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Realization and Characterization of P-typed Polythiophene Based Organic Photovoltaic Cells

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In this work, an organic photovoltaic cell experimental study was performed to improve the electrical characteristics (current and voltage) and the conversion efficiency. Three Schottky organic photovoltaic cells that based polythiophene are realized experimentally for several cell surfaces and transparent electrode types. According to the obtained results, the best conversion efficiency is registered for the organic cell fabricated by {ZnO:Al/PTH/Al}. The photovoltaic cell performances are highly dependent on their geometry and the rearrangement of the polymer grains in contact with the metal that reflects the surface state significance of the two parts (metal and polymer). The electrode type used in the cell manufacturing possesses a very important influence on the cell electrical characteristics.

Keywords: Organic photovoltaic, Solar cell, Schottky P-doped polythiophene.

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1. INTRODUCTION

Research on organic solar cells has a significant infatuation because they have very interesting properties and many advantages [1, 2], including the cell flexibility and the ability to be exploited in large areas, the low costs of materials and the low fabrication cost [3, 4]. However, their stability and efficiency must be considerably improved compared to their current state.

In 1994, Heeger et al [5] have studied the active layers that based on the conjugated and derived polymers C60 on the structure of ITO/MEH-PPV:C_{60}/Calcium. During the following year, Hummelen et al [6] have employed the synthesized fullerene derivatives that possessed a better solubility, they obtained performances 2.9 % under illumination of 20 mW·cm^{-2} for the structure of ITO/MEH-PPV:[6.6]PCBM(1:4)/Calcium. In addition, Heeger et al [7] have added interface layers between the electrodes and the active layer. From 2003, cells based on P3HT: PCBM exceeded 3 % performance [8, 9]. In 2005, performances of 5 % were obtained [10, 11]. At 2007, a performance near to 6 % was reached [12]. During the last decade, 7 % performance is obtained for the PCDTBT, PBDTT-DPP and PBDTTT-C polymers [13, 14], for PTB7 polymers the obtained performance is 8.37 % [13].

Recently, the research on organic photovoltaic (PV) devices has made significant progress. However, the achieved organic photovoltaic power conversion efficiencies are still lower than those of inorganic solar cells. The main limiting factor of the high-efficiency organic PV devices realization is the short exciton diffusion length in most organic semiconductors (typically a few nanometers) [15, 16]. Currently, donor–acceptor (D-A) bulk heterojunctions (BHJs) fabricated by controlling phase separation in D-A mixtures are widely utilized to avoid such an exciton diffusion bottleneck [17].

This present work is related to the realization and characterization of organic photovoltaic cells based on a polymer of the Schottky type. The used material for the anode construction is the aluminum, the used polymer in the active layer is the synthesized polythiophene that is doped by $FeCl_3$ (*p*-doping) and the used transparent electrodes a cathode in these prototypes are SnO_2 and ZnO. Three Schottky organic photovoltaic cells that based polythiophene are realized experimentally for several cell surfaces and transparent electrode types. The objective of this work is the electrical characteristics improvement study (current and voltage) and the conversion efficiency of this organic photovoltaic cell type.

2. ORGANIC PHOTOVOLTAIC CELL

2.1 Organic Semiconductor

An organic semiconductor is an organic component in the form of a crystal or a polymer that has properties similar to a semiconductor inorganic. These properties are the conduction by electrons-holes and the band gap characteristic. This material type has given birth of the organic electronics or the plastic electronics. It is important to clarify that the polymeric conductors rival the metallic conductors in certain applications. In fact, under the normal conditions, the metallic conductor electrical conductivity values are comprised between 10^1 and 10^6 S·cm^{-1}, for example, the copper has an electrical conductivity of order 10^6 S·cm^{-1}. The semiconductor electrical conductivity values are comprised between 10^{-7} S·cm^{-1} and 10^1 S·cm^{-1}, for example, the silicon has an electrical conductivity of 10^{-4} S·cm^{-1}. In contrast, the non-conductor materials have electrical conductivities less than 10^{-7} S·cm^{-1}. In general, the polymers have a wide interval of electrical conductivities, 10^{-18} to 10^5 S·cm^{-1}, they have utilization flexibil-

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ity, and they can be used as insulators, semiconductors and conductors. The polythiophene polymer family have an electrical conductivity range of 10^{-11} to 10^3 S·cm^{-1} [18].

2.2 Photovoltaic Effect in the Organic Solar Cells

The photovoltaic effect is a photoelectric effect which serves the electrical energy production through a light source (sunlight, lumpfish, nergy solar to electrical energy. The photovoltaic effect is influenced by the illumination intensity, temperature, position and PV cell component material types etc. The photovoltaic effect in the organic solar cell is characterized by the short-circuit current (*Isc*), the open circuit voltage (*Voc*) and the conversion efficiency (η) [18].

