Improvement of the organic solar cells functional parameters

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Abstract: By changing the concentration ratio (zinc-phthalocyanine-ZnPhTc:Fullerene-C\textsubscript{60} from ZnPhTc:C\textsubscript{60} = 1:0 through ZnPhTc:C\textsubscript{60} = 1:1, to 1 C\textsubscript{60}: ZnPhTc = 1:0) in the active layer, as well as the architecture of the organic solar cells (OSC), a substantial increase of their short-circuit current is achieved. We suggest that the blurred interlayer boundaries lead to an enhanced motion of the holes and the electrons to the electrodes – ITO and Al respectively. Regardless of the shorter distances between the places of excitons creation, the excitons have enough “life-time” for diffusion to the suitable places where their decomposition to the charge carriers – holes and electrons, takes place. This is one of the well-known approaches to achieve a higher efficiency of the OSCs. We thus suggest that the possible interactions and processes discussed are obviously essential prerequisites for improving the functional parameters of the OSCs.

1. Introduction

The possibilities for improving the functionality and the production facilities of the OSCs have increased in the last few years due to the combination of theoretical and material advances and the particularly improved understanding of the processes occurring in the interaction of light with matter. This allowed the introduction of a variety of new materials (e.g., dyes, organic low-molecular weight compounds and polymers) in the production of organic solar cells (OSC) or organic light emitting diodes. The organic materials are attractive not only because of the almost unlimited number of compounds, but also due to the combination of their influence on the OSCs functional parameters and the low production costs [1]. At present, the efficiency achieved of the OSCs is about 10 \%, which is too low. One of the possible ways of improving these devices’ efficiency is to develop contacts of a heterojunction layer or an add-layer which would affect the velocity of holes and electrons in order to reach close values. The aim of the present work is to study this assumption by following the changes of the electrical parameters and structure of vacuum-deposited (VD) donor – zinc phthalocyanine (ZnPhTc) and acceptor – Fullerene (C\textsubscript{60}) layers as active films in the OSCs.

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2. Experimental
Most of the experiments were carried out on VD films consisting of condensed ZnPhTc and C₆₀. In the basic SC configurations, the upper layer is located between the donor – ZnPhTc and the cathode – a 100 – 120-nm Al film. The substrate used was a flexible polymer band – polyethylene-terephthalat (PET) covered by electroconductive films of indium thin oxide (ITO), 30 Ω/sq., fabricated by Kintec Ltd., Hong Kong. It is well known [2] that the characteristics – roughness, defectlessness and granularity of the final condensed films, depend on the growth, the microstructure and the size of the microcrystallites of each preceding deposited layer. Therefore, one of the goals of the experiments was to ensure evaporation conditions for producing a one- or multi-layer organic SC with the desired reproducible composition and microstructure. The dyes studied were evaporated from three independently heated vessel sources [3], thus overcoming the difficulties in evaporating at controlled rates because of the low and insufficient thermal stability and thermal conductivity of the substances used. Deposition rates of 0.1 – 0.4 nm/sec were achieved at 550 ºC for ZnPhTc, 700 ºC for C₆₀ and 130 – 160 ºC for bathocuproine (BCP) at a basic pressure of 4×10⁻³ Pa. The composition and thermal stability of VD ZnPhTc layers on KBr substrates were studied by Fourier transform infrared spectroscopy (FTIR). The FTIR absorbance spectra were recorded by a Bruker Tensor 27 spectrometer in the range 4400 – 450 cm⁻¹ with a resolution of 2 cm⁻¹. The surface morphology of the layers was studied using scanning electron microscopy (SEM Philips 515). The films’ structure and crystallinity were studied by TEM (HRTEM JEOL JEM 2100). The electrical characteristics were measured by a Keithley 617 (USA) high-precision electrometer.

3. Results and discussion
3.1. FTIR investigations
This part of the study aimed to follow the possible changes of the composition from the precursor ZnPhTc bulk material during the VD of the layers. The results from the FTIR studies are presented in figure 1, namely, the FTIR spectra of initial ZnPhTc dispersed on a KBr pellet. The spectra are normalized with respect to the band at 720 cm⁻¹. The peaks at 720 cm⁻¹, 1120 cm⁻¹, 1165 cm⁻¹ and 1333 – 1335 cm⁻¹ in figure 1 – curves 1 and 2, are typical and characteristic of the existence of the ZnPhTc compound. It is obvious that these essential peaks are present in both the bulk and the evaporated materials, which confirms the similarity of the composition.

![FTIR spectra](image)

**Figure 1.** FTIR spectra of vacuum deposited ZnPhTc; 1 – untreated, 2 – thermally treated at 200 ºC, 3 – FTIR spectrum of initial ZnPhTc on a KBr pellet.
Moreover, it can be concluded that the composition of the vacuum-deposited dyes used is identical to the initial one and the thermal treatment up to 200 °C (figure 1, curve 2) for both kinds of films has only a negligible effect on their compositions. This allows thermal annealing of the deposited films as a way of reducing their structural defects.

