

CHAPTER-7
SUMMARY AND CONCLUSION

Bulk heterojunction OPV devices have a significant role in the development of high performing organic semiconductor based solar cells. Three major thrust areas of research have been enumerated in great details in the literature, namely, organic semiconductor materials, device architecture, and interface engineering. In recent years, a prominent focus has been on to devise ways to improve charge extraction through the development of new buffer layers and architectural change at the fundamental level. However, the understanding of the interaction of organic active layer with inorganic buffer layers (CBL and ABL) is still in infancy and highly desired to improve charge collection from the OPV devices. Several approaches have been applied to minimize the impediment of charge transport at the interfaces but eventually, such efforts are limited to difficulties in the processing.^{89-90,133} The present work has been motivated by the pressing need to establish the appropriate characterization techniques and to develop an environment-friendly low-temperature process for a cathode buffer layers. With this backdrop, we have worked on various processes and doped cathode buffer layers and tried to develop an understanding of the underlying physical phenomenon using a series of electrical, chemical, structural, and optical characterization techniques.

In this thesis, we have established the inverted OPV device fabrication in an ambient condition and studied the electrical and optical properties of the devices made with D-A type of conjugated polymers as active layer and sol-gel processed ZnO cathode buffer layer. Apart from this, X-ray reflectometry has been done to develop an understanding about interface layer formed between the organic active layer and inorganic CBL. We have done the systematic study of interfacial modifications using two different approaches. In the first method, we have applied the different route of ZnO processing as well as the controlled doping of ZnO layer with fullerene molecules.

Further, these CBLs were studied extensively using structural (AFM, and contact angle), optical (UV-Vis, Raman, and FTIR) and chemical (XPS, NMR, and SIMS) investigation techniques. The OPV devices were made using these CBLs and the performances were compared. In the second method, a top-down approach is implemented to improvise the morphology of active layer and the interfaces around. A ternary OPV devices were fabricated using the molecular-shape-induced phenomenon in an active layer having one donor and two acceptors (PC61BM and PC71BM). We have tried to analyze the morphological and interfacial changes in the devices, and hence the impact on the efficiency of OPV devices. During our studies, we have fabricated and characterized each set of the devices in more than 5 batches and the reproducibility of the data was ensured.

Study of inverted OPV device with ZnAc precursor based ZnO as CBL

In this section, we have studied the OPV devices based on two different donor polymers, an in-house synthesized donor polymer PDPP-TNT and a commercially resourced donor polymer PTB7-Th. In these devices, we have used ZnAc precursor based ZnO as CBL. The PDPP-TNT:PC71BM based OPV devices with 3.8% PCE were studied for charge transport and recombination parameters within the device by fitting the impedance measurement. The electron mobility and lifetime were estimated in the range of $1.3\text{-}3.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ and $0.03\text{-}0.25 \text{ ms}$ respectively and found similar to the results from well-established SCLC technique. Further, The V_{bi} and N_A were calculated using MS analysis as $\sim 0.77\text{V}$ and $1.5 \times 10^{16} \text{ cm}^{-3}$, respectively to understand the processes at PDPP-TNT:PC71BM/ZnO interface.

On the similar line, the PTB7-Th:PC71BM based OPV devices with optimized PCE of 6.4% were studied. The electron mobility using IS analysis was found $\sim 1 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which was in good agreement with mobility obtained from SCLC technique as well as the reported values in the literature. The V_{bi} and N_A were calculated using MS analysis as $\sim 0.96\text{V}$ and $1.2 \times 10^{17} \text{ cm}^{-3}$, respectively for PTB7-Th:PC71BM based OPV device. Further, the R_{rec} was found in the range of $10^3 - 10^4 \text{ }\Omega\text{-cm}^2$ for both PDPP-TNT:PC71BM based and PTB7-Th:PC71BM based OPV devices, similar to the reported results for D-A copolymers.

We have established the impedance spectroscopy technique for the determination of physical parameters related to the charge transport and recombination in and at the interface of the OPV devices. Further, the devices were tested for environmental stability. We found that the commercially resourced PTB7-Th:PC71BM based devices has better aspects as room temperature processable device for our further studies.

