered if a suitable dielectric with high-$k$ ($k$: relative dielectric constant), compatible with the PFET process and in a flexible form factor with thicknesses that are controllably thin was identified.

This chapter focuses on the organic dielectric film component of the PFETs required for all-polymer PFETs by tailoring high-$k$ polymer films. The much needed advances in this area pose difficult challenges in terms of materials science considerations.
8.1 Motivation

One such problem centers on the fact that carbon based organic films have inherently low-$k$, having $k$ values significantly less than those of ceramic (inorganic) materials. Additionally, leakage currents through the film also pose potential problems given the generally porous nature of organic based polymeric films. On the other hand, organic films offer more favorable prospects to satisfy flexible form factors envisioned for many inexpensive all-polymeric devices.

As in the case of the semiconductor research, development of organic based dielectrics has received increasing attention in recent years [166-170]. A number of innovative approaches have been explored and encouraging results obtained. An example of a recent notable advance in this area is the development of $\sigma$-$\pi$ molecular organosiloxane dielectric multilayers having very low threshold voltages and high-$k$ ($k \approx 16$) [171].

Another frequently employed approach is to increase the $k$ values of organic films by incorporation of ceramic fillers [172, 173]. Although these fillers can provide a substantial increase in the $k$, they simultaneously introduce undesirable complications associated with interactions in the composite inorganic-organic film, leading to increased porosity and ultimately poor adhesion between the composite and the purely organic circuit boards.

More recently, an interesting report describe polymer composite films containing silver metal (Ag) nanoparticles, with the metal loading approaching the percolation threshold [174]. The Ag particles were coated with a carbonaceous layer to prevent
interparticle electrical contact and to improve compatibility between the polymeric matrix and the filler particles. Very favorable electrical properties ($k$ values, breakdown voltages, leakage current) were measured for these composite dielectric films. However, it is not clear, at this time, if these composite materials will exhibit long-term stability in that particle aggregation over time would be a concern since the particles are not co-valently bound to the polymer matrix molecules.

The present study involves an innovative approach to synthesis of totally organic dielectric films based on multilayered bipolar films produced by plasma enhanced chemical vapor deposition (PECVD). The layered structures were obtained by the successive polymerization of a carboxylic acid monomer followed by that of an amine containing monomer. The process involves production of alternating ultra thin layers of each monomer to create the bipolar interfaces between layers as achieved by spontaneous proton transfer from the acid to the amine.
8.2 Experiment

8.2.1 Pulsed plasma deposition of bipolar film

Figure 8.1 shows a schematic of the reaction system plus associated electrical components employed in this study. Further details on the operation of this system have been provided by Sanchez-Estrada [175, 176]. Pulsed plasma deposition provides better control over the quality of the deposited films. During plasma on periods, reactive species are generated from the monomer. These reactive species settle on substrate and form a low damage film during plasma off periods.

![Schematic of the plasma reactor system and associated electronic components](image)

Figure 8.1 A schematic of the plasma reactor system and associated electronic components used in this study. (Adopted from Ref. [24])
A carboxylic acid (-COOH) containing monomer, vinylacetic acid (VAA), and an amine (-NH\textsubscript{2}) containing monomer, allyl amine (AA), were polymerized under pulsed plasma operational conditions. For pulsed plasma deposition of VAA, a plasma duty cycle of 2/30 (plasma on-time, ms/ plasma off-time, ms) was used at a monomer pressure 160 mTorr and 150 W power input. Allyl amine was plasma polymerized at a duty cycle 10/30, monomer pressure 70 mTorr and 100 W power input. The polymer films were deposited on metal-insulator-semiconductor (MIS) substrates, which were assembled and cleaned, as described below. A polymeric thin film of allyl amine was first plasma deposited on the substrate which was then followed by the deposition of polyvinylacetic acid. The sequential deposition of AA and VAA films was performed to obtain a multi-layered structure containing polar groups localized at the interfaces between each consecutive layer. Plasma deposition time was varied to control the thickness of the deposited films. Initial studies, using profilometry, revealed that deposition rates of both monomers varied linearly with deposition time under the pulsed plasma conditions employed. From the deposition rates measured, it was possible to control both the VAA and AA film thickness to desired values by use of appropriate deposition times.

