Engineering and investigation of Zinc oxide cathode interfacial layer in inverted organic solar cells: Implications for charge transport and collection

A Thesis

Submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

by

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SHIV NADAR UNIVERSITY

(December, 2017)

DECLARATION

This is to declare that the thesis entitled **ENGINEERING AND INVESTIGATION OF ZnO CATHODE INTERFACIAL LAYER IN INVERTED ORGANIC SOLAR CELLS: IMPLICATIONS FOR CHARGE TRANSPORT AND COLLECTION** submitted by me to **Shiv Nadar University**, Gautam Buddha Nagar in partial fulfillment for the award of the degree of Doctor of Philosophy is a record of work carried out by me at Shiv Nadar University. The work, in full or in parts, has not been submitted to any other University/Institute for the award of any other degree. Any information/material used in the thesis from external sources has been appropriately acknowledged.

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CERTIFICATE

This is to certify that the thesis entitled "**ENGINEERING AND INVESTIGATION OF ZnO CATHODE INTERFACIAL LAYER IN INVERTED ORGANIC SOLAR CELLS: IMPLICATIONS FOR CHARGE TRANSPORT AND COLLECTION**" submitted by **'Shashi Bhushan Srivastava (Roll No. 1310120041)'** to the **Shiv Nadar University**, Gautam Buddha Nagar for the award of the degree of **Doctor of Philosophy** is a bonafide record of research work carried out by him/her under my/our supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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Dedicated to

My Family

With all that was before and all that is to come

ACKNOWLEDGEMENT

Pursuing PhD at ***Shiv Nadar University*** had been an astonishing experience and remarkable journey of my life. It was not only a journey for achieving a degree but also to gather and share knowledge from the others, realize the self-weaknesses and eventually improve myself to a greater height each and every day. In this process, I feel thankful to many people, without their support this work would not have been a reality.

First of all, I would like to convey my sincere thanks and heartiest gratitude to my research advisor ***Dr. Samarendra Pratap Singh*** for leading me to the exciting field of semiconductor devices. I really feel grateful to have a supervisor who has kept his door open for any scientific discussions at any time. He has helped in shaping me through all these years not only in scientific field but also improving other skills. Moreover, his broad research experience and way of tackling problems has inspired me a lot. The last four years, working with him had helped me to grow as an individual in the field of research and no doubt, it will remain as most significant part of my professional life.

I also take an opportunity to thank ***Prof. Rupamanjuri Ghosh***, (Vice chancellor, Shiv Nadar University) and other faculty members of the Department of Physics for their constant support and motivation during my PhD.

I express my deepest gratitude to ***Dr. Sankar Dhar*,** (Head, Department of Physics, Shiv Nadar University) for his valuable support in establishment of semiconductor lab. I always admire his very humble nature towards students.

I also feel thankful to our collaborators ***Dr. Sajal Kumar Ghosh*** (Department of Physics, Shiv Nadar University), ***Dr. Bimlesh Lochab*** (Department of Physics, Shiv Nadar University), and ***Dr. Sanjay Kumar Srivastava*** (NPL, New Delhi) for their continuous experimental support throughout my thesis work. I would also like to thank our international collaborator ***Dr. Prashant Sonar*** (QUT, Australia) for his support in providing organic semiconductor materials.

I take an opportunity to express my heartfelt gratitude to the members of the doctoral committee ***Dr. Sajal Kumar Ghosh*** (Chairperson), and ***Dr. Syed Kamil*** (Member) for their valuable inputs and constructive suggestion to shape the thesis.

It was an experience of life time to work in such a friendly and helpful environment at SNU with the support and encouragement from all the faculty members, staffs, lab mates, project students.

I would like to thank my colleagues from Department of Physics specially ***Gourav Bhattacharya***, ***Arabinda Barman***, and ***Chetan Prakash Saini*** for their support in carrying out experiments and the valuable discussion we had together. Also the co-workers, ***Swapnil Shukla, Kunal Kumar Jha, Divambal Appavoo, and Ashish Chalana***, from Department of Chemistry need special mention for their unconditional help. I would also like to thank ***Anurag Pritam*** for sharing many joyful moments during my thesis writing.

