

Study the Important Parameters Affecting Performances of P3HT:PCBM Organic Solar Cells

ABSTRACT

Aims: Organic solar cells were realized and characterized. The structure of the device is Glass/ Transparent conducting oxide/ poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)/ poly(3-hexylthiophene): : [6,6]-phenyl-C61-butyric acid methyl ester/ Aluminum (Glass/ TCO/ Pedot:Pss/P3HT:PCBM/ Al). Where P3HT: PCBM is used as active layer. The J(V) characteristics and the parameters of the cells as function of concentration of the blend of the active layer, the thickness of the active layer and the type of substrate are given.

Study design: Theoretical study of the performances of organic solar cells is given. Followed by an experimental study. The cells were realized and characterized.

Place and Duration of Study: Laboratory of Advanced Technologies of Genie Electrics (LATAGE) Faculty of Electrical and Computer Engineering Mouloud MAMMERI University (UMMTO), BP 17 RP 15000, Tizi-Ouzou, Algeria.

Methodology: we discuss general mechanisms leading to generation and transport of charge carriers and parameters which govern the behavior of organic solar cells.

The absorption spectra of P3HT: PCBM is measured using SAFAS 200 instrument for different temperatures. Solar cells were realized and characterized as function of different parameters: transparent electrodes, concentration of the active layer and thermal annealing.

The current density characteristic results for the cells realized were compared for two substrates (indium tin oxide (ITO) and Fluor doped tin oxide (FTO)) and the concentration effect of the blend is studied. The decay of performances of these devices in the time is due to the degradation mechanisms which are a result of diffusion of H₂O and O₂ species through the organic layers.

Results: The current density characteristic depends on various parameters, the type of the substrates, the concentration of the blend, thickness of active layer and thermal annealing.

Conclusion: Our study shows that the performances of the organic solar cells depend on different parameters. In order to improve the performances of the cells, optimization of the concentration and thickness and the use of transparent electrodes with high transmittance and high conductivity must be used.

Keywords: organic solar cells, performances, P3HT: PCBM, transparent electrodes, temperature, AFM, concentration.

1. INTRODUCTION

Polymer solar cells have attracted much attention during the last years due to their lower fabrication cost and possibility of using flexible substrates [1]. However, their efficiency is usually less than 5%. In recent year the energy efficiency of the organic photovoltaic solar cells (OPVs) has significantly increased. The energy efficiency reached a record of 12% [2]. The active layer morphology related to blending preparation and annealing, is one of the most important factors affecting solar cell efficiency [1], [3], [4]. Organic solar cells undergo many degradation pathways during their lifetime. Efficiency loss is due to light, oxygen and water [3]. The exposure to oxygen leads to an enhanced charge carrier concentration

and a decreased charge carrier mobility. A lower mobility leads to a higher extraction time for the charge carriers and therefore to an enhanced bimolecular recombination probability which results in the decreased FF. The open circuit voltage is slightly increased because the Langvin recombination rate is lower when the mobility decreased. The higher charge carrier densities reduce the internal field and therefore increase the open circuit voltage [3]. Thermal annealing improves cell efficiency. A detailed comparison of stability of P3HT: PCBM devices in relation to the sequence in which the devices have been annealed, evaporated, and exposed to different degradation stress is studied [2]. The behavior of bulk heterojunction (BHJ) OPV after thermal degradation is generally correlated to morphological changes occurring in the active layer that can affect: (i) charge separation process by formation of fullerene aggregates in polymer, fullerene blends which leads to a PCE loss due to the reduction of the donor: acceptor (D:A) interfacial area, (ii) charge extraction by a migration of skin layer of either polymer or fullerene adhering to the top contact, generating barriers of selective transport regions depending on the device architecture, (iii) transport properties by modification of the polymer packing in the blend, (iv) recombination by an increase of the number of defect states in the bulk of the active layer, and (v) optical properties by generation of a charge transfer complex between donor and acceptor molecules which acts as an excitons quencher [6]. To predict the thermal stability of BHJ solar cells a capacitance method was used [6]. Solar cells are multi-layered structures the decay in their performances reflects not only the degradation of the photoactive layer, but of each of its constituent layers [7]. In this work we have studied the performances of OPV as function of the transparent conducting oxides (TCO) used as anode. We have realized cells with indium tin oxide (ITO) and cells with Fluor doped tin oxide (FTO), the parameters of the devices have been compared. The current density characteristics of the cells as function of the active layer concentration are presented. Another factor which affects the performances is the annealing temperature of the device. The measurement spectra of the absorption of the active layer show that the absorption is improved when the layer is annealed. The morphology of the active layer is given by Atomic Force Microscopy (AFM) topography, the crystallinity of the active layer is improved after the thermal annealing.

