INFLUENCE OF PEDOT:PSS LAYER ON THE PERFORMANCES OF „BULK-HETEROJUNCTION" PHOTOVOLTAIC CELLS BASED ON MEH-PPV:PCBM(1:4) POLYMERIC BLENDS

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Photovoltaic cells having as active layer a mixture between poly{[2-[2',5'-bis(2"-ethyhexyloxy)phenyl]-1,4-phenylenevinylene]-co-[2-methoxy-5-(2'-ethylexyloxy)-1,4-phenylenevinylene]} (MEH-PPV) regioregular polymer and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) fullerene derivative were prepared on ITO covered optical glass and plastic sheets, as substrates. The samples have the same architecture, the main difference between them being the presence or not of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). For all the prepared structures, the morphological, optical and electrical characterization was carried out, comparatively. The current-voltage (I-V) characteristics in monochromatic light and the action spectra of the prepared structures were recorded, at room temperature. The parameters characterizing photovoltaic cells (short-circuit current, open circuit voltage and fill factor) were calculated and compared for prepared structures with or without PEDOT:PSS "buffer" layer.

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1. Introduction

In the last decade organic photovoltaic cells became of major importance taking into account that these devices have some important advantages like a low cost production and common processing techniques [1-3]. Many important scientific groups have focused on the research of these structures, studying the influence of morphology on the performances of photovoltaic cells [4-7] and different preparation methods [8-10]. Special attention is given to bulk heterojunction structures in which the electron acceptor and the donor are mixed together in a solution and then is spin-coated and deposited as a thin layer [11-13]. The major problem of these devices is related with their time stability [14], even if many researchers are trying to solve this.

To improve the photovoltaic performances of the prepared samples, as "buffer" layer between the anode and the active film is frequently used PEDOT:PSS. The architecture of the organic photovoltaic structures is important, so matching the energy level of the active layer with the work function of electrodes becomes necessary. With a high transparency in the visible range, a good thermal stability and a very easy processing [15-17] PEDOT:PSS is an ideal candidate for preparing organic photovoltaic cells. Although its electrical conductivity is not very high (0.05 – 0.8 S/cm) [15], it can be improved by adding carbon nanotubes [18-22] and ZnO nanoparticles [7, 23] mixed together in PEDOT:PSS solution.

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The goal of this study is to demonstrate the importance of PEDOT:PSS “buffer” layer on the performances of the bulk-heterojunction photovoltaic cells, based on MEH-PPV:PCBM polymeric blends, observing the induced changes on the physical properties of the prepared cells containing this film as compare with those which do not contain it.

2. Experimental details

5 mg of MEH-PPV polymer (poly{[2-[2',5'-bis(2''-ethylhexyloxy)phenyl]-1,4-phenylenevinylene]-co-[2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylenevinylene]}) and 20 mg of PCBM fullerene derivative ([6,6]-phenyl C_{61} butyric acid methyl ester) were dissolved in 1 ml cholobenzene and sonicated 24 hours to obtain a good homogeneity. The MEH-PPV and PCBM powders were purchased from Sigma Aldrich Company and used without further purification.

As substrates were used optical glass and plastic sheets (PET) covered with a thin layer of indium tin oxide (ITO) and before polymer's deposition these were cleaned as follows: for Glass/ITO: 15 minutes ultrasonicated in acetone, 15 minutes in ethanol and 15 minutes were treated with an UV-OZONE lamp and for PET/ITO was performed only the UV-OZONE irradiation.

Then the PEDOT:PSS and MEH-PPV:PCBM(1:4) polymer layers were deposited by spin-coating technique. After each deposition a thermal treatment was made, for samples only with PEDOT:PSS for 60 minutes at 100ºC and for the structures with blend for 30 minutes at 50ºC. To complete the photovoltaic devices an aluminum (Al) cathode was deposited by thermal vacuum evaporation.

The schematic structure of the realized samples is presented in figure 1.

