POLYMER PHOTODETECTORS: DEVICE STRUCTURE, INTERLAYER AND PHYSICS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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December, 2013
PUBLICATIONS


ABSTRACT

Photodetectors are light responsive devices that convert optical signals into electric signals. Photodetectors have wide applications in image sensing, environmental monitoring, day- and night-surveillance, chemical and biological detection, industrial process control, communication, planetary probing and so on. Currently, photodetectors based on GaN, ZnO, Si, InGaAs and bulk PbS cover different sub-bands from UV to infrared region. These photodetectors are expensive and some of them require to be operated at low temperature, which certainly limits their applications.

Polymer photodetectors made with conjugated polymers possess the unique features, including room-temperature operation, high sensitivity, low working voltage, low cost, thin profile, large area and flexibility. Ultrasensitive polymer photodetectors with high response speed and spectral response ranging from UV to near infrared have been demonstrated. However, new device structure, high responsivity and stable polymer photodetectors needs to be developed to extend their applications. In my dissertation, we reported various methods to enhance the performance of polymer photodetectors.

By solvent annealing and post-production thermal annealing, we were able to demonstrate that polymer photodetectors possess comparable responsivity to inorganic counterparts. We have, for the first time, developed the inverted device structure for polymer photodetectors. By utilizing inorganic nanowires and quantum dots as either cathode or anode buffer layer, we were able to demonstrate robust polymer
photodetectors. We also investigate the device performance versus energy offset between
the workfunction of anode electrode and the valance band of conjugated polymers, band
offset at the heterojunction and purity of conjugated polymers.
Polymer photodetectors (PDs) are promising for a wide variety of industrial and scientific applications, owing to the advantages of room-temperature operation, low cost manufacture, thin profile, flexibility, large area and low working voltage. Spectral response, responsivity, detectivity and linear dynamic range are important figures of merit used to characterize device performance of PDs. In order to enhance the performance of polymer PDs, this dissertation is focused on: (1) improving external quantum efficiency (EQE) of polymer PDs; (2) developing polymer PDs with an inverted device structure; (3) using ZnO nanowire array as an electron extraction layer in the inverted polymer PDs; (4) using wide bandgap CdTe quantum dot to substitute PEDOT:PSS anode buffer layer in the polymer PDs with a normal device structure; (5) analyzing device performance of polymer PDs correlated with band offsets at bulk heterojunction and impurity density. Following are the highlights of my dissertation:

We employed bulk heterojunction (BHJ) structure instead of bilayer or multilayer structure for polymer PDs. By combined treatments of solvent annealing to photoactive layer and post-production thermal annealing to finished devices, the polymer PDs based on poly(3-hexylthiophene) (P3HT): phenyl-C61-butyric acid methyl ester (PC_{61}BM) exhibited external quantum efficiency (EQE) as high as 80% and responsivity of 320 mA/W, respectively. We further found that enhanced performance is attributed to
enhanced charge transport by better packing of P3HT and improved contact between BHJ active layer and electrodes. (ACS Applied Material and Interfaces 2012, 4, 3701−3705)

In order to explore the application of polymer PDs, polymer PDs with an inverted device structure need to be developed. We first reported polymer PDs with an inverted device structure and manifested the functional roles that ZnOx and MoO$_3$ played in the inverted device. Optimization of photoactive layer was carried out by processing additive 1,8-diiodooctane (DIO). And the optimized polymer PDs based on poly[2,6-(4,4-bis-(2-ethyhexyl)-4H-cyclopenta[2,1-b;3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT):PC$_{61}$BM exhibited detectivities greater than $10^{12}$ Jones(cm Hz$^{1/2}$/W) from 400 to 850 nm. (Organic Electronics 2012, 13, 2929–2934)

When plain ZnO$_x$ interlayer was replaced with nanostructured vertical aligned ZnO nanowire (NW), an increased contact area for effectively extracting electrons and blocking holes were expected. Mid-infrared polymer PDs based on poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)diathiazole-thiophene-2,5) (PDDTT):PC$_{61}$BM with ZnO NW incorporated inverted device structure exhibited detectivities greater than $10^{10}$ Jones from 400 to 1450 nm. (The Journal of Physical Chemistry C 2012, 116, 13650−13653)

We further explored the application of wide bandgap CdTe quantum dot (QD) as a hole extraction layer in substitution of poly(3,4-ethylendioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) for polymer PDs with normal device structure. Polymer PDs incorporated with CdTe QD exhibited dark current density more than 1 order of magnitude lower, detectivities up to $10^{12}$ Jones and lifetime 4 times prolonged, as compared to those

For better understanding dark current density from device physics perspective, we investigated its relations with offset energies at the BHJ ($\Delta E$), electrode contact barrier and impurity concentration ($N$). We found that the dark current was reverse proportional to offset energy and dependent on $\sqrt{N(\Delta E - V)}$. The contact barrier led to an increase in dark current density by generation process from the Schottky contact and apparently behaved like a reduction of $\Delta E$. These studies suggested the challenges of infrared detection with a relatively small $\Delta E$, and emphasized the purity of organic semiconducting materials, morphology control and ohmic contact for high performance infrared polymer PDs.

In summary, BHJ polymer PDs demonstrated device performance fairly comparable to inorganic counterparts. Improvements of polymer PDs have been accomplished from perspectives of morphology, device structure and interface engineering. Furthermore, in-depth study on dark current density in polymer PDs provided insights into challenges from materials impurity, morphological control and energy level alignment for high detectivity infrared polymer PDs.
ACKNOWLEDGEMENTS

A dissertation is not a work of individual effort. I would like to take this great opportunity to acknowledge people who have contributed to this work and supported me to make it possible during my past years at The University of Akron. I thank them for every piece of education, instruction, advice and friendship that helped me grow, progress and start my career.

Foremost, I owe most to Dr. Xiong Gong, my generous, caring and patient advisor. I am extremely grateful for his continuous support to my PhD study and research. He led me into one of the most exciting and vigorous research fields and taught me from the fundamentals and basics. He has been a motivated, knowledgeable and generous advisor that provided the vision, encouragement, challenges and advice necessary for me to proceed. He created a great deal of opportunities for me including managing instrumentation, public presentations and internships and mentored me in academics and personality, which will definitely have long and beneficial influence on my future career and life. I could not have imagined having a better advisor.

I also would like to express my sincere gratitude to my doctoral committee members: Dr. Stephen Z.D. Cheng, Dr. Alamgir Karim, Dr. Matthew L. Becker and Dr. Yi Pang. I appreciate wholeheartedly their support, encouragement, insightful comments and helpful suggestions. In particular, I thank Dr. Stephen Z.D. Cheng for joint group
meetings and thermodynamic classes that taught me knowledge and broadened my views. His valuable critics allowed me to perceive my incompleteness and inspired me to learn more. Dr. Alamgir Karim has taught me advanced characterizations of functional polymers, and I really thank him for the discussions and suggestions about morphology studies using advanced electromagnetic characterization techniques. I sincerely acknowledge Dr. Matthew L. Becker for his collaboration and considerable input on the quantum dot project. I am especially grateful to his fruitful discussion and his review and improvements on the manuscripts before submission. Moreover, I want to thank Dr. Yi Pang very much for great helps on optical and electrical characterizations at the Department of Chemistry. I appreciate his help, accessibility and discussions very much.

Outside the committee, my sincere thanks also go to Dr. Deli Wang at the University of California San Diego. It has been delighted to collaborate with him on ZnO nanowire project and a device prototype was born and successfully demonstrated. I thank Dr. Li Bradshaw at System Seals, Inc for the intern opportunities, her logic management, mentor and kind caring.

In addition, the students who have inspired and helped me deserve my honest gratitude. I particularly appreciate Mr. Jinjun Zhou, Mr. Ke Sun, Dr. I-Fan Shieh, Mr. Chi-Hao Hsu, Mr. Hao Liu, Mr. Mingjun Huang and Mr. Yusheng Chen for collaborations and helps throughout my research. And I really treasure the friendship with and the support from my former and current group members: Dr. Tianzhi Yu, Dr. Wanzhu Cai, Dr. Tingbin Yang, Dr. Chien-Lung Wang, Mr. Hangxing Wang, Mr. He Ren, Mr. Wei Zhang,
Mr. Chao Yi, Mr. Bohao Li, Mr. Kai Wang, Ms. Chang Liu, Mr. Xiaowen Hu, Mr. Peng-cheng Du, Mr. Tianyu Meng, Mr. Guanyu Fang, Mr. Chang Liu, Mr. Zhan Zhang.

Besides, I would be remiss to not thank the graduate students, staff and professors in the Department of Polymer Engineering at The University of Akron. I am glad and thankful to be a member of the family. And I especially thank Mrs. Sarah Thorley and Mrs. Cheryl Slusarczyk for academic consultant, Mrs. Deborah Wilhite for numerous helps about supply purchases, and Mr. Jeff Long and Mrs. Karen Jackson for technic supports and solving problems. The listing is incomplete but a mere subset of the total people involved.

Finally, and most importantly, I would like to thank my father, mother and families for their unconditional love and devotions to me. They always have confidence in me and inspire me to chase my dreams.
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7.7 Dark current density $J_d$ at -0.2 V and at -0.5 V versus offset energies $\Delta E$ and the linear approximations respectively............................ 92
Photodetectors (PDs) are the devices for detecting and measuring properties of lights by photoelectric effect, which usually manifests as a photocurrent. Over more than a century of exploration and development, enormous progresses have been made in the field since the very first photomultiplier tube was invented by Elster and Geiter. Nowadays, PDs have been widely used in applications such as image sensing, environmental monitoring, chemical/biological detection, industrial process control, telecommunication, optical interconnect and planetary probing.\(^1\)\(^-\)\(^8\) And the market is expanding at a growth rate of about 10% every 5 years and forecasted faster in coming years with increasing demands in industrial automation, defense and information technology (IT) sectors.\(^9\),\(^10\)

Predominant PDs are made of inorganic semiconductors. Particularly, ZnO, Si, InGaAs and PbS based PDs are used for four important sub-bands, 0.25 μm-0.4 μm (UV), 0.45 μm-0.8 μm (visible), 0.9 μm-1.7 μm (near IR), 1.5 μm-2.6 μm (mid-IR), respectively.\(^11\) The technology has become mature and reliable, however, complex and expensive manufacture, mechanical inflexibility, large operational voltage (>40 V)\(^12\) and low working temperature (e.g. InGaAs, <4.2 K)\(^11\) have limited the spread, compatibility and versatility to broad applications and new technologies. Therefore, it is of great interest
to pursue PDs of simplicity, low cost, flexibility, large area, low power consumption and room-temperature detection.

In the past years, organic/polymer PDs emerged as an alternative to the traditional PDs. Although organic PDs are still in the development stage, their unique properties set themselves apart from the conventional PDs, making them interesting and promising into various types of applications. The distinct features of organic PDs include light weight, thin profile, low-cost and high-throughput manufacture, large area, flexibility, low working voltage, room-temperature detection and more. Firstly, room-temperature detection of low energy photons will be most attractive. This roots in the intrinsic differences between organic semiconductors and inorganic semiconductors and will save cumbersome and energy-consuming cooling systems for economic detection. Secondly, solution processing of organic PDs by printing and coating technologies can elevate production speed, reduce unit fabrication price and scale up sizes. Thirdly, low working voltage of organic PDs enable them more competitive and adaptable than inorganic counterparts for portable consumer electronics. Last but not the least, the switch from silicon to carbon opens great opportunities to organic PDs because of material variety, tunability and budget.

Based on organic materials, organic electronics can be typically classified into conjugated small molecules and conjugated polymers. With superior solution processability than small molecules, polymer based electronics possess bright prospect for realistic production and application that demand low-cost manufacture. As a characteristic of organic materials is low dielectric constants and rather high exciton binding energies (0.1-1.4 eV), effective polymer photovoltaics are based on the concept of bulk heterojunction
(BHJ) structure, in which semiconducting polymers as the electron donor and fullerene derivatives as the electron acceptor are mixed in the bulk, phase separated in micron and nanometer scale, and form junctions with great interface area to dissociate excited electron-hole pairs. In this dissertation, we discuss polymer photodetectors based on bulk heterojunction photoactive layer, and arrange our work as follows. In chapter II, organic/polymer photodetectors are overviewed. In particular, the operational principles, device characterization, device optimization are summarized. In chapter III, we present our work on how to enhance external quantum efficiency of polymer PDs. By treatments of solvent annealing and thermal annealing, the $EQE$ of polymer PDs is as high as 80%, which is comparable to that of inorganic counterparts. In chapter IV, we focus on development of polymer PDs with an inverted device structure. Inverted polymer PDs are easier to be integrated with back panel and thin film transistors than polymer PDs with a conventional device structure. We are firstly demonstrating polymer PDs with an inverted device structure. In chapter V, we exploit vertical ZnO nanowire array as an electron-extraction and hole-blocking layer in the inverted polymer PDs. Our results define a promising pathway for inverted polymer PDs using ZnO NW array cathode interlayer to function with large area and in vicinity of photocurrent generation. In chapter VI, we investigate wide bandgap CdTe QD in substitution of conventional poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) for polymer PDs. Polymer PDs incorporated with CdTe QD successfully demonstrate lower dark current density, higher detectivity and longer lifetime, as compared to those with PEDOT:PSS. In chapter VII, we discuss the influence of band offsets and impurity density on the perfor-
mance of polymer PDs. The results demonstrate that saturation dark current density is a function of band offsets, impurity density and contact barrier when generation process at depletion regions is taken into consideration. Lastly, in chapter VIII, a summary of works and outlooks is put forwards as the end.
CHAPTER II

OVERVIEW OF POLYMER PHOTODETECTORS

2.1 Polymer Photodetectors

Organic electronic and optoelectronic devices, such as light-emitting diodes, field effect transistors, solar cells and photodetectors (PDs), have drawn increasing interests and investigation over the past decades, owing to their potential of being fabricated on flexible and light-weight substrates using low-cost and high-throughput printing and coating techniques. Among these, organic PDs are well suited to applications requiring room temperature and large area and become a serious contender for new generation photodetection. These applications include multi-color imaging, X-ray imagers biomedical sensing, vision mimicking systems, near-field scanning microscope, fluorescence detection and data communications.

PDs are light responsive devices driven by photoelectric effects, namely photovoltaic effect and photoconductive effect. As organic semiconducting materials require two to three orders of magnitude higher energy than inorganic semiconductor to dissociate photo-induced exciton and delocalize electrons, electric fields by heterojunction interfaces are widely utilized. The photocurrent generation responding to the incident light has
four successive steps in the mechanism: 1) Excitation of light-absorbing materials to form bound electron-hole pairs (excitons); 2) Diffusion of excitons to heterojunction interface within effective diffusion length, otherwise recombination takes place; 3) Generation of free charge carriers, holes and electrons, via dissociation of exciton at the depletion interface; 4) Interaction of charge carrier with external circuit to provide output electric signals. The process is schematically illustrated in Figure 2.1.\textsuperscript{13}

Spectral response determines the usage and application for any PDs. In last decade, organic PDs from deep ultraviolet (DUV) to mid-infrared (MID) have been demonstrated. For ultraviolet (UV) light detection, wide bandgap small-molecule donors 1,3,5-tris(3-methyl phenyl-phenylamino)triphenylamine (m-MTDATA)\textsuperscript{23–27} with dual UV absorption
peaks located at 330 nm and 365 nm, respectively and N,N’-diphenyl-N,N’-bis(3-
methylphenyl)-(1,1’-biphenyl)-4,4’-diamine (TPD)\textsuperscript{28} with absorptions at 305 nm and 354
nm are generally used. The electron acceptors used with m-MTDATA include bathocu-
proine (BCP),\textsuperscript{23} 4,7-diphenyl-1,10-phenanthroline-(bathophenanthroline) (Bphen),\textsuperscript{27} tris-
(8-hydroxy-quinoline) aluminum (Alq\textsubscript{3})\textsuperscript{25,28} and 1,3,5-tris(N-phenyl benzimidazol-2-
yl)benzene (TPBi).\textsuperscript{26} Wide bandgap polymer poly(N-(2-ethylhexyl)carbazol-3,6-diyl)
(PCz) has been reported for UV detection peaked at around 350 nm.\textsuperscript{29} In addition, organ-
ic-inorganic hybrid systems, in which inorganic semiconductors such as ZnO dominate
the UV light detection, and small molecules or polymers enhance the absorption and pho-
toconductivity of ZnO, exhibited effective and fast response.\textsuperscript{30–32}

Visible light detection has been greatly promoted by practical applications such as
color image sensors and scanners. For example, a highly sensitive red light photodetector
based on a copper phthalocyanine (CuPc)/C60 bilayer was demonstrated by Higashi et
al.\textsuperscript{33} And semiconducting polymers with band gaps at around 2.0 eV are widely used in
visible light photodetectors, such as poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bi-
 thiophene)] (F8T2) nanowires,\textsuperscript{34} poly(2-methoxy,5(2-ethyl-hexyloxy)-p-
phenylenevinylene) (MEH-PPV),\textsuperscript{35} poly(3-octylthiophene) (P3OT),\textsuperscript{16,35} and poly(3-
hexylthiophene) (P3HT).\textsuperscript{36,37} To tune monochromatic light detection for specific applica-
tion and preciseness, one approach is to develop and use proper dyes or pigments with
narrow absorption, and another way is by screening the incident light. Higashi incorpo-
rated a thiophene derivative (P6T) layer of 100 nm and another thiophene derivative
(BP3T) with wider bandgap and higher conduction band of 20 nm in front of photoactive
heterojunction CuPc/C60 and realized red light detection at 620 nm with internal photon-to-electron conversion efficiency (IPCE) of 51.7% and detectivity ($D^*$) of $4.0 \times 10^{11}$ Jones (1 Jones = 1 cmHz$^{1/2}$/W). The screening was achieved by P6T layer absorbing and preventing blue light from reaching the photoactive layer, and the thin BP3T layer blocking excitation energy transfer from P6T to CuPc, as shown in Figure 2.2.

