Active Layer Thickness Optimization for Maximum Efficiency in Bulk Heterojunction Solar Cell

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Abstract. Organic solar cell (OSC) is one of the best promising candidate for harvesting energy mainly due to their simple and economic fabrication process, the reduced manufacturing cost, and easy integration to other products. Bulk heterojunction solar cell in which the active layer is a blend of donor –acceptor materials are one of the best organic photovoltaic device with highest efficiency and a significant improvement in the device performance occur over last years. Bulk heterojunction architecture gives a high interfacial surface area for efficient charge dissociation. In this study, bulk heterojunction solar cell is simulated using General Purpose Photovoltaic Device Model Software. A donor- acceptor blend of Zinc pthalocyanine (ZnPc) fullerene C60 is used as the active layer. The power conversion efficiency for various thickness of the active layer is studied. Optimization of active layer thickness for maximum power conversion efficiency are done. The dependence of various electrical parameters such as short circuit current density (J_{sc}), Open circuit voltage (V_{oc}), fill factor (FF),average carrier mobility on power conversion efficiency are also studied.

1. Introduction
Organic solar cells (OSCs) comes in the third generation solar cells where solar cells being categorised into first second and third generation solar cells and light absorbing layer is the carbon based (organic polymer) material [1, 2]. Bulk heterojunction (BHJ) (organic) solar cells are applicable for the large scale device fabrication. Simple and economic fabrication process, device stability, mechanical flexibility, device performance makes the organic solar cell technologies scalable. The attractive unique properties of organic semiconductors including their low cost production, and lasers fabrication can be done using OSCs with high feasibility and efficiency. The organic molecules which is the building block of organic semiconductor are formed by π conjugated system [3]. Tang proposed the first two-component OSC in 1986 from the observation of photoelectric effect in the Tang cell [4]. The efficiency of two component OSC was very low [5]. This drawback was solved by the advent of bulk heterojunction (BHJ) solar cells in 1995 by Heeger and co-workers[6]. The active layer of a BHJ solar cell is a combination of a donor and acceptor material mixed in nanoscale [7, 8]. This gives required thickness for absorption and an appropriate diffusion distance across the active layer. The probability of charge dissociation is increased in bulk heterojunction architecture because of the increased interfacial surface area. Many researches have done since that time to discover new acceptors and donors and on their morphology.

This report consolidates bulk heterojunction (BHJ) solar cell simualtionalongwith ITO/PEDOT: PSS/ZnPc: C60/Al device structure. The active layer used is amixture of fullerene C-60 and Zinc
Phthalocyanine in the ratio 1:1. Furthermore the HTL (hole transporting layer) constitutes PEDOT: PSS, ITO (indium tin oxide) takes place of the transparent front contact and as the metal back contact Aluminium is used. The four isoindole units which provide conjugated 2 dimensional π electron system is the core structure of Zinc phthalocyanine (ZnPc) macrocycle. The trouble free synthesizing of ZnPc and its non-toxicity towards environment makes it a promising applicant in solar cell applications. ZnPc has high thermal and photo chemical stabilities. Phthalocyanine is enormously used as the donor material in the OSCs field [9]. Good carrier transport, high short circuit current density and efficiency is achieved using the best combination of C-60 as the electron acceptor. Organic solar cells with high power conversion efficiency can be fabricated using the blend ZnPc: C-60. In this study, thickness of the active layer ZnPc: C-60 is varied from 50nm to 500nm and the corresponding efficiencies are reported. The dependence of power conversion efficiency on parameters like open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), fill factor (FF) of the bulk heterojunction (BHJ) solar cell with the variation in active layer thickness is determined using the electrical simulation in the General Purpose Photovoltaic Device Model (GPVDM) software. Such an analysis will help the experimental scientist to optimise the active layer thickness of their device.

