Studies on Effect of Interface Layer at the Organic-Cathode Interface on PCE of OSCs

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The effect of exciton blocking layer (EBL) on the performance of bilayer copper pthalocyanine (CuPc)/fullerene (C_{60}) photovoltaic devices is studied and the results are presented here. CuPc and C_{60} are the electron donor and acceptor respectively. The application of EBL enhances the fill factor (*FF*) and short circuit current (J_{sc}), which results in the enhancement of the overall efficiency of the devices. Bathocuproine (BCP) and bathophenanlthroline (BPhen) are used as the EBL materials in these studies. With respect to the standard device (device containing no EBL), an enhancement of ~ 48 times in efficiency is observed for the device containing BCP. The application of BPhen in place of BCP enhances further the efficiency by ~ 70 %, which is attributed to better electron transportation through BPhen.

Keywords: Exciton blocking layer (EBL), Fill factor (FF), Organic semiconductors (OSCs).

1. INTRODUCTION

An OSCs can be prepared by using a single light absorbing organic layer between two electrodes but it will possess low efficiency due to a variety of reasons. We can understand all these reasons only by understanding the device mechanism. For example, low absorption by a single layer and generation of charge carriers only in a thin layer near the meta-organic interface results such devices to be intrinsically inefficient and low quantum yield of charge photo generation. Exciton quenching at metal-organic interfaces [1] can also reduce photocurrent yields. The most successful OSCs are based on charge generation at the interface between donor and acceptor materials. Our main objective is to study the effect of different interface layers on the performance of bi-layer OSCs. Interfaces among the organic layers and between organic and metal electrodes play a very important role in the determination of device performance and its improvement. The interface layers introduced at different interfaces can serve different purposes like enhancement in J_{sc}, V_{oc}, *FF* resulting enhanced efficiency and life time. In this paper our objective was to improve the performance of OSCs via introduction of interface layers at the organic and metal cathode interface. The results with insertion of different interface layers are discussed below in detail.

2. EXPERIMENTAL DETAILS

It has been found that CuPc, H_2Pc and ZnPc phthalocyanines are quite suitable for photovoltaic studies. The devices based on phthalocyanine were fabricated on cleaned

Received: 10.05.18; Accepted: 12.05.18

and pre-patterened indium tin oxide (ITO) coated glass substrates in ITO/Pc/C_{60}/Al configuration. The investigations were carried out on the optimized devices without interface layers. The optimized layer thicknesses/configuration for CuPc, H_2Pc and ZnPc based materials were found to be ITO/H_2Pc(23nm)/C_{60}(40nm)/Al(150nm) (**Device 1**), ITO/CuPc(20nm)/C_{60}(40nm)/Al(150nm) (**Device 2**) and ITO/ZnPc(25nm)/C_{60} (37nm)/Al(150nm) (**Device 3**), respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the dark and illuminated *J-V* characteristics of **Device 1** at room temperature. The device was illuminated with a tungsten halogen lamp irradiance of ~ 80 mW/cm^2. The device exhibited J_{sc} = 0.58 mA/cm^2, V_{oc} = 0.27 V, FF = 31 % and η = 0.06 %. This device exhibited very poor performance and a detailed analysis of the dark *J-V* characteristics resulted into determination of series resistance (R_s) = 20.3 Ω, shunt resistance (R_{sh}) = 4.4 x 10^3 Ω, with rectification ratio of 4.6x10^2 at ± 1 V. Under illumination the series and shunt resistances were calculated to be 18.4 and 1.5x10^3 Ω respectively. The change in the series and shunt resistances can be attributed to the change in conductivity of the active layer due to photo-generated charge carriers.

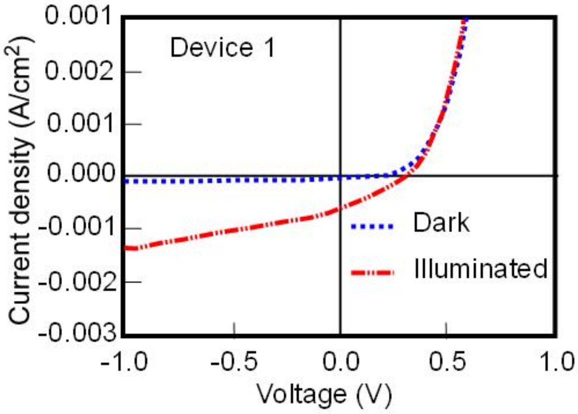

Fig. 1: Dark and illuminated J-V characteristics of the Device 1 (under illumination intensity of ~ 80 mW/cm^2).