Finally, I like to express my sincere thanks to ***Shiv Nadar Foundation*** for providing scholarship and infrastructure, otherwise this work would not have been possible.

I am highly indebted to my parents who played an important role in shaping a lot of me. Their encouraging words constantly inspired me to pursue my dreams. The constant support and the patience my wife ***Ruchika*** showed towards me in this whole journey is worth appreciating.

Synopsis

The bulk heterojunction (BHJ) organic solar cells (OSCs) are made by assembling a multi-layered structure where each layer has a specific role in devices. In a BHJ active layer (AL), the donor and the acceptor materials have their presence on both electrodes which increases the probability of recombination at interfaces of the active layer and electrodes. Hence, the introduction of electrode buffer layers at both electrodes have become crucial in forming a selective contact for one type of charge carriers. These buffer layers offer manifold advantages such as,

1. Tuning of energy level alignment between electrodes and the active layer
2. Preventing a feasibility of the physio-chemical reaction between electrodes and the active layer
3. Tailorability of the local composition of bulk-heterojunction active layer

The introduction of these buffer layers was successfully exploited in inverted OSC device architecture which has resulted in an improved lifetime of the devices with easy fabrication steps in ambient condition. However, there are still many challenges which need to be dealt promptly to understand the designing/selection rules of interface buffer layers and its impact of electrode buffer layers on the morphology of the active layer. Additionally, charge transport and charge collection mechanisms at interfaces of the active layer/electrode buffer layers and electrode buffer layers/electrodes also need to be understood.

Several works have been done to highlight and address the interfacial issues between cathode (anode) buffer layers and their roles in OSC devices. The additional layer of fullerene has been tried to reduce the interaction of donor polymers with electron collecting electrode. The use of fullerene-based self-assembled monolayers as a chemical modifier has drawn much attention towards getting the solution for interface issues in OSCs. We have reviewed the works reported by various researchers, and have planned our research with this background. These studies emphasize on the requirement of a series of electrical, optical, structural and chemical characterization tools to establish a structure-property correlation in the context of the role of electrode buffer layers in OSC devices. We believe such studies will pave the way for an efficient engineering of electrode buffer layers in OSCs.

The aim of this thesis is to investigate and engineer Zinc oxide (ZnO) cathode buffer layer which bridges the transparent electrode and the active layer in an inverted OSC. We have used current density-voltage (J-V), space charge limited current (SCLC), capacitance-voltage (C-V) and impedance spectroscopy (IS) techniques to study charge transport, charge carrier recombination and charge collection efficiency in devices. A quantitative and qualitative analysis of the structural and surface aspects of sol-gel processed ZnO was done using X-ray reflectivity (XRR) and atomic force microscopy (AFM) techniques. On the basis of our understanding of the structural-property correlation in the sol-gel processed ZnO based inverted OSC devices, we developed an approach to engineer the ZnO layer by using an alternate precursor. Further, with the same precursor, we developed a PC61BM doped ZnO-organic hybrid cathode buffer layer and implemented in OSC devices. A self-assembled approach to realize an ideal p-i-n structure in conjunction with ZnO buffer layers is employed and investigated in inverted OSCs. Here, we have used a specifically designed a ternary active layer involving one donor (PTB7-Th) and two structurally different acceptors, ellipsoidal PC71BM and a spherical PC61BM. The inverted OSC devices having the ternary active layer with ZnO cathode buffer layer(s) are investigated to understand the impact of these improvisations on the electron transport and their collection. Further, the improved device performances and their electrical characteristics are interpreted in the context of structural and chemical changes occurred in ZnO buffer layer and at their interfaces.

In order to present a reliable study on the topic of our focus, we have used commercially available standard materials and their devices fabricated in ambient conditions. The stability of inverted OPV devices was verified to ensure ideal conditions for performing subsequent electrical characterizations.

The thesis is organized in seven chapters and we briefly describe their contents here-

Chapter 1 briefly introduces the research on organic solar cells, the current challenges in this area and the motivation of this thesis.

