

Master in Photonics

MASTER THESIS WORK

Study about the performance of Small Molecule Organic Solar Cells, Fabricated Based on Bulk-Hetrojunction and PIN-Junction

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Study about performances of Small Molecule Organic Solar Cells, Fabricated Based on Bulk-Hetrojunction and PIN-Junction

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Abstract. Organic solar cells have the potential to provide low-cost photovoltaic devices as a clean and renewable energy resource. In this thesis, we focus on understanding the energy conversion process in organic solar cells, and improving the power conversion efficiencies via controlled growth of organic components.

Keywords: Small molecule, Organic photo-voltaic, DBP, Intrinsic, Bulk Heterojunction

1. Introduction

Organic solar cells have made significant progress in the past two decades due to their potential for providing a low cost alternative to inorganic solar cells such as Si. This progress has been made possible by several important advances in the understanding of organic semiconductor materials, and their ability to convert solar energy into electric current. Perhaps the most important advance in organic photovoltaics (OPV) has been the use of an organic donor-acceptor (DA) heterojunction (HJ) as a means to achieve highly efficient carrier generation from tightly bound excitons characteristic of small molecules.[1,2] With the synthesis of novel organic molecules and the design of new device structures, the PV efficiency has led to recent and significant improvements in both small molecular weight and polymeric solar cells.[3-5]

2. Organic Semiconductor

The structure of an OPV cell is inherently different from architectures employed for inorganic cells.[6] This is due to the differences in physical properties between organic and inorganic semiconductors. For instance, photon absorption in an organic semiconductor results in the creation of a tightly bound exciton, or electron-hole pair, as opposed to the generation of free charge carriers in inorganic materials. Excitons are the result of the weak interactions between molecules; this results in a low intermolecular orbital overlap and low dielectric constant for the solid. Furthermore, organic semiconductors tend to have low carrier mobilities (typically 10^{-7} to $2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) as well as a small exciton diffusion length ($L_D < 40 \text{ nm}$). However, most organic materials possess high absorption coefficients of $\alpha > 10^5 \text{ cm}^{-1}$, allowing for layer thicknesses that can be kept thin yet still highly absorptive.

2.1. Organic solar cell

Due to new materials and concepts, e.g., bulk heterojunctions [7], [8] doping of organic molecular matrices with donor or acceptor molecules [9], the p-i-n structure [10] and tandem architecture [11] have led to efficiencies of up to 12% by Heliatek.[12]

In addition to high potential to improve the power conversion efficiency, the main advantages of organic photovoltaic are:

- Low-cost production due to use of cheap and abundance materials;
- Tailoring Molecular Properties. Organic semiconductors can have their chemical and electrical properties tailored in numerous ways by modifying the chemical structures.
- Low weight and flexibility. There are organic materials with exceptionally high absorption coefficients in the visible range, allowing the realization of ultra-thin photovoltaic cells.
- Large area devices. Thanks to fabrication techniques may lead to realize organic solar cells in large area substrates.

The deposition of organic materials can be roughly divided in two major families. Both techniques depend on different physical and/or chemical properties of the materials.

2.1.1. Small molecule organic solar cells

The first family consists of gas phase based depositions. The organic material is heated above the evaporation temperature, and subsequently transported to the substrate. If the temperature of the substrate is low enough, the molecules condense on it and a layer can be formed. The transport itself can be done in vacuum, with a carrier gas, or via diffusion.

2.1.2 Polymer organic solar cells

The second deposition family is solvent based. The material is dissolved or dispersed in a solvent, and this solution is applied to a substrate, where, after evaporation of the solvent, a thin organic layer is formed.

2.2. Working principles

The conversion of photon energy into free charge carriers is explained in the follow simplified steps:

- *Light absorption* of the molecule in one of the respective absorber layers;
- *Exciton creation* within the photoactive layer;
- *Exciton diffusion* to the interface of the two different absorber layers;
- *Charge transfer state*: exciton gets separated due to a favourable energy offset overcoming the exciton binding energy;
- *Charge transport*: charge free carriers are generated and transported through the layer, respectively;
- *Collection the charges* at the electrodes, realized by Ohmic contacts.

