

Study of electrical and optical properties of ITO/PEDOT/P3HT:PCBM(1:1)/LiF/Al photovoltaic structures

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ITO/PEDOT/P3HT:PCBM(1:1)/LiF/Al photovoltaic cells were prepared by spin coating technique, using optical glass substrates covered with a thin ITO layer. The samples have the same structure, differing by LiF layer thickness. I-V characteristics in dark and under monochromatic light were recorded, at room temperature. The fill factor and the power conversion efficiency were calculated for each sample. The cell parameters in regime of photo-element were determined and their dependence on the thickness of the LiF layer are presented and discussed.

(Received September 30, 2010; accepted October 14, 2010)

Keywords: Polymer blends, P3HT, PCBM, Bulk-heterojunction, Photovoltaic cells

1. Introduction

Conjugated polymers are frequently used in organic solar cells [1], especially because they have some important advantages like low cost, low temperature processing and flexibility [2]. Since Sariciftci et al. [2] have discovered the charge separation in polymer/fullerene systems, they have been intensively investigated. After the first reports on polymer blend devices, many researchers tried to improve the power conversion efficiency by combining different materials and controlling their morphology [3]. The first organic photovoltaic cells were Schottky type, M1/Organic Layer/M2 (M1 and M2 were metals with different work functions, in such a way that one contact should be ohmic and the other one a blocking contact). The organic layer was typically monomeric: phthalocyanines, merocyanines or porphyrins were used [4]. The power conversion efficiency for these structures was small, of the order of 10^{-2} % [5]. Trying to increase the conversion efficiency, two- and three- layered devices were prepared, with better results. The structures based on polymeric blends, seem to be much more promising for these devices, with relatively high efficiency of about 4-5 % [6], also they are cheaper than the organic thin films, based on small molecules.

Over the past decade, many research groups have focused on regio-regular poly(3-hexylthiophene) (P3HT) as the standard electron-donor in polymer bulk-heterojunction solar cells [7]. Usually it is used in a mixture with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) [4].

Our study is related with ITO/PEDOT/P3HT:PCBM(1:1)/LiF/Al photovoltaic cells. The prepared samples have the same structure, but with

varying LiF layer thickness. We present a complete characterization of these devices and the differences between them, taking into account the LiF layer thickness.

2. Experimental procedures

As anode we used ITO-coated glass (100 nm thick), commercially available from Praezisions Glass und Optik (CECO20P). The substrates were cleaned by ultrasonication using isopropanol, acetone and helmanex, an alkaline detergent. Poly(ethylenedioxythiophene):polystyrene sulfonic (PEDOT:PSS) acid layer (100 nm thick) was deposited by spin coating technique.

After PEDOT deposition, substrates were heat treated in an oven at 140°C during 2 hours. This layer is used to facilitate the hole transfer between the active layer and the ITO electrode, due to its ability to help smooth the surface roughness, and also to the fact that its work function lies between the work function of ITO (4.7 eV) and the HOMO levels of the most *p*-type organic semiconductors. The polymeric films (P3HT:PCBM, 1:1) were deposited by spin coating technique in two steps: first during 70 seconds with an angular velocity of 1500 rot/s and second step in 20 seconds with an angular velocity of 2000 rot/s. We prepared two sets of samples differing by LiF thickness layer (P1 sample – 200 nm and P2 sample – 75 nm). LiF layer was deposited by thermal vacuum evaporation. To complete the photovoltaic structures an Al top contact was deposited by thermal vacuum evaporation. The residual pressure in the deposition chamber was 10^{-5} mbar. A cross section through the prepared samples is shown in Fig. 1.

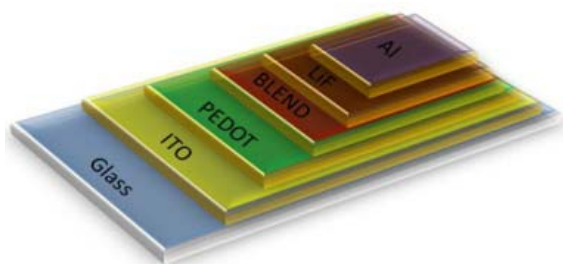


Fig. 1. Structure of the photovoltaic cells based on P3HT:PCBM(1:1).

The morpho-structural characterization of the component thin films was performed using atomic force microscope (Ape Research SPM; AFM A100-SGS apparatus). The roughness and thickness of the films were determined by X-ray reflectometry using Bruker D8 Discover XRD diffractometer.