Based on the analysis of dark and illuminated *J-V* characteristics of **Device 2** at room temperature it was observed that this device exhibited very poor photovoltaic performance with the J_{sc} = 0.19 mA/cm^2, V_{oc} = 0.35 V, FF = 10 % and η = 0.01 %. This device exhibited very poor rectification ratio of 0.35 at ± 1 V. As expected the series and shunt resistance were observed to change from 22x10^3 to 14x10^3 Ω and 1.8x10^5 to 6.3x10^2 Ω respectively. From the analysis of dark and illuminated *J-V* characteristics of **Device 3** at room temperature it was observed that this device also exhibited poor photovoltaic performance with J_{sc} = 0.6 mA/cm^2, V_{oc} = 0.31 V, FF = 30 % and η = 0.06 %. The device exhibited the R_s and $R_{sh}$to be 183 and 2339 Ω respectively, which changed to 141 and 960 Ω respectively after illumination. The device exhibited very poor rectification ratio of 0.63 at ± 1 V.

From the results discussed above it can be concluded that performance of these devices was not good and a better geometry/configuration is required for enhanced efficiency. For that purpose we introduced different interface layer at different places and observed tremendous enhancement in the efficiency. Interface layer was introduced at the organic and metal interface which worked as the exciton blocking layer (EBL). Due to the thermalization and fast rate of evaporation of hot metal cathode the surface defect states are produced at the organic-cathode interface. These surface states result in the quenching of excitons. To prevent the quenching of excitons the active region should sufficiently be far away from the cathode interface. The insertion of an interface layer, which does not absorb the incident light and does not allow the diffusion of the excitons to the cathode interface, confine the excitons within the active layer and it may be one of the effective approaches for efficient device fabrication. Such layers are called exciton blocking layers (EBL). Application of EBL in small molecular OSCs has proved to be an efficient approach [2]. EBL prevents the migration of excitons to the cathode interface, which reduces exiton quenching at the cathode and more exiton contribute to the generation of electricity. Bathocuproine (BCP) is a very important material for such applications. We have carried out the studies on the performance of OSC devices using Bathophenanthrolene (BPhen) as the EBL and the results are compared with those containing BCP. The device containing BPhen showed enhanced efficiency compared to that incorporating BCP. The devices fabricated for these studies are designated as **Devices 4**, **5**, **6** and **7** and the configurations are as follows:
Device 4: ITO/CuPc (20nm)/C_{60} (40nm)/BCP (8nm)/ Al (120nm).
Device 5: ITO/CuPc (20nm)/C_{60} (40nm)/BPhen (8nm)/Al (120nm).
Device 6: ITO/H_2Pc (23nm)/C_{60} (40nm)/BPhen (8nm)/Al (120nm).
Device 7: ITO/ZnPc (25nm)/C_{60} (37nm)/BPhen (8nm)/Al (120nm).

The *J-V* characteristics of the devices have been studied in dark and under tungsten halogen lamp illumination at irradiance of ~ 80 mW/cm^2, using a programmable Keithley 2420 source meter unit interfaced with computer. The lower performance of **Device 1**, **2**, **and 3** are attributed to the interface defect states which are generated in organic layer at the time of deposition of hot metal over organic layer. The metal cathode diffuses into the organic layer which may result shorts in the devices. Standard devices showed almost no rectification, which can be attributed to the very high series resistance (including the contact resistance between C_{60} and Al cathode) and very low parallel resistance.

Energy level diagram of different device are shown in Figure 2. It is supposed that improvement in performance with EBL will be difficult as EBL introduces a very high energy barrier for collection/injection of electrons between C_{60} and Al cathode. For example BCP has very high ionization potential (HOMO ~ 7.0 eV) and low electron affinity (LUMO ~ 3.5 eV). The LUMO energy level of C_{60} lies below that of BCP. It is expected that the application of BCP will introduce a barrier for electron injection from C_{60} to BCP. Because of very high electron and hole injection barriers from C_{60} to EBL the excitons do not diffuse to cathode and remain in the C_{60} layer only.

