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Vacuum-deposited diphenyl-diketo-pyrrolopyrroles structures with photoelectrical applications

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Abstract. Modern organic semiconductor devices are designed as stacked organic/inorganic thin films. In such multilayer structures, strong requirements are set forth to the properties of the specific films, e.g., film homogeneity, thickness uniformity and roughness. The physical vacuum deposition (PVD) technique fulfils all of these requirements having even the capability of producing the whole multilayer structure in the same vacuum cycle. Diphenyl-diketo-pyrrolopyrroles (DPP) are low-molecular-weight materials with promising luminescence and photoelectrical properties. This study deals with PVD of thin DPP films and measurement of their properties. The organic films and inorganic electrodes of the multilayer structures were prepared in the same vacuum cycle, and then the structures were encapsulated in a glove box avoiding exposure to oxygen. ITO|composite|Al structures were prepared with active DPP-C₆₀ composite films (ratio 60:40 mass %) of about 100 nm thicknesses. The surface morphology of the films was studied by SEM imaging, which revealed uniform films containing separate spherical structures. The dark current and the photoconductivity were measured and the photoelectrical behavior of the structures was estimated. It was found that the optimized preparation of the structures under the aforementioned conditions leads to an improvement of their photoelectrical properties.

1. Introduction

Diphenyl-diketo-pyrrolopyrroles (DPP) are low-molecular-weight materials with promising luminescence and photoelectrical properties. The first known derivative, 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-c]-pyrrole (DPP) was described for the first time in 1974, having been synthesized by mistake.

In 1986, the first derivative was introduced to the market and, since then, many other derivatives have fulfilled their potential, especially in the industry of colorants. The interest in these pigments has grown recently and they have become subjects of patents in many areas of applications.

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These compounds have been the object of intensive research for pigment applications; they exhibit a variety of shades in the solid state and, especially, chemical, light and thermal stability [1]. DPP itself has a high molar absorption coefficient, as well as a high fluorescence quantum yield; therefore, the low-molecular-weight derivatives of DPP have been extensively studied concerning their optical and photophysical properties [2–4]. Potential applications have been reported of DPP derivatives as luminescent media in a polymer matrices [5], solid-state dye lasers [6], OLED devices [7] and organic field-effect transistors [8].

Thin films of low-molecular-weight semiconductors are usually prepared by means of a variety of complex techniques, including physical or chemical vapor deposition, organic molecular-beam epitaxy or solution-based deposition techniques. The performance of small molecular organic devices has been shown to be highly sensitive to the films' morphology and processing conditions. Often, the solution-deposited active layers of devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates, whereas the vapor deposition techniques provide high-quality crystalline films characterized by improved charge-transport properties compared with those of solution-deposited films. The relationship between the organic thin film morphology and the device performance is nowadays subject of comprehensive research activities.

DPP based polymers, as well as small molecules, have found their place in the organic electronics. This paper deals with 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, denoted hereinafter as DPP (figure 1). Using this material as a donor for bulk-heterojunction-based solar cells leads to a photovoltaic conversion efficiencies up to 4,4 % [9]. Conjugated systems provide high charge-carrier mobility across the structure.

In the present paper, DPP-C₆₀ donor-acceptor composite films were prepared by vacuum co-deposition and the photoelectrical properties of ITO|composite| films were investigated.

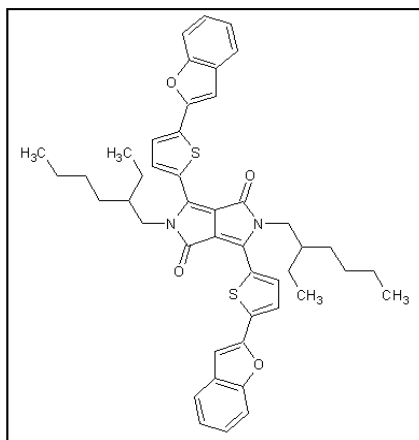


Figure 1. Chemical structure of the active material DPP.