Absorption spectra were recorded at room temperature using a UV-VIS Perkin-Elmer Lambda 35 Spectrophotometer. Action spectra were performed with a set-up consisting of a Cornerstone 130 monochromator and a Keithley 2400 Source Meter, controlled by computer. The current-voltage characteristics of the cells both in dark and under illumination with monochromatic light were measured at room temperature. The fourth quadrant I-V characteristics were recorded under monochromatic light with different wavelength related with the maximum in action spectrum of each investigated structure.

3. Results and discussion

X-ray reflectivity is sensitive to thin films having the thickness in the range of atomic dimensions to many tens of microns, by virtue of the X-ray wavelengths employed at the very high diffraction space resolutions attainable. The strong interference between the different boundaries of refractive index give rise to fringing from which the

thickness can be estimated using
$$t = \frac{(i-j)\lambda}{2\sin(\omega_i - \omega_j)}$$
,

where i and j are the fringe orders and ω_i and ω_j their corresponding angles, respectively. This is simply derived from Bragg's law and was first use for thickness determination with reflectometry by Keissing [8]. The reflectometry curves recorded for ITO/PEDOT/P3HT:PCBM/LiF/Al cells with the Cu $k_{\alpha 1}$ line, $\lambda = 1.5406 \text{ \AA}$ are shown in Fig. 2a.

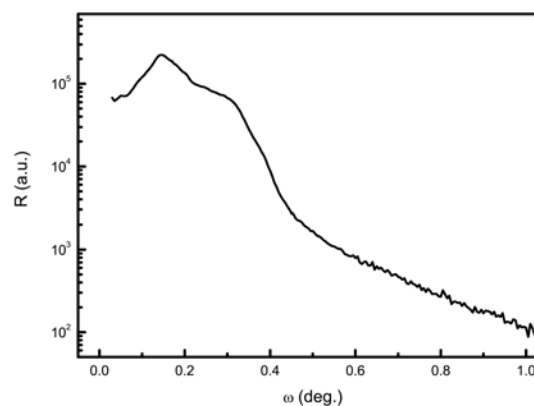


Fig.2a. Reflectometry curve for ITO/PEDOT/P3HT:PCBM film

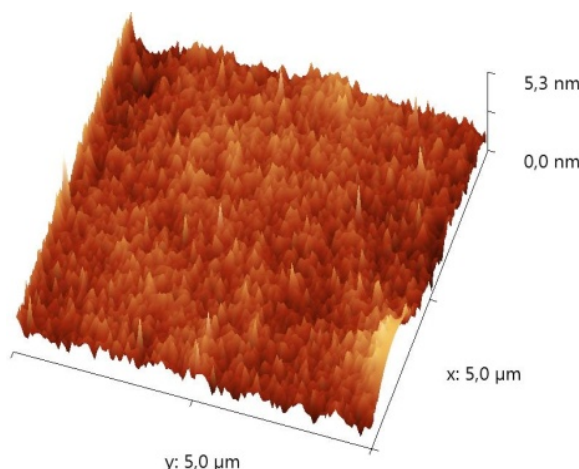


Fig.2b. AFM image for ITO/PEDOT/P3HT:PCBM surface

The thickness and roughness of P3HT:PCBM layer had been calculated from the experimental curves using LEPTOS software package, and the values obtained were 123 nm and 14 nm, respectively. Such values are typical for spin coating polymeric films. It is known that a reduced thickness of the films should lead to reduced compressive stresses, conferring to the structure a good mechanical integrity.

I-V characteristics both in dark and under illumination with 550 nm monochromatic light obtained for P1 are presented in Fig. 3.

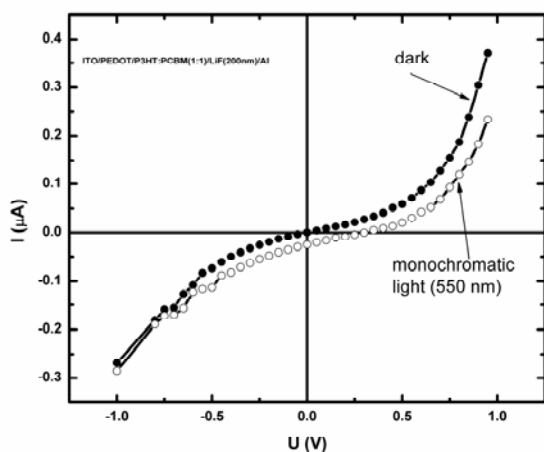


Fig. 3. I-V characteristics in dark (filled circles) and in monochromatic light of $\lambda=550$ nm (empty circles) for ITO/PEDOT/P3HT:PCBM(1:1)/LiF (200 nm)/Al photovoltaic cells.

