Inverting the organic solar cell

M S Vaishnav, P Saranga, V R Harikrishnan, Abhiraj Gopinadh, S Jayaraj and P Predeep

Laboratory for molecular photonics and electronics (LAMP), Department of physics, National Institute of Technology, Calicut 673601, India

Department of Mechanical Engineering, National Institute of Technology, Calicut 673601

sarangssajeev@gmail.com

Abstract

The immediate requirement to reduce Green House Gas emissions and the diminishing petroleum reserves are forcing the world to switch into greener sources of energy. Organic Solar Cells are one of the most impressive solutions for the clean energy demands. They have interesting advantages which can be translate into potential applications in the future. It is due to this reason, that efforts to improve both the efficiency and stability of OSCs are garnering worldwide attention. But the conventional architecture has crippling disadvantages which impacts the performance of OSCs. This has led to a growing interest in OSCs with inverted architecture- a structure with the transparent electrode acting as cathode and high work function metal as anode. This review will go over the existing mechanisms and researches taking place in the fabrication of Inverted OSCs.

1. INTRODUCTION

The sun is our largest source of energy. It is estimated that the average solar irradiation on the earth surface is around 1050 W/m². Still, the contribution of solar energy in meeting the global energy demands remains limited. This is mainly due to the financial and technical difficulties associated with the fabrication and installation of Photo voltaic cells. In the practical scenario, Photovoltaic energy generation is almost synonymous with semiconductor based solar cells, with silicon dominating the market. They are being used by industries and households for decades. Even though advancements in solar cell technologies has helped Silicon solar cells to achieve higher efficiency and a substantial decline in prices, it is still not affordable by many, especially the ones living in poor or developing nations. Moreover, the requirement of vast expanses of land and related infrastructure imposes further barriers in its large-scale adoption. It is difficult to integrate Silicon solar cells into buildings, glass panes and other surfaces. Also, with the world shifting towards electric- vehicles, solar cells that can be integrated into automobile bodies with minimal effort and without ruining the aesthetics, are being sought for.

Another issue lies in the fabrication of semiconductor-based devices. The manufacturing methods are highly energy intensive. Melting Silicon and forming ingots require high temperature treatment, which offsets the very intention behind going for solar energy. Moreover, one can notice that silicon
solar cells have reached a certain saturation level, from which further breakthroughs in terms of performance are not expected.

Organic Solar cells, or Plastic solar cells as they are popularly known, consists of a polymer layer sandwiched between two electrodes. This polymer acts as the photovoltaic material instead of inorganic semiconductors used in conventional solar cells. OSCs can solve most of these aforementioned issues. Thinner solar cells which can be integrated into a wide variety of substrates can be made using such polymer-based materials. Transparent solar cells which can be integrated into buildings and automobiles may be one among the most lucrative applications of OSC technology. Availability of a wide variety of materials with different properties can help in fine tuning the range of spectrum which is to be absorbed. Also, their fabrication can be done at comparatively lower temperatures, or even at room temperature. Viability to fabricate them using simpler processes like industrial screen printing, can give a boost to productivity as well. It is possible to fabricate 1000-100,000 m² per day using such techniques. This is impressive because manufacturing silicon solar cells of similar area will require almost a year. Thus Organic Solar cells open a window of opportunities and a future of clean energy.

But everything is not so attractive about Organic Solar cells. It has comparatively lower Power Conversion Efficiency compared to inorganic semiconductor solar cells. Another major drawback is the stability of such solar cells. The shelf life or OSCs is pretty low in comparison with silicon solar cells. The materials used are sensitive to ambient conditions which leads to rapid degradation of such cells. There were many reports about the efforts to improve upon these deficiencies like Nano structuring of the absorbing layer, using additional buffer layers, inverting the device structure etc. Out of these the inverting the device structure brought much improvement in the efficiency and also simplified the fabrication process of OSCs (Figure 1). In this review various of aspects of inverting the device structure of OSCs are discussed.