![Figure 2.2](image)

Figure 2.2 (a) Conceptual energy diagram of red-light-only sensitive organic photodiode based on CuPc and C60, (b) sectional device structure, and (c) structures of chemicals and their abbreviations used.

Meanwhile, it is of great interest to pursue organic PDs that can sense the light from near-infrared (NIR) (750-1400 nm) all the way up to short-wavelength infrared (SWIR) (1400-3000 nm). There needs organic materials of low bandgap or small energy transitions in order to absorb infrared lights. Binda et al. reported photodetectors with
squiraine dyes/ [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) that have a broad response extending from 600 nm to 900 nm.\textsuperscript{38} Zimmerman et al. demonstrated a NIR photodetector using porphyrin tape molecules/C60, which sensed from near visible to deep into NIR, with an external quantum efficiency $\eta = 6.5\%$, $D^* = (2.3 \pm 0.1) \times 10^{10}$ Jones, and a response time of $2.12 \pm 0.02$ ns at 1350 nm.\textsuperscript{39} Gong et al developed broad-band photodetectors based on polymer poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)diathiazole-thiophene-2,5) (PDDTT) with spectral response from 300 to 1450 nm, $D^*$ greater than $10^{12}$ Jones and linear dynamic range over 100 decibels (dB) at room temperature.\textsuperscript{11} Figure 2.3 gives the molecular structure of PDDTT and the spectral absorption of the PDDTT, PCBM, PDDTT:PC61BM films as well as the response detectivities versus wavelength of the polymer PDs biased at -0.1 V, exhibiting great potential to compete and cover inorganic PDs. Gong et al also demonstrated polymer PDs based on low bandgap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopental[2,1-b;3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) with spectral response up to 950 nm and $EQE$ of 40% at 800 nm.\textsuperscript{40} In addition, IR colloidal quantum dots (QDs) are exploited for their bandgap tenability with size effects in PDs. Konstantatos et al reported solution processed organic/inorganic hybrid NIR photodetectors with colloidal PbS nanoparticles capped with oleic acid onto gold interdigitated electrodes with spectral response up to 1300 nm.\textsuperscript{12} Clifford et al demonstrated oleate-capped PbS QDs with simple device structure of ITO/PbS QDs/Al could sense lights from 400 nm to 1800 nm with peak responses at 580 nm, 750 nm, 1150 nm and 1480 nm, respectively.\textsuperscript{41} The hybrid
systems offer possibilities and great potential to combine advantages of inorganic and organic materials to advance broad-band deep IR photodetection.

Figure 2.3 (a) Molecular structures of PDDTT and PC61BM. (b) Absorption spectra of thin films PDDTT (black curve), PC61BM (green curve), and PDDTT:PC61BM bulk heterojunction composites (blue curve). The inset shows the absorption spectra of the three materials from 300 to 500 nm. (c) Energy-level diagrams of PDDTT, PC60BM, PVK, PS-TPD-PF6CB, C60, ITO, PEDOT, and Al. (d) Detectivities of Si photodetector, InGaAs photodetector, and polymer photodetector versus wavelength.11
Among all organic PDs, conjugated semiconducting polymer based PDs stand out as a significant proportion. Because small molecules are mostly layered by vacuum deposition method and polymers can be fabricated by solution processing, polymer PDs are more promising and compatible to printing and coating technology, that best offer low-cost and large-area manufacture in the future. Moreover, polymer PDs possess the highest responsivity and \( EQE \) at low working voltages. This is extremely attractive for easy alternation to polymer PDs and for low power operation that fits energy saving purposes and portable devices. Last but not the least, the flexibility of polymers is exceptional for non-planar and bendable photon detection. Herein, in this dissertation, we are focused mostly on polymer PDs, from device physics, characterization to processing.

2.2 Operational Principles of Polymer Photodetectors

Following the initial discovery of ultrafast photoinduced electron transfer from semiconducting polymer to fullerene derivatives,\(^{42}\) a number of polymer PDs with high detectivity and fast response to various spectra range have been reported.\(^{11,35,43-45}\) The results demonstrated that the performance of polymer PDs is comparable or even better than the inorganic counterparts.

Polymer PDs sense difference between active illuminated state and inactive dark state by photoelectric effect, as seen in Figure 2.4. Polymer PDs are made of a photoactive layer, which is a BHJ blend of the D and the A, sandwiched between the indium tin oxides (ITO)-glass as the anode and a low-work-function metal as the cathode. The de-
vices are operated at zero bias or reverse voltages where bare dark current is allowed to flow across the junctions. When photons with energy larger than bandgap of either D, A or both are incident onto the polymer PDs, significant photocurrent comes out of the detectors by photovoltaic effect and indicates the incident lights. The photocurrent generation processes are identical to that of polymer solar cells, which requires successful and successive steps of exciton creation and dissociation at D/A interface, ultrafast charge transfer over recombination, free charge transport and collection at respective electrodes, as discussed in Chapter 2.1.

Figure 2.4 J-V Characteristics of polymer PDs in dark and under illumination
An equivalent circuit model for the polymer PDs is shown in Fig. 2.5. And the J-V characteristics of polymer PDs can be described by the standard diode equation:

\[
J = J_0 \left[ \exp \left( \frac{q(V - JR_s)}{nkT} \right) - 1 \right] + \frac{V - JR_s}{R_{SH}} - J_{ph} \tag{2.1}
\]

where \( J_0 \) is the saturation dark current density, \( k \) is the Boltzmann constant, \( V \) is the applied voltage across PDs, \( n \) is the ideality factor, \( R_S \) is the series resistance, \( R_{SH} \) is the shunt resistance and \( J_{ph} \) is the portion of the current density resulted from photoexcitation. In the dark \( J_{ph} \) is equal to 0, above equation describes the total dark current.

The first term at the right side of the equation comes from Shockley equation derived from ideal p-n junction based on depletion approximation. The depletion approximation assumes dipole layer with abrupt boundaries and outside the boundaries the semiconductor is electrically neutral. By one-dimensional approach, electron and hole current densities are sum of the drift component and diffusion component with applied Einstein relation \( D_{n,p} = \frac{kT}{q} \mu_{n,p} \).

\[
J_n = q\mu_n nE + qD_n \frac{dn}{dx} = q\mu_n \left( nE + \frac{kT}{q} \frac{dn}{dx} \right) = \mu_n n \frac{dE_n}{dx} \tag{2.2}
\]
where \( q \) is the element charge, \( T \) is the absolute temperature, \( x \) is the distance from the junction edge, \( E \) is electric field, \( n \) and \( p \) are densities of electron and hole, \( \mu_n \) and \( \mu_p \) are electron and hole mobilities, \( D_n \) and \( D_p \) are diffusion constants of electron and hole, \( E_{F_n} \) and \( E_{F_p} \) are quasi Fermi levels for electrons and holes, respectively. Using continuity equations for the steady-state condition in the n-side of the p-n junction and assuming low-injection for \( p_n \ll n_n \) is the n-type semiconductor, there is

\[
-U - \mu_p E \frac{dp_n}{dx} + D_p \frac{d^2 p_n}{dx^2} = 0 
\]

in which \( U \) is the net recombination rate and

\[
\tau_p \equiv \frac{p_n - p_{n0}}{U} 
\]

where \( p_{n0} \) is the equilibrium hole density on the p-side. There is no electric field in the neutral region, eqn (2.4) reduces with eqn (2.5) to

\[
\frac{d^2 p_n}{dx^2} = \frac{p_n - p_{n0}}{D_p \tau_p}. 
\]

The solution of eqn (2.6) with the boundary conditions of \( p_n(W_{Dn}) = p_{n0} \exp(qV/kT) \) at depletion edge and \( p_n(x=\infty) = p_{n0} \) at neutral region gives

\[
p_n(x) - p_{n0} = p_{n0} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right] \exp\left(-\frac{x-W_{Dn}}{L_p}\right) \quad (2.7)
\]

where \( L_p \equiv \sqrt(D_p \tau_p) \) is the diffusion length. At \( x=W_{Dn} \) the hole diffusion current is

\[
J_p = -qD_p \frac{dp_n}{dx} |_{W_{Dn}} = \frac{qD_p p_{n0}}{L_p} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right]. \quad (2.8)
\]

Similarly, the electron diffusion current in the p-side is

\[
J_n = -qD_n \frac{dn_p}{dx} |_{-W_{Dp}} = \frac{qD_n n_{p0}}{L_n} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right]. \quad (2.9)
\]
The total current is given by the sum of eqn (2.8) and eqn (2.9) as

\[ J = J_p + J_n = J_0 \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right], \quad (2.10) \]

and the saturated reverse current density is given

\[ J_0 = \frac{qD_p N_D}{L_p} + \frac{qD_n N_A}{L_n} = \frac{qD_p n_i^2}{L_p N_D} + \frac{qD_n n_i^2}{L_n N_A} \quad (2.11) \]

in which \( N_D \) and \( N_A \) are donor dopant concentration in n-type semiconductor and acceptor dopant concentration in p-type semiconductor, respectively, \( n_i \) is the intrinsic carrier density with\(^{48}\)

\[ n_i^2 = N_C N_V \exp \left( - \frac{E_g}{kT} \right) \quad (2.12) \]

where \( E_g \) is the bandgap of the semiconductor, \( N_C \) and \( N_V \) are effective density of states in conduction band and valence band of the semiconductor.

### 2.3 Characterization of Polymer Photodetectors

Several figures of merits (FOMs) are used to evaluate the quality and effectiveness of polymer PDs. These FOMs are responsivity \((R)\), external quantum efficiency \((EQE)\), noise equivalent power \((NEP)\), detectivity \((D)\) and linear dynamic range \((LDR)\).\(^{11}\)

\[ R = \frac{J_{ph}}{L_{light}} \quad (2.13) \]

where \( J_{ph} \) is the photocurrent and \( L_{light} \) is the incident light intensity.
EQE is described by the number of charge carriers generated out of the number of incident photons under working condition. Then \( R \) can be converted from \( EQE \) by following formula:

\[
R = EQE \times \frac{q}{h \nu} = EQE \times \frac{q \lambda}{hc} = EQE \times \frac{\lambda}{1240} \quad (2.14)
\]

where \( \lambda \) (nm) is the incident light wavelength, \( h \) is Planck’s constant, \( \nu \) is the frequency of incident light and equals to light speed in vacuum \( c \) divided by \( \lambda \). Now it is obvious that \( R \) is related to the incident wavelength and \( EQE \), which can be directly measured by the instrument.

Another important FOM is \( NEP \), that is, the minimum impinging optical power that a detector can distinguish from the noise.

\[
NEP = (A \Delta f)^{1/2}/D \quad (2.15)
\]

where \( A \) (cm\(^2\)) is the effective area of the detector, \( \Delta f \) (Hz) is the electrical bandwidth, and \( D \) is the detectivity measured in units of Jones (1Jones = 1 cmHz\(^{1/2}\)/W). \( D \) is given by the following equation:\(^{11}\)

\[
D = (A \Delta f)^{1/2} R/i_n \quad (2.16)
\]

where \( i_n \) (A) is the noise current.

Noise refers to spontaneous fluctuations in the current passing through semiconductor bulk materials or devices. There are three types of noise: thermal noise or Johnson noise, flicker noise and shot noise. Thermal noise is universal and roots in random thermal motion of the current carriers. The open-circuit mean square voltage of thermal noise is given by\(^{47}\)

\[
<V^2_n> = 4kT \Delta f Z \quad (2.17)
\]
where $Z (\Omega)$ is the real part of the dynamic impedance between terminals. At room temperature, thermal noise is generally very small for a semiconductor device with 1 k $\Omega$ resistance.\textsuperscript{47} Flicker noise is also called $1/f$ noise that is inversely proportional to frequencies and affected by surface states. Shot noise comes from discreteness of charge carriers that contribute to current flow and it is the major noise in most semiconductor devices. The mean square noise current of shot noise for a p-n junction is given by\textsuperscript{47}

$$< i_n^2 > = 2q f |J|$$  \hspace{2em} (2.18)

where $J$ is the current density. If, as expected, the shot noise from $J_d$ is the major noise, a projected $D, D^*$, can be expressed as\textsuperscript{11}

$$D^* = \frac{R}{(2q J_d)^{1/2}} = \frac{(J_{ph}/L_{light})}{(2q J_d)^{1/2}}. \hspace{2em} (2.19)$$

$J_d$ is given by the diode equation regardless of series resistance and shunt resistance as

$$J_d = J_0 \exp(qV/nkT). \hspace{2em} (2.20)$$

Consider the bulk heterojunction composite as one semiconductor material with highest occupied molecular orbital (HOMO) constituted by semiconducting polymer and lowest unoccupied molecular orbital (LUMO) by the acceptor material, the saturated dark current can be suggested as eqn (2.11) and (2.12) by

$$J_0 = \frac{qD_a n_i^2}{L_a N} = \frac{qD_a N_C N_V}{L_a N} \exp\left(\frac{-\Delta E}{kT}\right) \hspace{2em} (2.21)$$

in which $D_a$ is the ambipolar diffusion constant, $\Delta E=E_{LUMO(A)}-E_{HOMO(D)}$ as illustrated in Figure 2.6. This suggested that a small $\Delta E$ would lead to a large $J_d$. 

\hspace{2em} 17
The last FOM is \( LDR \) or photosensitivity linearity (typically quoted in dB). \( LDR \) is calculated as\(^{11}\)

\[
LDR = 20 \log(J_{ph}/J_d) \quad (2.22)
\]

where \( J_{ph} \) is the photocurrent measured at light intensity of 1 mW/cm\(^2\).

Accordingly, high performance polymer PDs would feature high \( EQE \), high \( R \), high \( D^* \) and large \( LDR \), aside from the spectral response requirement.

### 2.4 Methods to Improve Device Performance of Polymer Photodetectors

#### 2.4.1 Materials

Currently, the detection range of a polymer PD is primarily determined by the bandgap of the conjugated semiconducting polymer. And the maximum detectable wavelength can be estimated with the empirical equation\(^{49}\)

\[
\lambda_{max} = \frac{hc}{E_g} \quad (2.23)
\]
where $h$ is Planck constant, $c$ is the speed of light in vacuum and $E_g$ is the bandgap of the semiconductors. As such, bandgaps of semiconducting polymers play a crucial role in determining the fundamental capability of photodetector device. For UV detection, $E_g$ should be as large as 3 eV; Visible light or color detectors utilize semiconducting polymers with $E_g$ between 1.5 eV and 3 eV; And NIR photodetection requires $E_g$ to be less than 1.5 eV.