2. PARAMETERS AFFECTING CHARACTERISTICS OF ORGANIC SOLAR CELLS

2. 1. Charge transport in polymer fullerene films

A polymer: fullerene bulk hetero-junction solar cell can be regarded as an insulator sandwiched between two electrodes. The light entering the transparent electrode is considered to be uniformly absorbed by the active layer, which results in a uniform generation of electron-hole pairs throughout the specimen. In photovoltaic cells the recombination probability of the free charge carriers depends on the mean carrier drift length mean carrier drift length.

$$w_{e,h} = \mu_{e,h} \tau_{e,h} E \quad (1)$$

Where: $w_{e,h}$: the mean carrier drift length of electrons (e) and holes (h)

μ : charge carrier mobility

τ : charge carrier lifetime before trapping or recombination

E: the electric field.

If the mean carrier drift lengths of electrons and holes are smaller than the device thickness L ($w_{e,h} < L$), the both charge carriers are accumulated in the layer. At steady state, the distance which they travel increases linearly with applied voltage (V) and the photocurrent J_{ph} follows Ohm's law:

$$J_{ph} = q G (\mu_e \tau_e + \mu_h \tau_h) \frac{V}{L} \quad (2)$$

Where q: the electric charge

G: the generation rate of electron-hole pairs.

The photocurrent density J_{ph} as a function of the applied voltage V is given by the equation (3):

$$J_{ph} = q G L (1 + b) \frac{-b + \left(b^2 + \frac{4(1-b)V\mu_h\tau_h}{L^2} \right)^{1/2}}{2(1-b)} \quad (3)$$

Where b is the drift length ratio defined here as

$$b = \mu_h \tau_h / \mu_e \tau_e$$

For equal electron and hole $\mu\tau$ products ($b=1$), it can be seen that equation (2) equal to equation (1) and at higher voltages the photocurrent saturates at $q G L$. according to equation (2), for very different charge transport properties of electrons and holes ($1 \gg b \rightarrow 0$), the J_{ph} approaches one half power on V :

$$J_{ph} = q G (\mu_h \tau_h)^{1/2} V^{1/2} \quad (4)$$

2.2. Current density in a structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al

The current density J_D depends quadratically on voltage. This behavior is characteristic for a space-charge limited current (SCLC) [18] given by:

$$J_D = \frac{9}{8} \epsilon_0 \epsilon_r \mu_e \frac{V^2}{L^3} \quad (5)$$

Where $\epsilon_0 \epsilon_r$ is the permittivity of PCBM. For PCBM the relative dielectric constant $\epsilon_r=3.9$.

$\mu_e = 2.10^{-7} \text{ m}^2/\text{Vs}$.

$\epsilon_0=8.854.10^{-14} \text{ F/cm}$ is the constant dielectric of free space.

2.3. Temperature effect on the electrical transport of organic solar cells

Thermal annealing improves cell efficiency. During thermal annealing, growth and perfection of polymer crystallization occurred, which increases the charge transport capability. However, a prolonged annealing process will increase the crystallization of P3HT and force the aggregation of PCBM [4], [8]. The ordered structure facilitates the charge transport [9], [10]. Figure (1) shows the AFM (Atomic Force Microscopy) image of P3HT: PCBM deposited with spin coater. After annealing at 130 °C during 30 min the structure was ordered.