2. GPVDM Software

General Purpose Photovoltaic Device Model (GPVDM) Software is a general-purpose tool (free), which is used in simulating opto-electronic devices like solar cells, LEDs, diodes, FETs. During its initial time GPVDM is used to simulate the organic solar cell but now it is developed to simulate crystalline silicon solar cells, organic LEDs (OLEDs), a-Si solar cells, organic Field Effect Transistors (OFETs), CIGS solar cells [10]. GPVDM solves the poisson equation, carrier continuity equation using finite difference method. It solves the equation of drift diffusion and also solves the optical equation by applying the ray tracing or transfer matrix method [11]. The equations used to simulate the device is shown as equations 1-5.

\[
\frac{d}{dx} \varepsilon_0 \varepsilon_r \frac{\partial \phi}{\partial x} = q(n - p) \quad (1)
\]

\[
J_n = q\mu_n \frac{\partial E}{\partial x} + qD_n \frac{\partial n}{\partial x} \quad (2)
\]

\[
J_p = q\mu_p \frac{\partial E}{\partial x} - qD_p \frac{\partial p}{\partial x} \quad (3)
\]

\[
\frac{\partial J_n}{\partial x} = q(R_n - G + \frac{\partial n}{\partial x}) \quad (4)
\]

\[
\frac{\partial J_p}{\partial x} = -q(R_p - G + \frac{\partial p}{\partial x}) \quad (5)
\]

3. Electrical parameters

In this work, a bulk heterojunction (BHJ) solar cell having an active structure ITO/PEDOT: PSS/ZnPc: C60/Al is simulated. This BHJ organic solar cell device contains 4 layers. The front contact transparent layer is ITO of thickness 140nm and the n-k values are also imported from the reference [12]. The polymer contact layer is PEDOT: PSS of thickness of 100nm and the n-k values of PEDOT: PSS is extracted from the reference [13] and imported to GPVDM. The metal back contact layer is Aluminium of thickness 100nm and their n-k values are extracted from the reference [14]. The active layer is the mixture of fullerene C-60 and Zinc phthalocyanine (ZnPc)(1:1). The n-k values of ZnPc: C-60 is imported to the GPVDM from the reference [15]. The thickness of the active layer ZnPc: C60 is ranged from 50nm to 500nm by a step of 50. The efficiencies corresponding to each thickness is noted [16]. The electrical parameters like open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), and fill factor (FF), average carrier mobility are to be determined. The device structure of simulated bulk heterojunction solar cell for 300 nm thickness ZnPc: C60 is shown in figure 1.
4. Results and Discussion

4.1. Electrical Parameters and Power Conversion Efficiency of Simulated BHJ Solar Cells

The power conversion efficiency and some of the electrical parameters such as short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), voltage (maximum power) ($V_{max}$), current density (maximum power) ($I_{max}$), maximum power ($P_{max}$) and average carrier mobility of simulated ITO/PEDOT: PSS/ZnPc: C60/Al bulk heterojunction solar cells of different thickness of ZnPc: C-60 active layer is shown in table 1.

| Thickness (nm) | $V_{oc}$ (V) | $J_{sc}$ (mAcm$^{-2}$) | FF  | $V_{max}$ (V) | $J_{max}$mAcm$^{-2}$ | Max power (mW) | Average Carrier mobility(m$^2$V$^{-1}$s$^{-1}$) | Efficiency (%) |
|----------------|--------------|------------------------|-----|---------------|----------------------|----------------|-----------------------------------------------|----------------|
| 50             | 0.56         | 5.24                   | 0.76| 0.48          | 4.68                 | 22.22          | 8.85                                          | 2.22           |
| 100            | 0.56         | 10.77                  | 0.73| 0.45          | 9.84                 | 44.07          | 9.21                                          | 4.40           |
| 150            | 0.55         | 11.31                  | 0.71| 0.45          | 9.84                 | 44.13          | 8.26                                          | 4.41           |
| 200            | 0.54         | 12.17                  | 0.67| 0.43          | 10.42                | 44.67          | 8.11                                          | 4.47           |
| 250            | 0.54         | 15.90                  | 0.57| 0.41          | 12.04                | 48.87          | 8.00                                          | 4.89           |
| 300            | 0.54         | 16.21                  | 0.56| 0.41          | 12.10                | 49.17          | 7.87                                          | 4.92           |
| 350            | 0.54         | 15.71                  | 0.55| 0.41          | 11.53                | 46.86          | 7.73                                          | 4.68           |
| 400            | 0.54         | 15.23                  | 0.57| 0.41          | 11.45                | 46.82          | 7.62                                          | 4.68           |
| 450            | 0.54         | 15.18                  | 0.57| 0.41          | 11.37                | 46.62          | 7.52                                          | 4.66           |
| 500            | 0.54         | 14.04                  | 0.61| 0.41          | 11.18                | 45.88          | 7.44                                          | 4.59           |