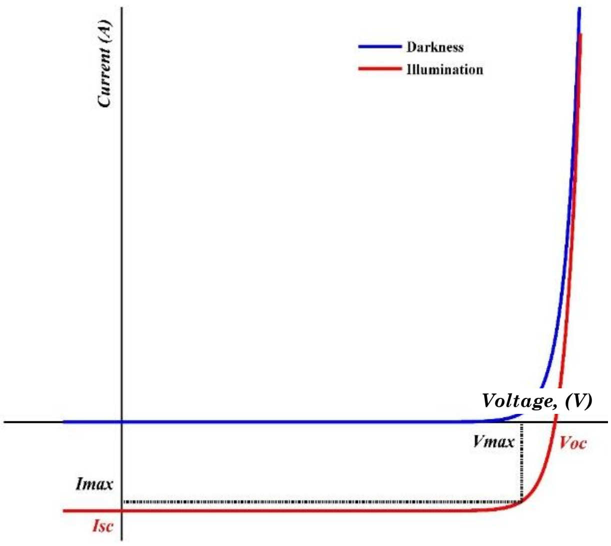

Fig. 1 – Current-voltage characteristic and the photovoltaic cell electrical parameters

Fig. 1 Shows the current-voltage characteristic in the dark and under typical illumination of the PN junction solar cell. The electrical parameters characterizing the organic solar cell are clearly shown in Fig. 1 [19].

– **Short Circuit Current:** The short-circuit current is achieved by shorting the cell electrodes ($V = 0$ V), in other words, it is the largest current that can be obtained with a solar cell. It linearly increases with the cell illumination intensity; it also depends on the illuminated surface, the radiation wavelength, the carrier mobility and the cell temperature.

– **Open Circuit Voltage:** To obtain the open circuit voltage value, it is necessary to ensure that the current intensity through the cell is zero. In the organic solar cell case, *Voc* is linearly dependent on the donor material level HOMO and the acceptor material level LUMO. The charge losses in the interface electrode/semiconductor decrease the cell performance *Voc*, the open circuit voltage decreases with increasing temperature; it varies slightly depending by the light intensity [18].

– **Form factor:** The form factor is the ratio between the maximum power supplied by the cell and the product of the open circuit voltage and the short circuit current. Eq. (1) [18].

$$FF = \frac{P_{\max}}{I_{sc} \cdot V_{oc}}. \quad (1)$$

– **Conversion Efficiency:** The essential mechanisms involved in the photovoltaic conversion process are summarized in Fig. 2 [20], [18]. These mechanisms are affected by recombination phenomenon, which reduces the cell performance.

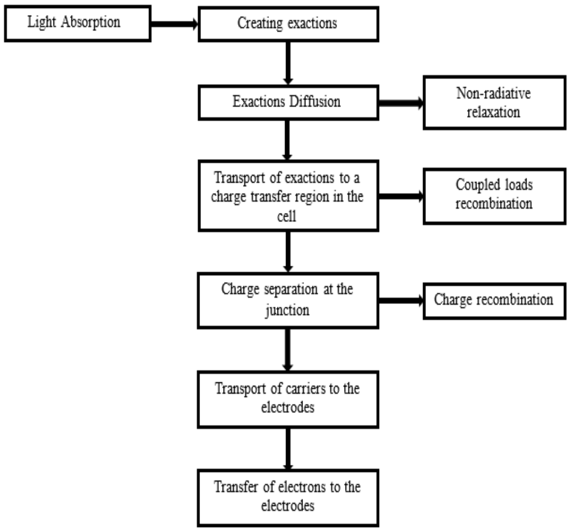

Fig. 2 – Conversion steps and the power losses mechanism

The photovoltaic cell conversion efficiency is defined by the ratio between the delivered maximum power ($P_{\max}$) and the incident light power (P_{in}) Eq. (2) [19]:

$$\eta = \frac{P_{\max}}{P_{in}} = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_{in}}. \quad (2)$$

The photovoltaic conversion efficiency improvement of the organic solar cells (conjugated polymer in our case) equires the improvement of mechanisms brought intoplay in this process by making a good choice of the device structure [19].

3. EXPERIMENTAL METHOD

3.1 Choosing the Organic Cell Material Type

The organic photovoltaic cell construction materials have a very important influence on the photovoltaic conversion efficiency, absorption and current density delivered by the cell.