I-V dependence is non-linear and asymmetric for both samples, with a low rectifying factor, but increasing for higher applied voltages.

The action spectra for P1 sample together with the absorption spectra are presented in figure 4. The absorption spectrum of the P3HT:PCBM(1:1) blend layer, was enlarged with respect of the absorption spectra of the P3HT and PCBM layer, respectively [4], ranging from 300 to 700 nm.

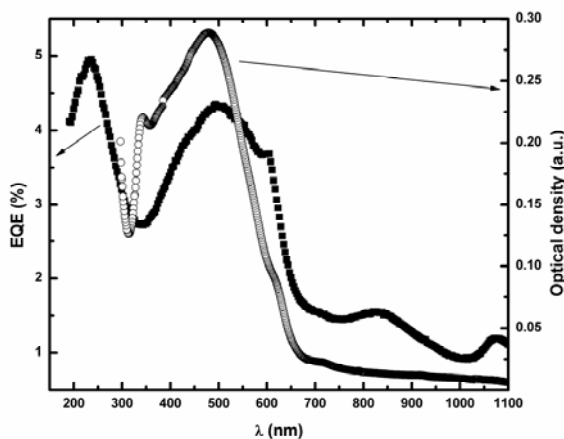


Fig. 4. Action spectrum (filled squares) and absorption spectrum (empty circles) for ITO/PEDOT/P3HT:PCBM(1:1)/LiF (200 nm)/Al as prepared samples

The measured spectra seems to be batic, the maximum photocurrent is obtained for a maximum in absorption, showing that the D/A bulk heterojunction are responsible for photovoltaic response, and the filtering effect, present in the case of ITO/PEDOT/P3HT:PCBM(1:1)/Al cells,

disappears [4], most probably due to the presence of LiF thin film. Comparing with the Schottky structures which have only P3HT or PCBM as organic absorber [4], the action spectra of ITO/PEDOT/P3HT:PCBM(1:1)/LiF/Al cells, was extended in the range 350-650 nm.

While the PEDOT layer facilitates the holes transfer, the LiF layer has the same action for electrons, facilitating their collection. But the series resistance of the cell was increased leading to a low fill factor.

I-V characteristics in dark for P2 samples are presented in Fig. 5.

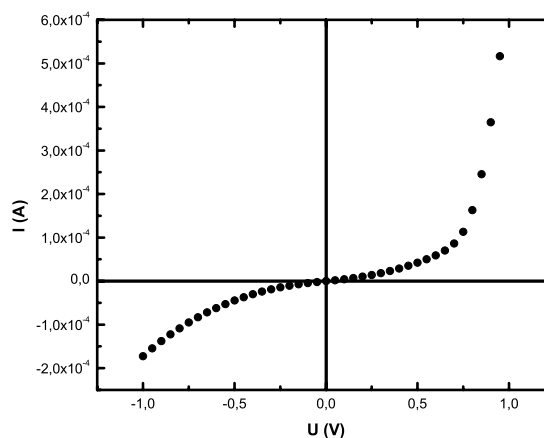


Fig. 5. I-V characteristics in dark for ITO/PEDOT/P3HT:PCBM(1:1)/LiF(75 nm)/Al

I-V characteristics were recorded at room temperature for both forward and reverse bias. The forward bias corresponds, like for P1 samples, to positive voltage on the ITO contact. The rectifying factor was increased with respect to that of sample P1.

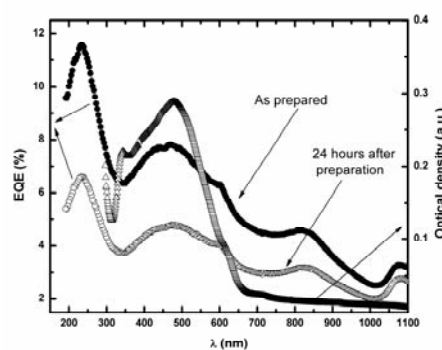


Fig. 6. The action spectra normalized to the power of the light source of the ITO/PEDOT/P3HT:PCBM(1:1)/LiF(75 nm)/Al cell, for as prepared samples (filled circles) and after 24 hours preparation (empty circles) and the absorption spectrum of P3HT:PCBM(1:1) films (empty triangles)

Action spectra together with the absorption spectra for P2 samples are presented in figure 6.