4.2. Variation of Average Carrier Mobility with Thickness

The carrier mobility increases from 50nm to 100nm then keeps on decreasing for all thickness. Figure 2 shows the variation of carrier mobility with thickness. The maximum value for average carrier mobility is obtained for the BHJ OSC simulated at 100nm thickness of ZnPc: C-60, which is equal to 9.21x10$^{-8}$ m$^2$ V$^{-1}$s$^{-1}$. The decrease in carrier mobility is due to the increased blend thickness [17].
4.3. Disparity of Open Circuit Voltage with Thickness
Varying thickness did not affect the open circuit voltage much. Almost $V_{oc}$ remains constant over the thickness only slight changes are noted before 100 nm thickness of the active layer. $V_{oc}$ value shows notable variation up to 200 nm and thereafter remains constant. The slight decrease in $V_{oc}$ is due to the decreased crystallinity which increases the defect density and hence decreased average carrier density at $V_{oc}$ [10]. The figure 3 shows the active layer thickness dependence of open circuit voltage ($V_{oc}$) of simulated ITO/PEDOT: PSS/ZnPc: C60/Al BHJ OSC.

4.4. Disparity of Short Circuit Current Density ($J_{sc}$) with Thickness
Thickness variation makes a noteworthy change in short circuit current density ($J_{sc}$). As thickness increases from 50nm to 500nm, the short circuit current density also upsurges up to 300 nm and then as the thickness increases the short circuit current density gets decreased. The maximum short circuit current density obtained is at 300 nm of 16.21 mA/cm$^2$. The increase in $J_{sc}$ from 50nm to 300nm is due to the increased charge carriers which are created by the absorption of light. The short circuit current variation ($J_{sc}$) with active layer thickness of ITO/PEDOT: PSS/ZnPc: C60/Al BHJ OSC is shown in the figure 4.
Figure 4. Disparity of Short circuit current density ($J_{sc}$) of ITO/PEDOT: PSS/ZnPc: C60/Al bulk heterojunction solar cell with varying thickness of active layer

4.5. Variation of Power Conversion Efficiency with Thickness

By simulating ITO/PEDOT: PSS/ZnPc: C60/Al BHJ organic solar cell for different thickness of ZnPc: C60, it is clearly understood that efficiency of the BHJ OSCs is dependent on thickness of the photo active layer (ZnPc: C60). At 300nm efficiency is maximum (4.92%). Fig 5 shows that as the thickness of the active layer varies from 50 nm to 300 nm the efficiency of BHJ OSCs increases and indicates maximum at 300 nm and again decreases as the thickness increases beyond 300 nm. This may be due to the efficiency dependence on various parameters like open circuit voltage, short circuit current density, fill factor etc. The variation in efficiency with active layer thickness shows similar pattern to variation in efficiency of short circuit current density with thickness. Thus efficiency variation with thickness can be explained in terms of short circuit current density. It increases from 50 nm to 300 nm thus it increases the efficiency while after 300 nm the short circuit current density shows a decreasing pattern with increasing thickness which decreases the efficiency beyond 300 nm. The decrease in average mobility as shown in the figure 2 can also decreases the efficiency. The maximum short circuit current density ($J_{sc}$) is 16.21mA/cm$^2$ which corresponds to the maximum efficiency 4.92% at 300nm. Thus the optimum thickness obtained is 300 nm of active layer ZnPc: C60.