2.3. Structures

In the following a brief summary, including the strengths and weak points, of the four most used architectures of organic solar cells is given:

2.3.1. Schottky diode

Early solar cells made use of Schottky diodes employing an organic semiconductor where charge separation occurred between the non-ohmic metal-semiconductor interfaces. Fig.1-(a)

2.3.2. P-N junction

More recently, devices have been made using a *p-n* junction to separate charges – an *n*-type Organic semiconductor forms a *p-n* junction with a *p*-type Organic semiconductor in similar way as *p* and *n*-type Silicon. The benefit over Schottky diodes is that open circuit voltages are generally higher due to the hole blocking properties of *n*-type Organic semiconductor. Fig.1-(b)

2.3.3. Bulk heterojunction

The strong point of this type is the large interface area if the molecular mixing occurs on a scale that allows good contact between alike molecules and most excitons to reach the D/A interface. This can usually only be partly achieved so the defects of the network structure, particularly the connectivity with the correct electrode, is the big weak point of this structure. Fig.1-(c)

2.3.4. P-I-N junction

This relatively recent type represents the successful attempt to unify the advantages of the two structures above. Charge separation occurs in the blend layer and charge transport can only occur via the correct transport layer. Fig.1-(d)

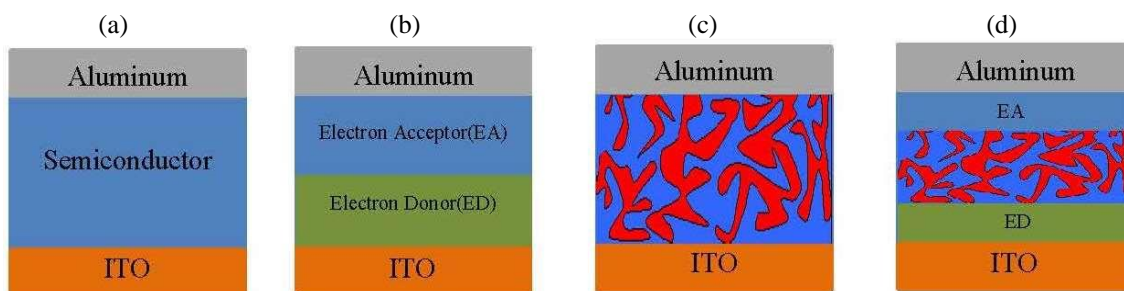


Figure 1. (a) Shottky diode. (b) P-N junction. (c) Bulk Heterojunction. (d) P-I-N junction.

3. Experimental

In this chapter I will mainly discuss about materials and those methods which have been used in our experiments.

3.1. Materials

Depending on the background free carrier concentration, the organic materials can be either p-type or n-type.[13-15] However a more significant feature of an organic semiconductor is whether the electron or hole mobility is higher, which is an intrinsic characteristic of the organic material, determined by the HOMO (LUMO) overlap between adjacent molecules.[13] It is thus more appropriate to refer to a particular material.

3.1.1. Photoactive materials

3.1.1.1. Tetraphenyldibenzoperiflanthene (DBP)

A highly efficient organic thin-film solar cell based on a P-I-N structure employing a novel electron-donor (ED) material, tetraphenyldibenzoperiflanthene(DBP)[16], has been studied in this work. Fig.2 (a)

3.1.1.2. Fullerene (C_{70})

Comparing the optical absorption of C_{70} with C_{60} , we could get the conclusion that using C_{70} as our n-type material would help to increase the efficiency of our cells. Fig.2 (b)

3.1.2. Transport Materials

3.1.2.1. Bathocuproine (BCP)

Bathocuproine, also called BCP, is a wide-gap electron transport and exciton blocking material. The role of BCP as buffer layer inserted between active layer and aluminium contacts. The BCP layer is believed to be: first, prevent the recombination of excitons at the interface between the organic layer and the metal; second, prevent damage to the acceptor layer by the metal deposition, third, prevent penetration of metallic atoms into organic active layer; fourth, prevent Oxygen and Water molecule to damage the organic active layers below. Fig.2 (c)

3.1.2.2. Molybdenum trioxide

Molybdenum trioxide is chemical compound with the formula MoO_3 . MoO_3 interlayer between the ITO anode and the hole transporting layer has been used for small molecule solar cells to enhancement in the fill factor due to the reduction in series resistance. Fig.2 (d)