Other than PCz, MEH-PPV, P3HT, P3OT, PCPDTBT, PDDTT mentioned in Chapter 2.1 for polymer PDs, there are ongoing efforts made to synthesize new materials especially low-bandgap polymers for NIR sensing. Generally, two commonly ways are used. One is ‘push-pull’ polymers with alternating electron-donating and electron-accepting units, and the other scenario is introduction of a methine group at the bridge of two rings to maintain a flat structure and extend conjugation length.\(^{50}\) Yao et al reported polythieno[3,4-b]thiophene (PTT) for NIR polymer PDs sensing from 400 nm all the way up to 1000 nm.\(^{44}\) Hu et al used poly[2,6-(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene)-alt-5,5-(4’,8’-di-3-hexylthiophen-2-yl)-6-(2-ethylhexyl)-[1,2,5]thiadiazolo-[3,4-f] benzotriazol (PTZBTTT-BDT) whose bandgap is as narrow as 1.1 eV and demonstrated high detectivity polymer PDs responsible from 400-1100 nm.\(^{51}\)

Approach from sensitized acceptor materials or additional absorbers is alternative ways to better extends the spectral response of the polymer PDs. Prototypes of quantum dots used as absorbers,\(^{52-56}\) and bulk heterojunction polymer photovoltaics incorporated with dyes or quantum dots for additional photon capture\(^{57-61}\) have been developed. Though fundamental principles are under extensive investigation, electronic response attributed
from the incorporated sensitizers is clearly indicated by \( EQE \) spectra. Such systems exhibited the potential for use in photodetector applications that need exotic detection at specific wavelengths.

2.4.2 Device Configurations

The first organic photovoltaic cells pioneered was made in a way of bilayer structure,\(^6^2\) The only heterojunction is formed with limited contact, and this mostly resulted in a waste of photon energy and a relatively low responsivity of the PDs. To overcome the drawbacks of bilayer structure, Yu\(^6^3\) brought forth a blend of electron donor and electron acceptor components, the bulk heterojunction (BHJ) structure which significantly enhance the interfacial contact between the electron donor and electron acceptor. This concept is also workable for polymer photodetectors.

In BHJ photoactive layer, two networks resulted from phase separation of electron donor and electron acceptor are presented. As the morphology of the active layer can be quite random, each phase in reality contacts both electrodes with possibly unfavorable surface traps, leading to leakage current that affects detectivity of polymer PDs. Gong et al addressed the problem and improved the situation by inserting an electron-blocking layer at the anode and an hole-blocking layer at the cathode, as seen in Figure 2.7.\(^4^0\) Energy-thermally, copolymer PS-TPD-PFCB with high LUMO and \( C_{60} \) with low HOMO prevented electrons and holes from moving to the anode and cathode, respectively. As a result, a significant low dark current was observed, which brought about detectivity as high
as $10^{13}$ Jones at $\lambda= 800$ nm. This also belongs to interface engineering by interlayer materials, which will be discussed in next section.

Figure 2.7 (a) Molecular structure of C$_{60}$ and PS-TPD-PF CB; (b) Energy level diagram of the device; $J$-$V$ characteristics of photodetectors at $\lambda= 800$ nm with identical intensity.$^{11}$
In addition, tandem architecture photovoltaics attract lots of research interests.\textsuperscript{64–67} Figure 2.8 sketches typical organic tandem cells comprising a bottom cell and a top cell connected by interlayer in series to cover a broad photon spectrum. In other words, the design is intended to exploit light that is not utilized by the first device by the second one which compensates the whole absorption range. The notion is also applicable for polymer PDs in that one compact device can be made of several single-junction cells, each of which detects separated optical sub-bands. Tandem organic PDs based on small molecules have been reported by Matthew Menke et al for efficient broad detection from 300 to 1100 nm.\textsuperscript{68}

2.4.3 Morphology and Interfacial Engineering

The ideal morphology of BHJ photovoltaics has always been described as a bicontinuous composite of electron donor and electron acceptor with massive interfacial area
and a mean domain size commensurate with the exciton diffusion length (10-20 nm). The two components should phase segregate to facilitate effective charge transfer and charge transport in continuous pathways to respective electrodes to generate $J_{ph}$. Separate domains out of the ideal networks will act like recombination centers, thus reducing $J_{ph}$ and increasing $J_d$. As such, the performance of polymer PDs is significantly dependent on the morphology of active layer. And the effect of photoactive layer morphology has been long discussed for polymer photovoltaic cells, and morphology is a complex function of chemical composition, processing solvent, annealing and additives.

Thin film morphology is firstly dependent on the chemical compositions of the film. An example can be the morphology study of poly[2-methoxy-5-(3,7-dimethylctyloxy)]-1,3-phenylenevinylene (MOMD-PPV) blended with poly[oxa-1,4-phenylene-1,2-(1-cyanovinylene)-2-methoxy,5-(3,7-dimethylctyloxy)-1,4-henylene-1,2-(2-yanovinylene)-1,4-phenylene](PCNEPV) of different molecular weight (MW) by Loos et al. It was found that distinct phase separation could only occur to PCNEPV of medium and large MW and that PCNEPV rich domain became larger as MW increases. And the best $J$-$V$ characteristics of the polymer photovoltaic devices were observed from PCNEPV of medium MW with optimum domain sized 20-50 nm.

Then, morphology of photoactive layers is highly connected with solvent, solution concentration, D/A ratios and processing methods in film preparation. For example, Hoppe et al prepared and imaged solid-state blended films of poly[2-methoxy-5-(3,7-dimethylctyloxy)]-1,3-phenylenevinylene (MOMD-PPV) and PC$_{61}$BM from chlorobenzene and toluene, with D/A from 1:1 to 1:4 and solution concentration from 0.10 wt% up
to 0.30 wt%. They found that large PC$_{61}$BM clusters hundreds nanometers in width are associated to poor device performance and that optimization can be made by loading ratio of MDMO-PPV/PC$_{61}$BM with morphologies showing no significant PC$_{61}$BM clusters (smaller than 50 nm).

Further morphology control utilized external stimuli to treat the photoactive composites, such as thermal annealing and solvent annealing. Certain systems, such as P3HT based polymer photovoltaics, work dramatically with these treatments. In a P3HT:PC$_{61}$BM solar cells, the $J_{ph}$ increased efficiency reached to nearly 5% by thermal annealing$^{72}$ at 150 °C and to 4.4% by slow-drying coating. These effects were understood as enhanced interchain stacking of P3HT and higher crystallinity with increased charge-carrier mobility, optimized domain size and network of D and A, and improved interfacial contact between photoactive layer and electrodes, which result from materials self-adjustment at higher molecular mobility at high temperature and solvent atmosphere.$^{72–76}$

Other than these, processing additives become a positive way to refine film morphologies especially for complicated materials systems. Here, the processing additives used are typically a class of high boiling point solvents such as 1,8-octanedithiol, 1,8-diiodooctane, nitrobenzene and chloronaphthalene. The reason why the added solvents are called processing additives is their amount needed in the common solution of photoactive layer materials is typically limited to a few percent. And it has been found that the additives need to be vacuumed under FT-IR traceable value before next processing steps. In 2007, alkanedithiols draw great attention by pumping PCE of polymer solar cells of low bandgap polymer [2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b,c]-
dithiophene)-alt-4,7-(2,1,3-benzothia-diazole)] (PCPDTBT) and PC$_{71}$BM from 2.8% to 5.5%. It was explained by an optimum nano-morphology as a result of alkanedithiols selectively dissolving the fullerene component, whereas the polymer is less soluble. Cho et al observed higher and more stable transport characteristics and charge carriers mobilities of films processed with the additives.

Interface engineering also demonstrates the influence on performance of polymer photovoltaics, including polymer solar cells and polymer PDs. It brings up the importance of layer contacts on film morphology and charge extraction/recombination. By means of interface engineering, it is promising to passivate charge trap state, well align energy levels, facilitate charge collection, guide film morphology, enhance materials compatibility and alter work function of electrodes as desired. For polymer PDs, contacts and interlayers that will produce low series resistance and high shunt resistance would enhance $J_{ph}$, reduce $J_d$ and promote responsivity and detectivity.

The most used interfacial layer is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which increases workfunction of ITO for normal OPV structure and planarizes the substrates for better compatibility with organic film and high reproducibility. However, PEDOT:PSS is not ideal, because it is acid and hygroscopic, and it has deep workfunction without electron blocking capability. A vigorous development of hole-transporting/electron-blocking layers for anode was inspired, like carbon nanotubes (CNTs), molybdenum oxide(MoO$_3$), nickel oxide (NiO), and tungsten oxide (WO$_3$), and self-assembly monolayers (SAMs) with electron withdrawing –CF$_3$ groups and so on.
On the other anode side, early interface engineering utilized thermal deposited Ca, Ba and lithium fluoride (LiF) to form ohmic contact for electron collection. Besides, n-type transparent metal oxides, for instance zinc oxides (ZnO\textsubscript{x}) and titanium oxides (TiO\textsubscript{x}), played its part for in conventional device structure, but also supported reversing the device polarity for inverted organic photovoltaics.\textsuperscript{98–100} Preparation of these metal oxides also evolve from vacuum thermal deposition to sol-gel solution processing, which brings much easy and economic fabrication.\textsuperscript{98–102} Besides, ZnO\textsubscript{x} and TiO\textsubscript{x} in between the photoactive layer and back metal electrode lead to high photocurrent of polymer photovoltaics and were explained by a spatial redistribution of the light intensity.\textsuperscript{101,102}

Last but not the least, a series of water/alcohol soluble conjugated polymers for electron transporting layer is of particular interest.\textsuperscript{103} These materials can enable easy solution processing without interfacial mixing or destroy in multi-layer fabrication. The feasibility of water/alcohol soluble conjugated polymers for electron-transporting and hole-blocking in both conventional and inverted OPV has been demonstrated. Yang et al modified ZnO\textsubscript{x} surface with an alcohol/water-soluble conjugated polymer poly\{9,9-bis(6’-(N,N,N-trimethylammonium)hexyl)fluorene-alt-co-1,4-phenylene\}bromide (PFN-Br) and achieved inverted polymer solar cells with power conversion efficiency of 8.4\%.\textsuperscript{104} Hu et al demonstrated NIR PDs with increased EQE and suppressed dark current by incorporation poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as an electron extraction layer at cathode.\textsuperscript{51}
2.5 Issues of Polymer PDs and Researches of Interests

Development of high performance polymer PDs is of particular interest in this dissertation. As discussed above, an excellent polymer PD needs to have both high photocurrent and low noise current to accomplish high responsivity and high detectivity. Therefore, to maximize photocurrent and minimize dark current photocurrent is the center topic in exploring high performance polymer PDs. Issues of polymer PDs that need to be addressed include but not limited to:

a. Low responsivity and \( EQE \) of polymer PDs;
b. Surface contacts between stacking layers;
c. Stability of polymer PDs;
d. How to reduce noise current of polymer PDs;
e. Polymer PDs sensing into mid- and far-infrared;
f. Polymer PDs with up-conversion and down-conversion mechanism;
g. Flexible polymer PDs.

In this dissertation, we approach high performance polymer PDs by addressing some of above issues and seek a better understanding of material-structure-performance relations. Firstly, we strive for high \( EQE \) of polymer PDs by simple and affordable processing techniques. With comprehension of photocurrent generation processes, we proposed that \( EQE \) is dependent on factors of mobility, interfacial contact and film morphology. Therefore, we explored combinatorial treatment of solvent vapor annealing and post-production thermal annealing and processing solution with solvent additives respectively in chapter III and IV. Secondly, we developed and investigated inverted device
structure of polymer PDs for circuitry integration requirement, stability and solution processability in chapter IV and V. We have employed functional interlayers, ZnO$_x$ and MoO$_3$, and tried to understand their roles in inverted polymer PDs. And when the plain amorphous ZnO$_x$ interlayer was engineered to vertically aligned crystalline ZnO nanowire array, it was of our interest to learn the feasibility and potential of such prototype for a wide application. Moreover, we searched for ways to lower dark current density and enhance detectivity. Specifically, we studied CdTe quantum dot (QD) interlayer with dual function of hole-transporting and electron-blocking in polymer PDs and investigate the effect of interfacial properties on device performance. Finally, we desired to systematically understand the source of dark current that influence the detectivity of polymer PDs. Therefore, we consider the factor of generation current from depletion region and seek correlated relations between dark current density and several elements such as energy offsets between electron donor and electron acceptor, impurity concentration in the p-n junction and contact barriers. Through the exploration, we hope to provide insights about origins of dark current density and challenges in high detectivity polymer PDs.
CHAPTER III

SOLUTION-PROCESSED POLYMER PHOTODETECTORS WITH HIGH EXTERNAL QUANTUM EFFICIENCY AND DETECTIVITY

3.1 Introduction

With the discovery of ultrafast photoinduced charge transfer from semiconducting polymers to buckminsterfullerene and its derivatives, sensitive and fast temporal response polymer photodetectors (PDs) have been demonstrated. As demonstrated in the previous chapter, the photocurrent density ($J_{ph}$) of polymer PDs depends on the intensity of light illuminated on the devices and the magnitude of external quantum efficiency ($EQE$). Although organic PDs with high $D^*$ (more than $10^{10}$ Jones; 1 Jones = 1 cmH$^{1/2}$/W) have been already demonstrated through utilization of multilayer device architecture, the external quantum efficiency ($EQE$) was only a few percents. For example, Forrest’s group has demonstrated the organic PDs with $D^*$ over $10^{10}$ Jones, nevertheless, the $EQE$ was only 6.5%. Polymer PDs with $D^*$ over $10^{13}$ Jones has been demonstrated, but the $EQE$ under zero bias was less than 10%. In general, the $EQE$ of polymer PDs and other organic PDs with spectral response at wavelength ($\lambda$) less than 800 nm is around 40%; and the $EQE$ at $\lambda > 800$ nm is only a few
percent. These values are much lower than those of inorganic counterparts,\textsuperscript{49,106} and the low responsivities would demand higher read-out capability. Hence, polymer PDs with high $EQE$ have to be developed for applications.

Meanwhile, an additional important device performance parameter is the detectivity ($D^*$), which relies on both $J_{ph}/EQE$ and dark current density ($J_d$).\textsuperscript{11} Only if a high $EQE$ couples with a low $J_d$, polymer PDs with high $D^*$ can be accomplished. As $J_{ph}$ and $J_d$ are strongly affected by the spatial distribution of the separated phases of electron donor (D) and electron acceptor (A) in the bulk heterojunction (BHJ) active layer, modification of morphology has been crucial and a key strategy in the optimization of device performance. In this chapter, we report solution-processed polymer PDs with approximately $EQE$ up to 80\%, $D^*$ of over $10^{13}$ Jones, $J_d$ of the magnitude of nA/cm$^2$ and linear dynamic range over 120 dB. All these performance parameters were achieved by combined treatment of polymer PDs with solvent vapor annealing and post production annealing.

3.2 Experimental

Materials

Poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals Inc. and (6,6)-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) was provided by 1-Material Inc. used without further purification.
Device Fabrication and Characterization

Polymer PDs were fabricated on indium tin oxide (ITO) glass in the glovebox with nitrogen atmospheres. The active layer, composed of P3HT blended with PCBM (1:0.8 by weight), was cast from 2 wt% ortho-dichlorobenzene (o-DCB) solution followed with thermally annealing at 80°C for 30 minutes. P3HT:PCBM layer with thickness ranged from 60 nm to 310 nm were obtained by tuning the speed of spin-casting. The anode, metal Al with thickness exceeding 200 nm, was thermally deposited onto the top of polymer active layer. The active device area was 4.5 mm².

Optimization of device performance was carried out by solvent-vapor annealing treatment and post-production thermal annealing treatment. The solvent-vapor annealing treatment was exposing the fresh P3HT:PCBM active layer to saturated o-DCB solvent vapor at room temperature and atmosphere pressure in a closed jar for 10 minutes before 30-minute thermal annealing at 80 °C. Post-production treatment was that the final devices were thermally annealed at 150 °C for 10 minutes in the nitrogen atmospheres.