2. EVOLUTION OF DEVICE STRUCTURE OF OSCS

![Figure 1](image)

**Figure 1** Evolution of device architectures of polymer-based solar cells: (a) single layer; (b) bilayer; (c) “disordered” bulk heterostructure; and (d) ordered bulk heterostructure. Adapted with permission from.[1] Copyright 2004 American chemical society.

When light falls upon the active layer, an exciton is formed, which is basically an electron- hole pair. This exciton diffuses through the material in which it is formed within its lifetime. The typical value of diffusion length in most of the polymers used falls somewhere between 5 and 20 nm. Excitons
formed in such polymers have binding energies falling between 0.1eV and 1eV. This necessitates a mechanism for the dissociation of excitons. In single layer Organic solar cells, the strong electric field at the depletion region of a Schottky contact helps in dissociation. But such single layered structures are seldom used in modern studies. This is due to the extremely low efficiencies recorded. Almost all of the modern OSCs use a donor and an acceptor as active layer.

Introduction of bilayer solar cells happens to be one of the most important improvements to OPV cells. As light is absorbed by the donor, an excited state is attained, from which electron is transferred to the Lowest unoccupied molecular orbital (LUMO) of the acceptor. The difference between ionization potential and electron affinity of donor and acceptor is what leads to this separation. This means that excitons have to reach a donor-acceptor interface within its lifetime. More the chances of an exciton reaching an interface, the more will be the efficiency. Thus, the efficiency of bilayer cells is limited by the fact that only those excitons formed near the junction contributes to current generation. This severe limitation has been overcome with the introduction of Bulk Heterojunction (BHJ) OSCs. In such solar cells, the donor and acceptor polymers are intimately mixed up, creating junctions throughout the bulk of the material, and hence the name bulk heterojunction. Therefore, excitons need not travel long distances before reaching a D-A interface leading to higher possibilities of charge separation and hence larger photocurrent and Power conversion efficiency (PCE). Using the state-of-the-art technologies, bulk heterojunction OSCs with PCE of about 10% have been fabricated.

Electrode choice also affects the efficiency and operation of OSCs (Figure 2a). The electrodes are usually modified by using buffer layers to improve charge induction properties and reduce energy barrier heights. One of the most common buffer layers used in the anode side is PEDOT: PSS (poly[3,4-(ethylenedioxy) thiophene]: poly (styrene sulfonate)). But this material can lead to etching of indium tin oxide (ITO) over a period of time, raising concerns with the device stability. Another issue with this device structure is the requirement of high vacuum deposition of low work function metal, which raises the fabrication costs. Also, the low work function metal gets degraded when exposed to ambient conditions. [2]

3. INVERTED DEVICE STRUCTURE

A major problem with conventional OSC device structure is the unfavorable Vertical Phase Separation. It is desired that the electron donor, which aids hole transportation should gradually distribute towards the anode and the electron acceptor which helps in transportation of electrons should distribute towards the cathode. But, due to the lower surface energy of donor materials, for instance, Poly(3-hexylthiophen-2,5- diyl) (P3HT), compared to that of electron acceptor component, for instance, PCBM, the donor layer tends to get distributed towards the surface. This is an unfavorable distribution for a regular cathode on top architecture[3].

Based on these considerations, an inverted structure was proposed in which the transparent ITO/(fluorine doped tin oxide)FTO now forms the cathode and a high work function metal forms the anode. [4] To ensure a reduced work function for the cathode, ITO has to be treated with appropriate material so as to form a composite electrode. With this structure, it is now possible to remove PEDOT: PSS at the ITO interface. Also, the high work function metal can be coated without vacuum deposition processes. Use of a high work function metal which does not degrade when subjected to ambient conditions, improve the overall lifetime of the cell, as well. Moreover, the Vertical Phase Separation occurring will be favorable for charge transportation. A typical Organic Solar Cell with inverted structure is shown in figure 2(b).
Figure 2 Structure of a typical OSC with (a) conventional architecture and (b) inverted architecture.