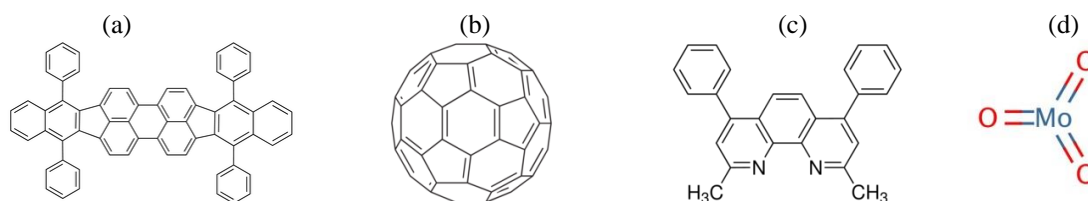


Figure 2. (a) DBP. (b) C₇₀. (c) BCP. (d) MoO₃.

3.2. Substrate preparation

Preparation of the substrates is very important for obtain reproducible results. All of the solar cells presented in this research used glass coated with the transparent conductor indium tin oxide (ITO).

ITO has been supplied by Luminiscence Technology Corporation. Glass substrates with thick 1200~1600 Å have a sheet resistance of 9~15 Ω/sq and the transmission is higher than 84% at 550 nm. Fig. 6

All substrates were cleaned with acetone during 30 minutes and with isopropyl during 30 minutes in deionized water. After being dried by N₂-gas, the ITO glass exposure to an ultraviolet-ozone surface treatment during 30 minutes to increase the work function [17] and remove any remaining carbon residues.

3.3. Material deposition

3.3.1. Hole transport layer deposition

MoO₃ was deposited by thermal evaporation at base pressure of 10⁻⁶ mbar. The evaporation rate was fixed at 0.1 Å/s. The thickness of the film is estimated from the frequency of the quartz oscillator.

3.3.2. Deposit of organic layers

Organic solar cells were fabricated by thermal evaporation of small molecules. The manufacturing process was carried out in a Nitrogen atmosphere using the glove box MBraun200B.

Organic layers were grown by thermal evaporation in a home-made system. The system is composed by five evaporation sources, one sample holder, provided with heater, and quartz crystal set inside vacuum chamber. In order to avoid cross contamination each type of material always is evaporated in the same source. There are three temperature controllers allowing to establish specific substrate temperature during the deposition process and co-evaporate different organic materials. Fig. 3

3.3.2. Deposit of organic layers

Metal deposition is an extremely critical point in small molecules solar cells. Higher deposit rates may short the device. Aluminium is the metal used as a cathode in all devices. The metal was deposited on organic layers through shadow mask to give an active are of 0,075 cm². Deposit rate was below than 0,2 Å/s during first 20 nm and 1 Å/s up to required thickness. During the evaporation process the samples rotated at 30 rpm to obtain a uniform layer. Fig.4