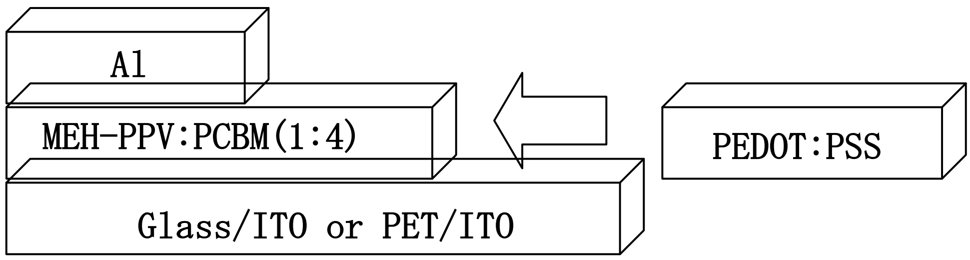

Fig. 1. Schematic structure of photovoltaic cells based on MEH-PPV:PCBM(1:4)

The morphological investigations were performed using an Ape Research SPM atomic force microscope. The absorption spectra were recorded at room temperature with a Perkin Elmer spectrophotometer in 190 – 1100 nm range. The action spectra were performed using a set-up consisting of a Cornerstone 130 monochromator and a Keithley 2400 Source Meter, controlled by a computer. The electrical characterizations were performed at room temperature containing the current –voltage (I-V) measurements carried out both in dark and under A.M.1.5. conditions. The parameters characterizing the photovoltaic cells, such as: short-circuit current (Isc), open circuit voltage (Voc), fill factor (FF), and power conversion efficiency (η), were determined for all prepared cells.

3. Results and discussion

All the samples have as active layer the polymeric blend MEH-PPV:PCBM(1:4), the differences were the presence or not of the PEDOT:PSS buffer layer and the type of used substrate, optical glass or plastic sheets.

The AFM images of the prepared thin active layers were presented in figure 2, comparatively for the structures with and without PEDOT:PSS.

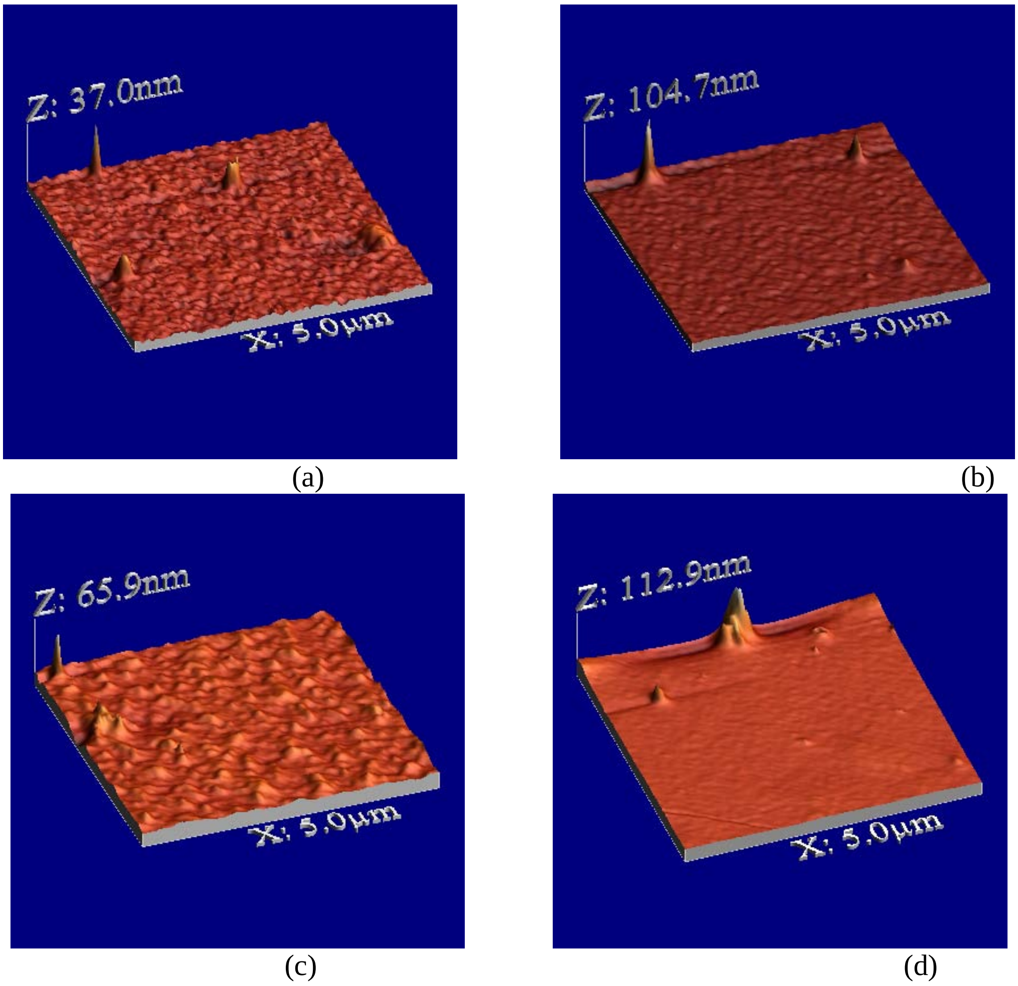

Fig. 2. AFM images of (a) Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4), (b) Glass/ITO/MEH-PPV:PCBM(1:4), (c) PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) and (d) PET/ITO/MEH-PPV:PCBM(1:4) thin layers