8.2.2 Characterization of pulsed plasma deposition of bipolar film

The number of layers and film thickness varied among the 3 sets from 4 layers to 10 layers, having nominal total thicknesses of 200, 120, and 50 nm, corresponding to individual layers of 50, 20 and 5 nm, respectively. For the 10, 6, and 4 layer thin films, the refractive index was estimated to be 1.55, 1.58 and 1.67, respectively, as measured by
single wavelength ellipsometry. The flexibility property of the films was examined by SEM analysis of the films deposited on thin PMMA substrates. No cracking or delamination was noted after repeated flexing of the samples through 30° angles.

8.2.3 Fabrication of a metal-insulator-semiconductor (MIS) capacitor

Metal-insulator-semiconductor (MIS) capacitors were fabricated on 2” Boron-doped (100) p-type Si wafers with a resistivity of 4.2-4.4 Ω-cm. The substrates were processed through standard degreasing and RCA cleaning procedures prior to plasma polymerization. After deposition of multilayer stacks of thin films was carried out under pulsed RF plasma conditions, the Au back contact (100 nm) were then electron beam evaporated in a low pressure range on the back side of the Si wafer. The MIS capacitors were completed by shadowmask electron beam evaporation (~10⁻⁷ Torr) of the Au electrode, about 100 nm thick, directly onto the multilayer stack surface. The final MIS structure fabricated was a Au/p-Si/10-layer stack of PP-AA and PP-VAA/Au. The active area of each MIS capacitor studied was 0.283 mm².

8.2.4 Electrical characterization of pulsed plasma deposition of bipolar film

Capacitance-voltage (C-V) measurements were carried out with an LCR meter (Agilent 4284A) coupled with CSM/Win analysis software (Material Development Corporation, MA) at a frequency range from 1 KHz to 1 MHz at room temperature under darkness. For C-V measurements, the MIS capacitors were biased from −t/10 V to +t/10
V with voltage step of 0.1 V, where \( t \) is the total thickness (nm) of multilayer film. The hysteresis behaviors of the MIS capacitors were recorded at a frequency of 1 MHz. A correction procedure was employed to compute the series resistance of MIS capacitor. Current density-voltage (\( J-V \)) measurements were performed with a semiconductor parameter analyzer (Agilent 4156) at room temperature. All capacitors fabricated were tested without any postdeposition annealing.
8.3 Results and discussion

Figure 8.2 provides a simple visualization of the nature of the bipolar interface between the two films. A radio frequency (RF) pulsed plasma reactor system was employed to provide deposition conditions that permit retention of the requisite monomer functionalities (i.e., –COOH and –NH₂ groups) while simultaneously providing improved film thickness control over that encountered under conventional continuous wave (CW) plasma operations [176-178]. Film characterizations, using X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform-IR (ATR FT-IR) spectroscopy, provide unequivocal evidence for the presence of the –COO⁻ and -NH₃⁺ polar entities as shown in Figures 8.3 and 8.4, respectively.

Figure 8.2 Schematic diagram of the interfacial boundary between the plasma polymerized allyl amine (PP-AA) and vinylacetic acid (PP-VAA) thin films.
Figure 8.3 1A, 1B, 1C are high resolution C1s X-ray photoelectron spectra of plasma polymerized allyl amine (PP-AA), vinylacetic acid (PP-VAA) and the double layer bipolar film respectively. 2A and 2B are high resolution N1s for PP-AA and the double layer bipolar film respectively. 3A and 3B are high resolution O1s for PP-VAA and the double layer bipolar film respectively.
Figure 8.3 shows a compilation of high resolution XPS data for C(1s) [panels 1A,1B,1C], N(1s) [panels 2A,2B], and O(1s)[panels 3A,3B]. Spectra of polymer films obtained from pure allyl amine and vinylacetic acid, along with the assigned chemical functionalities, are shown in panels 1A and 1B. These spectra can be contrasted with the C(1s) spectrum recorded when a thin polyallyl amine film (2 nm) was deposited on a polyvinylacetic acid film (panel 1C). As shown in 1C, the high binding energy –COOH peak (at 289 eV) has been broadened and the peak maximum shifted to a slightly lower binding energy of 288.5 eV, a shift which is consistent with the formation of COO⁻ groups. The high resolution N and O atom spectra provide additional verification of the formation of polar groups. The N(1s) spectra reveal the presence of a peak at 401.7 eV in the layered film [2B] not present in the pure allyl amine film [2A]. This high binding energy peak is consistent with the presence of ammonium ion functionality. Finally, the high resolution O (1s) spectrum of the layered film reveals a low binding energy peak at 531.7 eV, which is not present in the film obtained from pure vinylacetic acid. This low binding energy peak is also consistent with the presence of COO⁻ groups in the layered film.

