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Electric transport in organic system with planar DBP/F_{16}ZnPc junction on the basis of direct current and small signal admittance spectra analysis

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ABSTRACT

The objective of this work was to determine electric transport in the organic device based on a planar junction of electron donor and electron acceptor materials, namely ITO/MoO_3/DBP/F_{16}ZnPc/BCP/Ag. The analysis reported herein was based on direct current-voltage measurements and small-signal admittance spectra in the dark and under illumination. Such analysis may provide information on potential barriers, parasitic resistances and presence of space charge affecting the electric current flow within the device. Therefore, this approach could be applied for determination of physical processes related to electric charge transport within multilayer structures, such as photovoltaic cells or photodetectors.

In the case of the investigated system, the parallel parasitic resistance, the resistance of electrodes, and the geometric capacitance of 10 MΩ, 55 Ω, and 1.6 nF respectively were found. It was also shown that the direct current flowing from ITO to Ag was limited by charge carrier injection from electrodes, while in the case of current flowing from Ag to ITO no essential barriers at electrodes were noticed.

1. Introduction

Solid photovoltaic systems operating on the basis of charge carrier separation at a single heterojunction can be generally divided into inorganic and organic semiconductor devices. Operation principles of inorganic solar cells are well known and efficiencies of particular processes occurring in these systems, starting from absorption of photons and ending with charge carrier collection by electrodes, can be estimated quite accurately. The resultant total efficiencies evaluated from efficiencies of particular processes are in agreement with experiments and the most effective inorganic systems [1] have almost reached the efficiency limit predicted by Shockley-Queisser theory [2]. In the case of organic devices, the most effective systems reach power conversion efficiencies 3 times lower than their inorganic counterparts [1] and processes involved in energy conversion do not seem to be well described. In particular, electric properties of organic junctions raise many doubts. First of all, it is hard to confirm or to rule out the development of space charge region near the junction. Moreover, if it does occur, we can put the question if the width of the region is modified by external electric field, and eventually, if this region provides proper conditions for charge separation. These issues are important for the operation of the device in the dark as well as under illumination.

In this work we analyse electric transport in a planar bilayer organic device in the dark and under illumination with light from the spectral range of strong absorption of both active materials. Our analysis is based on direct current-voltage characteristics and small signal admittance spectra obtained within the 50 Hz - 1 MHz frequency range. Our reasoning regards simultaneous analysis of both components of complex admittance and their relation to direct current-voltage curves collected in the dark and under illumination. Although there are many articles that present the analysis of small signal admittance of organic devices, such an analysis is usually carried out under the assumption of a certain process determining these spectra. As a result, these studies are often limited to consideration of only one component of small signal admittance spectra. Assuming the presence of a depletion region near the interface one may determine the width and capacity of this region, distribution of trapping states or the height of a potential barrier on the basis of Mott-Schottky plots (e.g. [3]). Capacity of such a depletion region should be independent of frequency and drop with the increase in reverse voltage. Another example of the analysis regarding only one component of small signal spectra is the analysis of susceptance used to determine mobility of free charge carriers whenever space charge limited current flows through the investigated system. In this case we observe a modulation of the spectrum related to the time of flight of free charge carriers. This method attracts considerable attention since it enables determination of relatively low free charge carrier mobilities in

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thin organic layers (e.g [4,5]). Another common example of small signal admittance analysis reported in literature is representation of the data in the form of Cole-Cole type of graphs, usually as the negative reactance (-Z'') vs resistance (Z') (e.g [6]). This approach enables determination of elements of the equivalent circuit, namely the number of capacitors and resistors necessary to model the device under study. Although it is possible to evaluate the values of resistance, one cannot easily determine the values of capacity on the basis of such plots. The latter are useful whenever changes in the values of chosen elements induced by external factors are the matter of interest (e.g [7,8]). Nevertheless, to assess the values of all the elements the equivalent circuit is comprised of one has to consider both components of frequency dependent small signal admittance. Moreover, knowledge on the effect of DC voltage on small signal spectra is useful for attribution of these elements to geometrical elements of studied system, such as resistance of electrodes or geometrical capacity of the layers, and determination of processes related to charge transport. The correlation between low frequency conductance and current-voltage dependence, as well as the influence of illumination on small signal spectra are also worth studying. There are not many papers showing the analysis of both components of small signal admittance spectra collected for photovoltaic cells under different DC biases. Furthermore, the number of publications dealing with such spectra measured under illumination and referring them to current-voltage characteristics is very limited. Herein, we present a complete analysis of admittance spectra collected for our samples in the dark and under illumination, relating these results to data acquired during DC experiments, and show the application of this approach in the analysis of processes determining electric charge transport in similar systems.