– **Active Layer:** Among several types of conjugated polymers available (PPV 2.7 eV, MDMO-PPV: 2.48 eV, MEHPPV 2.1 eV, PPP: 3 eV ... etc.), the polythiophene (PTH) have a small band gap of 2 eV, a good chemical stability compared to other semiconductor polymers and a good electrical conductivity of 5.62 10^{-3} S·cm^{-1}. These three characteristics support the choice of polythiophene as an active layer.

– **Transparent Electrode:** The choice of F-doped SnO_2 or Al-doped ZnO as transparent electrodes is based on the optical and electrical properties, cost, toxicity ... etc. These two materials have the following criteria: the good electrical conductivity, the high transmittance that is more than 85 % in the visible, the availability of SnO_2, the low construction cost, the stable characteristics (thermal, chemical and mechanical) and the low toxicity. Moreover, these transparent electrodes (SnO_2 and ZnO) are the most used in the photovoltaic cell manufacturing domain. According to these criteria, the SnO_2 and ZnO are the best candidates for the replacement of ITO [21, 22] in the organic solar cell manufacturing. In this work, the proposed organic cell structure uses two transparent electrode types (SnO_2 and ZnO film) on the glass substrate; these two transparent electrodes have an output works of 4.85 eV and 3.3 eV, respectively.

– **Metal Electrode:** The nature of metallic electrode material conception is a factor limiting the current density delivered by the cell. The metallic electrode output work should be large, the electrode conception material must be available and the cost of this material should be minimal Table1. According to these criteria, the aluminum is an acceptable candidate for the realization of metallic electrodes. In addition, the aluminum is the electrode material most used for the inorganic and organic cell construction.

Table 1 – Out work and cost of different materials

Material	Out Work (eV)	Cost ($) of 1 Kg
ITO	5.14-4.5	299-405
PEDOT	5.2-5.3	1000
Aluminum	4-4.2	1.666
Gold	5.1	4521.28
Silver	4.3	624.85
Calcium	2.8	0.22

3.2 Organic Solar Cells Development

After completing the first step that consists in the choice of the organic photovoltaic cell component materials, the second step concerns mainly the choosing of the photovoltaic cell structure type.

There are several mounting types of the organic and inorganic photovoltaic cells. The assembly type choice is linked to the component materials availability, the used equipment availability in the organic cell development, the technology mastery, the implementing cost and the used method mounting reliability. The choice of the Schottky structure type is determined according to these criteria.

The Schottky structure consists of an active layer (polythiophene P-doped in the present case) and two electrodes, the first electrode represents a transparent anode (SnO_2:F or ZnO:Al in the present case) and the second electrode represents a metal cathode (aluminum in the present case), and a glass substrate. To realize the Schottky structure, the transparent electrode must be placed on the glass substrate. Then, the active layer is placed on the transparent electrode; the aluminum electrode is placed on the active layer, so that the obtained composition must be in the form of a sandwich. This elaborate structure allows the light passage through the glass and transparent electrode towards the active layer, which leads to the photoelectric conversion process. Therefore, the electrical charges gathering in the metal electrode (aluminum) supplying an electric current Fig. 3.

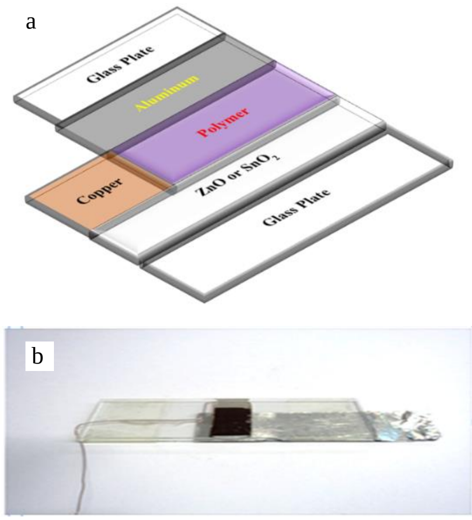

Fig. 3 – Organic solar cell: structure (a), photo (b)

The present work focuses on the realization and characterization of three organic photovoltaic cells of Schottky type. The three realized cells contain the same active layer of polymer (polythiophene P-doped), the same metal electrode of aluminum and the same glass substrate. The first completed test concerns the used material type for the transparent electrode preparation, the first made cell has a transparent electrode of SnO_2:F and the second cell has a transparent electrode of ZnO:Al [21]. For knowledge the best transparent electrode, it is necessary to keep the same cell dimensions (the thickness of each component must be 100 nm and the contact surfaces between the different components must be 1 cm^2) and the same climatic conditions (Lighting, temperature ... etc.). The second test concerns the production of the third cell with an active surface area of 1.5 cm^2, for determinate of the photovoltaic cell characteristic behavior according to the active surface area variation.