3.2. SEM and TEM investigations
Electron-microscopy observations of the surface morphology of the various substrates (figure 2 a, c) types were carried out prior to and after a deposition of ZnPhTc films with different thickness, given in relative units (figure 3). It was thus proved that the PET/ITO–60 Ω/sq. flexible substrates (figure 2 a, c and 2 b, d) are the most suitable ones from the point of view of the fine surface morphology and defectlessness of the active layer.

On the other hand, the use of 30 Ω/sq. ITO layers is more suitable for OSCs because of the low sheet resistance providing a better OSC performance. To reduce the influence of the substrate on the structure of the active film, an additional buffer layer must be added. Thus, a pyromelithec diaihnydride (PMDA) blocking layer was chosen \[4\] as a way of reducing the transport of holes towards the ITO anode.

![Figure 2. SEM images of ZnPhTc evaporated on PET/ITO substrates:](image)

- a, b – 30 Ω/sq.; c, d – 60Ω/sq.,
- a, c – thickness 193 nm; b, d – thickness 63 nm.

![Figure 3. TEM images taken from a composite of ratio 1:1; the thicknesses are measured in relative units (ru), where 5000 ru ≈ 100 nm:
- a) (ZnPhTc+Fullerene) ≈ 5000 ru,
- b) (ZnPhTc+Fullerene)/BCP ≈ 6000 ru,
- c) (ZnPhTc+Fullerene)/BCP ≈ 7500 ru.](image)

![Figure 4. Simplified equivalent circuit diagram for modelling the DC behavior of a solar cell.](image)

3.3. Electrical measurements
Figure 4 presents a simplified equivalent circuit diagram of an OSC. The important cell parameters are the parallel \(R_p\) and serial \(R_s\) resistance. The values of \(R_p\) (table 1) influence mainly the slope of the curve in the range around 0 V (3\textsuperscript{rd} and 4\textsuperscript{th} quadrant). At a lower \(R_p\), the open-circuit voltage \(V_{oc}\) drops, while the short-circuit current \(I_{sc}\) remains unchanged. \(R_s\) defines the slope of the \(J/V\) curve (figure 5) in the 1\textsuperscript{st} quadrant, i.e. in the range above the \(V_{oc}\) (transmitting diode direction). The fill factor \(FF\) and the \(I_{sc}\) decrease, while the \(V_{oc}\) remains unchanged when \(R_s\) increases \[5\].
Analyzing these results (figure 5 and table 1), one can see that the deposition of C$_{60}$ leads to increased $R_s$, which is associated with the contact barrier. This barrier creates an electric field which is opposite to the field of the cell. This is confirmed by the decrease of the $I_{sc}$ and $V_{oc}$. However, the same result may be due to the difference between the donor and acceptor LUMO levels, as well as to the not very good quality of the electrical contacts.

As already discussed, an approach to create OSCs with good functional characteristics is to provide an effective separation of excitons in the entire volume of the active film. Therefore, our study aimed to establish conditions for creating “blurred boundaries” of the active composite (figure 6, 2 and 3) layer with a ratio of 1:1. This assumption was proved by the best parameters of the structures studied (figure 6, 2 and 3). These samples are composed of a film of donor ZnPhTc and acceptor C$_{60}$ with blurred boundaries at the molecule-molecule contact in the largest part of the volume of the active layer. It is also seen in figure 6, 2 and 3 that increasing the thickness of the active layer leads to an increase of the $I_{sc}$, $V_{oc}$, $FF$, and the energy conversion efficiency ($\eta$).

**Table 1.** Parallel ($R_p$) and serial ($R_s$) resistance values.

| $\Omega$ cm$^2$/samples | 1  | 2  | 3  | 4  | 5  | 6  |
|-------------------------|----|----|----|----|----|----|
| $R_s$                   | 758| 337| 199| 513| 377| 280|
| $R_p$                   | 3585| 680| 559| 2796| 3541| 1742|

**Figure 5.** Current density – voltage ($J/V$) characteristics of organic photovoltaic devices with various layer structures illuminated by white light at 6 mW cm$^{-2}$.

**Figure 6.** Different structures of OSC – 1, 4, 5, 6 develop the idea of a PMDA buffer layer; 2, 3 – layers with “blurred” boundaries.

aTh- thicknesses in relative units.
4. Conclusions
We discussed and experimentally confirmed a novel idea for improvement of some functional OSC parameters, namely, the enhanced exciton decay and subsequent charge separation on the grain boundary of the ZnPhTe-C$_{60}$ donor – acceptor composite layer. Complementary PMDA and C$_{60}$ layers were added to the OSC structure in view of facilitating the extraction of the photogenerated charge carriers through the electrodes.

Acknowledgment
The present work was financially supported by the National Science Fund at the Ministry of Education and Science of Republic of Bulgaria under contract DO-02/254-2009 and by the Grant Agency of the Czech Republic under contract: No. P205/10/2280.

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