For all these samples the roughness (RMS – root mean square roughness) and Skewness factor (S_{sk}) values were detailed in table 1. The S_{sk} parameter, defined as (ISO 4287/1 ASME B46.1): $S_{sk} = \frac{1}{MNS_q^3}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left[z(x_k, y_l)-\mu\right]^3$ exhibited a positive value greater than 1 ($S_{sk} > 1$) for all thin films, indicating a flat surface with extreme peaks (grains).

Table 1. Calculated values for RMS *and Skewness factor of prepared samples.*

Sample	RMS (nm)	Skewness (nm)
Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)	1.20	4.1
Glass/ITO/MEH-PPV:PCBM(1:4)	2.80	17.5
PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)	2.00	3.5
PET/ITO/MEH-PPV/PCBM(1:4)	4.00	9.5

As can be observed from the data published in Table 1, the roughness of the samples with PEDOT:PSS buffer layer is smaller than the values obtained for the structures without this layer, particularly is almost half. The role of PEDOT:PSS layer was to smooth the surface between the electrode, Glass/ITO or PET/ITO, and the active layer, MEH-PPV:PCBM(1:4), contributing in our opinion to the decreasing of defect interface states and then improving the holes collection to the ITO electrode.

The optical characterization, representing the measurements of absorption spectra in the range of 190 – 1100 nm, revealed that the absorbance for Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) thin films is higher than the value obtained for the same samples but without PEDOT:PSS layer (see figure 4). The same behavior was observed for thin films prepared on PET sheets. For the samples without PEDOT:PSS layer the absorbance was less than for those which have this film deposited (see figure 5). For all devices the PEDOT:PSS layer was deposited by spin-coating technique following the procedure described above. The influence of PEDOT:PSS layer on the optical properties of the prepared thin films is more pronounced for samples on PET substrates. On the interest range, between 400 and 800 nm, the absorbance is almost double for those films with PEDOT:PSS (samples on PET). For films deposited on glass substrates the difference wasn't significant. A possible explanation can be related with the thickness of the substrates, the PET sheets are less thick than the optical glass.

To obtained a complete imagine of the prepared structures in figure 3 is presented the energy band diagram for these.

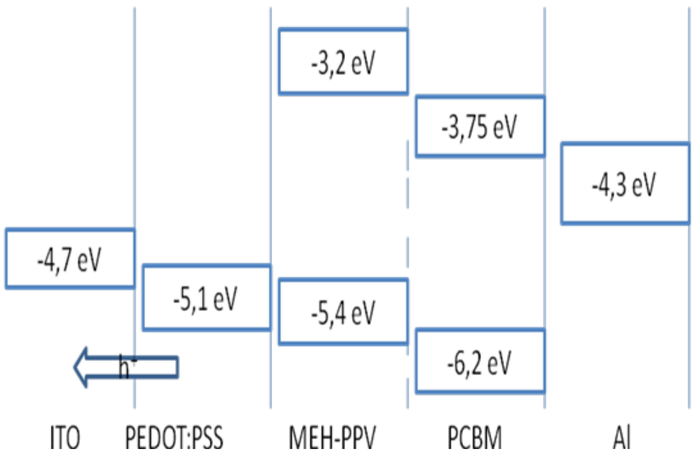

Fig. 3. Energy band diagram for the ITO/PEDOT:PSS/MEH-PPV:PCBM/Al photovoltaic cells

PEDOT:PSS layer is a holes collector, facilitating the holes transport to the anode because its work function is between the work function of the ITO and HOMO level of the active layer, as can be observed in figure 3.

The action spectra for the devices with and without PEDOT:PSS thin film are shown in figures 4 and 5, comparatively, together with the absorption spectra of Glass/ITO/(PEDOT:PSS)/MEH-PPV:PCBM(1:4) and PET/ITO/(PEDOT:PSS)/MEH-PPV:PCBM(1:4) thin films, respectively.