Finally, the volt-amperometric method is used to determinate the characteristic curves $I(V)$ under illumination and in the dark to obtained the short-circuit current, the open circuit voltage, the maximum power and the conversion efficiency of each elaborated organic photovoltaic cell.

4. RESULTS AND DISCUSSION

4.1 Electrical Characterizations of Realized Schottky Cells

This part focuses on the measuring electrical characteristics and the proposing an electrical model for the organic photovoltaic cells, as well as the determination of parameters that influence on the organic photovoltaic cell efficiency, particularly the cell surface and the used material type in the transparent electrode conception. The produced photovoltaic cells are presented according to the conception material type and the contact surface Table 2.

Table 2 – Developed organic photovoltaic cells

Cell	Polymer	Transparent electrode	Surface (cm^2)
N°1	PTH	SnO_2:F	1
N°2	PTH	ZnO:Al	1
N°3	PTH	SnO_2:F	1.5

The first realized cell contain a P-doped polythiophene film which has an electrical conductivity of $13.5\ 10^{-3}$ S·cm^{-1}. The used transparent electrode is based on SnO_2 (doped by 14 % F in 400 °C), which has an electrical resistivity of $1.6\ 10^{-3}$ Ω·cm. the area of the first realized organic photovoltaic cell is identical to the 1 cm^2.

Table 3 (cell 1) shows the short-circuit current and the open circuit voltage of the first realized organic cell under illumination of $G = 500$ W·m^{-2} and in the dark, for an ambient temperature of 28 °C.

For a better representation of the generated current evolution by the PV cell as an electrical voltage function between its bounds, the two curves are traced in the darkness and under illumination Fig. 4.

The electrical characteristics (current and voltage) which are showing in the Fig. 4 indicate that the cell actually behaves like a diode (junction). In addition, in the illimitation case, the solar radiation photonic effect on the electric charge creations is clearly visible in this figure, which is logically reflected by an increasing in the recorded current values.

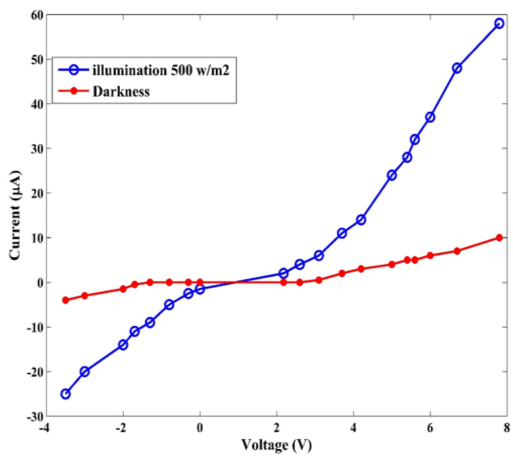

Fig. 4 – Current-voltage characteristic of the first cell of a surface of 1.0 cm^2

With respect to the obtained curve in the darkness, the unregistered observations in the illumination case are valid in darkness case for the direct and reverse polarizations of the metal/polymer junction.

The second realized cell contain a P-doped polythiophene film that has an electrical conductivity of $13.5\ 10^{-3}$ S·cm^{-1}. The used transparent electrode is based on ZnO (doped by 1 % Al in 450 °C) which has an electrical resistivity of 0.11 Ω·cm. the area of the second realized organic photovoltaic cell is identical to the 1 cm^2.

Table 3 (cell 2) Shows the short-circuit current and the open circuit voltage of the second realized organic cell under illumination of $G = 500$ W·m^{-2} and in the dark, for an ambient temperature of 28 °C.

In order to demonstrate the luminance effect on the characterizations $I(V)$ of the second realized photovoltaic cell, the two delivered current curves are plotted on the same graph in function of the voltage V in darkness and under illumination Fig. 5.

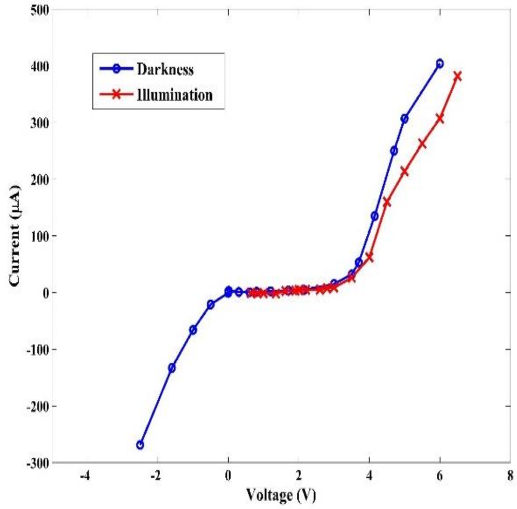

Fig. 5 – Current-voltage characteristic of the second cell of a surface of 1.0 cm^2

The photonic phenomenon is presented also in this second cell, the electrical magnitudes order is important comparatively to the first cell, also the magnitude value has an order of tens µA. This augmentation is caused by the ZnO transparent electrode that presents a good electrical conductivity and a law electrical resistivity compared to SnO_2.