The system under study was the ITO/MoO_3/DBP/F_{16}ZnPc/BCP/Ag cell, where ITO is indium tin oxide, MoO_3 is molybdenum trioxide, DBP is tetraphenyldibenzoperiflanthene, F_{16}ZnPc is perfluorinated zinc phthalocyanine and BCP is bathocuproine. DBP was applied as an electron donor [9,10] due to high absorption coefficients of this material reaching over $4 \times 10^5\,cm^{-1}$ [10–12], while F_{16}ZnPc as an electron acceptor [13,14] that absorbs light of longer wavelengths compared to DBP. Both of these materials form homogeneous layers upon thermal evaporation [12,13]. Complementarity of their absorption spectra should enable harvesting of light from the whole visible range, while the energetic offset between the donor and acceptor layers, shown in Fig. 1, confirms proper conditions for exciton dissociation at the DBP/F_{16}ZnPc junction. We suppose that excitons with energies higher than the difference between LUMO of F_{16}ZnPc and HOMO of DBP can effectively dissociate at the DBP/F_{16}ZnPc interface and as a result of this process electrons populate F_{16}ZnPc, while holes populate DBP. Thin layer of MoO_3 was incorporated into the cell to prevent exciton quenching at the ITO electrode and to enable better hole extraction from DBP to ITO [9,15], while BCP played two roles, namely reduction of exciton quenching at Ag [9,10,13,16,17] and protection of F_{16}ZnPc layer from penetration of Ag atoms during evaporation of the latter. We have to add here, that it is known that vacuum evaporation of MoO_3 does not lead to pure MoO_3 layer but rather to the growth of a MoO_x film [18,19]. Although there are two different views on the energetic structure of such films and mechanisms of electric conduction within these layers (see Fig. 1a), applicability of MoO_3 as a buffer layer has been confirmed by many experiments [9,15,6,20].

2. Experimental

Samples were fabricated under high vacuum of 5×10^{-6} hPa (Auto 306 Turbo, Edwards). Substrates were neither heated nor cooled during the process, and special shields for evaporation sources were used to avoid cross contamination. Glass substrates partially covered with ITO were cleaned in ultrasonic bath with isopropanol, blow-dried with hot air, and transferred into a vacuum chamber, where the following layers were subsequently evaporated: MoO_3 (5 nm), DBP (17 nm), F_{16}ZnPc (65 nm), BCP (15 nm), and Ag (50 nm). Organic materials and MoO_3 were evaporated in one vacuum cycle. The rate of evaporation of all the layers was equal to 0.2 nm/s. The active area of the samples was ca. 6 mm^2. The experimental setup used to collect current-voltage characteristics and short-circuit current spectra was reported in [13], while small signal admittance spectra were recorded by PM6306 FLUKE LCR meter. The root mean square voltage of 50 mV was applied in the case of all small signal measurements, while all the experiments involving illumination of the samples were run under monochromatic illumination through ITO with light of intensity $I_0 = 10^{14}$ photons/(cm^2s) and either variable wavelength from the 375 nm – 900 nm range (in the case of short-circuit current action spectra) or wavelength of 600 nm.

3. Analysis and discussion

The wavelength of illumination used in all subsequent measurements was selected due to the peak value exhibited by the short-circuit current (Fig. 2a) and open-circuit voltage (Fig. 2b) action spectra within the 600–610 nm range, in which both active materials show high absorption (normalized absorbance of these materials, i.e. A/A_{max} where A stands for the absorbance of the layer, while A_{max} is the maximum value of this parameter recorded in the 380–900 nm range, where shown in Fig. 2a and b for the reference; values of A equal to 0.43 and 0.32 were recorded for the F_{16}ZnPc layer at λ = 635 nm and the DBP layer at λ = 608 nm, respectively). The direction of current flow and symbatic character of both action spectra (i. e. the correspondence between the maxima of current or voltage and absorption of light by active materials) within the whole investigated spectral range confirm that photovoltaic effect observed in this system is driven by exciton dissociation at the DBP/F_{16}ZnPc junction. After dissociation holes are transported through DBP to ITO, while electrons reach Ag via F_{16}ZnPc. Moreover, symbatic character of the short-circuit current action spectrum indicates that even excitons generated near the MoO_3 layer are capable of dissociation at DBP/F_{16}ZnPc interface and contribute to current flow.

Fig. 3 shows current-voltage characteristics collected in the dark (solid squares) and under illumination (circles). Positive voltage corresponds to higher potential at ITO. Solid circles show current flowing from ITO to Ag, while open circles correspond to current flowing from Ag to ITO. At λ = 600 nm and under such relatively low light intensity the short-circuit current reaches ca. 0.8 μA/cm^2, while the open-circuit voltage yield 0.35 V. According to R. A. J. Janssen and J. Nelson [27] the offset between the hole-transporting level of DBP and the electron-transporting level of F_{16}ZnPc of 0.9 eV should be sufficient to provide the V_{oc} of about 0.6 V under higher illumination intensities. The inset of Fig. 3 shows a semi-log plot of the dark current-voltage curve that cannot be fitted to the modified diode equation characteristic for semiconductor p-n junctions, since we would observe an increase in the diode ideality factor n (extracted in the same manner as in [28]) from 1.4 at 0.1 V to 6.5 at 0.8 V, that cannot be explained within the frame of Shockley equation [29]. Such a situation is quite common for organic solar cells.

Spectra of small signal conductance and capacitance collected for the investigated system in the dark and under illumination are presented in Figs. 4 and 5 respectively in the form of conductance (Y'), i.e. a real part of admittance, and the real part of capacitance (C'). Firstly, it is worth noticing that the spectrum of C' does not depend on applied steady voltage nor illumination. In this spectrum we distinguish two nF capacitances independent of frequency in a wide range of frequencies. Thus, spectrum of capacitance seems to be determined by two ideal capacitors. Situation changes in the case of conductance - for higher frequencies (just above ca. $6{\cdot}10^3$ Hz) the curves are practically independent of steady voltage, while for lower frequencies a clear effect of steady voltage is seen. Looking from lower to higher frequencies we can generally notice three steps of the curves. The lowest one depends on steady voltage and is explicitly noticeable at V = 0.8 V. The middle