Capacitance Voltage of P3HT:Graphene Nanocomposites Based Bulk-Heterojunction Organic Solar Cells

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Abstract. After the discovery of conjugated polymer and bulk-heterojunction concept, organic solar cell has gain many interest in the photovoltaic world. The main problem for organic solar cells is that the power conversion efficiency (PCE) is still considered low even though it is much more low cost compared to inorganic solar cell such as Silicon (Si). Therefore, the objective of this research is to investigate the effect of Poly(3-hexylthiophene) (P3HT) thickness and concentration towards the capacitance voltage of the P3HT:Graphene solar cells. A simulation software called SCAPS is used in this research to simulate the effect on the solar cells. SCAPS is specialized for photovoltaic simulation studies. The solar cell’s structure will be drawn inside the simulation and the parameters for each layers is inserted. The voltage range will be fixed and the capacitance voltage will be calculated by the software and all the results will be put into one graph. For thickness results, P3HT’s layer at a thickness of 100nm has the lowest value of capacitance and clearly shows a peak at 0.86V. Where for the concentration, 1x10^{16} \text{cm}^{-3} is the only value that clearly shows there is the built-in voltage \( V_{bi} \) in the solar cells. Therefore, P3HT’s thickness of 100 nm and concentration of 1x10^{16} \text{cm}^{-3} has the best overall results.

1. Introduction
Recent research has shown by adding Graphene into polymer solar cells can improve the solar cell’s efficiency [1], [2], [3]. More understanding needed to be done on the physics of charge transport in order to improve the solar cells performance [4],[5]. To analyse the charge transport in organic semiconductor devices, capacitance \( C \) is being used. The capacitance-voltage characteristics can be give a better insights into these devices when combined with current density-voltage \( (J-V) \) data [6]. \( C-V \) measurements can also provide wealth info of the device characteristic and can determine the semiconductor’s parameters. Recent research has showed that the built- in voltage \( (V_{bi}) \) of the device can be obtained at the peak in the \( C-V \) characteristic [7]. In \( C-V \) characteristic, it is usually observe that only one peak is visible when the polarity is changed from reverse to forward when the bias is applied through the organic semiconductor [8],[9],[10]. Deep traps also affect the capacitance through dynamic response to the small-signal frequency. This forms the capacitance – frequency (C-f) measurements, also termed as admittance spectroscopy, which relies on a frequency differential (where the DC bias is constant) and the AC small signal frequency is varied. Many research has been
Poly(3-hexylthiophene) (P3HT), which has many excellent properties such as high electrical conductivity, high solubility in various solvent and can be deposit over a large area, under low deposition temperature and using low-cost deposition technique. The main problem for P3HT is it possesses a high electrical mobility ($\mu_{\text{hole}} = 0.2 \text{ cm}^2/\text{Vs}$) [2], [11] in conjugated polymers but it is still low compared to the electrical mobility of inorganic solar cells. P3HT is p-type semiconductor and also a donor material, that is why it is high in hole mobility while the electron mobility is low.

Graphene will be used as the carbon polymorph composites and will be mixed with P3HT to form an active layer in the organic solar cells. Since the discovery of Graphene in 2004, many research on Graphene’s properties has been done and it has been proven that Graphene has an excellent electrical characteristic such as an electron mobility of 10000 cm$^2$/Vs and has a higher mobility & conductivity than carbon nanotubes (CNTs). Graphene is also said to be an excellent electron acceptor [2]. Therefore Graphene will be an excellent combination with P3HT in order to achieve a higher power conversion efficiency. With the aid of Graphene, the mobility can be increase and will effect positively on the photocurrent.

A simulation software that is used in this research is call SCAPS. SCAPS was developed by Marc Burgelman from University of Gent, Belgium. This simulation program is to simulate the electrical characteristic of a thin film heterojunction solar cell. This simulation program will be used in this research to calculate the $C-V$ characteristic of P3HT:Graphene solar cells.

The main propose of this research is to investigate the $C-V$ characteristic of the P3HT:Graphene nano composite and see whether the presences of Graphene in P3HT effect the active layer’s performance. The $C-V$ measurements will be simulated using SCAPS and its characteristic will be measured.

2. Methodology

The structure of the solar cell is drawn in the software definition panel. The parameters such as the bandgap are fixed at 2.1 eV for P3HT layer and 0.25 eV for Graphene layer while electron affinity are fixed at 3.40 eV for P3HT layer and 4.5 eV for Graphene layer. For Graphene, the thickness will be fixed at 20 nm while the thickness of P3HT layer will be evaluated from 60nm to 100nm. For each thickness of P3HT, the carrier concentration will be evaluated from $1 \times 10^{13}$ till $1 \times 10^{16} \text{ cm}^{-3}$. The capacitance voltage will be calculated by the simulation software and all the result will be plotted into a graph.