In the same context, the third realized cell contain a polythiophene film has an electrical conductivity of $13.5\ 10^{-3}$ S·cm^{-1}. The used transparent electrode is based on SnO^2 (doped by 14 % F in 400 °C), which have an electrical resistivity of $1.6\ 10^{-3}$ Ω·cm. The area of the third realized organic photovoltaic cell is identical to the 1.5 cm^2.

The open circuit voltage values and the short circuit current values are giving in Table 3 (cell 3), for $G = 500$ W·m^{-2} and $T = 28$ °C.

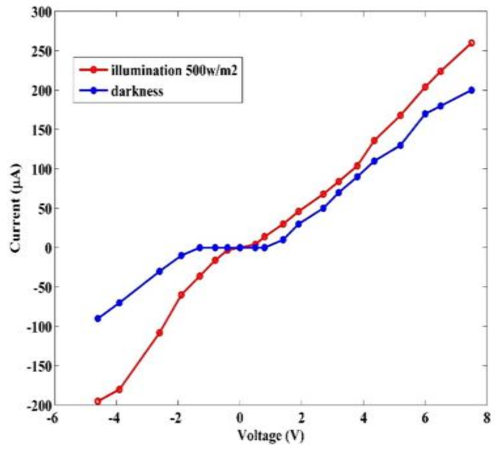

Fig. 6 – Current-voltage characteristic of the third cell of a surface of 1.5 cm^2

Fig. 6 shows two graphic representations of the electrical characteristics (current and voltage) in the darkness and under illumination of the third realized cell.

The observed phenomena in the first cell of 1 cm^2 area are the same observed phenomena in the third cell that has a surface of 1.5 cm^2. The principle difference between these two cells is the current amplitude that increases proportionally with increased surface. This increase is in the order of 30 times in the darkness, and it is in the order of 9 times when the cell is exposed to the illumination.

4.2 Organic Solar Cell Performance

P_{max} is defined by the product (I_{max}*V_{max}) [23] which must be maximal. The external photovoltaic efficiency is defined by the ratio between the maximum output electric power and the product of the generator surface and the incident radiation Eq. (3) [18].

$$\eta = \frac{I_{max} \cdot V_{max}}{S \cdot G}. \quad (3)$$

The conversion efficiency is an essential parameter in the organic photovoltaic cell development. In effect, the knowledge of its value allows evaluating the cell performances. In the obtained experimental measures, one can also compare the performance of different realized photovoltaic cells by the conversion efficiency.

Table 3 regroups the photovoltaic parameters of the three realized cells. The second photovoltaic organic cell is the most effective because it contains a transparent electrode of ZnO. This cell delivers a short circuit current of 22.54 μA and an open circuit voltage of 0.65 V under illumination of 500 W·m^{-2}, logically their yield is equal to 0.029 %.

Table 3 – Electrical parameters of all realized cells

N°	Cells	V(V)		I(μA)		η %
		500W/m^2	Darkness	500W/m^2	Darkness	
1	SnO_2 / PTH / Al, S = 1 cm^2	0.820	0.570	2.5	0.2	0,0041
2	ZnO / PTH / Al, S = 1 cm^2	0.65	0.43	22.54	2.3	0.029
3	SnO_2 /PTH/Al, S = 1.5 cm^2	0.929	0.324	22	6	0,027

5. CONCLUSION

This modest paper can be considered as a contribution in the renewable energies domain and specifically in the conversion photovoltaic, it presents many perspectives for the organic solar cell development. Organic photovoltaic cell experimental study was performed to improve the electrical characteristics (current and voltage) and the conversion efficiency.

Three Schottky organic photovoltaic cells that based polythiophene are studied according to the cell surface and transparent electrode type. The obtained results show that the best performances are obtained by the large cell; this proves that the cell efficiency is proportionally increasing with the contact area increasing. In addition, the best-used material for the electrode transparent conception is the ZnO, it delivers a good efficiency compared to the delivered efficiency by SnO_2.

In perspectives of this work, these cells can be significantly improved by the use a type of PN junction, which guarantees the drainage of all the electrical charges created by solar radiation and preventing recombination.

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