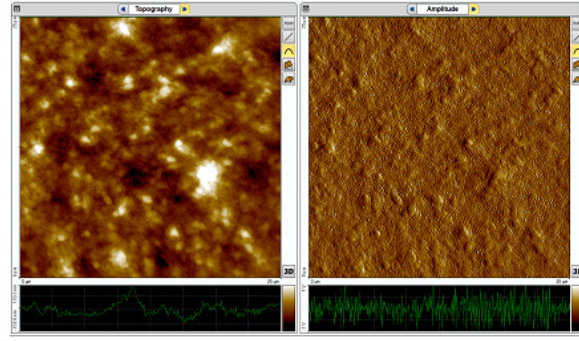
The open circuit voltage of the organic solar cells depends on temperature [15] as in Eq. (6)

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{ph}}{J_0} + 1 \right) = \frac{E_g}{q} - \frac{n k_B T}{q} \ln \left(\frac{N_v N_c \mu K_B T}{J_{sc} L N_A} \right) \quad (6)$$

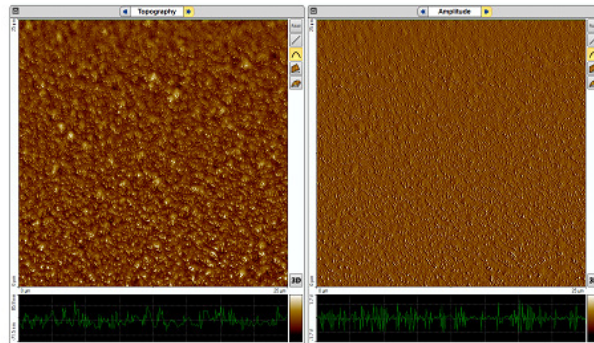
For $T=0^\circ\text{K}$, $V_{oc}=E_g/q$.

Where $E_g = \text{LUMO}_{\text{acceptor}} - \text{HOMO}_{\text{donor}}$

K_B is a Boltzmann constant $= 1.38 \cdot 10^{-23} \text{ m}^2 \text{ kg/sK}^\circ$, q is the elementary charge $= 1.6 \cdot 10^{-19} \text{ C}$, L is the thickness of the active layer, μ is the mobility of carriers, N_c and N_v are the state density of electron and hole respectively, n is the ideality factor of the diode and N_A is the doping concentration of acceptor.



a- P3HT:PCBM without annealing



b- P3HT:PCBM annealed at 130°C during 30 min

Fig.1. AFM topography of P3HT:PCBM

a- without annealing, b-annealed at 130°C

2.4. Effect of solvent annealing

Under solvent annealing conditions the polymer is seen to be ordered. Devices with ordered structure show higher efficiency [5].

2.5. Series and shunt resistances

The increase in both series and shunt resistances can be caused by the reduction in the mobile charge density and mobility associated with the creation of traps produced by the interaction of oxygen and water with the polymer.

Several factors contribute to increase the series resistances when the device is left in ambient conditions such as reduction of mobility, metal corrosion at the contact or changes in the contact barrier and charge space regions [11].

The J-V characteristics of an organic solar cell can be simulated with [17] the equation (7)

$$J = J_0 \left\{ \exp \left(\frac{V - J R_s A}{n K_B T / q} \right) - 1 \right\} + \frac{V - J R_s A}{R_p A} - J_{ph} \quad (7)$$

Where , J_0 is reverse saturation current density, V is the applied voltage, n is the ideality factor, R_s is the series resistances, R_p is the shunt resistance, J_{ph} is the photocurrent, A is the active area, K_B is the Boltzmann constant, T is the temperature, and q is the elementary charge.

2.6. Influence of the buffer layer

The BHJ (bulk heterojunction solar cells) [16] are very promising device structure exploited in the production of organic solar cells. away from the development and optimization of novel active materials, like novel acceptors or low band-gap polymer donors, the correct optimization and choice of the HTL (*Hole transport layer*) together with the ETL (*Electron transport layer*) play a fundamental role in order to get the best performance from a device. An improved Jsc was observed for the G - PEDOT: PSS devices due to the improved charge collection compared to PEDOT: PSS devices [12]. The electrical conductivity of PEDOT:PSS films can be increased by more than two order of magnitudes by spin-coating a compound containing one or more polar groups—such as ethanol, methoxyethanol, 1,2-dimethoxyethane, and ethylene glycol EG—onto the films. When the PEDOT:PSS films were modified with ethylene glycol (G-PEDOT) the sheet resistance decreased. Which contribute to improve transport of the carrier of charge. Alcoholic solvents enhance the conductivity as it is discussed in reference [13]. Highly conductive (443 S/ cm) and transparent (89%) PEDOT:PSS thin films with thickness of 93 nm [14] was shown in Fig. 2.