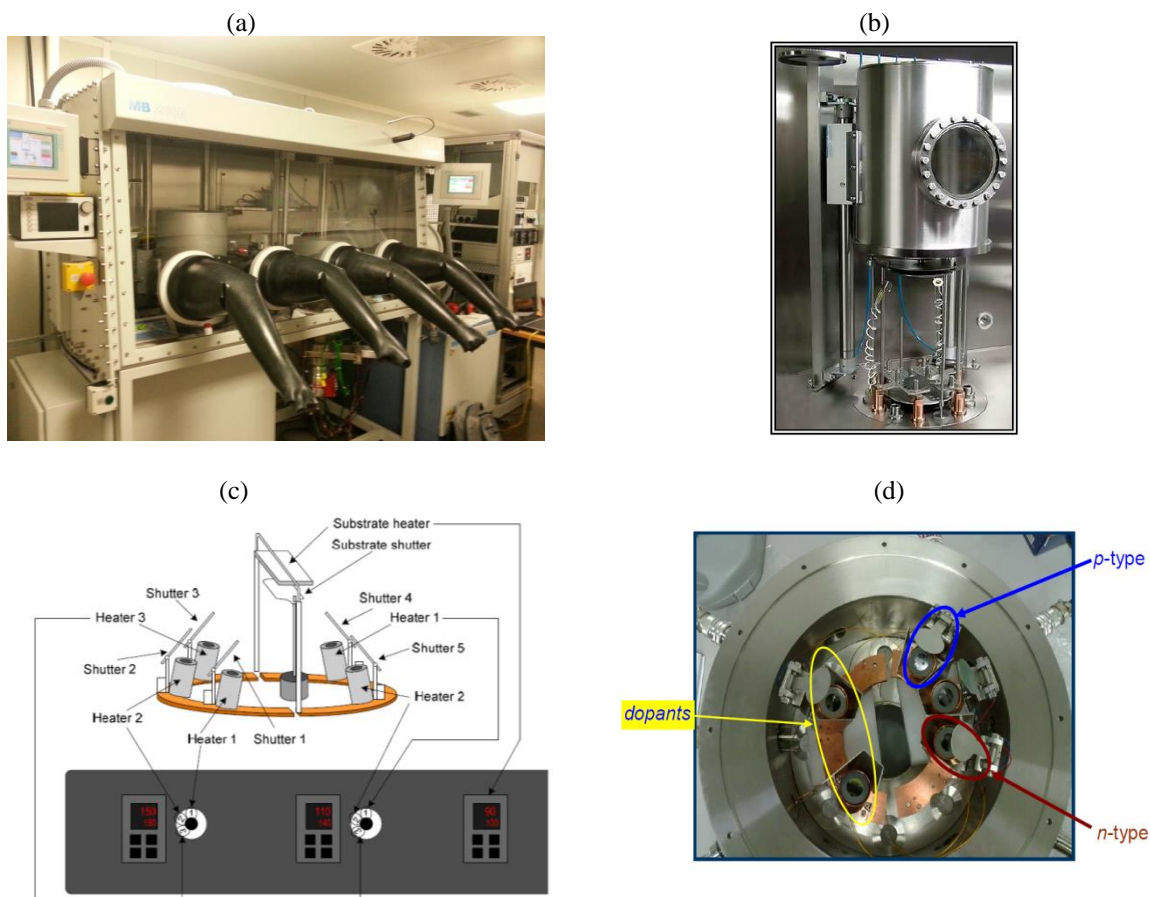


Figure 3. (a) Glovebox. (b) Metal chamber for evaporating metals or material with high molecular weight. (c) Schematic form of Organic Chamber. (d) Location of each source in Organic Chamber.

3.4. Characterization of the fabricated OPVs

Current–voltage curves and external quantum efficiency (EQE) were measured in nitrogen ambient using a prototype designed specifically. Using this prototype it is possible to measure 4 different substrates with 4 cells in each substrate in nitrogen atmosphere. The prototype has been fabricated by microLIQUID.

Devices were measured at room temperature using a HP 4142B DC Source measurement unit and an AM1.5 solar simulator (Newport Oriel Instruments [18]) at the light intensity of 100 mW/cm² calibrated with a pyranometer.

EQE characterization of photovoltaic cells was carried out on a QEX10 integrated system by PV Measurements Co. under standard measurement conditions. [19] Chopping frequency was fixed at 80Hz to avoid any perturbation from light ambient.

UV-visible-NIR Spectrometer (Shimadzu 3600) with UV-probe software for fomoteric analysis of solid and liquid materials in the 185 to 3300 nm range has been used for optical measurements. Spectrometer is equipped with ISR 3100 Integrating Sphere.

Absorption measurements were performed in air at ambient circumstance without device encapsulation.

4. Results and discussion

In this section I will discuss about the effect of the thickness of intrinsic layer- Co-evaporated-layer on the performance of small molecule solar cells. The intrinsic layer introduced in Organic Solar Cells in order to increase the absorption of light which led to increase in Short Circuit Current.

In this work, I analysed the effects in varying the thickness of co-evaporated DBP and C₇₀. The fabricated devices have either “Bulk hetrojunction” structure or “PIN junction” structure and for

showing that we did increase the performance of our cells, I will compare the results with simple “PN-junction” cells’ results.