The current density versus voltage (J-V) characteristics was measured using a Keithley 2400 Source Measure Unit. The photocurrent of polymer PDs was characterized using a Newport Air Mass 1.5 Global (AM1.5G) full spectrum solar simulator at the wavelength of 500 nm with the light intensity of 0.32 mW/cm². The EQE was measured under short-circuit conditions and reverse bias using the lock-in amplifier technique.
Film Characterization

The surface morphologies of the active layer with and without o-DCB vapor treatment were characterized by tapping-mode atomic force microscopy (AFM) (Digital Instrument).

3.3 Results and Discussion

3.3.1 Photoactive Layer Thickness and Device Performance

Table 3.1 summarizes device performance parameters of polymer PDs with different thicknesses of active layer. As the active layer was about 60 nm, polymer PDs exhibited both high \( EQE \) and responsivity \( R \), a ratio of photocurrent to incident-light intensity) but poor \( D^* \); as the active layer was about 310 nm, polymer PDs showed both

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>( J_d ) ( \text{A/cm}^2 )</th>
<th>( J_{ph} ) ( \text{A/cm}^2 )</th>
<th>( EQE ) ( % )</th>
<th>( R ) ( \text{mA/W} )</th>
<th>( D^* ) (Jones)</th>
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</thead>
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<tr>
<td>60</td>
<td>3.48E-7</td>
<td>9.03E-5</td>
<td>70</td>
<td>282</td>
<td>6.8E+11</td>
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<td>130</td>
<td>2.43E-8</td>
<td>8.65E-5</td>
<td>67</td>
<td>270</td>
<td>2.5E+12</td>
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<tr>
<td>190</td>
<td>7.09E-9</td>
<td>6.50E-5</td>
<td>50</td>
<td>205</td>
<td>4.0E+12</td>
</tr>
<tr>
<td>210</td>
<td>1.52E-9</td>
<td>5.84E-5</td>
<td>45</td>
<td>182</td>
<td>8.3E+12</td>
</tr>
<tr>
<td>310</td>
<td>1.42E-9</td>
<td>4.32E-5</td>
<td>33</td>
<td>135</td>
<td>6.3E+12</td>
</tr>
</tbody>
</table>

\( a \): thickness of active layer; \( b \): photocurrent measured at \( \lambda = 500 \) nm with an light intensity of 0.32 mW/cm\(^2\) and at bias of -0.5 V; \( c \): \( EQE \) measured at \( \lambda = 500 \) nm; \( d \): responsivity at \( \lambda = 500 \) nm; \( e \): the detectivity at \( \lambda = 500 \) nm and at bias of -0.5 V.
poor EQE and R but a relatively high $D^*$. The best $D^*$ and moderate EQE and R were observed from polymer PDs with the thickness of active layer about 210 nm. These data indicated that device performance (EQE, R and $D^*$) of polymer PDs were active layer thickness dependent.

3.3.2 Effects of Combinatorial Solvent and Post-production Annealing

Optimization of polymer PDs was carried out on the devices with a thickness of about 210 nm. The $J$-$V$ characteristics of polymer PDs with and without combined treatment are shown in Figure 3.1. In the dark, polymer PDs showed a rectification ratio more than $10^4$ at $\pm 1$ V, indicating the formation of well-made diodes. The $J_d$ observed from polymer PDs with and without combined treatments were nearly identical. The $J_d$ were smaller than 40 nA/cm$^2$ under the bias from 0 V to -1 V. These $J_d$ were significantly lower than those from inorganic PDs. Under the illumination of monochromatic light at $\lambda = 500$ nm, polymer PDs showed $J_{ph}$ was over 4 orders of magnitude higher than $J_d$ at the reversed bias. This indicated that efficient exciton dissociation and ultrafast photoinduced charge transfer occurred among the P3HT:PCBM BHJ composite. Moreover, it was observed that $J_{ph}$ from polymer PDs with combined treatments was approximately twice those without any treatment. This result demonstrated that $J_{ph}$ of polymer PDs was enhanced by both solvent-vapor annealing treatment and post-production thermal annealing treatment.
EQE spectra of polymer PDs are presented in Figures 3.2a and 3.2b, respectively. The EQE under reversed bias of -0.5 V from polymer PDs with combined treatments were nearly twice as high as those without any treatment over the entire spectra. And the EQE values were persistent under the reverse bias from 0 V to -1.0 V. This observation was consistent with the enhanced $J_{ph}$ from polymer PDs with combined treatments. Under the bias of -0.5 V, EQE of polymer PDs at $\lambda = 500$ nm was 79.5% electron per photon. Accordingly, the $R$ was calculated to be 320 mA/W. These are the highest values reported in the literatures so far.

The performance was also evaluated by detectivity, one of the most important figures of merits (FOM) used for evaluating the performance of PDs. Projected
detectivity, $D^*$, described by eqn. (3.1), was used to estimate the signal-to-noise ratio of polymer PDs.\textsuperscript{11}

$$D^* = \frac{J_{ph}/I_{light}}{\sqrt{2\alpha J_d}} \quad (3.1)$$

Figure 3.2 (a) The external quantum efficiency under -0.5 V bias of polymer PDs versus light wavelengths; (b) The external quantum efficiency of polymer PDs at $\lambda=500$ nm versus bias voltage
where $L_{\text{light}}$ is the incident light intensity and $q$ is the electron charge. The plots of $D^*$ at a bias of -0.5 V versus wavelengths for the polymer PDs are shown in Figure 3.3. The $D^*$ was over $10^{11}$ Jones for whole visible spectral range whereas 350 nm - 650 nm was the premium detection range with $D^*$ over $10^{13}$ Jones. These results are comparable to those observed from inorganic counterparts.

![Figure 3.3 Detectivities at bias of -0.5 V for polymer photodetectors with and without combined treatments](image)

Previous studies in polymer solar cells indicated that the phase separation of crystalline P3HT aggregates and PC$_{61}$BM domains was a complex exothermic process which could be affected by solvent vapor annealing and post-production thermal annealing. Both techniques concentrated on improving the nanoscale lateral phase separation of the two-component system. Solvent-vapor annealing method was used to control the polymer nano-morphology through the solvent removal speed. By slowing down the film-growth rate, P3HT molecules can be self-organized into more ordered
structure where interlaid distance and nanoscale crystallinity of polymer chains would be higher. As a result, the hole mobility and optical absorption of P3HT were enhanced. In order to confirm this hypothesis, AFM was carried out to study the film morphology. Figure 3.4 displayed the tapping mode AFM images of P3HT:PCBM films without (Figures 3.4a and 3.4b) and with solvent-vapor annealing (Figures 3.4c and 3.4d). The AFM phase images in Figures 3.4b and 3.4d showed the emergence of crystalline nanofibrils and a higher contrast of separated phases upon the solvent-vapor treatment.
These indicated that more ordered packing and crystallinity of polymer. As a result, enhanced charge mobility in the spontaneously separated phases could be expected. In addition, a rougher surface for film with solvent-vapor annealing (Figure 3.4c, $R_{RMS} \sim 3$ nm) was induced as compared to that without the treatment (Figure 3.4a; $R_{RMS} \sim 1.8$ nm). This slight change would facilitate a strong interaction and more contact areas between the active layer and top electrode.72

Post-production thermal annealing has been widely used for improving the performance of P3HT:PC$_{61}$BM solar cells.72,74,112–114 X-ray diffraction (XRD) studies have demonstrated that a lifted intensity of thiophene ring $\pi-\pi$ stacking peak and an emerging peak resulting from side-chain inter-digitations appeared after the solar cells were treated at 150 °C for 5 minutes.72 These enhanced packing of molecules and/or nanoscale crystallinity would certainly enhance the mobility of charge carriers. Moreover, AFM and transmission electron microscopy (TEM) studies also demonstrated that more complete phase separation and the formation of bi-continuous interpenetrating networks from the active layer occurred by the post-production treatment.72 Therefore, better charge carrier transport was promoted from the BHJ composite to the corresponding electrodes, resulting in enhanced photocurrent. Accordingly, $EQE$ of polymer PDs were dramatically enhanced by the combined solvent-vapor annealing treatment and post-production thermal annealing treatment.

Linear dynamic range ($LDR$) is another FOM used for evaluation of PDs. $LDR$ is given by $LDR = 20 \log (J_{ph}^*/J_d)$, in which $J_{ph}^*$ is the photocurrent measured at light intensity of 1 mW/cm$^2$.106 The $LDR$ for polymer PDs with combined treatments was
shown in Figure 3.5. It can be seen that polymer PDs can response linearly to the light intensity till 100 mW/cm$^2$, and the $LDR$ was greater than 120 dB, which is even higher than that from Si PDs.$^{11}$ These results are the best up-to-date and are comparable to or better than those of inorganic silicon based PDs.

3.4 Conclusions

Solution-processed polymer photodetectors based on P3HT:PCBM BHJ composite were demonstrated with spectral response from 350 nm to 750 nm. By combined solvent-vapor annealing treatment of active layer and post-production thermal annealing treatment of formed cells, polymer photodetectors with external quantum efficiency approxi-
mately 80%, detectivity over $10^{13}$ Jones, linear dynamic range over 120 dB and dark current a few decades nA/cm$^2$ were obtained. These high performance parameters demonstrated that polymer photodetectors are comparable to or better than inorganic counterparts.
CHAPTER IV

POLYMER PHOTODETECTORS WITH AN INVERTED DEVICE STRUCTURE

4.1 Introduction

Currently, ongoing research are mainly focused on polymer PDs with a conventional device structure, in which the bulk heterojunction (BHJ) composite of semiconducting polymers (D) and fullerene derivatives (A) are sandwiched between poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) modified indium tin oxides (ITO) anode and low-work-function cathode (e.g. Al). However, there is latent instability with this conventional device structure. First, the contact of acid PEDOT:PSS and ITO is reactive. Not only the contact failure but also the etching products degrade the performance of devices.\textsuperscript{87,115} Second, the top air-sensitive cathodes, including relatively stable Al, are inherently flawed giving poor long-term stability. Moreover, low-work-function metal inks is unlikely accessible; Hence, continuous low-cost printing technology for depositing large-area Al cathode will be a processing issue. In order to address these problems, inverted device structures have been recently developed.\textsuperscript{116} In the inverted device architecture, the polarity of the device is reversed by using high workfunction metal, such as Ag or Au, which are stable in air and can be printed from
paste inks, as the anode and ITO as the cathode. The elimination of acid PEDOT:PSS in the inverted device structure implies the devices can possess better stability.

Inverted polymer solar cells (PSCs) with comparable efficiency and enhanced stability have been reported. However, few inverted polymer PDs has been demonstrated. In this work, we report inverted polymer PDs with a device structure in which ITO acts as the cathode and Ag as the anode. By inserting ZnO and MoO₃ as an electron extraction layer and a hole extraction layer, respectively, the asymmetric characteristics of the photodiodes and the detection function of the device were accomplished. The influence of processing additive 1,8-diiodooctane (DIO) in fabrication of photoactive layer on the performance of inverted polymer PDs was also investigated.

4.2 Experimental

The inverted polymer PDs were built up with the structures of ITO/PCPDTBT:PC₆₁BM/Ag and ITO/ZnOₓ/PCPDTBT:PC₆₁BM/MoO₃/Ag, where PCPDTBT was poly[2,6-(4,4-bis-(2-ethyhexyl)-4H-cyclopenta[2,1-b;3,4b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] and PC₆₁BM was [6,6]-phenyl C₆₁-butyric acid methyl ester. Figure 4.1a and 4.1b present the device architecture of the inverted polymer PDs and the molecular structures of PCPDTBT, PC₆₁BM and processing additive, DIO, respectively. The photoactive layer, PCPDTBT:PC₆₁BM, was spin cast from chlorobenzene (CB) solution composed of 8 mg mL⁻¹ PCPDTBT and 24 mg mL⁻¹ PC₆₁BM. For inverted polymer PDs with both ZnOₓ and MoO₃ buffer layer, the ZnOₓ layer with a thickness of approximate 35 nm was prepared prior to the photoactive layer
by spin-coating 0.5 mol L\(^{-1}\) ZnO\(x\) precursor solution consisting of zinc acetate, ethanola-mine and 2-methoxyethanol solvent on the pre-cleaned ITO/glass substrate, followed by annealing at 200 °C in the air for 1 hour. The thin MoO\(_3\) layer with a thickness of approximate 10 nm was vacuum deposited on the top of the photoactive layer with an evap-

Figure 4.1 (a) Device architecture of the inverted polymer photodetectors; (b) molecular structures of PCPDTBT, PC\(_{61}\)BM and DIO; (c) Energy levels of PCPDTBT, PC\(_{61}\)BM, ZnO\(x\) and MoO\(_3\), with the workfunctions of ITO and Ag.
oration rate of 0.1 Å s\(^{-1}\). Top electrode Ag was thermal deposited through shade mask with the effective device area of 16 mm\(^2\).

4.3 Results and Discussion

4.3.1 Validation of Inverted Device Structure for Polymer Photodetectors

Figure 4.1c shows the energy levels of PCPDTBT, PC\(_{61}\)BM, ZnO\(_x\) and MoO\(_3\), and workfunctions of ITO and Ag electrodes. Since ZnO\(_x\) is a n-type semiconductor with high electron mobility\(^{98,124}\) and the valence band maximum of ZnO\(_x\) is up to -7.6 eV, ZnO\(_x\) is expected to be an electron extraction layer as well as a hole blocking layer. On the other side, MoO\(_3\) functions as a hole extraction and electron blocking layer in the inverted polymer PDs, as it is used as an efficient anode buffer layer in organic photovoltaics\(^{91,93,98,100,125,126}\) because of nontoxicity, high stability and very deep lying electronic states.\(^{127}\)

The current density versus voltage (J-V) characteristics of the inverted polymer PDs are shown in Figure 4.2a and 4.2b. It was found in Figure 4.2a that the inverted polymer PDs without both ZnO\(_x\) and MoO\(_3\) buffer layers exhibited symmetrical J-V characteristics, both in dark and under illumination of white light. The device behaves as a photo-switch with symmetric photocurrent but no built-in potential. While the inverted polymer PDs with both ZnO\(_x\) or MoO\(_3\) buffer layers possess a good asymmetric dark J-V curve with a rectification ratio over 10\(^3\) at ±1V. Notable photovoltaic effect with photoinduced current at short circuit and built-in potential are well observed.
To break the symmetry is an essential request for BHJ organic photovoltaic cells. Since D and A are intimately intermixed in the bulk volume, there is no intrinsic direction

Figure 4.2 (a) $J$-$V$ characteristics of the polymer photodetectors without ZnO$_x$ and MoO$_3$ buffer layers; (b) $J$-$V$ characteristics of the polymer photodetectors with ZnO$_x$ and MoO$_3$ buffer layers.

To break the symmetry is an essential request for BHJ organic photovoltaic cells. Since D and A are intimately intermixed in the bulk volume, there is no intrinsic direction...
of the internal fields for free charges, i.e. electrons and holes have no preferred way they should move to.\textsuperscript{69,128} Due to similar workfunctions, ITO (-4.7 eV) cathode and Ag (-4.7 eV) anode did not provide such an electrical field, the photodiodes, such as the inverted polymer PDs without the buffer layers, showed symmetric \textit{J-V} characteristics. In this case, the devices could not effectively collect photoinduced charge carriers under small bias, making it inappropriate for photon detection purpose. When ZnO\textsubscript{x} and MoO\textsubscript{3} were introduced into the inverted architecture as buffer layers, symmetry breaking was constructed for the inverted polymer PDs. As a result, the detection of light could be accomplished at small reverse bias where the photo-induced charge carriers were effectively collected and photocurrent distinguished largely from the dark current. These results demonstrated that to break the symmetry of the photodiodes by the buffer layers, ZnO\textsubscript{x} and MoO\textsubscript{3}, is crucial for the inverted polymer PDs.