Inverted OSCs can be of two types- top illuminated and bottom illuminated. In top illuminated structure (Figure 3), the top layer should be semitransparent to allow reach the active layer. There will be a reflective electrode buried at the bottom. In one example, a layer of Aluminum is coated over glass, followed by a layer of Titanium. Active layer is coated over it, and the HTL above it. Finally, a grid layer of a high work function metal is coated which acts as the anode[5].

Figure 3. An example of a top illuminated Inverted OSC[5].

In the bottom illuminated configuration, we have a transparent electrode at the bottom, a buffer layer over it, to modify its work function. The active layer is deposited above it, followed by the hole transport layer (HTL) and then the high work function metal electrode. The electron transport layer (ETL) and the bottom electrode should be transparent and the ETL should be thin enough so that light can reach the active layer. Due to the difficulties in finding a suitable transparent electrode at the top,
most of the research is focused on bottom-illuminated configuration.

4. SELECTION OF ELECTRODES AND BUFFER LAYERS IN INVERTED ORGANIC SOLAR CELLS

The open circuit voltage is limited by the difference between highest occupied molecular orbital (HOMO) of the donor and LUMO of the acceptor. But the short circuit current is found to change when different materials are used as the top electrode. Cells with metals like Au, Ag, Pt, Cu etc. shows almost similar PCE and V_oc. But the ones with Al, Ca/Al etc. shows a lower PCE. The most promising results have been obtained for cells with Ag electrodes. Interestingly, cells with copper electrodes are also having similar efficiencies, which makes it possible to fabricate low cost solar cells. Moreover, using high work function metals as the top electrode can eliminate the requirement of high vacuum deposition, making fabrication easier. Also, they remarkably improve the stability of the cell.

Buffer layers are generally used to modify the work function of electrodes and to enable selective transportation of charges. Some interface layers to enable electron collection at the ITO side, are Ca, Cs2CO3, ZnO, TiO3 etc. These layers are to be made very thin to allow the passage of light to the active layer. Efficiency can be further improved by doping the ETL with salts like Cs2CO3 and SnCl2. These salts are used as sources of Cs or Sn dopants and they improve the charge extraction properties by modifying the energy level of the buffer layer[6]. Introducing an 1 mm layer of Ca at the ITO/C60 interface can improve the fill factor and PCE. This is because the calcium layer reduces the series resistance and increases the shunt resistance of the cell[7].

Since the solar cell performance can get degraded if the active layer comes into direct contact with the top metal electrode, hole transportation or electron blocking layers are deposited in between. Transition metal oxides like MoO3, WO3, V2O5 and conducting polymers like PEDOT: PSS, Semen persical decoction for purgation with addition (SPDPA) are used for this purpose. Cells are also being made with a combination of buffer layers- spin coating a thin film of MoO3 Nano particles between active layer and PEDOT: PSS. These cells offer better J_sc compared to the ones without MoO3.

5. IMPROVING CELL EFFICIENCY USING INVERTED STRUCTURE

Highly efficient inverted OSCs with around 9.2% efficiency has been fabricated (Figure 4) by using PFN to tune the properties of ITO cathode. The energy level alignment at the ITO/PFN interface is thought to be due to the formation of an interface dipole. This, in turn, helps in collection of electrons. Ag is used as the top electrode and MoO3 as the hole transport layer. These solar cells exhibit such a high PCE because of a combined effect of reduced bimolecular recombination and higher photon absorption. This cell, also has a 10% increase in J_sc value in comparison with the previous best. They retain their performance even after being exposed to ambient conditions for over 62 days, in comparison with regular structures that get degraded within 10 days. This shows that along with better performance, inverted OSCs also have a higher life time. [8]
Figure 4. Device structure and energy levels of the fabricated cell. (a) Schematic of the inverted OSCs, in which PFN-modified ITO is used as cathode and anode is Al, Ag-based. Energy level diagrams of (b) and regular structure (c) inverted cell fabricated, under flat band conditions. Adapted with permission from.[8] Copyright 2012 Nature publishing group.