The “Bulk heterojunction” structure or “PIN junction” structure that we used in our experiments is shown in Fig. 4.(a)

The structure used to fabricate PIN-Junction cells, was:

$$ITO / MoO_3 \text{ 3nm} / DBP \text{ xnm} / DBP+C_{70} (1:1) \text{ xnm} / C_{70} \text{ xnm} / BCP \text{ 8nm} / Al \text{ 100nm}$$



Figure 4. (a) Device structure for intrinsic layer optimization. (b) The structure used to fabricate PIN-junction cells

For the fabrication of our cells, first we measure the optical absorption of those materials that we want to use. Measuring optical absorption, we could have ideas about how each molecule absorb in solar spectrum which is quite important for the later characteristics such as in EQE. Below it is shown the optical absorption of our used materials consist of BCP, MoO₃, DBP, C₇₀ and transmittance of coated glass with ITO. It should be mentioned that the absorption of glass was removed from the absorption of the materials since the transparency of the coated glass that we are using will decrease extremely when we reach around 300 nm in the wavelength, we only consider the absorption of our materials up to 350 nm; another consideration was due to the optical absorption instrument that we have been using which cause of increase after around 750 nm which also omitted from both transmittance and absorption diagrams. Fig. 6

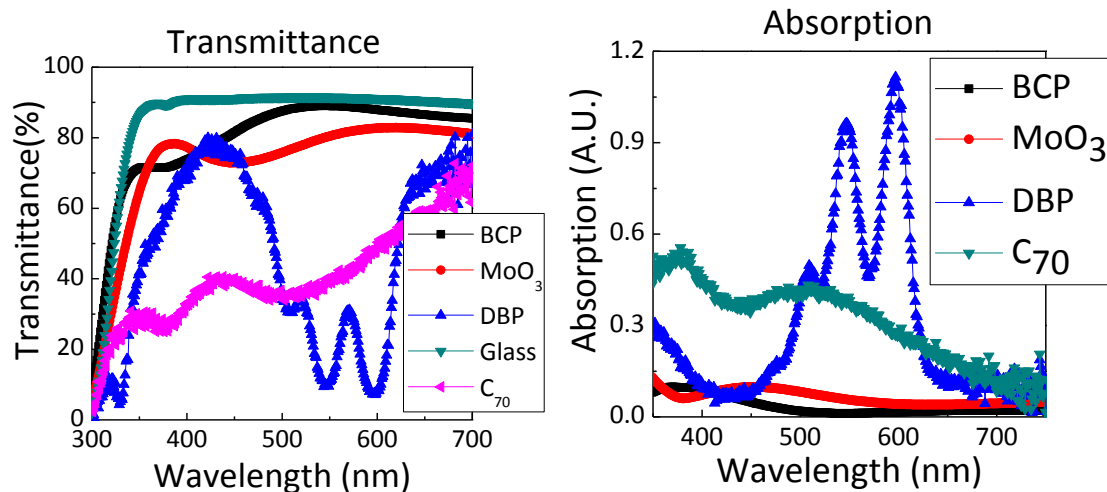


Figure 6. Transmittance and absorption of our materials including our transport materials and photoactive materials.

From absorption and transmittance diagrams, it could be easily seen that our transport materials are almost transparent while our photo-active materials absorb a big portion of photons, mainly in visible regime which the sun spectrum has the maximum number of photons.

Below, it is shown the absorption and transparency of few of our best fabricated Organic Solar Cells. Fig. 7