Chapter 2 discusses the selected organic semiconductor donor (D) and acceptor (A) and other materials used for the processing of ZnO buffer layer(s). Further, the fabrication of BHJ OSC for the two different material systems is described. The electrical, optical, structural and chemical characterization techniques used for characterization of materials and OSC devices are briefly introduced. Many of the device fabrication processes, in the ambient condition, and characterization techniques have been set-up and standardized during the course of this work which remains common to all the subsequent chapters.

Chapter 3 presents the standardization of fabrication of the inverted OSC device having a sol-gel processed ZnO buffer layer, their electrical characterization, and photovoltaic performance evaluation. In these devices, Molybdenum oxide (MoO_x) was used as an anode buffer layer. The inverted bulk heterojunction OSCs, for two donor copolymers (PDPP-TNT and PTB7-Th) with PC71BM (acceptor), were fabricated and characterized using J-V characteristics under dark and light, SCLC technique and results were analyzed. The stability of these devices was studied and ensured to perform further experiments for studying charge transport, their recombination, and collection at electrodes. To overcome the stability issue, we have encapsulated the devices using the microscopic cover slide and a binder glue. Through which the devices survived for more than two months and enabled us for further detailed studies.

In order to understand charge dynamics at the active layer/ZnO and ZnO/ITO interfaces, C-V and IS were performed and standardized on these devices. The IS data were analysed using equivalent model circuits and the fitting parameters, corresponding to the various physical mechanisms occurring in devices, were extracted. The charge carrier concentrations at the interfaces, built-in potential, electron and hole mobility, charge carrier lifetimes, and recombination characteristics were determined.

The PTB7-Th:PC71BM based OSCs demonstrate a high performance with the power conversion efficiency (PCE) of 6.4%. On the basis of the superior performance over PDPP-TNT and a low batch to batch variation of material, we have chosen PTB7-Th as a donor for our further studies.

Chapter 4 discusses the structural and surficial characteristics of sol-gel ZnO based PTB7-Th:PC71BM BHJ device architecture, and gives the insight about structural arrangements at the interfaces in the OSCs. After having adequate information about electrical interface parameters, we have used a non-destructive technique XRR for the detailed structural investigation at the buffer layer. XRR was done on the OSC devices using soft X-ray (wavelength, 80 Å) and found the presence of buried interface at AL/ZnO and MoO_x/AL structures. AFM is performed for further investigations, and their findings were interpreted to establish a structure-property correlation of electrode buffer layers in these devices.

Chapter 5 presents our approach to engineer ZnO cathode buffer layer. We have developed a low-temperature solution processed Diethylzinc (DEZ) precursor based ZnO and a PC61BM doped DEZ precursor based ZnO-PC61BM hybrid cathode buffer layers. The processing and a detailed electrical, optical, structural and chemical investigations of these cathode buffer layers are presented. A systematic efficiency enhancement in PTB7-Th:PC71BM inverted OSCs, having DEZ processed ZnO (PCE~8.0%) and DEZ:PC61BM processed ZnO-PC61BM cathode buffer layer (PCE~8.3%), is noticed. The inverted OSCs with our engineered cathode buffer layers show better fill factor than the devices with high-temperature treated zinc acetate (ZnAc) precursor processed ZnO.

The work function of ZnO:PC61BM layer is changed, towards the LUMO level of PC71BM, which is confirmed by scanning Kelvin probe microscopy (SKPM). In this case, the devices have shown an improvement in PCE with an increase in the short-circuit current (J_{sc}). X-ray photoelectron spectroscopy (XPS) and chemical analysis of ZnO:PC61BM suggest the presence of carbonyl group at the surface and attachment of Zinc atom to it which could be a possible cause for the observed interfacial modification. Further, work in this direction may pave the way for the interfacial engineering in OSCs, in general.

Chapter 6 discusses the characteristics of a strategically designed ternary active layer, having two structurally different fullerenes with PTB7-Th, based OSCs in conjunction with the cathode buffer layers discussed in the previous chapters. In this ternary active layer, an ellipsoidal PC71BM and a spherical PC61BM have a different precipitation kinetics which results in a downward percolation of PC61BM. Eventually, these self-assembled active layers favor formation of an ideal p-i-n kind of molecular assembly of donor and acceptor materials. The downward percolation of PC61BM may also modify AL/ZnO interface in devices.