6. STABILITY OF INVERTED OSCS

To study the stability of inverted OSCs in comparison with the conventional ones, unencapsulated solar cells of both types were maintained at ambient conditions and variation in their performance was noted down. The conventional cell with LiF/Al as its top electrode had its efficiency halved in a day and it got completely degraded within 4 days. On the other hand, the cell with inverted structure (Ag electrode) showed more or less a consistent performance even after a period of 40 days. The improved stability is thought to be due to the Ag electrode and PEDOT: PSS layer. The Ag electrode oxidized to form a silver oxide layer and thus the effective work function became -5.0 eV which matches with the HOMO of PEDOT: PSS (-5.1 eV).[9] Furthermore, the introduction of materials like TiO₂ as an electrode buffer layer has also improved the performance of Inverted OSCs since TiO₂ has a superior air-stability in comparison with other semiconductor oxides used.[10]
7. CONCLUSION

Organic solar cells made using inverted architecture shows better stability and efficiency compared to the conventional structure. It also allows much easier and better fabrication techniques for creating flexible solar cells over large areas. This reduces the fabrication costs and brings Organic Solar cells closer to commercial application. Moreover, application of different materials as buffer layers, further improves their performance. Also, tandem cells, made by integrating OSCs with silicon solar cells have achieved much higher efficiencies. Still, further research is required to improve the lifetime, efficiency and processability of OSCs.

References

[1] M. C. Kevin and M. D. Michael, “Conjugated Polymer Photovoltaic Cells,” Chem. Mater., vol. 16, no. 23, pp. 4533–4542, 2004, doi: 10.1061/9780784487059.062.
[2] K. Wang, C. Liu, T. Meng, C. Yi, and X. Gong, “Inverted organic photovoltaic cells,” Chem. Soc. Rev., vol. 45, no. 10, pp. 2937–2975, 2016, doi: 10.1039/c5cs00831j.
[3] I. I. Jeon and Y. Matsuo, “Vertical phase separation and light-soaking effect improvements by photoactive layer spin coating initiation time control in air-processed inverted organic solar cells,” Sol. Energy Mater. Sol. Cells, vol. 140, pp. 335–343, 2015, doi: 10.1016/j.solmat.2015.04.017.
[4] F. Zhang et al., “Recent development of the inverted configuration organic solar cells,” Sol. Energy Mater. Sol. Cells, vol. 95, no. 7, pp. 1785–1799, 2011, doi: 10.1016/j.solmat.2011.02.002.
[5] M. Glatthaar et al., “Organic solar cells using inverted layer sequence,” Thin Solid Films, vol. 491, no. 1–2, pp. 298–300, 2005, doi: 10.1016/j.tsf.2005.06.006.
[6] S. Nho et al., “Highly efficient inverted bulk-heterojunction solar cells with a gradiently-doped ZnO layer,” Energy Environ. Sci., vol. 9, no. 1, pp. 240–246, 2016, doi: 10.1039/c5ee03045e.
[7] F. J. Zhang, D. W. Zhao, Z. L. Zhuo, H. Wang, Z. Xu, and Y. S. Wang, “Inverted small molecule organic solar cells with Ca modified ITO as cathode and MoO3 modified Ag as anode,” Sol. Energy Mater. Sol. Cells, 2010, doi: 10.1016/j.solmat.2010.08.031.
[8] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, “Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure,” Nat. Photonics, vol. 6, no. 9, pp. 591–595, 2012, doi: 10.1038/n photon.2012.190.
[9] Z. Lin, C. Jiang, C. Zhu, and J. Zhang, “Development of inverted organic solar cells with TiO2 interface layer by using low-temperature atomic layer deposition,” ACS Appl. Mater. Interfaces, vol. 5, no. 3, pp. 713–718, 2013, doi: 10.1021/am302252p.
[10] L. Sun et al., “Simple solution-processed titanium oxide electron transport layer for efficient inverted polymer solar cells,” Thin Solid Films, vol. 573, pp. 134–139, 2014, doi: 10.1016/j.tsf.2014.11.011.