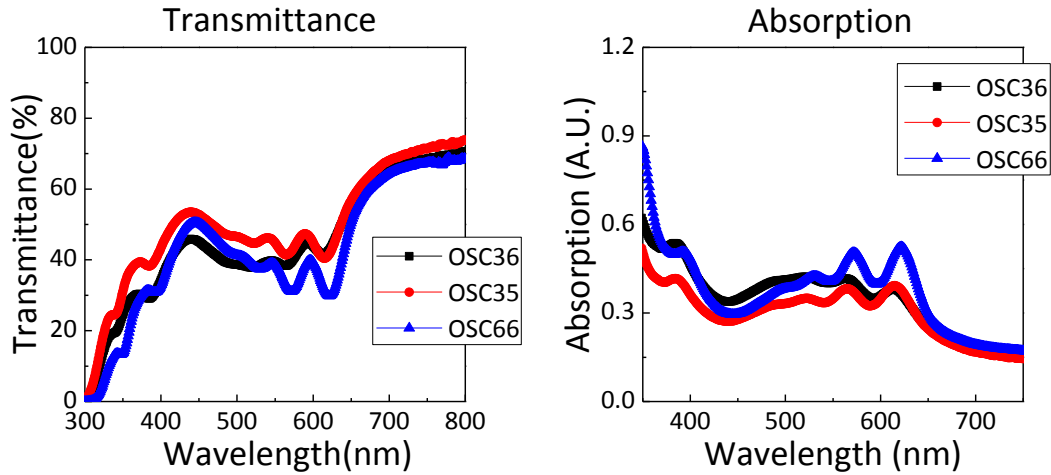


Figure 7. Comparison between absorption and Transmittance of three of our best fabricated cells- OSC35, OSC36 and OSC66.

Here, we characterize the best Solar Cell in each substrate through their JV-curves. Fig. 8

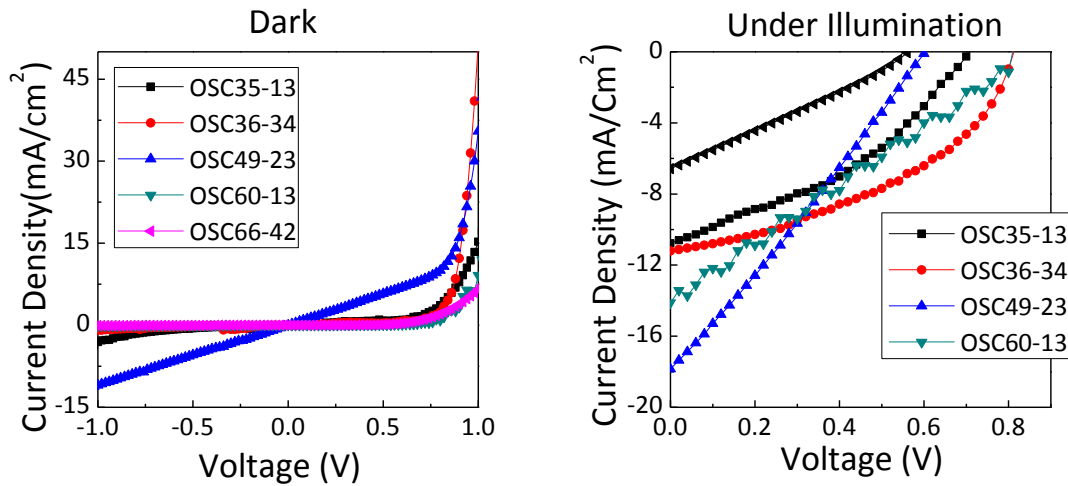


Figure 8. Current-Voltage in Dark- Dark-Logarithmic and under illumination.

In table 1, I compare those results that we obtained only from “Bulk hetrojunction” which depend on co-evaporation thickness. There we can see a sweet spot in the thickness of co-evaporation thickness.

Table 1. Variation of Solar Cells’ performance due to change in intrinsic layer thickness

Thickness(nm)	Open circuit voltage(V)	Efficiency(%)	Short circuit current(mA)	Filling Factor(%)
30	0.71	2.82	10.78	36.8
40	0.81	3.93	11.2	43.3
60	0.81	3.12	14.12	27.3
70	0.61	2.90	17.84	26.6
100	0.57	1.01	6.57	27.0

The best performances are obtained with 40nm of intrinsic layer considering efficiency, filling factor, open circuit voltage. According to the results we got, it is clear that by increasing the thickness of intrinsic layer, we could increase the generation of photo-current, which will increase the efficiency, however, after we kept increasing the thickness of the intrinsic layer,, other factors started to affect the output results, like recombination of hole and electrons of generated excitons, or losing the best filling factor that we could have obtained from our samples, etc. By looking at Fig. 9, you can see all necessary factors of our cells vs. thickness, drew in the same diagram with Efficiency, in order to have an idea about how they correlate with each other.