4.3.2 Effects of Processing Additive Diiodooctane for Photoactive Layer

Optimization of device performance via controlling BHJ composite morphology has been a common strategy.\textsuperscript{109} Thermal annealing and solvent annealing have been critical for optimizing the charge separation and migration in the phase separated morphology of several BHJ blends, however, they have not been successful to improve the performance of PCPDTBT:PCBM mixture yet.\textsuperscript{129,130} Whereas, with a small amount of processing additives, modified nanomorphology leading to a nearly doubled power conversion efficiency of PCPDTBT:PCBM PSCs has been reported.\textsuperscript{77,131} In order to optimize the performance of the inverted polymer PDs, devices with photoactive layer of
Figure 4.3 (a) Dark currents and photocurrents measured under illumination of $\lambda=800$ nm monochromatic light for the inverted polymer photodetectors processed with different concentration of DIO; (b) Projected detectivity at $\lambda=800$ nm of the inverted polymer photodetectors processed with different concentration of DIO.
approximately 200 nm thick processed from CB solutions containing 0, 1.0%, 3.0% and 5.0% (by volume) of DIO were investigated. Note that DIO was removed by vacuum pumping before deposition of the following layers. Figure 4.3a shows the dark currents and photocurrents measured under monochromatic light at wavelength $\lambda = 800$ nm with the light intensity of $0.9 \text{ mW cm}^{-2}$. Under the biases of -0.1 V, -0.5 V and -1 V, the photocurrents were at the same magnitude, however, the highest photocurrent was observed from the inverted polymer PDs processed from CB with 3.0% of DIO. Moreover, a decreasing dark current was observed from the inverted polymer PDs processed from CB solution with increasing content of DIO. Based on observed photocurrents and dark currents, we have calculated the detectivities of the inverted polymer PDs. The detectivities of the inverted polymer PDs processed from CB solution with different concentrations of DIO were shown in Figure 4.3b. The detectivities of the inverted polymer PDs were enhanced by processing active layer from CB solution with DIO. But the detectivities tended to decrease when active layer was processed with DIO beyond 3.0%. The highest detectivity, more than $7 \times 10^{11}$ Jones, was observed from the inverted polymer PDs processed from CB solution with 3.0% of DIO.

Further device optimization has been carried out by fabricating devices of photoactive layer processed from CB solution with 3.0% of DIO with thickness of 150 nm, 200 nm and 320 nm. Table 4.1 summarizes the detectivities of the inverted polymer PDs with different active layer thickness. It is manifested that the performance of the inverted polymer PDs is active layer thickness dependent. And the best detectivity was observed from the inverted polymer PDs with the thickness of active layer about 200 nm.
In order to understand how processing additive DIO affects the dark current and photocurrent of inverted polymer PDs, atomic force microscopy (AFM) was used to study the film morphology of active layer. Figure 4.4a and 4.4b show the AFM tapping-mode height images of PCPDTBT:PC61BM films processed from CB solutions with and without 3.0% of DIO, respectively. A rougher film surface has been observed from the film processed from CB with DIO than that without DIO. This rough surface can ensure a strong interaction and large contact areas between the active layer and top electrode, resulting in less contact series resistance and high photocurrent. Moreover, the phase image of the BHJ composite film processed from CB solution with 3.0% of DIO, shown in Figure 4.4d, displayed coarsened phase separation with larger length scale as compared with that without DIO, shown in Figure 4.4c. This phase separation at more favorable length scale would probably constitute better bicontinuous network, thus facilitate charge transporting through BHJ composite to corresponding electrodes, resulting in enhanced

Table 4.1 The performance of the inverted polymer photodetectors with 3.0% DIO

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$J_d^b$ (A/cm²)</th>
<th>$J_{ph}^b$ @ $\lambda=500$nm (A/cm²)</th>
<th>$D^c$ @ $\lambda=500$ nm (Jones)</th>
<th>$J_{ph}^b$ @ $\lambda=800$ nm (A/cm²)</th>
<th>$D^c$ @ $\lambda=800$nm (Jones)</th>
</tr>
</thead>
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<td>150</td>
<td>6.44×10⁻⁶</td>
<td>3.66×10⁻⁴</td>
<td>9.11×10¹⁰</td>
<td>4.14×10⁻⁴</td>
<td>3.20×10¹¹</td>
</tr>
<tr>
<td>200</td>
<td>1.43×10⁻⁶</td>
<td>3.56×10⁻⁴</td>
<td>1.88×10¹¹</td>
<td>3.67×10⁻⁴</td>
<td>6.03×10¹¹</td>
</tr>
<tr>
<td>320</td>
<td>2.06×10⁻⁶</td>
<td>2.52×10⁻⁴</td>
<td>1.11×10¹¹</td>
<td>2.31×10⁻⁴</td>
<td>3.16×10¹¹</td>
</tr>
</tbody>
</table>

$^a$: thickness of active layer; $^b$: photocurrent measured at bias of -0.5 V with light intensities of 2.8 mW/cm² and 0.9 mW/cm² at 500 nm and 800 nm respectively; $^c$: detectivity calculated at -0.5 V.
photocurrent and reduced dark current due to fewer isolated domains which act as recombination centers. Besides, it was noted that the PCPDTBT:PC$_{61}$BM film processed from CB with 3.0% DIO exhibited more fibril-like phase. This indicated that polymer molecules moved towards the free surface. Consequently, fullerene molecules was rich
near the bottom cathode in the inverted device.\textsuperscript{30} This proposed vertical profile of component distribution would reduce the probability of recombination at the interface between active layer and adjacent electrode, leading to reduced dark currents.

The external quantum efficiencies ($EQE$) were also measured under short circuit condition. Figure 4.5 shows the $EQE$ spectra of the inverted polymer PDs processed from CB solution with and without 3.0\% of DIO. The spectral response of these inverted polymer PDs are from 400 nm to 900 nm. The $EQE$ profile from inverted polymer PDs processed from CB solution with 3.0\% of DIO was significantly enhanced as compared with that without DIO. Moreover, the $EQE$ profiles revealed that the responsivity of the inverted polymer PDs processed with 3.0\% of DIO have a broader peak centered at $\sim$750 nm.

Figure 4.5 $EQE$ profiles of the inverted polymer photodetectors processed without and with 3.0\% DIO
nm as compared with those without DIO. This broadened and slightly red-shifted peak suggested enhanced intermolecular interaction of the semiconducting polymer. And this may indicate more ordered phases with possible improved crystallinity of PCPDTBT induced by DIO. Similar effect of 1,8-octanedi-thiol (ODT) on PCPDTBT:PC$_{71}$BM films which has been evidenced by grazing incidence X-ray diffraction (GIXRD).

4.4 Conclusions

In conclusion, inverted polymer PDs fabricated from narrow bandgap polymer PCPDTBT and PC$_{61}$BM have been successfully demonstrated. It was found that electron extraction layer ZnO$_x$ and hole extraction layer MoO$_3$ played important roles in the performance of inverted polymer PDs. Processing additive DIO has an impact on the film morphology of photoactive layer and thus affects the polymer PDs performance. Operated at room temperature, the inverted polymer PDs exhibited the detectivities greater than $10^{11}$ Jones from 400 nm to 850 nm. These results demonstrated that the NIR inverted polymer PDs are feasible and comparable to inorganic counterparts.
CHAPTER V

ZINC OXIDE NANOWIRE ARRAY AS AN ELECTRON-EXTRACTION LAYER
FOR POLYMER PHOTODETECTORS WITH AN INVERTED DEVICE STRUC-
TURE

5.1 Introduction

With the development of new narrow bandgap conjugated polymers and better con-
trol of the nanoscale morphology of the interpenetrating electron donor/acceptor net-
works, the detectivity of solution-processed polymer photodetectors (PDs) with the spec-
tral response from ultraviolet (UV) to infrared (IR) region have reached $10^{13}$ cm·Hz$^{1/2}$/W
(1 Jones = 1 cm·Hz$^{1/2}$/W).\textsuperscript{11} Most polymer PDs are built in conventional device structures,
where an photoactive layer (a mixture of polymer and fullerene derivative) is sandwiched
between the bottom transparent conductive anode (e.g., indium tin oxide, ITO) modified
with poly(3,4-ethylenedioxythiophene):poly-(styrene sulfonate) (PEDOT:PSS) and a low-
work-function metal cathode (e.g., Al, Ca, Ba). However, there are flaws in long-term
stability and processing with regard to this architecture. And inverted device structure,
where the direction of charge collection is reversed with ITO as the cathode and a high-
work-function metal (typically, Au or Ag) as the anode, has been developed.\textsuperscript{98,132}
In the inverted photovoltaic cells, n-type metal oxides such as zinc oxide (ZnO), titanium oxide (TiOx) and cesium carbonate (Cs₂CO₃) are developed onto the ITO electrode to break the symmetry. The elimination of the PEDOT:PSS layer and good contact between ITO and polymer active layer by n-type metal oxides improve PSCs stability. Moreover, the top anode of high work-function metal, such as Ag, Au, is stable and can be processed by coating or printing technology to simplify and lower the manufacturing cost.

ZnO nanowire (NW) is a promising candidate as an n-type buffer layer onto top of ITO due to its outstanding electronic properties. The intrinsic electron concentration of ZnO NW is up to $1−5 \times 10^{18}$ cm$^{-3}$, and electron mobility is $1−5$ cm$^2$/V·s. This large electron mobility indicated that ZnO NW is a good electron transporter. And a large surface-to-volume ratio and vertical alignment make ZnO NW in good contact with the polymer composite, which allows ZnO NW to collect the electron in a close distance. The deep highest occupied molecular orbital (HOMO) energy level up to $−7.72$ eV prevents holes from transporting to the cathode, which greatly reduces the charge recombination. Moreover, ZnO NW arrays have high transmittance in the visible spectral range and high absorption coefficient in the UV range. The feature of blocking/absorbing the UV radiation to the active conjugated polymer layer may result in better stability of the devices.

Herein, we report the fabrication of high-performance broadband polymer PDs based on narrow bandgap conjugated polymers with an inverted device structure, where electrons and holes are collected on ITO and metal contact with high work function. High-quality wide bandgap vertically aligned ZnO NW array offers an enhanced surface
area and is used as the cathode buffer layer in this device for effectively extracting electrons and blocking holes from the active polymer layer. The room-temperature detectivity of polymer PDs with such an inverted device structure is greater than $10^{10}$ Jones with the spectral response from 400 to 1450 nm.

5.2 Experimental

Materials

Poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)-diathiazole-thiophene-2,5) (PDDTT)$^1$ blended with (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) (ratio = 1:3 by weight) was dissolved in dichlorobenzene with a concentration of 2 wt %. The above solution was used for preparing the active layer.

ZnO NW Array Preparation

To prepare the ZnO NW array, we first deposited ZnO seeding layer (∼45 nm in thickness) on the ITO substrate using low-pressure RF magnetron sputtering on 99.99% ZnO target for 16 min with the chamber pressure at 1.7 mTorr. Solvothermal growth of ZnO NW,$^{139,140}$ using 25 mM solutions of zinc acetate and hexamethylenetetramine (HMTA, Sigma) in deionized water (>17.6 MΩ·cm), was carried out with gentle agitation at 85 °C for 3.5 h. The as-growth samples were then rinsed with de-ionized (DI) water and sonicated at 30 W for 1 min to remove surface residual particles and blow-dried with N$_2$.  

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Polymer Photodetectors Fabrication

To fabricate polymer PDs, the PDDTT:PCBM solution was first spin-cast on top of the ZnO NW, followed by drying at 80 °C for 10 min. The top of this layer was totally embedded in the composite material layer, and the polymer thickness is ∼150 nm. Then, a thin layer of MoO$_3$ film (∼15 nm) was deposited on the top of the active layer with an evaporation rate of 0.5 Å/s. Finally, the anode (Au, 80 nm) was deposited through a shadow mask by thermal evaporation in a vacuum of ∼10$^{-6}$ Torr. The active area of polymer PDs was 0.45 mm$^2$.

5.3 Results and Discussion

Figure 5.1a shows the molecular structures of PDDTT and PC$_{61}$BM. Figure 5.1b shows a cross-sectional SEM image of the vertical ZnO NW array grown on the ITO glass. Most of the ZnO NWs grow vertically on ITO glass substrate and have a hexagonal cross-section, indicating a growth along the c direction with an average diameter of 200 nm and length of ∼2 μm. The space between ZnO NW varies from 50 to 150 nm. Figure 5.1c shows the schematics of an inverted polymer PDs structure. Figure 5.1d shows the energy band diagram of the inverted polymer PDs, and the step-like energy level alignments can reduce the energy barriers for charge transport. With such configuration, the incident light traveled through the ITO glass and ZnO NW and shined on the polymer
active layer. The top Au contact also served as light reflection mirror, which enhanced efficient light absorption.

For the evaluation of the function of ZnO NW in the polymer PDs, the inverted polymer PDs without ZnO NW were fabricated and characterized. The current density-voltage (J-V) characteristics are shown in Figure 5.2. In the dark, the J-V curve did not show the rectify behavior, indicating this diode is a symmetric diode. The symmetric diode is further confirmed by applying a reversed bias and illuminating light (white light with 100 mW/cm² intensity) to the diode. There is a small photocurrent observed from the diode, and the J−V characteristics still show symmetry curve. Because of similar workfunctions of ITO (−4.7 eV) cathode and Au (−5.1 eV) anode, PDDTT and PC₆₁BM
Figure 5.2 $J$−$V$ characteristics of inverted polymer PDs with a structure of ITO/PDDTT:PCBM/MoO$_3$/Au under AM1.5G illumination from a calibrated solar simulator with the intensity of 100 mW/cm$^2$ and in dark.

Figure 5.3 $J$−$V$ characteristics of polymer PDs under AM1.5G illumination from a calibrated solar simulator with the intensity of 100 mW/cm$^2$ and at 800 nm with the intensity of 0.22 mW/cm$^2$ and in the dark.
are intimately intermixed in the bulk volume, there is no intrinsic direction of the internal fields for free charges. In this case, the diode could not effectively collect photoinduced charge carriers under small bias, making it inappropriate for photon detection purpose. Therefore, the diode with a structure of ITO/PDDTT:PCBM/MoO₃/Au is not fully fulfilled. To break the symmetry of this diode is an essential request to perform as a photovoltaic cell. Therefore, ZnO NW is expected to be used for breaking the symmetry of the diode.

The $J-V$ characteristics of inverted polymer PDs with a structure of ITO/ZnO NW/PDDTT:PCBM/MoO₃/Au are shown in Figure 5.3. In the dark, the $J-V$ curve shows the rectify behavior. This indicated that symmetry of the diode was broken by inserting of ZnO NW between ITO cathode and polymer active layer. Polymer PDs were measured under an illumination of 100 mW/cm² with an AM1.5G solar simulator (Oriel model 91192) and 0.22 mW/cm² at 800 nm. When the reversed bias was applied to the polymer PDs and light was illuminated, the photogenerated charge carriers greatly increased the reversed current; however, there was not much change in the forward current. The increased electron-hole pairs generated at the polymer PDs were responsible for the observed photocurrent under reversed bias condition. Photocurrent response of the polymer PDs increased to $4 \times 10^{-6}$ A/cm² under illumination of 800 nm (0.22 mW/cm²) and further to $1.9 \times 10^{-4}$ A/cm² under AM1.5G solar illumination (100 mW/cm²). The $J_{ph}$ and $J_d$ ratio is 1000 in this case. It confirmed that charge carriers can be efficiently generated by photoinduced electron transfer and subsequently transported via the bulk heterojunction (BHJ) nanomorphology to opposite electrodes.¹⁵
Responsivity was calculated from the measured photoresponse current density and can be expressed by\textsuperscript{11,141}

\[ R_\lambda = \frac{J_{ph}}{I_{light}} \] (5.1)

where \( R_\lambda \) is the responsivity of the polymer PDs in A/W, respectively, and \( J_{ph} \) is the measured current densities from polymer PDs in A/cm\(^2\), respectively. \( I_{light} \) is the incident optical power. The external quantum efficiency (\( EQE \)) was given by\textsuperscript{11,141}

\[ EQE = R_\lambda \frac{h\nu}{q} \] (5.2)

where \( q, h, \nu \) are the electron charge in C, Planck’s constant in J·s, and the frequency of the incident photon, respectively. \( \lambda \) is the wavelength in nanometers. If the dark current is the major contribution for the noise, then the detectivity can be expressed as\textsuperscript{11,141}

\[ D^* = \frac{R_\lambda}{\sqrt{2qJ_d}} \] (5.3)

where \( D^* \) is the detectivity in cm·Hz\(^{1/2}\)/W or Jones and \( J_d \) is the dark current density of polymer PDs in A/cm\(^2\). The measured \( EQE \) under short-circuit conditions and the absorption spectrum of PDDTT:PC\(_{61}\)BM thin film are presented in Figure 5.4. The similar profiles of absorption and \( EQE \) spectra of PDDTT:PCBM demonstrated that photons absorbed by PDDTT in the near-IR did indeed contribute to the photocurrent. Under zero bias, at \( \lambda = 800 \) nm, the \( J_{ph} \) is \( \sim 4 \times 10^{-3} \) A/cm\(^2\). According to eqn (5.1) and (5.2), the \( R_\lambda \) and \( EQE \) are 0.18 A/W and 27\%, respectively.
Figure 5.4 Absorption spectrum of PDDTT:PCBM thin film and EQE of polymer PDs under zero bias.