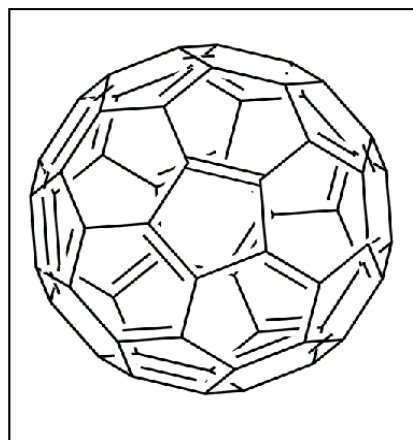


Figure 2. Chemical structure of the fullerene C₆₀.

2. Experimental

3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione was provided by our partner Center for Organic Chemistry Ltd. (COC), who synthesized it according to the route published in 2009 by Walker et. al. [9]. Fullerene C₆₀ PCBM ([6,6]-Phenyl-C₆₁-butyric acid methyl ester) (figure 2) was purchased from Ossila Ltd.

To fabricate our samples we used the Ossila OLED/OPV Pixelated Anode Substrate System and the Ossila Encapsulation System, which consist of a pre-patterned ITO-covered glass substrate with a standard size of 20×15 mm, an active area deposition mask, a cathode deposition mask, encapsulation epoxy, encapsulation glass slides and electrical connection legs with a standard 0.1-inch (2.54 mm) pitch. The pre-patterned ITO structure consists of one cathode strip along the long side of the substrate

and six fingers, which, combined with the deposition masks, form six active pixels with dimensions 4×1.5 mm and six anodes connected to them.

The composite thin film was deposited onto Ossila substrates in an MBraun vacuum system from two heat sources simultaneously at evaporation temperatures of 180°C for DPP and 420°C for C_{60} and deposition rates of 4.2 \AA/s and 2.5 \AA/s , respectively, through the active area deposition mask. After deposition of the active composite layer, the samples were taken out in nitrogen atmosphere, the mask was changed with the cathode deposition mask and the samples were returned back into the evaporation chamber. When the vacuum in the evaporation chamber reached sufficient levels, aluminum electrodes were deposited.

Finally, the samples were encapsulated according to a standard procedure.

An optical micrograph image of the sample prepared was taken and the overlapping of the layers was inspected.

Selected samples were studied by a Philips 515 scanning electron microscope (SEM). The SEM morphology characterization of the DPP- C_{60} composite films was carried out on the Ossila substrates without implementing the final encapsulation procedure and the result is shown in figure 3.

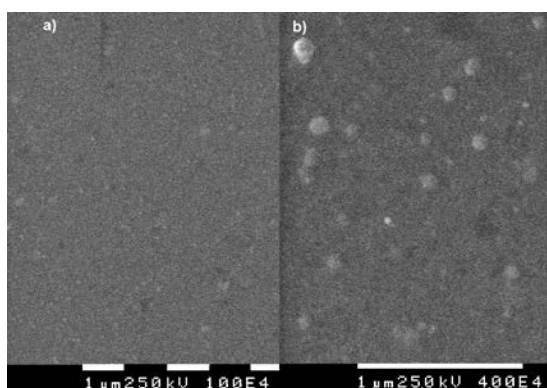


Figure 3. SEM images of the deposited composite thin films: a) magnification of 10 000; b) magnification of 40 000.

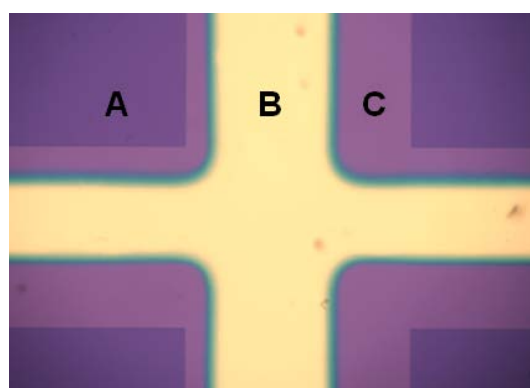


Figure 4. Optical micrograph in polarized light; the device structure is as follows: A is ITO, B is Al and C is the active composite layer.