The increase in efficiency with variation of the thickness from 50 nm to 300 nm is due to the larger absorption area of the photoactive layer which increases the incident photons and hence the generated excitons. After 300 nm increase of thickness decreases the efficiency which is due to the decrease in short circuit current density, and the recombination of charge carriers. Also the $V_{oc}$ value is slightly decreasing after 300 nm thickness. $V_{oc}$ shows the difference in energy between the HOMO of the donor and LUMO of the acceptor levels. Thus a decrease in $V_{oc}$ value reduces the HOMO-LUMO energy levels which can reduce the exciton dissociation. This reduced exciton dissociation can reduce the carriers and hence decreases the efficiency. The decrease in $V_{oc}$ can also increases the recombination. Thick absorbents can maximize the absorption, while the thickness should be less then the selected diffusion length for enhancing the charge collection. Therefore, the thickness greater than the optimum thickness can reduce the charge collection thus reduces the efficiency.
4.6. Current Density -Voltage Curves (J-V Curves)
Current density voltage (J-V) plots of the devices for ZnPc: C60 active layer is shown in figure 6. It is observed that the current density at zero voltage (J\textsubscript{sc}) remains constant over a voltage range then increases and reaches at zero at a particular voltage (open circuit voltage). At 300nm, the current density at zero voltage is 16.21 mA cm\textsuperscript{-2} and then it increases and reaches zero at 0.54V. At 50 nm the current density at zero voltage is 5.24 mA cm\textsuperscript{-2} and reaches zero at 0.56V. At 100nm the current density at zero voltage is 10.77 mA cm\textsuperscript{-2} and reaches zero at 0.56V. At 150nm current density at zero voltage is 11.31 mA cm\textsuperscript{-2} and reaches zero at 0.55V. At 200nm current density at zero voltage is 12.17 mA cm\textsuperscript{-2} and reaches zero at 0.54V. At 250nm, current density at zero voltage is 15.9 mA cm\textsuperscript{-2} and reaches zero at 0.54 V. At 350nm current density at zero voltage is 15.71 mA cm\textsuperscript{-2} and reaches zero at 0.54V. At 400nm current density at zero voltage is 15.23 mA cm\textsuperscript{-2} and reaches zero at 0.54V. At 450nm current density at zero voltage is 15.18 mA cm\textsuperscript{-2} and reaches zero at 0.54 V. At 500nm current density at zero voltage is 14.04 mA cm\textsuperscript{-2} and reaches zero at 0.54 V. From the plot also J\textsubscript{sc} is maximum for 300nm thickness of ZnPc: C-60 active layer of OSC.

4.7. Basic electrical parameters of the simulated BHJ Organic Solar Cell
The figure 7(a) shows the charge density voltage relation of ITO/PEDOT: PSS/ZnPc: C60/Al at 300nm. At 0V the charge density 1.71×10\textsuperscript{22} m\textsuperscript{3} from 0.3V there is notable increase in charge density. Figure 7(b) shows the total charge density voltage relation. The total charge contributed by both electrons and holes. At 0V the total charge density is 2.22×10\textsuperscript{22} m\textsuperscript{3}. The Figure 7(c) shows the current voltage relation of ITO/PEDOT: PSS/ZnPc: C60/Al at 300 nm. At 0V the current is 0.97 mA. Beyond 0.4 V there occur a notable increase in the current and at 0.57V current becomes zero.
5. Conclusion

ITO/PEDOT:PSS/ZnPc:C-60/Al bulk heterojunction solar cell is simulated for various active layer thickness (50 nm- 500nm with a difference of 50 nm). The power conversion efficiency along with the other electrical parameters such as open circuit voltage, short circuit current density ($J_{sc}$), fill factor, average carrier mobility are noted. The maximum obtained power conversion efficiency is 4.92% for 300nm optimum thickness of ZnPc: C-60 active layer of ITO/PEDOT: PSS/ZnPc: C-60/Al bulk heterojunction solar cell. The power conversion efficiency continuously increases from 2.22 % at 50 nm to 4.92% at 300nm and thereafter it decreases. The dependence of open circuit voltage($V_{oc}$), Short circuit current density ($J_{sc}$), fill factor(FF), average carrier density is studied. It was detected that short circuit current density is growing with thickness up to 300nm of the active layer thickness in simulated bulk heterojunction (BHJ) solar cell and thereafter decreases. Showing a similar pattern as in the case of power conversion efficiency with thickness. The strong dependence of short circuit current density($J_{sc}$) on power conversion efficiency is observed. The increase in short circuit current density with increase in thickness is due to higher light absorption area. The decrease in short circuit current
density after 300nm thickness is due to the increased recombination. A decreasing pattern of fill factor is observed previous to 400 nm thickness. A slight decrease in open circuit voltage ($V_{oc}$) is found below 100nm. This decrease in $V_{oc}$ is due to the reduced average carrier mobility. Average Carrier mobility get decreased with increasing thickness. Hopping mechanism of charge carriers reduces the carrier mobility at thick layers. This work is helpful for the experimental scientist to optimise the active layer thickness and thereby reducing their effort, time and materials.

Acknowledgement
The authors thank General Purpose Photovoltaic Device Model Software (GPVDM).

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