Also, the two spectra are batic, like in the case of sample P1, but External Quantum Efficiency (EQE) of this cell, was more than two times than that of sample P1. This behavior is due to smaller thickness of LiF film.

The fourth quadrant I-V characteristics for P2 samples in A.M. 1.5 conditions is presented in figure 7, these having the EQE higher than that of sample P1. For this set of samples, the open circuit voltage was 0.68 V and the short circuit photocurrent was 1.55 mA. Maximum power obtained was 0.3 mW, the fill factor was 0.28 and the power conversion efficiency calculated in A.M.1.5 conditions was 0.48 %. All these parameters are increased with the corresponding values obtained in the case of the cells without LiF [4].

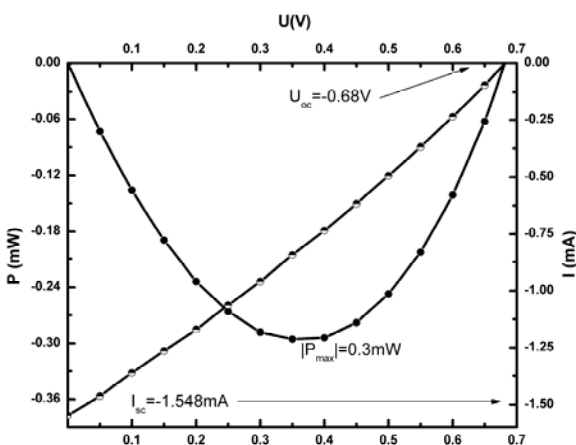


Fig.7. The fourth quadrant I-V characteristics of the ITO/PEDOT/P3HT:PCBM(1:1)/LiF(75 nm)/Al cells in A.M.1.5

Typical features of the photovoltaic cells based on the P3HT:PCBM blend polymers, is the fact that their stability in time is very poor [4], that is why, we have also addressed this problem in the case of our ITO/PEDOT/P3HT:PCBM(1:1)/LiF(75 nm)/Al cells. The action spectra measured after 24 hours (see figure 7), have the same shape as for prepared samples, but the values of EQE is 12 %, while after 24 hours the value is around 6 %. To explain this behavior, we measured the absorption spectra of P3HT:PCBM(1:1) layer at different time intervals, and we observed that, do not appear changes between them, resulting that no changes take place in the optical processes giving rise to the excitons creation in these materials [4]. But are dramatically changes in physical processes involved in the photo generation of the charge carriers, their separation and collection to the electrodes. As regarding the explanation of this behavior, we believe that the diffusion of In from ITO in polymers film, such as suppose different authors [9-12], could be one of the causes of the degradation of this type of organic photovoltaic cells. For example the decreasing in time of the open-circuit photovoltage could be explain in this hypothesis by the creation of more free electrons in ITO,

then the Fermi level of ITO will go up, so the differences between the work function of ITO and Al, respectively, decreases, then diminishing the internal electric field of the structures. So even the cell is not short-circuited by the paths created by the In to Al electrode, the photocurrent decreases due to the decreasing of the electric field. Now, systematically studies are carried out, devoted to explain these processes in view to the increasing the stability of the promising photovoltaic structures.

4. Conclusions

ITO/PEDOT/P3HT:PCBM/LiF/Al photovoltaic cells with different thickness of LiF were prepared by spin coating technique. Their I-V characteristics were measured in dark and under monochromatic light. The typical parameters as photoelement were determined from I-V characteristics in fourth quadrant under illumination in monochromatic light. The cells containing the LiF thin films showed better performances than those without LiF. The effect of the thickness of LiF layer was investigated.

The samples P2 with 75 nm LiF, showed increased values of the parameters ($I_{sc} = 1.55 \times 10^{-3}$ A, $U_{oc} = 0.68$ V, $FF = 0.28$ and $\eta = 0.48$ %) with respect to the values obtained for samples without LiF [4]. The EQE of the sample P2 was more than two times higher than that of the sample P1.

The stability in time of these structures, even though better than that of samples without LiF, still rest poor, that is why, now, systematically studies are carried out, devoted to explain these processes in view to the increasing the stability of the promising photovoltaic structures.

Acknowledgements

Romanian National Authority for Scientific Research supported this work under Bilateral Cooperation No.403CB/2008.

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