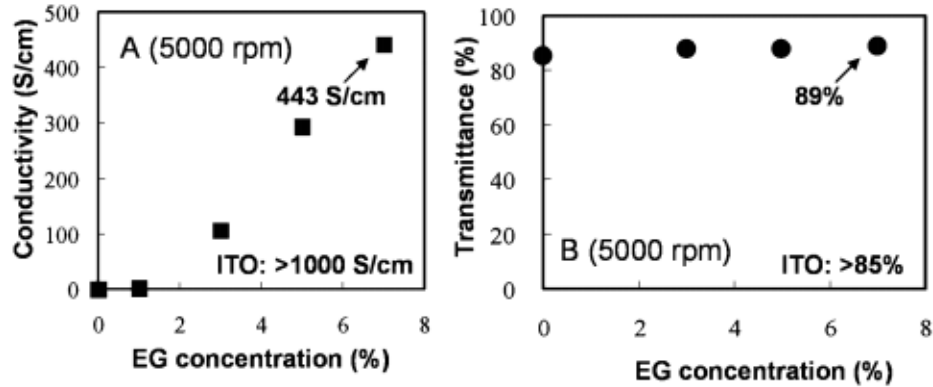


Fig.2. Plots of electrical conductivity (A) and visible-light transmittance (B) of the PEDOT/PSS thin films against concentration of (ethanol glycol) EG in the PEDOT/PSS dispersion used for the spin-coating [14]

3. EXPERIMENTAL RESULTS

The structure of the device realized are glass/TCO/Pedot:Pss/P3HT:PCBM/ZnO(NP)/Al. The active layer based is a blend of poly (3-hexylthiophene) (P3HT) and fullerene (PCBM). Pedot:Pss is used as hole transport layer (HTL), zinc oxide nanoparticles (ZnO (NP)) used as an electron transport layer (ETL). These layers are deposited by a spin coater. The cathode of Al is deposited by thermal evaporation under vacuum. The structure of the device is shown in Fig. 3.

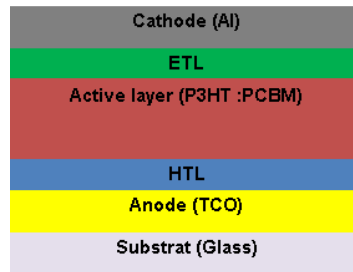


Fig.3. Structure of the device realized

3.1. Temperature and thickness effect in the absorption spectra of P3HT: PCBM layer

The absorption spectra of P3HT: PCBM films with varied thicknesses are presented in figure (4).The absorption enhances with the thickness of the layer.