The molecular organization of ternary BHJ active layer was investigated using Raman spectroscopy and AFM techniques. The inverted OSCs based on the ternary active layer shows a composition dependent efficiency and fill factor. The ternary blend devices with 20% PC61BM content exhibited the efficiency of 8.5% which is ~32% enhancement compared with the efficiency of the host PTB7-Th:PC71BM binary devices. A detailed C-V, impedance analysis and SCLC measurements of the binary and ternary devices confirm an improvement in charge transport and charge collection. A lowering in built-in potential and defect states can be attributed to a downward percolation of spherical PC61BM molecules towards BHJ/ZnO interface. A secondary ion mass spectroscopy (SIMS) experiments performed on a ternary BHJ AL/ZnO/ITO/Glass structure confirms our predicted molecular assembly of PTB7-Th, PC71BM, and PC61BM in devices. Our study also demonstrates that the molecular shape and size aspects of the third component in a fullerene-based ternary blend active layers in conjunction with the engineering of cathode buffer layer could be an important strategy to realize high performing OSCs.

Chapter 7 summarizes the results and their analysis cohesively in the context of engineering of cathode buffer layers in inverted OSC devices. The conclusions, based on the discussions from previous chapters, are also presented. Further, we believe that the work on low temperature processed PC61BM-doped ZnO will pave the way in achieving objectives of flexible OSCs.

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Abbreviations

AC	Alternating Current
Ag	Silver
Al	Aluminum
AFM	Atomic Force Microscopy
ABL (HTL)	Anode Buffer Layer (Hole Transport Layer)
AM	Air Mass
BE	Binding Energy
BHJ	Bulk Heterojunction
c-AFM	Conducting Atomic Force Microscopy
CA	Contact Angle
CBL (ETL)	Cathode Buffer Layer (Electron Transport Layer)
C-V	Capacitance-Voltage
$CHCl_3$	Chloroform
$CDCl_3$	Deuterated Chloroform
CPE	Constant Phase Element
CR	Confocal Raman
DI	De-ionized
DEZ	Diethyl Zinc
DIO	1,8-diiodooctane
D-A	Donor-Acceptor
EA	Ethanolamine
EQE	External Quantum Efficiency
FF	Fill Factor
FTIR	Fourier-transform Infrered
GIXRD	Grazing Incidence X-ray Diffraction
HOMO	Highest Occupied Molecular Orbital
IL-1	Interface Layer-1
IL-2	Interface Layer-2
I-V	Current-Voltage
J-V	Current Density-Voltage
IPCE	Incident Photon-to-Current Efficiency

ITO	Indium-doped Tin Oxide
IS	Impedance Spectroscopy
LUMO	Lowest Unoccupied Molecular Orbital
MEA	2-methoxy ethanol
MFM	Magnetic Force Microscopy
M-S	Mott-Schottky
Mo_2O_3	Molybdenum trioxide
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistor
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
OSC	Organic Solar Cell
ODCB	o-dichlorobenzene (1,2-dichlorobenzene)
PDPP-TNT	Poly{3,6-dithiophene-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c] pyrrole-1,4-dione-alt-naphthalene}
PTB7-Th	Poly{4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b ']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophene-4,6-diyl}
PC71BM	[6, 6]-phenyl-C71-butyric acid methyl ester
PC61BM	[6, 6]-phenyl-C61-butyric acid methyl ester
PCE	Power Conversion Efficiency
PSC	Polymer Solar Cell
PSPD	Position Sensitive Photodiode
SAM	Self-assembled Monolayer
SCLC	Space Charge Limited Current
SKPM	Scanning Kelvin Probe Microscopy
PVDF	Polyvinylidene Fluoride
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UV-Vis	Ultravoilet-Visible
XPS	X-ray Photoelectron Spectroscopy
XRR	X-ray Reflectivity
ZnAc	Zinc acetate
ZnO	Zinc Oxide