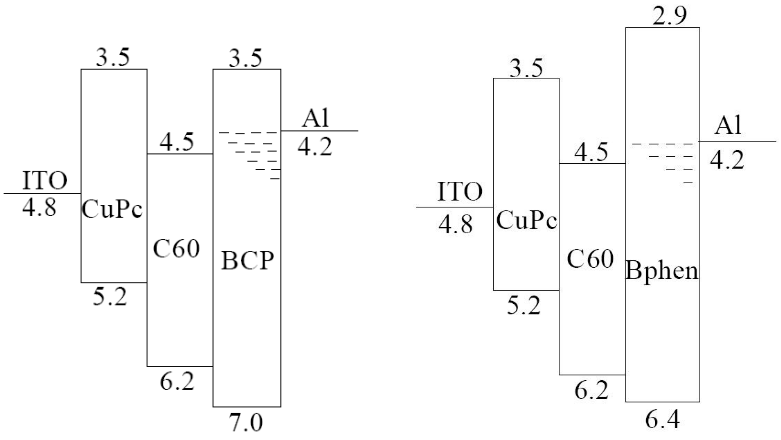

Fig. 2: Schematic energy level diagram of the devices incorporating EBLs.

Figure 3 shows the *J-V* characteristics of **Devices 4** in dark and under illumination. By the insertion of interface layer at organic/metal interface the rectification ratio was observed to increase. **Devices 4** to **7** shows improved rectification ratio of 7.18×10^2, 3.26×10^2, 3.01×10^2 and 7.18×10^2 at ±1 V respectively. It is clear evidence that the introduction of EBL in **Devices 4** to **7** improves the organic/cathode interface, which reduces the series resistance and enhances shunt resistance. Analysis of the dark and illuminated *J-V* characteristics of **Device 4** at room temperature showed that this device exhibits improvement in photovoltaic performance with J_{sc} = 2.5 mA/cm^2, V_{oc} = 0.35 V, FF = 43 % and η = 0.48 %. This device exhibited the series (R_s) and shunt resistance (R_{sh}) o be 13 and $85 \times 10^3\,\Omega$ respectively. Therefore insertion of EBL layer at the organic-cathode interface improves the performance of OSCs.

Even with high injection barrier in **Device 4**, the high performance in dark and under illumination compared to **Device 2** suggests improved electron injection/collection. The reason behind can be understood as follows. The thermalization of the hot metal cathode on EBL induces some defect states in energy band gap of EBL, which help the electron injection/collection between cathode and EBL [3]. These observations suggest that the electron transport across BCP is mainly through the defect states blow the LUMO, induced during the deposition of metal cathode. The application of BCP results in an enhancement in J_{sc} and FF that in turn results in enhanced efficiency. The enhanced J_{sc} can be attributed to the blocking of excitons and their confinement in the active layer that assists their dissociation in the active layer.

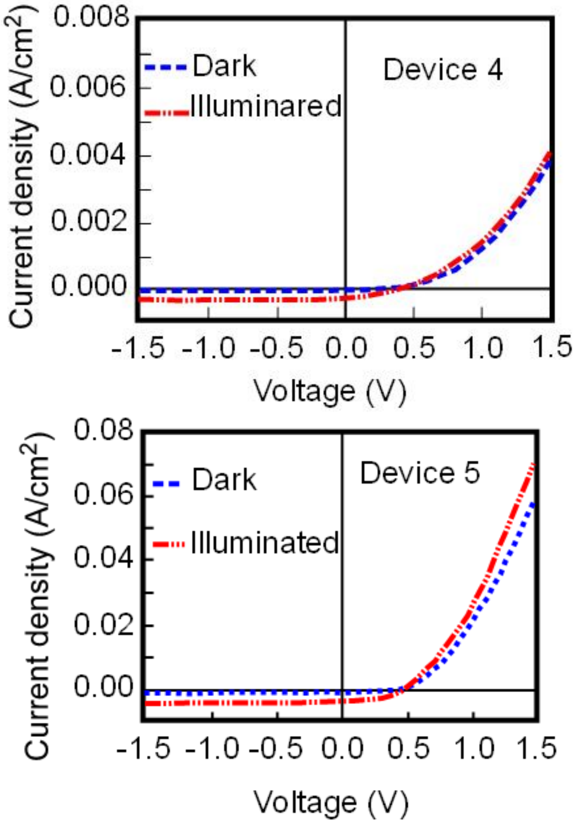

Fig. 3: Dark and illuminated *J-V* characteristics of the **Device 4, Device 5**.