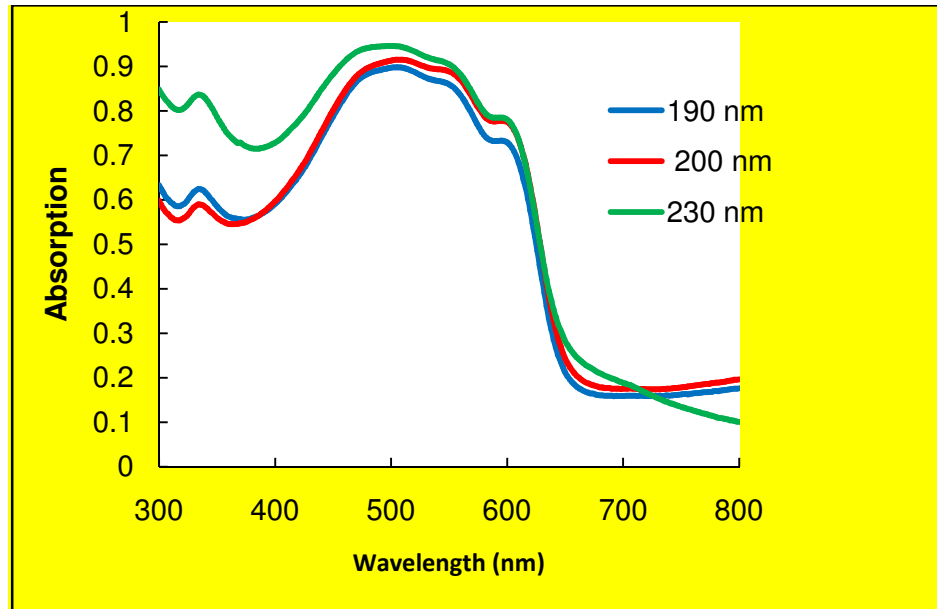


Fig.4. Absorption of P3HT: PCBM as function of the thickness

Annealing processing influenced organic photovoltaic device efficiency significantly. Generally, it is believed that annealing can improve the crystallization and orientation of polymer and found that the nano-scale phase separation occurred between polymer and fullerene after the thermal self-organization. Figure (5) shows the absorption spectra of P3HT: PCBM (1:0.8) ratio for different annealing temperature. The results shows that when the temperature increases the absorption increases. Optical absorption of thin films of blend of P3HT: PCBM with approximate thickness of 190 nm are investigated. The peak absorption of P3HT increases upon thermal annealing as is evident in Fig.5. On the contrary to P3HT the peak absorption intensity of PCBM reduces upon thermal annealing Fig.5. This is attributed to the diffusion of PCBM molecules forming needle like crystals and subsequently at higher temperatures forming clusters.

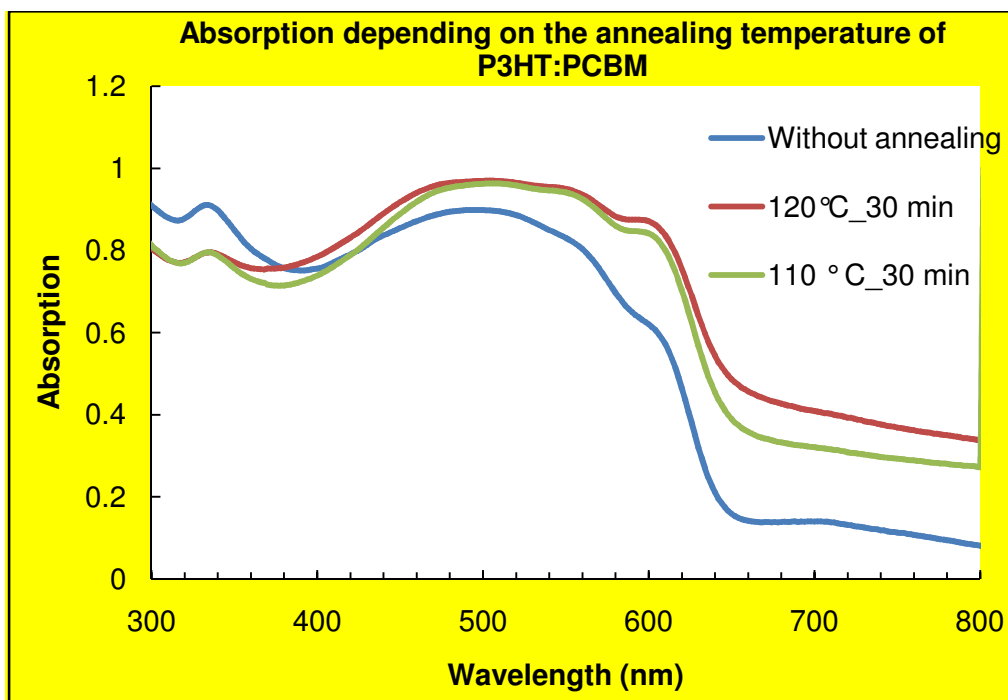


Fig.5.Absorption depending of the thermal annealing as function of the wavelengths

Fig. 6 and Table 1 show the influence of the thermal annealing in the performances of the OPV. The open circuit voltage V_{oc} and the efficiency η are improved with thermal annealing at 130°C.