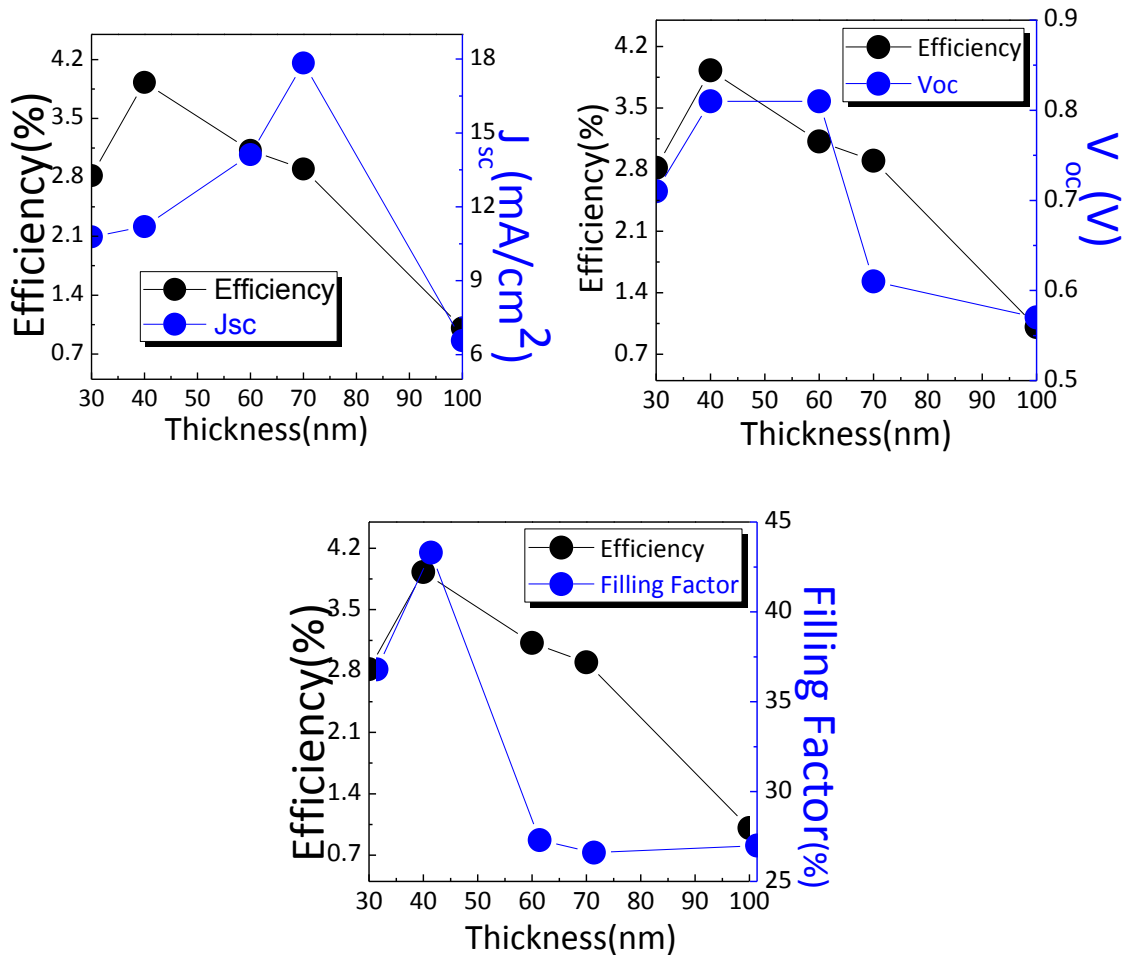


Figure 9. In this diagram, Short Circuit Current (Jsc), Open Circuit Voltage (Voc) and Filling-Factor(FF) draws vs. Thickness in all in the same diagram with Efficiency to display how the react with thickness more clearly.