Application of BCP lowers the series resistance (especially organic/cathode interface resistance) of the device, which results in the enhanced fill factor. We have taken 8 nm as the optimum thickness of BCP. The performance of the devices got deteriorated when the thickness of BCP was increased beyond 10 nm. These observations suggest that the defect states in BCP are induced only within the range of 10 nm. When the thickness of BCP is increased beyond 10 nm, the additional thickness (where defect states are not induced) introduces additional series resistance and electrons will have to face the interface barrier to inject from C_{60} to BCP, which is responsible for the poor performance of the devices. Ultimately the electrons are to transport through EBL to reach the cathode. Therefore the electron transport through BCP limits the efficiency of these devices. The use of an EBL with high electron mobility is expected to further enhance the efficiency of OSCs. Keeping this idea in our mind we employed BPhen in place of BCP. Figure 3 also shows the *J-V* characteristics of **Device 5** in dark and under illumination. **Device 5** includes BPhen instead of BCP. For the comparative studies the thickness of BPhen has also been taken to be 8 nm. The application of BPhen has been observed to be more efficient compared to BCP.

From the analysis of dark and illuminated *J*-*V* characteristics of **Device 5** at room temperature it was observed that this device exhibits good photovoltaic performance with J_{sc} = 2.7 mA/cm^2, V_{oc} = 0.5 V, *FF* = 43.5 % and η = 0.65 %. The device exhibited the R_s and R_{sh} to be 30 and 103x10^3 Ω respectively, which changed to 110.35 and 3620 Ω respectively after illumination. The enhanced performance of **Device 5** compared to **Device 4** can be attributed to the application of BPhen in place of BCP. An interesting feature which we have observed in these studies is ~ 40 % reduction in V_{oc} on the application of BPhen compared to BCP. The origin of V_{oc} in OSCs is not well understood. It has been suggested that usually V_{oc} in OSCs depends either on the difference between HOMO of the donor and LUMO of the acceptor [4,5] or on the difference of the work function of anode and cathode used [6]. In the present studies neither we have changed the donor-acceptor materials nor the electrodes, still a reduction in V_{oc} on the application of BCP suggests that there may be some other factor, which may be playing an important role in determining the V_{oc}. BPhen is a wide band gap (~ 3 eV) material with HOMO and LUMO levels at ~ 6.4 eV and 2.9 eV respectively and blocks the exciton diffusion to the cathode. The enhanced efficiency in **Device 5** can be attributed to the improved transportation of the photo generated electrons through EBL to the cathode. The electron mobility in BPhen is ~ 10^{-4} cm^2/Vs, which is almost two orders of magnitude higher than that in BCP (~ 10^{-6} cm^2/Vs) [7,8]. The much higher electron mobility in BPhen leads to better electron transport through the EBL and therefore increases the efficiency of OSCs.

A similar behaviour was observed in **Device 6** and **Device 7** which incorporated EBL at interface between H_2Pc/C_{60} (in **Device 1**) and $ZnPc/C_{60}$ (in **Device 3**) respectively. When we analyse the dark and illuminated *J*-*V* characteristics of **Device 6** it is observed that this device exhibited improvement in photovoltaic performance with the J_{sc} = 2.3 mA/cm^2, V_{oc} = 0.4 V, *FF* = 40 % and η = 0.53 %. This device exhibited the R_s and R_{sh} to be 32.3 and 38.4x10^3 Ω respectively, which changed to 19.3 and 1466 Ω respectively after illumination. Analysis of dark and illuminated *J*-*V* characteristics of **Device 7** shows that that this device exhibited improvement in photovoltaic performance with the J_{sc} = 5.6 mA/cm^2, V_{oc} = 0.5 V, *FF* = 40 % and η = 1.4 %. This device exhibited the R_s and R_{sh} to be 9.4 and 38.7x10^3 Ω respectively, which changed to 6.1 and 1380 Ω respectively after illumination.

4. CONCLUSION

We have introduced thin interface layers at the organic-metal interface and organic-organic interface. The interface layer introduced at organic-metal interface exhibited large band gap and did not absorb in the visible range. Due to high ionization potential and low electron affinity this layer worked as EBL and enhanced the efficiency of solar cells. Application of EBL with better charge carrier mobility improved the performance further. An interface layer absorbing in different spectral range introduced at the organic-organic donor-acceptor interface enhanced the performance further. This enhancement in efficiency has been attributed to the enhanced absorption and improved photon harvesting in the device. As such these results show that by the introduction of suitable interface layer at different places the efficiency of the OSCs can be enhanced further.

5. ACKNOWLEDGMENT

This work done at the time of Ph.D. I would like to pay my heartfelt gratitude to my supervisor Dr. S. Chand for their kind help and support. I heartily thank him for providing me the facilities and a healthy working environment at NPL.

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