3. Results & Discussion

The effect of the P3HT’s concentration towards the device’s capacitance is shown in Figure 1a). Here, the thickness of the active layer is fixed at 100nm and the concentration is evaluated from $1.0 \times 10^{13}$ cm$^{-3}$ to $1.0 \times 10^{16} \text{ cm}^{-3}$. From Figure 1, only (A) shows a drastic increase at 0.7 V while (B),(C) and (D) slowly decrease as the voltage increase. (A) also shows there is a built-in voltage inside solar cells. The capacitance increases in the forward direction and reach a peak at 0.86V. It has been reported that the peak came from mobile holes [8].This might occur due to the concentration of P3HT which increase from $1.0 \times 10^{13}$ cm$^{-3}$ to $1.0 \times 10^{16} \text{ cm}^{-3}$. P3HT is p-type semiconductor, therefore it is more rich in hole concentration. When the hole concentration increases, the capacitance value also increase.

Figure 1b) shows a closer look the capacitance at a carrier concentration of $1.0 \times 10^{16} \text{ cm}^{-3}$. It can be seen that the capacitance decrease at first until it reach a voltage of 0.58V. Starting form 0.58V the capacitance increased rapidly till reach its peak at around 0.86V. The capacitance then decrease till 0.94V due to the limitation of the minority carriers concentration in the neutral regions of the device [7]
Figure 1: a) shows the C-V characteristic for every concentration. b) C-V characteristic for concentration of $1.0 \times 10^{16}$ cm$^{-3}$.

Figure 2 show the effect of thickness towards the device’s capacitance voltage. The voltage is fixed from -0.8V to 1.0V and the concentration is fixed at $1.0 \times 10^{16}$ cm$^{-3}$. The thickness of P3HT is measured from 60 nm till 100 nm. As seen from Figure 2, capacitance is high when the thickness of the active layer is at 60 nm and the capacitance is at its lowest when the thickness is 100 nm. Therefore, the capacitance increases as the thickness decreases. There is a slight rise at 0.84V for very thickness but as the thickness decrease, the peak also decreases. As explained, the peak decreases due to the limitation of minority carriers concentration [7] in P3HT which is the hole concentration. When the thickness of the P3HT layer decreases, the hole concentration also decreases. This will lead to decrease in the peak. The peak for all thickness is also the same since it has been reported that the peak voltage is related to the bias voltage $V_{bi}$ [6]. The capacitance is inversely proportional to the thickness of the active layer, therefore the capacitance is lower for thicker active layers.
From the capacitance – frequency (C-f) result shown in Figure 3, it can be seen that the highest capacitance value is when the concentration is at $1.0 \times 10^{16}$ cm$^{-3}$ and under illumination. The capacitance is not really affected by carrier concentration as the frequency increases and it shows that even the concentration increases from $1.0 \times 10^{13}$ cm$^{-3}$ to $1.0 \times 10^{16}$ cm$^{-3}$, the capacitance range did not change a lot. (B) shows the highest capacitance value around 85.4125 nF/cm$^2$ while (E) has the lowest capacitance value at 84.832 nF/cm$^2$. The capacitance value remains constant when the active layer is under illumination occurs due to fixed temperature in the simulation program.

Figure 4 shows the effect of the active layer’s thickness towards the capacitance of P3HT:Graphene solar cell. The capacitance decrease as the active layer’s thickness increases. The thickness of 60nm has the highest capacitance value while a thickness of 100nm has the lowest. As seen in Figure 4, the capacitance of P3HT:Graphene stays static as the frequency increases but the capacitance value
between (B) and (F) has a larger gap compared to the one in Figure 3. This shows that the thickness has a greater effect towards the solar cell’s capacitance value than the carrier’s concentration. As shown in Figure 4, (A) shows a decrease in capacitance when the frequency increases. For all thickness under illumination, the graph is actually quite the same as (A) but because the decrease of capacitance is really small, it seen as a straight line. From the graph, it can be concluded that the thickness of the thin film has a small effect on the capacitance as the frequency increases because capacitance is mainly affected by the temperature [13]. The reason why the capacitance decrease when the active layer is thicker is because the distance between two electrodes of the solar cells increase, which cause the capacitance to slowly decrease.

4. Conclusion
In summary, P3HT at 100nm and the concentration at $1.0 \times 10^{16} \text{ cm}^{-3}$ shows the best results out of all the thickness and concentration of P3HT layer. This is because the peak at C-V characteristic appears really clearly at both results. Besides that, at forward bias, the capacitance value shows a strong sign that the minority charge carriers plays an important role. As the thickness increase, the capacitance decreases.

For C-f measurements, it can be concluded that the thin film’s thickness & concentration have a little effect on the capacitance as the frequency increases. Capacitance is greatly affected by the temperature and in this simulation, the temperature is fixed. The capacitance decrease as the thickness of the active layer increases due to the increase of distance from the two electrodes. The thickness of the active layer will separate the electrodes even more, which leads to the decrease in capacitance.

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