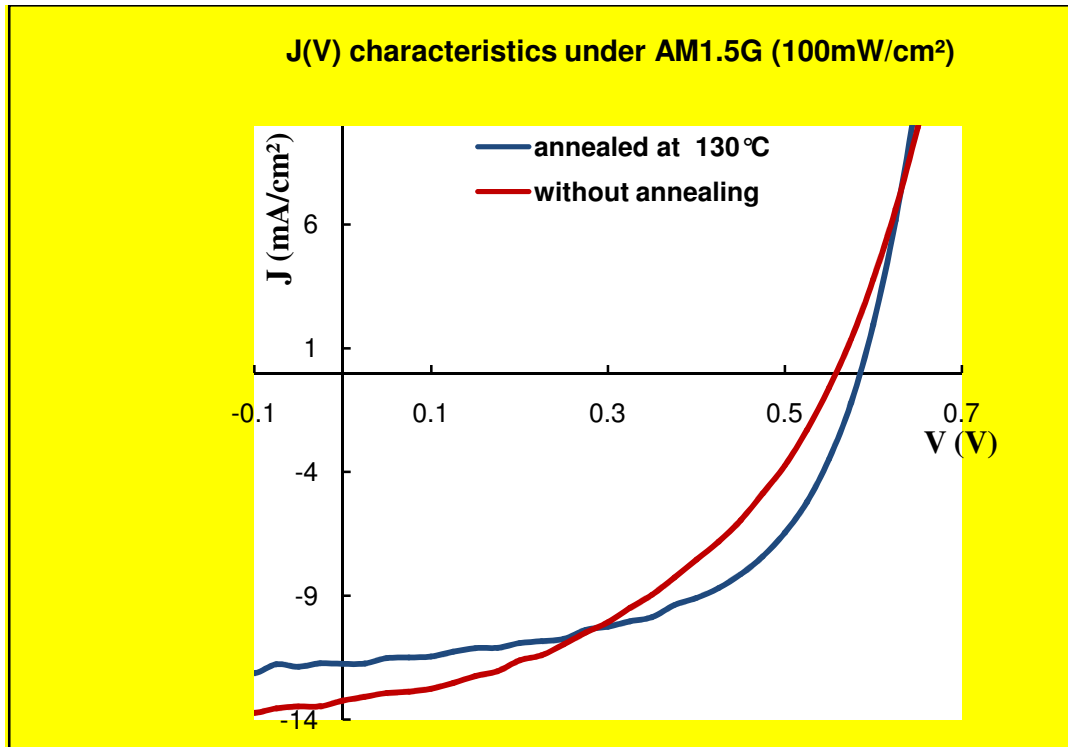


Fig.6. Effect of the thermal annealing on the performance of the OPV.

Table 1: Effect of the thermal annealing on the performances of the cells

	V_{oc} (V)	J_{sc} (mA.cm ⁻²)	FF	η (%)	R_{serie} (Ω)	R_{shunt} (Ω)
Annealed at 130°C	0.57	11.66	0.55	3.69	47.74	1995.68
Without annealing	0.55	13.14	0.43	3.13	73.58	1131.53

3.2. Concentration effect on the performances of organic cells

Fig.7 shows the current density (J) voltage (V) characteristics of the organic solar cells made with the different concentrations. The higher performances are obtained when the concentration of the blend is 70 mg/ml, efficiency = 3.2, V_{oc} =0. 52 V, J_{sc} =12, 74 mA/cm², FF= 48.56. When the concentration is higher the thickness of the active layer is higher, then the efficiency is better.