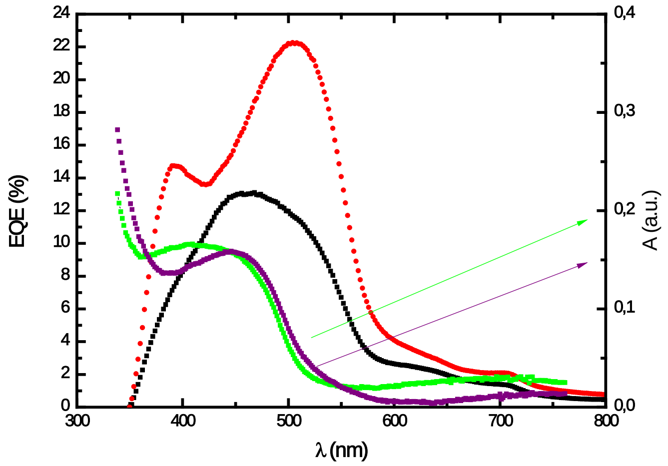

Fig. 4. Action spectra of Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al (red curve) and Glass/ITO/MEH-PPV:PCBM(1:4)/Al (black curve) photovoltaic cells respectively and absorption spectra of Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) (purple curve) and Glass/ITO/MEH-PPV:PCBM(1:4) (green curve) thin films

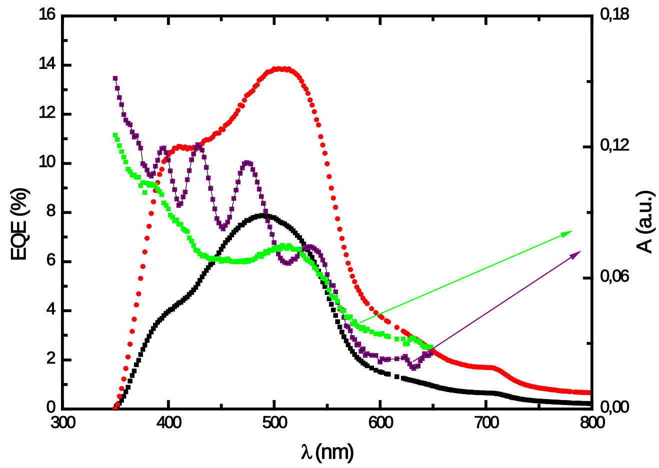

Fig. 5. Action spectra for PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al (red curve) and PET/ITO/MEH-PPV:PCBM(1:4)/Al (black curve) photovoltaic cells and absorption spectra of PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) (purple curve) and PET/ITO/MEH-PPV:PCBM(1:4) (green curve) thin films

As can be observed from figures 4 and 5 for the samples which have deposited the PEDOT:PSS thin film the external quantum efficiency (EQE) is higher than those who don't have it, almost doubled in value.

For samples on optical glass substrates the maximum in action spectra for both samples, with and without PEDOT:PSS layer, is slightly shifted to red, but as a whole range of wavelengths, the action spectra seems to be batic with absorption spectra, showing that the photo generation is highest for the wavelengths corresponding to the maximum in the absorption spectra.

For the structures deposited on PET sheets, the absorbance maximum is shifted to high wavelength, but we can notice the same behavior, the absorption and action spectra are batic.

These results confirm that PEDOT:PSS facilitates the holes collection to the anode and improves the obtained photocurrent values which can be influenced by the interfaces between the electrodes and the active layer [1]. If for electrons transporter were used different alkaline fluorides like LiF [24, 25], KF [26] or CsF [27, 28] as hole transporter for almost all photovoltaic devices is used PEDOT:PSS thin layer.

To extract the parameters characterizing the photovoltaic cells, the current-voltage characteristics in fourth quadrant were recorded at room temperature. In figures 6 and 7 are presented these for those structures with PEDOT:PSS film, taking into account that better results were obtained for analyzed samples with PEDOT:PSS layer, comparatively with those without this thin layer. The spectra were recorded at room temperature, at illumination through ITO electrode, in monochromatic light, λ=550 nm, for all the photovoltaic cells.