Figure 5.5 Detectivity versus wavelength for inverted polymer PDs under zero bias.
The detectivity of the polymer PDs with an inverted device structure as a function of wavelength is illustrated in Figure 5.5. According to eqn (5.3), at zero bias, the $D^*$ of polymer PDs at 800 and 1400 nm is $\sim 2 \times 10^{11}$ and $\sim 8 \times 10^9$ Jones, respectively. Operating at room temperature, the polymer PDs with an inverted device structure using ZnO NW as a cathode buffer layer exhibited spectral response from 400 to 1450 nm, with detectivity greater than $10^{10}$ Jones at wavelengths from 400 to 1300 nm and greater than $10^9$ Jones from 1300 to 1450 nm. The detectivity of the polymer PDs with an inverted device structure was comparable to those inorganic PDs with a conventional device structures.\textsuperscript{142}

5.4 Conclusions

In conclusion, we report a high-performance broadband polymer PD based on a blend of narrow bandgap conjugated polymers PDDTT and PCBM with an inverted device structure, where electrons and holes are collected on ITO and metal contact with high work functions. High-quality vertical ZnO NW array with a wide bandgap and an enhanced surface area acts as the cathode buffer layer for extracting electrons and blocking holes effectively from the active layer to the underneath electrode. The inverted device exhibits spectral response from UV to IR (400-1450 nm), with detectivity greater than $10^{10}$ Jones at wavelengths from 400 to 1300 nm and greater than $10^9$ Jones from 1300 to 1450 nm. The use of the inverted structure can also elongate device lifetime by minimizing the contact oxidation. Low work function metal contacts are not needed in this case. Our results here define a promising pathway for the fabrication of high-
sensitivity polymer PDs with an inverted device structure using ZnO NW array cathode
buffer layer for a wide range of applications.
CHAPTER VI

WATER-SOLUBLE CADMIUM TELLURIDE QUANTUM DOT AS AN ANODE INTERLAYER FOR SOLUTION-PROCESSED POLYMER PHOTODETECTORS

6.1 Introduction

Polymer semiconductors present different optical and electronic properties from the inorganic counterparts. Particularly, the exciton binding energy in semiconducting polymers is much higher than thermal energy $kT$ at room temperature (25.6 meV at 298K) due to its low dielectric constant,\textsuperscript{108,143,144} leading to reduced dark current density from thermal excitation. Meanwhile, when the bulk heterojunction forms by introducing intimate electron acceptor materials, such as fullerene derivatives, the dissociation of photon-induced excitons within effective diffusion length from the interface of semiconducting polymer/electron acceptor can be assisted by the energy offsets,\textsuperscript{42,145} followed by charge transfer and charge transport ideally in separated channels.\textsuperscript{69} Consequently, the reverse-biased device can yield electric flow under illumination orders of magnitude higher than in dark at room temperature. This enables room-temperature radiation detection, especially near-infrared (NIR) sensing without additional cumbersome cooling system, making semiconducting polymer based PDs exceptionally attractive,
promising, and valuable.

In the last decade, a number of polymer PDs with broad spectral response from visible to up to 1600 nm and high external quantum efficiency (EQE) have been studied and demonstrated. The basic operation principles of polymer PDs are similar to those of polymer solar cells. Nevertheless, there is an additional important device parameter for polymer PDs, that is dark current density ($J_d$). To obtain high detectivity, a polymer PDs with both high photocurrent ($J_{ph}$) and low $J_d$ are desired. $J_{ph}$, similar to short circuit current density ($J_{sc}$) for polymer solar cells, can be enhanced by thermal and solvent annealing, additives, light trapping masks and some interface engineering. However, only a few reports have addressed that $J_d$ is correlated to active layer thickness, composition, spatial distribution of the blend components, temperature and surface contacts. Among these, Gong demonstrated increased $J_{ph}$ and remarkably reduced $J_d$ of polymer PDs by wide-bandgap semiconductors as an electron-blocking layer and hole-blocking layer. The key is the wide-bandgap semiconducting layer conducts the major charge carriers and blocks the other type charge carrier by energy level alignment. In this chapter, we report NIR polymer PDs with wide-bandgap CdTe QD to replace PEDOT:PSS anode interlayer for the first time. In NIR polymer PDs, CdTe QD actively function as a hole extraction layer and an electron-blocking layer as well. We further demonstrated that NIR polymer PDs with CdTe anode interlayer possess higher detectivity and longer lifetime, as compared with those with PEDOT:PSS as anode interlayer.
6.2 Experimental

Preparation of 3-mercaptopropionic acid (MPA) capped CdTe QD

The CdTe QD were prepared similar to methods described previously. De-ionized water (99 mL) was degassed by bubbling with argon for 1 hour. CdCl₂·2.5H₂O (0.0583 g, 0.26 mmol) and MPA (0.0427 g) were added to the aqueous solution, and the pH was adjusted to 8.5 - 9 by the addition of a 5% NaOH solution. The mixture was further degassed with argon for ~30 min. Subsequently, freshly prepared NaHTe solution (1.00 mL) produced by the reaction of NaBH₄ (0.0183 g, 0.49 mmol) with tellurium powder (0.0231 g, 0.181 mmol) in an aqueous solution (1.00 mL) was mixed with the CdCl₂-MPA solution. The resulting mixture solution was refluxed under argon flow at 96 - 99 °C for 4 hours to obtain the CdTe QD. The obtained QD were further purified by ultrafiltration. Non-reacted MPA was removed by centrifugation with a 3000 MW filter at 3300 rpm for 60 min. The QD were washed with de-ionized water and centrifuged again. The upper phase was subjected to another ultrafiltration step on a 50 000 MW filter. The lower phase was concentrated with 3000 MW filter to reach a concentration of 6.0 µM QD. The CdTe QDs solution was further diluted with de-ionized water to 2 µM.

Fabrication of Polymer PDs

ITO-coated glasses were cleaned using an ultrasonic bath with successive detergent, de-ionized water, acetone and isopropyl alcohol and were dried overnight. The ITO substrates were treated with UV-ozone for 20 minutes. And the CdTe QD were spin-cast
from the aqueous solution, followed by annealing at 100 °C for 10 minutes. The active layer of PCPDTBT:PC$_6$T$_{61}$BM (1:3 by weight) was spun cast on top of CdTe QD layer from 6 mg/mL polymer chlorobenzene solution, followed by thermal annealed at 70 °C annealing for 10 minutes. The thickness of active layer is estimated 200 nm. Finally, top electrode calcium (~10 nm) and aluminum (~100 nm) were consequently thermally deposited through a shade mask with the active device area of 16 mm$^2$ under vacuum. For the polymer PDs using PEDOT:PSS as the anode buffer layer, ~35 nm thickness of PEDOT:PSS (Heraeus Clevios$^\text{TM}$ PH) was spin-cast from PEDOT:PSS solution and then annealed at 150 °C for 10 minutes before deposition of PCPDTBT:PC$_6$T$_{61}$BM active layer.

Characterization of Polymer PDs

The $J$-$V$ characteristics of the polymer PDs were measured using a Keithley 2400 Source Meter measure unit. Monochromatic light at 500 nm and 800 nm are produced by Newport Air Mass 1.5 Global (AM1.5G) full spectrum solar simulator covered with Newport bypass filter centered at 500 nm and 800 nm, respectively. The $EQE$ profiles were measured under -0.5 V bias with periodic monochromatic light by PV Measurement IPCE unit. The film morphology studies were carried out by tapping-mode atomic force microscopy (Digital Instrument).
6.3 Results and Discussion

6.3.1 Material Properties of CdTe Quantum Dot

The layout of the device architecture for NIR polymer PDs is shown in Figure 6.1 a. The molecular structures of poly[2,6-(4,4-bis-(2-ethyhexyl)-4H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDHTBT) and phenyl-C61-butyric acid methyl ester (PCBM) are shown in Figure 6.1b. The synthesized CdTe QDs are p-type nanocrystals passivated by hydrophilic MPA ligands in aqueous solution. The absorption and photoluminescence spectra of CdTe QD in aqueous solution are presented in Fig. 6.1c. As the well-known transmission and emission color of semiconductor nanocrystals are size-dependent because of quantum confinement, from the first absorption peak and photoelectron emission peak, the diameters of CdTe QD are estimated between 3 nm and 4 nm, and the valence band edge and conduction band edge are estimated to be -5.0 eV and -2.9 eV, respectively. Based on the band alignment of the materials (Figure 6.1d) used for fabrication NIR polymer PDs, it predicts that the CdTe QDs can serve as a hole-extraction layer (HEL) and an electron-blocking layer (EBL) as well. Figure 6.1e shown the absorption spectra of photoactive layer PCPDHTBT:PCBM spin cast on ITO, ITO/PEDOT:PSS and ITO/CdTe QD substrates, respectively. It is clear that there is a bare difference introduced by CdTe QD layer in contrast with blank ITO and ITO/PEDOT:PSS, which indicates that visible light is allowed to pass through CdTe QD layer and to be absorbed by PCPDHTBT:PCBM active layer.
Figure 6.1 (a) Scheme of the device architecture; (b) molecular structure of PCPDTBT and PC₆₁BM; (c) normalized absorption and photoluminescence spectra of CdTe QD measured from solution; (d) Energy levels of the stacking layers of the devices with CdTe QD; and (e) normalized absorption spectra of PCPDTBT:PCBM casted on ITO, ITO/PEDOT:PSS, and ITO/CdTe QD, respectively.
An ultrathin CdTe QD layer is cast from a dilute aqueous solution (~2×10⁻⁶ mol/L, 2 μM) followed by thermal annealing at 100 °C for 10 minutes. We found out that the annealing did not generate any changes of the CdTe QD, but it is for preventing moisture from the glovebox with nitrogen atmosphere. Figure 6.2 shows the AFM tapping mode

Figure 6.2 AFM tapping-mode height images of CdTe QD from 2 μM aqueous solution (a) as spun and (c) after annealing at 100 °C for 10 min; and AFM tapping mode phase images of CdTe QD from 2 μM aqueous solution (b) as spun and (d) after annealing at 100 °C for 10 min.
images of CdTe QD layers cast from 2 μM aqueous solution as spun and after annealing at 100 °C for 10 minutes. It demonstrates that the layers with and without annealing are characteristically identical in both height and phase images. However, in both cases, CdTe QDs by spin casting are randomly distributed with full coverage on top of ITO. For 10 μm×10 μm size, the surface root-mean-square roughness of ITO/CdTe QD is ~1.53 nm which is little rougher than that observed from blank ITO (R\text{RMS} = ~1.45 nm). The smoothness is attributed to small dimension of CdTe QD, and they can fill some of the dents as viewed in Figure 6.2d.

6.3.2 CdTe Quantum Dot as Electron-blocking and Hole-transporting Interlayer for Polymer Photodetectors

The current density–voltage (J-V) characteristics of the NIR polymer PDs are displayed in Figure 6.3a. The dark current density from NIR polymer PDs with CdTe QD as the anode interlayer is more than one order of magnitude lower than that with PEDOT:PSS as the anode interlayer. Under illumination of white light with the light intensity of 100 mW/cm², the polymer PDs with CdTe QD layer exhibited $J_{sc}$ of ~ 4.0 mA/cm², which is about 1.3 mA/cm² lower than those with PEDOT:PSS. However, at the reverse bias of -500 mV, the extracted $J_{ph}$ of polymer PDs with CdTe QD is no smaller than those with PEDOT:PSS. These results demonstrates the feasibility of CdTe QD as a HEL and an EBL resulting in reduced $J_d$ and sustained $J_{ph}$ for NIR polymer PDs. Fig. 6.3b shows both $J_{ph}$ and $J_d$ at monochromatic lights of wavelength ($\lambda$) = 500 nm and $\lambda$ = 800 nm with
Figure 6.3 (a) $J$-$V$ characteristics of polymer photodetectors with CdTe QD and PEDOT:PSS; (b) Photocurrent density at $\lambda = 500$ nm and $800$ nm, dark current and calculated detectivities versus bias voltage.
the light intensity of 2.8 mW/cm$^2$ and 0.9 mW/cm$^2$, respectively. It can be seen that the monochromatic $J_{ph}$ is almost 1000 folds of $J_d$ at the voltage of -500 mV, indicating high sensitivity of NIR polymer PD. Assuming the major noise is the shot noise from the dark current, the monochromatic detectivities$^{11}$ of the polymer PD with CdTe QD anode modification layer exceeds $5 \times 10^{11}$ Jones within -500 mV bias. The detectivities of polymer PDs at $\lambda = 500$ nm and $\lambda = 800$ nm versus different biases are plotted in Fig. 6.3b, respectively. Even under the bias of -2000 mV, the polymer PDs possessed the detectivity over $10^{11}$ Jones. These high detectivities at the bias from -400 mV to -2000 mV are comparable to Si-based PDs.

Figure 6.4 presents the incident photon to charge carrier efficiency (IPCE) spectrum of polymer PDs with CdTe QD as an anode interlayer. The IPCE profile is consistent with the absorption spectrum of PCPDTBT:PC$_{61}$BM, which further indicated that no influence of CdTe QD lay on the photoresponse of polymer PDs. Based on $D = \frac{EQE \times (\lambda/1240)/(2qJ_d)^{1/2}}{2}$, where D is the detectivity, $\lambda$ is the wavelength in nanometer and q is absolute value of an electron charge ($1.6 \times 10^{-19}$ Coulombs), respectively, the wavelength-dependent detectivities are calculated and depicted in Figure 6.4. Under bias of -500 mV, D are over $10^{11}$ jones and up to $10^{12}$ jones from 350 nm to 900 nm.

In order to better understand the device performance, the morphology of the active layer on ITO/CdTe QDs is observed by atomic force microscopy (AFM) and compared with that on ITO/PEDOT:PSS. Figure 6.5 shows the AFM phase images of PCPDTBT:PC$_{61}$BM on ITO/PEDOT:PSS and ITO/CdTe QD, respectively. Though there are some defects of the photoactive film on ITO/CdTe QD, the nano-scale phase separa-
tion between PCPDTBT and PC$_{61}$BM are featured and identical in both cases, indicating that the different anode contact does not alter the phase separation and distribution of BHJ active layer. Hence, photo-excitation, photocurrent generation and transport processes are preserved, providing basis of competitive photoresponse of the polymer PDs incorporated with CdTe QD.

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![Figure 6.4 External quantum efficiency and detectivity at -500 mV of the polymer photodetectors with CdTe QD versus incident light wavelengths](image)
that the different anode contact does not alter the phase separation and distribution of BHJ active layer. Hence, photo-excitation, photocurrent generation and transport processes are preserved, providing basis of competitive photoresponse of the polymer PDs incorporated with CdTe QD.