The setup for photoelectrical measurements consisted of a Keithley 6517A electrometer and voltage source; monochromatic light was produced by an LSH502 LOT-Oriel halogen lamp and an MSH101 LOT-Oriel monochromator. The light power was controlled by using gray filters and measured by a S120VC standard Si photodiode power sensor and a Keithley 485 picoammeter.

The photoelectrical measurements started with the spectral dependence of the photocurrent at zero applied voltage; the I - V characteristics were then measured in both directions of the voltage scale in dark and when exposed to monochromatic light. Finally, the dependence of the photocurrent on the incidental light power (irradiance) was measured. The sample was exposed to monochromatic light at the wavelength of 533 nm.

3. Results and discussion

3.1. Sample characterization

An optical micrograph image of the sample prepared for electrical characterization is presented in figure 4. As is seen, uniform films covering entirely the ITO electrode area were prepared.

A more precise film-surface characterization of the composite films was performed by SEM. SEM images taken at two different magnifications from the same sample without applying the encapsulation procedure are presented in figure 3. The image taken at the lower magnification of 10 000 (figure 3a) confirms that smooth and uniform DPP- C_{60} films without a presence of pinholes were produced. The

SEM image taken at a magnification of 40 000 (figure 3b) reveals the formation of spheres with a size of about 100 - 200 nm. The spheres observed could be related to the formation of a single phase of one of the components. To clarify this problem, further studies of samples with different DPP-C₆₀ ratios should be carried out. In general, one can conclude that the DPP-C₆₀ films deposited are suitable for electrical measurements in “sandwich” type samples.

3.2. Photoelectrical measurements

Figure 5 presents the spectral dependence of the photocurrent measured at zero applied voltage between the electrodes of ITO|composite|Al structures with active DPP-C₆₀ composite films. The maximum of the spectrum was found at 533 nm. A similar spectral dependence of the photocurrent taken from samples with the same DPP-C₆₀ ratio of a composite film prepared by spin-coating technique was published in the literature [9]. To excite this peak during the following experiments, a monochromatic light ($\lambda = 533$ nm) was used.

I-V characteristics measured in dark and under illumination of ITO|composite|Al structures with active DPP-C₆₀ composite films of about 100 nm thickness are presented in figure 6. To estimate the electrical parameters of the samples, the graphs are plotted on a semi-logarithmic scale (the negative values of the current are multiplied by -1).

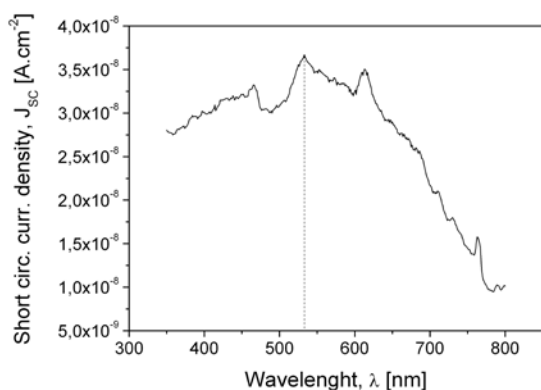


Figure 5. Spectral dependence of the photocurrent at zero applied voltage.

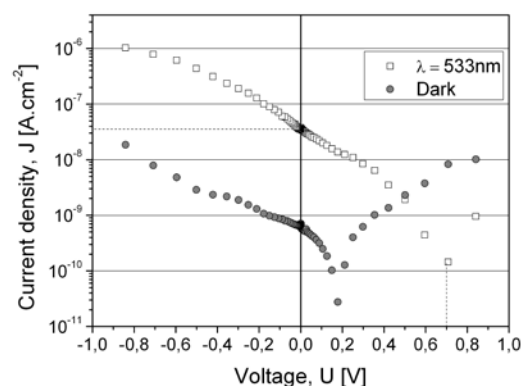


Figure 6. *I-V* characteristics measured in the dark and under monochromatic light with irradiance 0.35 mW cm^{-2}

The dark current measurements yielded non-linear and almost symmetrical characteristics with a contact barrier of about 0.2 V. These effects could be related to the imperfections of the electrodes.