The PIN-junction is a mixed of bulk-hetrojunction structure plus a thin layer of donor and acceptor molecules in the photoactive layer. The interface between donor and acceptor molecules is a critical point to achieve efficient organic solar cells. In order to study the influence of the bulk heterojunction layer were fabricated devices with p-i-n structure. The bulk heterojunction is the intrinsic layer in this architecture. In this study, I kept the thickness of donor and acceptor constant and change the thickness of intrinsic layer. Tab. 2

Table 2. Varying the thickness of intrinsic layer in the PIN structure:

Thickness(nm)	Open circuit voltage(V)	Efficiency(%)	Short circuit current(mA)	Filling Factor(%)
30	0.83	3.52	10.22	41.6
50	0.83	3.54	10.43	40.9

The structure used to fabricate PIN-Junction cells, was:

ITO/ MoO3 3nm/ DBP 10nm/ DBP+C70 (1:1) xnm/ C70 30nm/ BCP 8nm/ Al 100nm

Meaning, by keeping the thickness of acceptor and donor material constant, we only study the effect of the thickness of intrinsic layer. These cells are usually have higher Filling Factor than bulk-hetrojunction cells due to blocking effect of donor and acceptor material, while introducing those non-intrinsic layers prevent us from increasing the intrinsic layer due to exciton diffusion length which will end of having less short circuit current. Fig. 4 (b),11

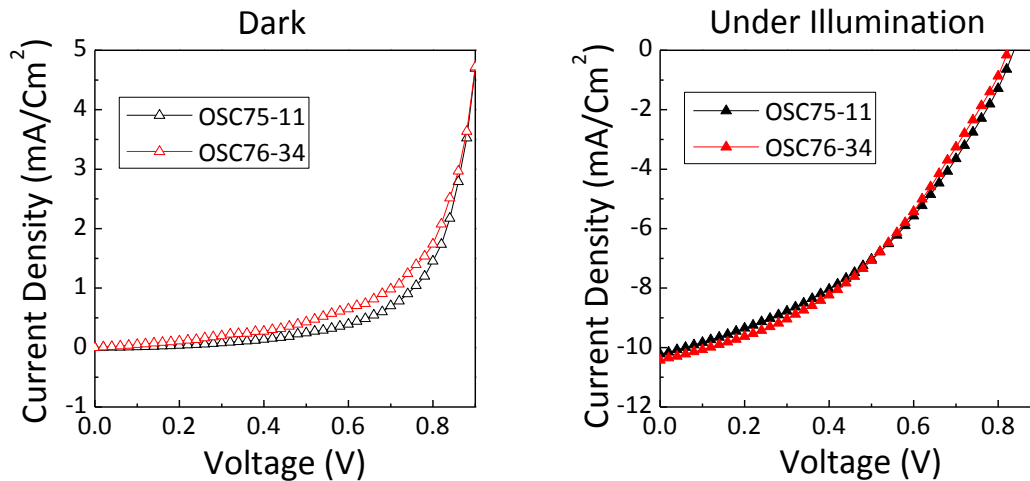


Figure 11. Voltage-Current curves show in dark, dark-logarithmic and under illumination

The external quantum efficiencies of the solar cells are represented in Fig. 12; it is clear that any device with higher short circuit current, will have an EQE which has more area under it diagram. In this case, both J_{sc} were similar, however due to the shifting in absorption of cells which cause because of the increasing in the thickness of intrinsic layer, the EQE. Diagrams are not similar although as it was mentioned before, the area under both of them are almost equal.

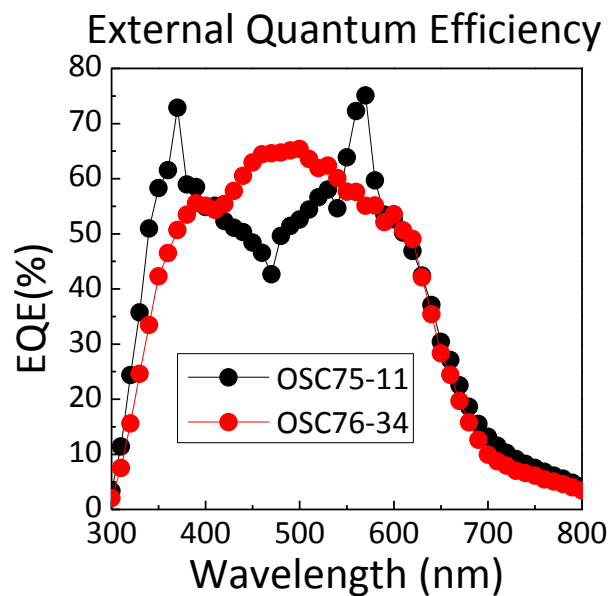


Figure 12. External Quantum Efficiency diagrams of the best cells in fabrication of OSC75 and OSC76.

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