![AFM phase images](image)

**Figure 6.5** AFM phase images of PCPDTBT:PC$_{61}$BM (a) ITO/PEDOT:PSS and (b) ITO/CdTe QD, respectively.

### 6.3.3 Effect of CdTe Quantum Dot Concentration

We further investigate the influence of CdTe QD concentrations on both $J_{ph}$ and $J_{d}$. Figure 6.6 shows the $J$-$V$ characteristics of polymer PDs with CdTe QD anode interlayer spun from $1 \times 10^{-6}$ mol/L (1 μM), 2 μM and 3 μM aqueous solutions, respectively. When the CdTe QD layer is cast from 1 μM solution, large $J_{d}$ is observed, indicating that electron-blocking effect does not exhibit. This is probably due to too sparsely distributed QD. As the concentration of CdTe QD in spin-casting solution increases to above 2 μM, the polymer PDs with significant reduction of $J_{d}$ and no loss of $J_{ph}$ are observed. With further
increased CdTe QD concentration, there is no obviously alternation in both \( J_{ph} \) and \( J_d \) observed. Thus, the surface coverage of CdTe QD on ITO anode is essential to the \( J_d \) suppression. It is worthy noted that CdTe QD layer processed from 2 \( \mu \)M solution is not continuous and homogeneous, as suggested by Figure 6.2c and d, but this CdTe QD layer can significantly reduce \( J_d \).

![Image of J-V characteristics](image_url)

Figure 6.6 J-V characteristics of the polymer photodetectors with CdTe QD layer spun from 1 \( \mu \)M, 2 \( \mu \)M and 3 \( \mu \)M aqueous solutions, respectively.

6.3.4 Stability

The self-stability of polymer PDs with CdTe QD anode interlayer is studied and compared with those with PEDOT:PSS anode interlayer. Fig. 6.7 presents the normalized responsivities and normalized detectivities versus storage time. As interpreted in Fig. 6.7a
Figure 6.7 Device performance decay profiles of the unencapsulated polymer PDs with respective PEDOT:PSS and CdTe QD biased at -500 mV: (a) normalized responsivity (b) normalized detectivity.
and b, the half-shelf lifetime of responsivity and detectivity of the polymer PDs are enhanced from 60 hours to 650 hours and from 120 hours to 480 hours, respectively, by using CdTe QD instead of PEDOT:PSS as the anode buffer layer. The prolonged stability of the polymer PDs with CdTe QD anode interlayer demonstrates the favorable inertness of the CdTe QD material and its compatibility with ITO and active layer.

6.4 Conclusions

In summary, solution-processed wide bandgap CdTe QD has been demonstrated as an effective and stable hole-extraction layer as well electron-blocking layer for NIR polymer PDs. Compared with polymer PDs with PEDOT:PSS as an anode interlayer, the polymer PDs incorporated with CdTe QD exhibit suppressed dark current while maintain comparable photoresponse, yielding enhanced detectivity over $10^{11}$ Jones in the spectral response from 350 nm to 900 nm. Moreover, by replacing PEDOT:PSS with CdTe QD, the lifetime of the polymer PDs extended from 60 hours to up to 650 hours. These results demonstrate that CdTe QD could be a simple and better solution-processable alternative to PEDOT:PSS functioning as a hole-extraction and electron-blocking layer in polymer PDs.
CHAPTER VII

INfluence of Band Offsets and Impurity Density on the Device Performance of Polymer Photodetectors

7.1 Introduction

Detectivity of polymer PDs measures how well the effective photocurrent is over the noise current. If the major noise current comes from shot noise, the normalized detectivity of a PD is given by\(^{11}\)

\[
D^*(\lambda, V) = \frac{J_{ph}(\lambda, V)}{L_{light}(\lambda)} \sqrt{2qJ_d(\lambda, V)}
\]

(7.1)

where \(J_{ph}\) is the net photocurrent density, \(L_{light}\) is the incident light optical power, \(J_d\) is the dark current density and \(q\) is the element charge. It is clear that not only high photocurrent density but also low dark current density are required for fabrication of high detectivity PDs.

Photocurrent generation has been extensively studied with polymer:fullerene bulk heterojunction photovoltaics. The profound enhance in \(J_{ph}\) can be achieved by thermal and solvent annealing,\(^{149}\) processing additive,\(^{105,147}\) light trapping masks\(^{150}\) and some interface engineering.\(^{84,151}\) However, \(J_d\) is less addressed and understood. Only a few
reports correlated $J_d$ with active layer thickness,\textsuperscript{147,149} composition,\textsuperscript{152} spatial distribution of the blend components,\textsuperscript{45,153} temperature\textsuperscript{45,153} and surface contacts\textsuperscript{11,40,154,159} experimentally. As further improvements are necessary to optimize polymer PDs, a more complete understanding of device performance governed by $J_d$ is needed.

In organic semiconductor devices, the offset energy ($\Delta E$), which is defined as the energy difference between highest occupied molecular orbital (HOMO) of electron donor (D) and lowest unoccupied molecular orbital (LUMO) of electron acceptor (A), is a critical parameter as described in eqn 2.21 and Figure 2.6. It determines the electric field at the interface for photocurrent generation.\textsuperscript{69} And it is interesting and meaningful to explore whether $J_d$ is a property of the heterojunction energetic and material characteristics. Meanwhile, by taking into consideration the generation current under reverse bias from depletion region, a dependence of $J_d$ on impurity concentration ($N$) can be correlated and discussed. It is highly expected to better understand device performances and reveal challenges and opportunities for accomplish low dark current and high detectivity polymer PDs.

In the following parts, we started with quantitative model using a generalized Shockley equation for p-n junctions. By adapting generation current under the reverse bias condition where polymer PDs are operated, the dark currents are modeled as a function of $\Delta E$ and $N$. Experimental results by constructing polymer photovoltaic cells with a series of $\Delta E$ with different polymers were tested to verify predicted relations. And the dependence of $J_d$ on factors of $\Delta E$, $N$ and contact barriers can be resolved.
The J-V characteristics of a polymer PD can then be expressed by the generalized Shockley equation for p-n junctions in deal cases as \(^{47}\)

\[
J = J_0 \left\{ \exp \left( \frac{qV}{kT} \right) - 1 \right\} - J_{ph} \quad (7.2)
\]

where \(q\) is elementary charge, \(k\) is Boltzman constant, \(T\) is absolute temperature, \(V\) is applied voltage, \(J_{ph}\) here refers to gross photocurrent, and \(J_0\) is the reverse saturation current, \textit{viz.} \(^{47}\)

\[
J_0 = \frac{qD_aN_CN_V}{L_aN} \exp \left( - \frac{E_g}{kT} \right) \quad (7.3)
\]

in which \(D_a\) is diffusion coefficient, \(L_a\) is diffusion length, \(N\) is impurity density, \(N_C\) and \(N_V\) are effective density of states in conduction band and valence band respectively, and \(E_g\) is the heterojunction energy barrier, equal to \(\Delta E = \text{LUMO (A)} - \text{HOMO (D)}\).

In the dark state \(J_d\) at reverse biases will saturate to \(J_0\) and exponentially decreases approximately as \(\Delta E\) increases. However, this accounts only the diffusion of minority carrier and dominant generation process in the depletion region under reverse bias will cause departure from the ideal. This is practical because charge carriers are depleted under reverse biases \((np < n_i^2; n_i\) is the intrinsic charge carrier density\) and thermal generation prevail to restore the system to equilibrium.\(^{48}\) Thus it is one of the reasons that reverse dark current gradually increases rather than saturate with voltage before junction breakdown. The current density due to generation in the depletion region is given as \(^{47}\)

\[
J_{ge} = \int_{W_D}^{\infty} q |U| dx = q |U| W_D = \frac{qn_i W_D}{\tau_g} \quad (7.4)
\]
where $W_D$ is the depletion layer width, $U$ is the rate of generation, $\tau_g$ is the generation lifetime and is defined as

$$\tau_g = \frac{\sigma_n \exp\left(\frac{E_l-E_f}{kT}\right) + \sigma_p \exp\left(\frac{E_i-E_l}{kT}\right)}{\sigma_p \sigma_n \nu_{th} N} = \frac{Q}{N} \quad (7.5)$$

in which $\sigma_p$ and $\sigma_n$ are the electron and hole capture cross sections, respectively, $\nu_{th}$ is thermal velocity proportional to $T^{1/2}$, $N$ is the impurities concentration and $Q$ is a representative of the $rac{\sigma_n \exp\left(\frac{E_l-E_f}{kT}\right) + \sigma_p \exp\left(\frac{E_i-E_l}{kT}\right)}{\sigma_p \sigma_n \nu_{th}}$. Meanwhile, depletion-layer width at the junction can be given by

$$W_D = \sqrt{\frac{2\varepsilon}{qN} (\Delta E - V)} \quad (7.6)$$

where $\varepsilon = \varepsilon_r \varepsilon_0$ is the dielectric permittivity of the material, $V$ is the applied bias. And

$$n_i^2 = N_C N_V \exp\left(-\frac{\Delta E}{kT}\right)^{48} \quad (7.7)$$

Substitute eqn (7.5), (7.6) and (7.7) into eqn (7.4), yielding

$$J_{ge} = \sqrt{N(\Delta E - V)} \frac{\sqrt{2\varepsilon q N_C N_V}}{Q} \exp\left(-\frac{\Delta E}{2kT}\right). \quad (7.8)$$

Therefore, the total saturation current can be approximated by the sum of diffusion current from neutral region by eqn (7.3) and $J_{ge}$ from the heterojunction:

$$J_0^* = \frac{qD_a N_C N_V}{L_a N} \exp\left(-\frac{\Delta E}{kT}\right) + \sqrt{N(\Delta E - V)} \frac{\sqrt{2\varepsilon q N_C N_V}}{Q} \exp\left(-\frac{\Delta E}{2kT}\right). \quad (7.9)$$

At zero and low reverse bias, eqn (7.9) may be arrange with ideal factor $x$ into

$$J_0^* = \left(\frac{qD_a N_C N_V}{L_a N} + \sqrt{N(\Delta E - V)} \frac{\sqrt{2\varepsilon q N_C N_V}}{Q}\right) \exp\left(-\frac{\Delta E}{xkT}\right). \quad (7.10)$$
Typically, the intrinsic charge carrier density in organic semiconductors are small, thus the generation current may be dominant. Therefore, the above derivation would predict \( \ln(J_d) \) linearly decays as \( \Delta E \) and proportional to \( \sqrt{N(\Delta E - V)} \).

7.2 Experimental

To understand and verify the fundamental physics governing \( J_d \), we measure the \( J_d \) at -0.2 V attainable from polymer bulk heterojunction photovoltaic cells based on selected combinations of different electron donor polymers and a common electron acceptor \((6,6)\)-phenyl-C61-butyric acid methyl ester (PC61BM). The semiconducting polymers are poly(3-hexylthiophene) (P3HT), poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), poly(thienothiophene-co-benzodithiophenes)7 with fluoride thienothiophene content 20% (PTB7-F20), Poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7), poly[2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene][3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7-DT) and Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diy]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diy]-2,5-thiophenediyl] (PCDTBT). The molecular structures of the polymers and PC61BM are shown below in Figure 7.1.
The energy levels of the semiconducting polymers are re-affirmed by combination of cyclic voltammetry (CV) and the optical bandgap. CV was conducted on BAS C3-Voltammetry Cell Stand with an Epsilon potentiostat at a scanning rate of 100 mV/s in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution at room temperature. A glassy carbon electrode, a Pt electrode and an Ag/Ag⁺ electrode were used the working electrode, counter electrode, and reference electrode, respectively. The sample was drop cast from 1 mg/mL chloroform solution on the working electrode. And the HOMO of the semiconducting polymers is determined by
HOMO = e\[− 4.8V − (E_{ox} − E_{1/2(Fe)})\] \hspace{1cm} (7.11)

where \(E_{ox}\) is the onset oxidation potentials of the tested polymers, \(E_{1/2(Fe)}\) is half-wave potential of ferrocene. And the LUMO is estimated by

\[
\text{LUMO} = \text{HOMO} + E_{opt} \hspace{1cm} (7.12)
\]

In which \(E_{opt}\) is the optical bandgap interpreted from the cut-off absorption energy.

The photovoltaic cells are fabricated with device structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/semiconducting polymer: PC\textsubscript{61}BM/Ca/Al. The D:A ratios of photoactive layers are selected as the best values that produce highest \(J_{ph}\). That is 1:0.8 for P3HT:PC\textsubscript{61}BM Blend, 1:3 for PCPDTBT:PC\textsubscript{61}BM blend, 1:1.5 for PTB7-F20/PTB7/PTB7-DT: PC\textsubscript{61}BM blends and 1:4 for PCDTBT:PC\textsubscript{61}BM blend. Meantime, the choice of 3% v/v diiodooctane (DIO) is also met for PCPDTBT, PTB7-F20, PTB7 and PTB7-DT systems. The photoactive layers were spin cast on ~35 nm PEDOT:PSS with controlled thicknesses of 100-110 nm measured by atomic force microscopy (AFM). And top electrode Ca/Al with thicknesses about 8 nm/110 nm were sequentially thermal deposited through shadow mask with the active device of 4.5 mm\(^2\). And the dark current density versus voltage (\(J-V\)) characteristics was measured using a black box by a Keithley 2400 Source Measure Unit.

The impurity concentration of the blends are estimated using Mott-Schottky analysis on capacitance-voltage (\(C-V\)) characteristics by Agilent 4830 impedance analyzer at frequency of 1 kHz. The Mott-Schottky analysis is based on abrupt space charge region at the junction and the charge in the region is entirely due to impurities, such as dopant atoms or trapped domains out of network as recombination centers. The capacitance originates from the depletion region is given\(^{160}\)
\[ C = \varepsilon_r \varepsilon_0 A/W \quad (7.13) \]

where \( W \) is the width of the depletion region, \( A \) is the area of the device, \( \varepsilon_r \) is the relative dielectric constant of the semiconductor, and \( \varepsilon_0 \) is the vacuum permittivity. The space charge width depends on the impurity density and modulates as applied direct circuit (DC) bias as

\[ W = \sqrt{\frac{2 \varepsilon_r \varepsilon_0 (V_{bl} - V)}{q N}} \quad (7.14) \]

in which \( V_{bl} \) is the built-in voltage. Therefore, Mott-Schottky plot of \( \frac{1}{C^2} \) versus \( V \) will yield a line, whose intersection give built-in voltage and slope inversely proportional to the impurity density. The impurity density thus can be estimated with \(^{(160,161)}\)

\[ N = -\frac{2}{q \varepsilon_r \varepsilon_0 A^2} \left( \frac{d \frac{1}{C^2}}{d V} \right)^{-1}. \quad (7.15) \]

7.3 Results and Discussion

Figure 7.2 shows the current-voltage curves for the semiconducting polymers regarding to CV measurements. From the first oxidation potential, the HOMO of the donor polymers are estimated and summarized in Table 7.1. And the test results are analogous to literature reports, confirming the compositions and energetics of the polymers. The LUMO of PC\(_{61}\)BM is also verified and identical to reported CV results to be -3.91 eV.\(^{(162,163)}\) Assuming abrupt flat-band junction between the donor polymers and electron acceptor PC\(_{61}\)BM, \( \Delta E \) constructed by the combinations varies from 0.98 eV to 1.52 eV.
Table 7.1 Donor semiconducting polymers and their corresponding energy levels and the offset energies $\Delta E$ with PC$_{61}$BM

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{\text{onset(ox)}}$ (V)</th>
<th>HOMO (eV)</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>LUMO (eV)</th>
<th>$\Delta E$ regarded with LUMO of PC$_{61}$BM at -3.91 eV (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>0.46</td>
<td>-4.89</td>
<td>1.90</td>
<td>-2.99</td>
<td>0.98</td>
<td>162,164</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>0.60</td>
<td>-5.03</td>
<td>1.45</td>
<td>-3.58</td>
<td>1.12</td>
<td>129</td>
</tr>
<tr>
<td>PTB7-F20</td>
<td>0.67</td>
<td>-5.10</td>
<td>1.60</td>
<td>-3.50</td>
<td>1.19</td>
<td>165</td>
</tr>
<tr>
<td>PTB7</td>
<td>0.79</td>
<td>-5.22</td>
<td>1.70</td>
<td>-3.52</td>
<td>1.31</td>
<td>166</td>
</tr>
<tr>
<td>PTB7-DT</td>
<td>0.84</td>
<td>-5.27</td>
<td>1.63</td>
<td>-3.64</td>
<td>1.36</td>
<td>167</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>1.00</td>
<td>-5.43</td>
<td>2.10</td>
<td>-3.33</td>
<td>1.52</td>
<td>168,169</td>
</tr>
</tbody>
</table>
Figure 7.3 Diagram of energy levels of ITO, PEDOT:PSS, P3HT, PCPDTBT, PTB7-F20, PTB7, PTB7-DT, PCDTBT, PC$_6$1BM, Ca, Al before contact.