It should be mentioned that no additional intermediate layers serving to reduce the contact barrier were used. The optimization of the stacked structures will be a subject of a future study. Under illumination by monochromatic light, the non-optimized samples produced photocurrent of almost two orders of magnitude higher than what was observed in the dark measurements. By processing the data for the DPP-C₆₀ structure, a short-circuit current of $J_{SC} = 36 \times 10^{-9} \text{ A cm}^{-2}$ and an open-circuit voltage of $U_{OC} = 0.71 \text{ V}$ were determined.

Using the area confined within J_{OS} and U_{OC} , the dependence of the electrical power on the voltage is plotted in figure 7, right y axis. The maximum electrical power found was $P_{MAX} = 1,2 \times 10^{-8} \text{ mW cm}^{-2}$ at $U_{MP} = 0.25 \text{ V}$ and $J_{MP} = 5,24 \times 10^{-9} \text{ A cm}^{-2}$.

The dependence of the photocurrent on the incident light power (irradiance) for samples with DPP-C₆₀ films under illumination by monochromatic light is plotted in figure 8. It was found that the photocurrent is proportional to G^γ , where G is the photogeneration rate and $\gamma = 1.15$ is the slope of the graph presented. This result could be connected to a monomolecular photogeneration mechanism.

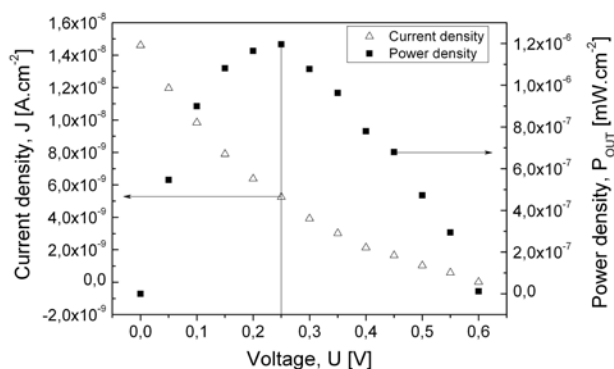


Figure 7. Dependence of the power density (right y axis) and current density (left y axis) on the voltage applied, as calculated from figure 6, light curve.

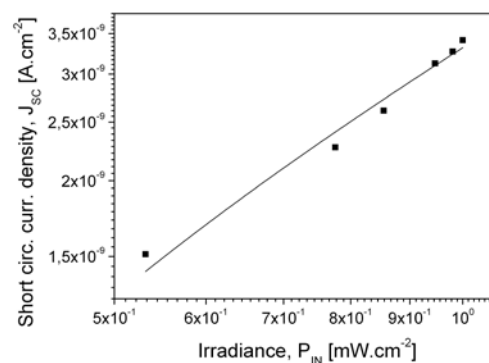


Figure 8. Dependence of the photocurrent on the light intensity at $\lambda = 533$ nm and applied voltage $U_{MP} = 0.25$ V.

4. Conclusions

ITO|composite|Al structures with active DPP-C₆₀ composite films of about 100-nm thickness were prepared by vacuum deposition and encapsulated in an inert atmosphere.

The surface morphology of the films prepared was studied by SEM imaging, which revealed formation of spheres with a size of about 100 - 200 nm.

Photoelectrical measurements were carried out. It could be concluded that the vacuum-deposited DPP-C₆₀ composite active layers have promising properties for incorporation in the future organic solar cells. Further optimization should be conducted in view of reducing the contact barrier and facilitating the excitation decay and charge carrier extraction through addition of intermediate interface layers.

Acknowledgements

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