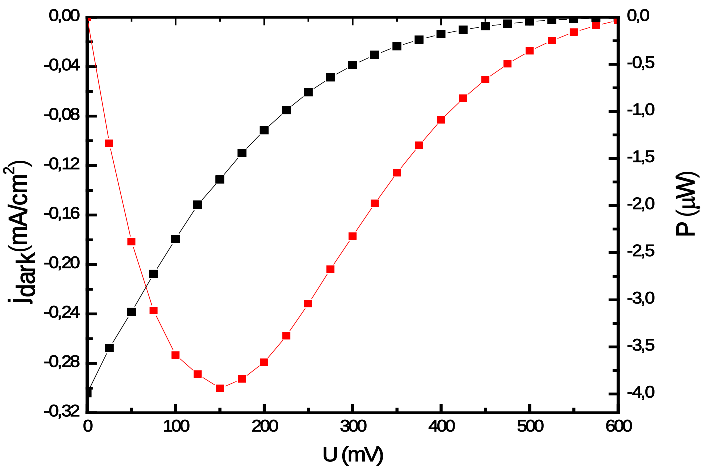

Fig. 6. I-V characteristics in fourth quadrant of Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al photovoltaic cells

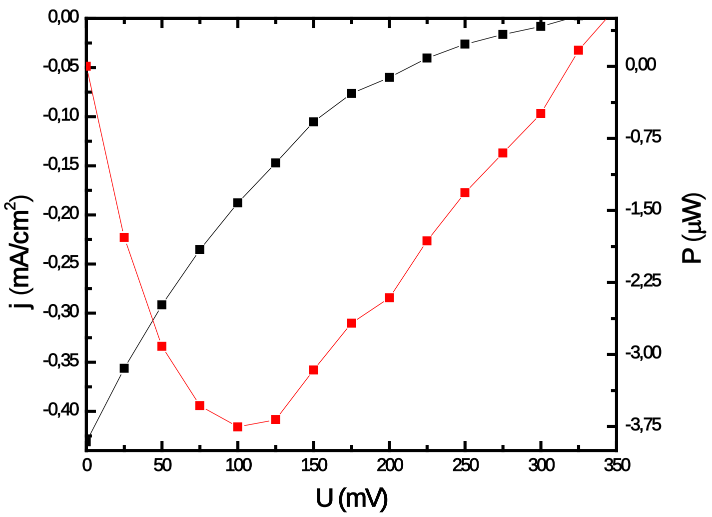

Fig. 7. I-V characteristics in fourth quadrant of PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al photovoltaic cells

Analyzing the I-V characteristics in fourth quadrant, the parameters characterizing a photovoltaic cell (short-circuit current, open circuit voltage, fill factor) were calculated and their values are given in table 2.

Table 2. Calculated parameters characterizing a photovoltaic cell.

Structure	V_{OC} (mV)	I_{SC}(mA/cm^2)	FF (%)
Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al	575	0.3	14
Glass/ITO/MEH-PPV:PCBM(1:4)/Al	275	0.045	8
PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al	325	0.4	13
PET/ITO/MEH-PPV:PCBM(1:4)/Al	425	0.09	13

In the case of the samples having the optical glass as substrate, the open-circuit photo voltage Voc for the structures containing PEDOT:PSS, is more than the double of its corresponding value in the case of structures without PEDOT:PSS. For samples with PEDOT:PSS, both on optical glass or PET sheets, the short-circuit values are higher than those obtained for the structures without this layer, particularly about two orders of magnitude for Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al photovoltaic cells and about five times higher in the case of PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al photovoltaic cells.

The fill factor was almost double for the structures deposited on optical glass substrates and with PEDOT:PSS layer than the value obtained for the same photovoltaic cells but without this layer. For PET samples we obtained the same value for structures with and without the ”buffer” layer.

4. Conclusions

Organic photovoltaic cells having as active layer the blend MEH-PPV:PCBM(1:4) were successfully prepared on optical glass substrates and flexible substrate (PET sheets), and the influence of PEDOT:PSS “buffer” layer on the structure’s performances was analyzed.

From morphological characterizations we can notice that samples which have deposited this thin film the roughness is less than for those without PEDOT:PSS layer, demonstrating the smoothing role of it. The optical absorbance is higher for Glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) and PET/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) thin film than for the same structures without PEDOT:PSS layer.

The action spectra of prepared samples revealed that the photovoltaic performances are improved for those which have this layer deposited, facilitating the holes transport between the active layer and anode and their collection to ITO electrode. This result is confirmed by the calculated values of parameters characterizing photovoltaic cells, short-circuit current, open circuit voltage and fill factor determined from the I-V characteristics in the fourth quadrant, in monochromatic light.

The importance of this layer was demonstrated by the obtained results for the prepared organic photovoltaic cells, but other new studies are needed to improve the efficiency’s values and their lifetime.

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