ATR FT-IR absorption spectral studies provide additional confirmation of the presence of a bipolar film. In these experiments, an ultrathin (2 nm) polyallyl amine film was again deposited on an equally thin 2 nm polyvinylacetic acid film, using a silicon substrate [179]. A comparison of the ATR-FT-IR spectrum of this composite sample, with spectra of pure polyallyl amine and polyvinylacetic acid, is shown in Figure 8.4. Of
special significance are the appearance of characteristic –COO\(^-\) and NH\(_x^+\) absorption bands, as indicated in Figure 8.4c, which are not present in the pure polyallyl amine (Figure 8.4b) or the pure polyvinylacetic acid films (Figure 8.4b).
Figure 8.4 ATR-FTIR spectra of plasma polymerized (A) allyl amine (PP-AA), (B) vinylacetic acid (PP-VAA) and (C) the double layer bipolar film.
Additionally, static sessile water drop contact angle measurements revealed the composite film to be significantly more wettable than either pure polyallyl amine or polyvinylacetic acid single-layer films, as shown in Figure 8.5. The increased wettability of the composite film would be in accord with expectations based on the polar nature of these films in light of the presence of the positive and negative ion centers.

![Figure 8.5 Static sessile-drop water contact angle measurements with plasma polymerized allyl amine (PP-AA), vinylacetic acid (PP-VAA) and the double layer bipolar film (PP-VAA/PP-AA).](image)

A variety of samples containing alternating thin layers of the –COOH and –NH₂ polymers were deposited on a p-doped Si substrate for use in determination of the dielectric and electrical properties of these bipolar containing films. Three different sets
of samples containing alternating layers of the –COOH and –NH₂ films were prepared. The number of layers and film thickness varied among the 3 sets from 4 layers to 10 layers, having nominal total thicknesses of 200, 120, and 50 nm, corresponding to individual layers of 50, 20 and 5 nm, respectively. Subsequently, the Au electrode was deposited on the uppermost organic layer thus completing the assembly required for measurement of electrical properties. The electrical characterizations included capacitance-voltage (C-V) and current density-voltage (J-V) measurements for alternating thin layers of the –COOH and –NH₂ polymers sandwiched between the p-Si substrate and the top Au electrode, in a metal-insulator-semiconductor (MIS) capacitor configuration.

Figure 8.6(a) shows a typical C-V response of a 10-layer stack of alternating allyl amine (5 nm) and vinylacetic acid (5 nm) at 1 MHz frequency in a bias ranging from -5 V to 5 V. The high frequency response clearly shows accumulation at negative bias voltage and depletion regions at positive bias voltage. The \( k \) of this structure was extracted from the measured accumulation capacitance, based on the capacitance formula for a parallel capacitor,

\[
\kappa = C \cdot t / \varepsilon_0
\]

where \( C \) is the accumulation capacitance per unit area (F/cm²) and \( \varepsilon_0 \) is the permittivity of vacuum. The \( k \) extracted here was 6.21 at 1 MHz. The inset of Figure 4a shows the hysteresis behavior of the capacitor, exhibiting \( \sim 3.0 \) V hysteresis at 1 MHz due to uniformly distributed charges trapped in the polymer films during plasma deposition process [180]. As the total thickness of the capacitors is increased, a large hysteresis is
observed. For each 4- and 6-layer stack of polymer film structure, a shift (Δ) of about 15 V and 7.2 V are observed, respectively. For all capacitors tested here, the trap charge density (\(N_t\)) in the dielectric layer is estimated \(\sim10^{12}\) cm\(^{-2}\) using the relation

\[
N_t = \frac{C \cdot \Delta}{q}
\]  