Figure 7.4 Dark $J$-$V$ characteristics of ITO/PEDOT:PSS/polymer:PC$_6$1BM/Ca/Al. The thickness of polymer:PC$_6$1BM is about 105 nm.
The energy level diagram of the polymer photovoltaic cells are depicted in Figure 7.3. The LUMO-LUMO differences between the polymers and PC$_{61}$BM are well above 0.3 eV, which indicates sufficient energy potential at the junctions for exciton dissociation and charge transfer that associate with photocurrent generation in the polymer PDs. The use of PEDOT:PSS essentially increases the workfunction of anode, allowing ohmic contact with photoactive layer whose D has a HOMO lower than the workfunction of PEDOT:PSS. It appears that the cases of P3HT, PCPDTBT, PTB7-F20, PTB7 and PTB7-DT are most likely have ohmic contact with the anode. But PCDTBT may have Schottky barriers due to too deep HOMO levels. Meanwhile, low workfunction Ca at the cathode, higher than LUMO of PC$_{61}$BM, enable ohmic contact at the cathode.

Figure 7.5 Mott-Schottky plots of ITO/PEDOT:PSS/polymer:PC$_{61}$BM/Ca/Al. The thickness of polymer:PC$_{61}$BM is about 105 nm.
The J-V characteristics of the photovoltaics cells with comparable photoactive layer thickness of 100-110 nm in dark are presented in Figure 7.4. The reduction of $J_d$ is apparent with the increment in $\Delta E$ except PCDTBT:PC$_{61}$BM, which will be discussed later. And Mott-Schottky plots of impedance results of D-A junctions are shown in Figure 7.5. The impurity concentrations can be interpreted using eqn (7.15) respectively. The parameters that may be associated are summarized and listed in Table 7.2. Simply assuming the bulk heterojunction is equivalent to abrupt p-n junction, no band bending at the contact and generation current dominant at reverse bias due to small intrinsic carrier density, eqn (7.10) predicts a linear dependence of $\ln(J_d)$ on $\Delta E$ given $\sqrt{N(\Delta E - V)}$ is identical, and $J_d$ is a function of $\sqrt{N(\Delta E - V)}$.

Table 7.2 Extracted parameters from J-V characteristics, energetics and Mott-Schottky analysis

<table>
<thead>
<tr>
<th>Polymer: PC$_{61}$BM</th>
<th>$J_d$ @ -0.2V (A/cm$^2$)</th>
<th>$J_d$ @ -0.5V (A/cm$^2$)</th>
<th>$\Delta E$ (eV)</th>
<th>$N$ (cm$^{-3}$)</th>
<th>$\sqrt{N(\Delta E + 0.2)}$ (eV cm$^{-3}$)$^{1/2}$</th>
<th>$\sqrt{N(\Delta E + 0.5)}$ (eV cm$^{-3}$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>3.04×10$^{-6}$</td>
<td>1.04×10$^{-5}$</td>
<td>0.98</td>
<td>3.70×10$^{16}$</td>
<td>2.09×10$^8$</td>
<td>2.34×10$^8$</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>2.08×10$^{-6}$</td>
<td>5.55×10$^{-6}$</td>
<td>1.12</td>
<td>2.90×10$^{16}$</td>
<td>1.96×10$^8$</td>
<td>2.17×10$^8$</td>
</tr>
<tr>
<td>PTB7-F20</td>
<td>1.86×10$^{-6}$</td>
<td>5.39×10$^{-6}$</td>
<td>1.19</td>
<td>5.57×10$^{16}$</td>
<td>2.78×10$^8$</td>
<td>3.07×10$^8$</td>
</tr>
<tr>
<td>PTB7</td>
<td>9.21×10$^{-7}$</td>
<td>2.64×10$^{-6}$</td>
<td>1.31</td>
<td>2.82×10$^{16}$</td>
<td>2.06×10$^8$</td>
<td>2.26×10$^8$</td>
</tr>
<tr>
<td>PTB7-DT</td>
<td>8.14×10$^{-7}$</td>
<td>2.23×10$^{-6}$</td>
<td>1.36</td>
<td>1.05×10$^{16}$</td>
<td>1.28×10$^8$</td>
<td>1.40×10$^8$</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>1.48×10$^{-6}$</td>
<td>4.20×10$^{-6}$</td>
<td>1.52</td>
<td>1.83×10$^{16}$</td>
<td>1.77×10$^8$</td>
<td>1.92×10$^8$</td>
</tr>
</tbody>
</table>
A plot of $J_d$ at -0.2 V vs $\Delta E$ is presented in Figure 7.6. The linear dependence of $\ln(J_d)$ on $\Delta E$ is estimated from P3HT:PC$_{61}$BM, PCPDTBT:PC$_{61}$BM and PTB7:PC$_{61}$BM, as the estimated $\sqrt{N (\Delta E - V)}$ of the blends are almost identical. Offsetting the linear relationship with respect to the values of $\sqrt{N (\Delta E - V)}$, PTB7-F20:PC$_{61}$BM device whose $\Delta E$ is 1.19 eV finds agreed $J_d$ in the vicinity of the predicted value at $\sqrt{N (\Delta E - V)} \sim 2.8 \times 10^8$ (eV cm$^{-3}$)$^{1/2}$. However, the $J_d$ observed from PCDTBT:PC$_{61}$BM photovoltaic cells, whose $\Delta E$ is 1.52 eV, deviated largely from the discussed relations. By a close examination, we propose a probable reason is the contact barrier at the interface between photoactive layer and ITO/PEDOT:PSS. According to Figure 7.3, the contact of PCDTBT with PEDOT:PSS are Schottky contact because of
deeper HOMO of the semiconducting polymers. And the barrier height before contact was roughly 0.23 eV. The Schottky contacts will also have generation currents due to surface states, which were not taken into consideration by eqn (7.10). As these contact barriers oppose $\Delta E$, the devices will see an apparent offset energy $\Delta E_{\text{app}} = \Delta E - \text{contact barrier}$. Through the observed $J_d$, the $\Delta E_{\text{app}}$ estimated using the linear relation given a tain $\sqrt{N(\Delta E - V)}$. And the contact barriers calculated by $\Delta E - \Delta E_{\text{app}}$ for PCDTBT:PC$_{61}$BM is 0.32 eV. These values are only slightly larger than the barrier heights estimated from flat band condition. Therefore, it demonstrates that the linear dependence of $\ln(J_d)$ may be on the apparent offset energy $\Delta E_{\text{app}}$, where the invariance on the linear approximation is related to the D-A junction $\Delta E$ and impurity concentration $N$.

![Graph](image)

Figure 7.7 Dark current density $J_d$ at -0.2 V and at -0.5 V versus offset energies $\Delta E$ and the linear approximations respectively.
Figure 7.7 depicts the $J_d$ at -0.2 V and at -0.5 V respectively as a function of $\Delta E$. At both reverse biases, $J_d$ regresses exponentially with $\Delta E$ and the slopes are similar. These again elucidate the reverse bias dependent dark current density $J_d$ and the consistent linear approximation. PCDTBT:PC$_{61}$BM show rises in $J_d$ at both voltages and the offset energies required to meet the deduced values from previous prediction are almost identical, which also suggests hypothetically the linear regression of $\ln(J_d)$ on the apparent energy offset $\Delta E$ with subtraction of a contact barrier.

The experimental results demonstrated the association between $J_d$ of polymer photovoltaics PDs and two physical parameters of the device: D-A junction $\Delta E$ and impurity concentration $N$. And the tendency agrees with the theoretical predictions. These information reveals that a large D-A junction $\Delta E$ and a low impurity concentration $N$ are needed to construct low shot noise polymer PDs. Meantime, the importance of ohmic contacts in between layers of the device is evident. With the understanding of the physics, the practical challenges in producing low-noise and efficient infrared polymer PDs can be comprehended, in that $\Delta E$ of type-II (staggered) heterojunction between D and A is limitedly small as a result of low bandgap semiconductor materials. To fabricate high performance IR polymer PDs, it would be highly demanded of low bandgap semiconductor absorber in high purity grade, fine device design as well as delicate processing method for bare contact barriers, and better morphology with minimum trap centers.
7.4 Conclusions

We have presented a device model that explores the interrelationships between the energetic characteristics, the offset energy $\Delta E$ between HOMO of D and LUMO of A, of organic heterojunction and the effect the characteristics imposed on dark current density in polymer photovoltaic photodetectors. The model based on the Shockley equation modified with generation process from p-n junction describes voltage dependent saturation dark current density, and predicts the linear decreasing of $\ln(J_d)$ with an increasing $\Delta E$ and $J_d$ is a function of $\sqrt{N\Delta E}$, where $N$ is the impurity density at the D-A heterojunction. Experimentally, the trend is tested and modified with impact from contact barriers, which apparently reduce the effective $\Delta E$. Ultimately, the results inform the requirements of a large $\Delta E$, a low $N$ from high purity material and better morphological control, as well as smooth and barrier-free contact for highly sensitive polymer PDs.
CHAPTER VIII

SUMMARY AND OUTLOOK

In this dissertation, polymer photodetectors (PDs) utilizing solution processed bulk heterojunction photoactive layers were fabricated and studied about the device electronic performances. Polymer PDs, with lower cost and easier fabrication, demonstrated comparable and even better capability than inorganic counterparts. The effects of processing techniques, device structure, morphology, interlayer materials, interlayer geometry and energetics were investigated and related to the responsivity, detectivity and stability of polymer PDs by bonded structure-processing-performance relationship.

Solution-processed Polymer Photodetectors with High External Quantum Efficiency and Detectivity

Polymer photodetectors based on P3HT:PC61BM BHJ composite were optimized by active layer thickness and combined solvent-vapor annealing and post-production thermal annealing. The electronic response and active layer surface and morphology change by the processing treatments were investigated. From the results we could conclude the following:
Device performance of polymer PDs were active layer thickness dependent. Both photocurrent density and dark current density decrease with increasing active layer thickness. The best performance with highest detectivity ($D$) and moderate external quantum efficiency ($EQE$) and responsivity ($R$) were observed from active layer about 210 nm.

By combined solvent-vapor annealing treatment of active layer and post-production thermal annealing treatment of formed cells, polymer photodetectors exhibited external quantum efficiency approximately 80%, detectivity over $10^{13}$ Jones and linear dynamic range over 120 dB. Solvent annealing induced a slightly rougher active layer surface by atomic force microscopy. Both solvent annealing and post-production thermal annealing promote better packing of polymers and surface contact between active layer and top electrode, resulting in significantly improved $J_{ph}$.

Future works related to this portion of the research could be optics to improve light available to active layer by reducing reflection and scattering. Possible approach could be anti-reflective coating, optical functional layer and light trapping techniques.

Polymer Photodetectors with an Inverted Device Structure

For stability and solution processability, polymer PDs with inverted device structures need developing. Polymer PDs based on PCPDTBT:PC$_{61}$BM in architecture of ITO/ZnO$_x$/photoactive layer/MoO$_3$/Ag were investigated. Optimization of the polymer
Polymers were synthesized by processing additive 1,8-diodooctane (DIO). From these experimental studies, we conclude that:

- Polymer PDs with the inverted structure have been successfully demonstrated with diode rectification ratio over $10^3$ at $\pm 1$V. Electron extraction layer ZnOₓ and hole extraction layer MoO₃ played important roles in constructing the asymmetric inverted polymer PDs.

- Processing additive DIO has an impact on the film morphology of the photoactive layer and the resultant performance of polymer PDs. $J_{ph}$ and $J_d$ are affected by the concentration of DIO, and the best ratio of $J_{ph}/J_d$ and detectivity is observed from polymer PDs processed with 3% v/v DIO. With the optimization, the inverted polymer PDs exhibited detectivities greater than $10^{11}$ Jones from 400 nm to 850 nm at room temperature.

Future work related to this portion of the research could be development of solution-processed MoOₓ on active layer for inverted polymer PDs. This will ultimately achieve the prototype of effective and stable polymer photovoltaics by solution processing of all layers. In addition, detailed thin film bulk morphology change as a function of processing additive type and concentration could help understand how processing additives work.

Zinc Oxide Nanowire as an Electron-Extraction Layer for Polymer Photodetectors with an Inverted Device Structure
Vertically aligned ZnO nanowire (NW) array were investigated in inverted polymer PDs as the cathode electron-transporting and hole-blocking layer. The ZnO NW array was prepared by solvothermal growth on preformed ZnO seeding layer. And the performance of the polymer PDs with device structure of ITO/ZnO NW/PDDTT:PC$_61$BM/MoO$_3$/Au were studied. We can conclude that:

- High-quality vertical ZnO NW array with a wide bandgap and an enhanced surface area can acts as the cathode buffer layer for extracting electrons and blocking holes effectively in inverted polymer PDs.
- The inverted polymer PDs exhibits broadband spectral response from UV to IR (400-1450 nm), with detectivity greater than $10^{10}$ Jones at wavelengths from 400 to 1300 nm and greater than $10^9$ Jones from 1300 to 1450 nm.

Future work related to this portion of the research could be structure-performance study of ZnO NW array on device performance, including factors like NW length, NW density and surface properties.

Water-soluble CdTe Quantum Dot as an Anode Interlayer for Solution-processed Polymer Photodetectors

Water-soluble cadmium telluride (CdTe) quantum dot (QD) used as an anode interlayer in solution-processed near infrared (NIR) polymer photodetectors was investigated. Comparative study of CdTe QD and PEDOT:PSS in terms of polymer PDs performance and stability was conducted. From the experiments, we conclude that:
• Wide bandgap CdTe QD can serve as an optical transparent and hole-extraction as well as electron-blocking layer for polymer PDs. The CeTe QD layer can be water processed at room temperature.

• Compared with polymer PDs with PEDOT:PSS as an anode interlayer, those with an ultrathin CdTe QD interlayer exhibit suppressed dark current while maintaining comparable photoresponse, yielding enhanced detectivity over $10^{11}$ Jones in the spectral response from 350 nm to 900 nm.

• By replacing PEDOT:PSS with CdTe QD, polymer PDs extended lifetime from 60 hours to up to 650 hours, indicating the robust and stable contacts using CdTe QD as the anode functional interlayer.

Future work related to this portion of the research could be application of solution processed wide bandgap QD interlayers for inverted polymer PDs. Besides, optical properties of QD interlayer can be further explored and discussed for potential use in sub-band detection and light conversion for polymer photonics.

Influence of Band Offsets and Impurity Density on Device Performance of Polymer PDs

Reverse biased dark current $J_d$ of polymer PDs were studied as a function of characteristic heterojunction energetics $\Delta E$ and impurity density $N$. The interrelation was approached from mathematic models and experimental observation. From our work, we can conclude that:

• $\ln(J_d)$ linearly decreases with $\Delta E$ and is dependent on $\sqrt{N \Delta E}$, according to mathematic model based on the Shockley equation modified with generation pro-
cess from p-n junction, which causes a generation current \( J_{ge} \) related with impurity density \( N \).

- Experimentally, the linear dependence of \( \ln(J_d) \) on \( \Delta E \) by a factor of \( \sqrt{N \Delta E} \) was observed. And the results reflected an impact from contact barriers, which modifies the dependence of \( \ln(J_d) \) on apparent \( \Delta E_{app} \) that was substracted by contact barriers.

- Messages from the work inform that high purity material, good morphology and minimum contact barriers are essential to fabricate high performance IR polymer PDs.

Future work related to this portion of the research could include verification and improvements on the theoretical model, comparative experiments about the effect of energetic contact barriers by constructing barrier-free and barrier variant devices, effect of surface states as well as the relationships between morphology and measured impurity density \( N \).
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