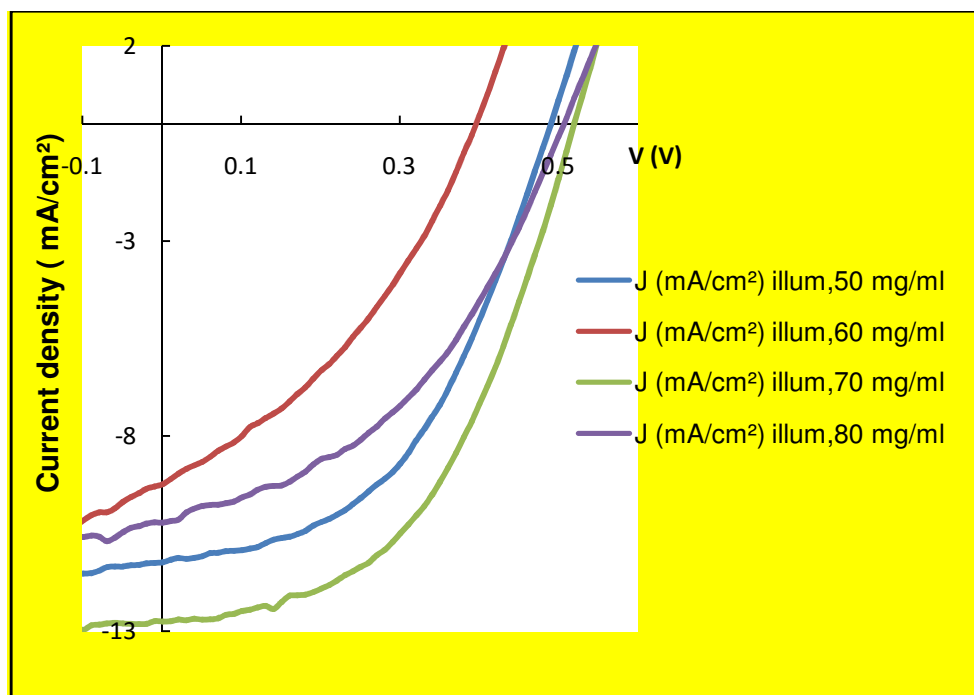


Fig.7. Characteristic J (V) with different the concentration of the P3HT: PCBM blend.

3.3. Effect of the substrates type ITO and FTO

The type of substrates is another parameter which affects the performances of the solar cells; flexible organic solar cells as a function of post-annealing temperatures were studied [9]. In this work we use two different transparent electrodes deposited on glass: ITO and FTO. The FF of cells with ITO is better than with FTO substrates because the transmittance and the conductivity of ITO are higher than of FTO. Fig.8 shows J (V) characteristics under illumination of organic solar cells with different substrates.

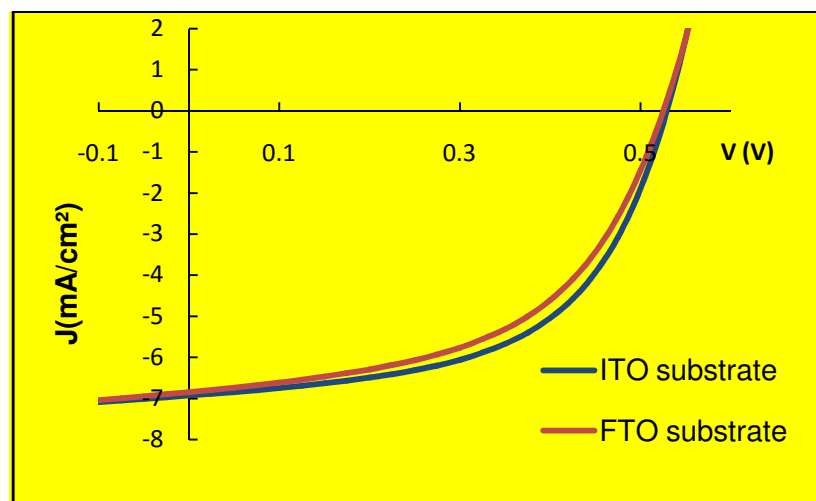


Fig.8. Characteristics J (V) of organic solar cells with different substrate.

4. CONCLUSION

Various parameters contribute to the stability of the performances of organic solar cells. The materials used in their elaboration such as the active layer and the electrode contact. The current density depends in temperature, the mobility of carrier charges, and substrate type. Thermal annealing reduce interface defect, and improves the crystalline structure which improves the mobility of carriers then improves photocurrent. Several factors contribute to increase the series resistances when the device is left in ambient conditions such as reduction of mobility, metal corrosion at the contact or changes in the contact barrier and charge space regions. The collection efficiency is determined by a collection length which depends on the quality of the active layer.

In general, there are six main important processes which might limit the power conversion efficiency of organic photovoltaic devices:

1. Light absorption in the film.
2. Free charge carrier generation.
3. Charge transport to the opposite electrodes and extraction by the electrodes.
4. Carrier recombination.
5. Architecture dimension and design of the device.
6. Temperature effect (annealing temperature of the active layer and the cells).

In order to improve the performances of organic solar cells we must use polymer with a small gap, adequate HTL and ETL, and transparent electrodes with high transmittance and high conductivity.

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