where \(q\) is the magnitude of electronic charge. The higher accumulation capacitance tends to shift to higher values when decreasing the frequency for all capacitors, as shown in Figure 8.6(b). A frequency dependent dispersion in the accumulation region is observed. The frequency dependence of the \(k\) is attributed to the slow polarization of the plasma polymerized multilayer stack at higher frequencies and this polarization can lead to an increase in the induced charge at lower frequencies [181]. Under zero bias the dielectric loss at 1 MHz of the 4-, a 6-, and a 10-layer stacks was 0.06 ± 0.001, 0.02 ± 0.001, and 0.02 ± 0.001, respectively.
Figure 8.6 (a) C-V characteristics of MIS capacitor at 1 MHz for a multilayer stack of plasma polymerized allyl amine (PP-AA) and vinylacetic acid (PP-VAA) film (Au/p-Si/10-layer stack of PP-AA and PP-VAA/Au). The inset shows the hysteresis behavior of the sample. (b) Frequency dependence of the accumulation capacitance for the three different films in four orders of magnitude over frequency.
The $k$ of multilayer stacks was calculated for four different frequencies, as shown in Figure 8.7(a). The phenomenon of higher $k$ at lower frequency is observed. For a 10-layer stack, the dielectric constant varied from 6.21 at 1 MHz to 6.55 at 1 KHz. Similar behavior was observed for each 4- and 6-layer stack of polymer layers. The variation of $k$ does not show any trend with varying the total thickness and number of multilayers, indicating that the thickness and the number of multilayers of the deposited films are not significant for controlling $k$. This phenomenon can be explained by the simulation results reported by Natori et al. when the $\varepsilon$ is independent of thickness for $\varepsilon < 10$ [182]. The dielectric constants of the three multilayer stacked films studied here show small temperature dependence from 27 °C to 147 °C, indicating a good thermal stability of their dielectric constants, as shown in Figure 8.7(b).
Figure 8.7 (a) The dielectric constant, $k$ estimated from $C-V$ measurement of a multilayer stack of plasma polymerized allyl amine (PP-AA) and vinylacetic acid (PP-VAA) film as a function of frequency. (b) The dielectric constant, $k$ of three multilayer stacked films studied here as a function of temperature at 1 MHz.
Figure 8.8 illustrates the $J$-$V$ characteristics of multilayer stacks. As the total thickness of a multilayer film is decreased, the leakage current density is significantly reduced. The leakage current density of a MIS capacitor with a 10-layer stack was 6.5 $\mu$A/cm$^2$ at 1 MV/cm, which is two orders of magnitude smaller than the 6-layer stack film structure and no breakdown in the voltage range. It should be noted that all the devices in this study were measured without any postdeposition annealing [24]. The inset of Figure 8.8 shows the hysteresis behavior of the $J$-$V$ characteristics for a 10-layer stack of polymer films. Some hysteresis is observed in alternating forward and backward voltage sweeps. A leakage current density at 1 MV/cm$^2$ is decreased two orders of magnitude when the total thickness of film is decreased while increasing the number of multilayers in the stack, indicating the number of interfaces within each deposited film is a more important factor to control the leakage current density in multilayer stacked bipolar polymer films than the aggregate thickness.

Under pulsed RF plasma polymerization conditions, efficient retention of monomer functional groups in the polymer film has been demonstrated [24, 178]. In this experiment, it is confirmed that a significant presence of the $-\text{COO}^-$ and $-\text{NH}_3^+$ polar entities, generated from the interaction of the polyvinylacetic acid and the polyallyl amine films, are present in the layered polymer films as shown by XPS and ATR FT-IR analysis. The $k$, in the range of 5.7–6.2 at 1 MHz obtained without any post-deposition annealing, are relatively high values for purely organic films containing only oxygen and nitrogen as heteroatoms. These high-$k$ values are attributed to the unique multilayer stack of alternating layers, combined with the significant presence of $-\text{COO}^-$ and $-\text{NH}_3^+$ polar entities that induce strong dipole orientation polarizability. The redistribution of charges
within a functional group with a net permanent dipole moment reorients itself in space in response to an external applied electric field. The relationship between $\varepsilon$ and the total polarizability ($\alpha$) is often described by the Clausius-Mossotti relationship. The $\alpha$ is generally additive, including electronic, atomic, and dipole orientation polarizability and, within the context of the Clausius-Mossotti relationship, can be used to estimate the contribution of each polarization group to the dielectric constant [183]. The total polarizability increases when dipole orientation polarizability increases. As a result, the $k$ also increases. In this experiment, the observed small variation of the $k$ with varying the total thickness and number of multilayer stack suggests that the $k$ is mainly due to the high dipole orientation polarizability induced between alternating charged layers.
Figure 8.8 $J-V$ characteristic for three different films without postdeposition annealing at room temperature. The inset shows the hysteresis behavior in the $J-V$ curves for 10-layer stack film of plasma polymerized allyl amine (PP-AA) and vinylacetic acid (PP-VAA) film.
8.4 Conclusions

In conclusion, a multilayer stack of polymeric thin films composed of alternating amine and carboxylic acid functional groups was deposited by pulsed RF plasma polymerization produced a composite structure having a relatively high-κ and low leakage current density as obtained without postdeposition annealing. This high-performance multilayer polymer film stack, deposited at ambient temperature and was not subjected to further treatment of any kind, is promising in terms of use as a flexible dielectric material.
References


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