Structural determination of interfaces at active layer/CBL or ABL

In this section, we have used the non-destructive XRR technique to understand the structural evolutions at the interface of various layers in the OPV device which are responsible for charge transport and extraction. The XRR results indicate the formation of additional layer (IL-1) with different optical density at ZnO/BHJ interface. It confirms the infusion of PC71BM molecules on top of ZnO layer. Such infusion of acceptor molecule planarizes ZnO CBL at ZnO/BHJ interface. However, the XRR analysis at the MoO_x /BHJ interface shows the presence of another interface layer, IL-2. The optical density of which indicates the molecular interdiffusion of MoO_x into the active layer. Further, the surface topography analysis of ZnO and BHJ active layer were interpreted to establish the structure-property correlation. These

findings have provided an in-depth understanding of interface activities in the device, and was helpful in deciding our further experimental plans.

The first approach: Engineering of ZnO cathode buffer layer

In this approach, we have carefully chosen the set of modifications in ZnO CBL layer. The DEZ based ZnO was used to ensure the effects of precursor and processing variation on the OPV device performance. Further, the DEZ based ZnO was doped using PC61BM fullerene to improve CBL and the same was applied to OPV devices. On the basis of the detailed analysis of different CBLs and their devices, we demonstrate that OPV device efficiency has increased to $\sim 8.0\%$ with low temperature processed DEZ based ZnO (effect of precursor change) and $\sim 8.3\%$ for PC61BM-doped ZnO (effect of PC61BM doping) compared to an efficiency of $\sim 7.2\%$ efficient devices using ZnAc based ZnO.

The preliminary investigations have shown the enhancement in the optical band gap of DEZ based ZnO and PC61BM-doped ZnO (3.44 eV and 3.53 eV respectively). Also, the contact angle was found the maximum (55.6°) for DEZ based ZnO and reduced to 45.1° for PC61BM-doped ZnO. The topographical change has been observed along with work function modulation suitable for the charge transport, confirmed from SKPM mode of AFM. To correlate these results, the CBLs were further investigated. The XPS measurements have confirmed that the DEZ based ZnO surface has lowest stoichiometric ZnO ($R_A \sim 0.39$) which is attributed to higher contact angle. However, PC61BM-doped ZnO layer has shown the presence of PC61BM molecules at the surface with $R_A \sim 0.53$, confirms the cause of the reduction in contact angle. The other chemical measurements have indicated the formation of a new stable PC61BM-Zn complex.

The C-V analysis confirmed the lowering of defect states ($N_A = 4.05 \times 10^{16} \text{ #cm}^{-3}$) at the CBL/BHJ interface and hence reduction in built-in potential. The recombination resistance, obtained from IS measurement, increased significantly. It shows the better charge collection efficiency in the OPV devices with PC61BM-doped ZnO as CBL.

The second approach: Self-assembled improvised interfaces

We have designed an efficient ternary BHJ active layer involving one donor (PTB7-Th) and two structurally different fullerene acceptors, an ellipsoidal PC71BM and a spherical PC61BM, through a prior investigation of Raman spectroscopy and thin film morphology. The addition of PC61BM to host binary system, PTB7-Th:PC71BM shows a percolation of PC61BM molecules towards the bottom in ternary thin films and have potential to alter morphology to facilitate charge transport and collection. The inverted OPV devices based on the ternary active layer show 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 blend 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 by reducing built-in potential and defect states which is apparently happening due to a downward percolation of spherical PC61BM molecules in ternary active layers towards BHJ/ZnO interface. We demonstrate that the molecular shape and size aspects of the third component in a fullerene-based ternary blend active layers are an important factor to realize high performing OPV devices.

In summary, a cohesive interface engineering based self-assembled and artificially modified ZnO interfaces could be an ideal approach to improve OPV devices performances and stability.

Suggestions for further studies and concluding remarks

The methodological contribution towards the engineering of the cathode buffer layers in OPV devices in this work immediately suggests a line of investigation for further studies, which have been already initiated in our laboratory. The combined approaches with engineered ZnO in ternary devices need to be explored extensively to find the easily processable direct methods for the fabrication of high performing OPV devices. The similar work can be extended to modify the anode buffer layer and its interaction with the organic active layer.

XRR is a useful technique and needs to be extended for further investigation of structural aspects of interfaces in organic solar cells. Thus a combination of structural, chemical, and electrical characterization techniques could be a useful way to probe interfaces in organic electronic devices.

In this work, we have shown the two different approaches towards interfacial modification and applied on a single type of donor polymer system. The low temperature processed DEZ precursor based inorganic-organic hybrid ZnO cathode interlayer can be used to realize flexible solar cells. It needs to be extended to the different polymeric material systems in an attempt to find the ideal structure for OPV devices.

Schematically, I have presented an overview of the work done in this thesis as depicted in figure 7.1.

Figure 7.1. An overview of work presented in this thesis.

