

Vacuum-deposited diphenyl-diketo-pyrrolopyrrole solar cell structures

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Abstract. Photoelectrical parameters were measured of solar cell ITO|PEDOT:PSS|composite|Al samples. The active composite film was deposited in vacuum by co-evaporation of 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 (DPP(TBFu)₂) and fullerene (C₆₀). Additional DPP(TBFu)₂:C₆₀ composite films were studied by spectroscopy in the ultraviolet and visible region (UV-VIS) and scanning electron microscopy (SEM). It was found that solvent annealing (SVA) of composite DPP(TBFu)₂:C₆₀ vacuum-deposited films with tetrahydrofuran vapors improves the solar cell parameters by increasing the efficiency more than tenfold. This could be related to the more homogenized structure of the SVA composite film, as observed by SEM. The increased light absorption, as shown by UV-VIS spectroscopy, around the peak at 350 nm contributed to the better SVA solar cell performance. Photogeneration in the samples follows a monomolecular mechanism.

1. Introduction

Diphenyl-diketo-pyrrolopyrroles (DPP) are low-molecular-weight materials exhibiting outstanding luminescence and photoelectrical properties. DPPs have been the object of intensive research in view of pigment applications. They exhibit a variety of shades in the solid state and, especially, chemical, light and thermal stability [1]. Chemical tailoring of DPP allows modification of various properties, as, for example, the molar absorption coefficient and fluorescence quantum yield. Thus, the low-molecular-weight DPP derivatives have been extensively studied concerning their optical and photophysical properties [2–4]. The optical properties are related to the conjugated system which provides charge-carrier mobility across the material structure.

Potential applications of DPP derivatives have been reported as luminescent media in polymer matrices [5], solid-state dye lasers [6], OLED devices [7] and organic field-effect transistors [8]. Therefore, DPP based polymers, as well as small molecules, have found their application in the organic electronics.

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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 the small molecular organic devices is 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. The vapor deposition techniques provide high-quality crystalline films characterized by improved charge-transport properties compared with those of solution-deposited films. The vacuum technique has the advantage of a dry film deposition process excluding the usage of solvents. Moreover, this technique offers more opportunities to control such important film parameters as film thickness and uniformity. As a consequence, the films deposited exhibit more stable and reproducible properties in comparison with solution-deposited films.

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(TBFu)₂. Using this material as a donor for bulk-heterojunction-based solar cells leads to photovoltaic conversion efficiencies up to 4.4 % [9]. Fullerene (C₆₀) was used as an acceptor material, which facilitates the charge separation on the heterojunction. These results are strongly dependent on the film structure. For example, solvent annealing causes morphology and structure changes in bulk heterojunction devices by electron donating and electron accepting phase separation. This effect contributes to the better transport of photogenerated charge carriers from the interface to the electrodes of a solar cell device leading to higher photogeneration efficiency.

In the present work, DPP(TBFu)₂:C₆₀ donor-acceptor composite films were prepared by vacuum co-deposition and the photoelectrical properties of ITO|PEDOT:PSS| DPP(TBFu)₂:C₆₀|Al solar cell samples were investigated.

2. Experimental details

The samples for photoelectrical measurements were prepared by the following procedure. Glass substrates with patterned ITO (Ossila) were preliminarily cleaned in an ultrasonic bath of 5% NaOH solution, then rinsed in water and subsequently washed twice in deionized water. Finally, ultrasonic treatment in an isopropanol bath was carried out for 10 minutes at room temperature. A PEDOT:PSS film was deposited by spin coating at 5500 rpm for 60 seconds. Subsequent annealing for 10 minutes at 150 °C in air and 10 minutes at 150 °C in nitrogen atmosphere was applied to remove the residual moisture.

Next, organic composite and electrode films were prepared in a clean room class C (M. Braun Inertgas-Systeme GmbH, Garching, Germany). DPP(TBFu)₂:C₆₀ composite thin films were deposited by co-evaporation of DPP(TBFu)₂ and C₆₀ on Ossila substrates through a proper deposition mask. The deposition was performed in a vacuum system from two thermally heated sources at evaporation temperatures of 180 °C and 415 °C. DPP(TBFu)₂ and C₆₀ deposition rates of 2 and 1 Å/s, respectively, were controlled independently by a two-channel quartz crystal microbalance (Inficon SQC 310). Thus, a DPP(TBFu)₂:C₆₀ mass ratio of 1.5:1 was achieved on a substrate rotated at 15 rpm.

Solvent vapor annealing (SVA) was carried out in nitrogen atmosphere at a temperature of 25 °C. Five ml of tetrahydrofuran (THF) was poured into a 40 mm glass Petri dish. The lid was closed for 20 min to achieve saturation vapor conditions. An as-cast film was attached on the back side of another Petri dish lid. The lids were quickly swapped on the solvent-containing Petri dish. In this way, the film was positioned about 5 mm above the solvent level in saturated THF vapors. After SVA for 20 s, the film was removed from the treatment chamber.

After that, the as-cast and the SVA samples were applied together without breaking the nitrogen atmosphere to a mask for Al deposition and put into the vacuum chamber. An Al cathode of 150 nm film thickness was thermally evaporated in a vacuum of 1×10^{-6} mbar at a deposition rate of 1 Å/s.

The solar cell samples of type ITO|PEDOT:PSS| DPP(TBFu)₂:C₆₀|Al were measured in nitrogen atmosphere. During the measurements, the samples were exposed to standard light produced by an LS0916 LOT Oriel class AAA solar simulator. This device provides a defined light beam according to the AM 1.5 standard. The light intensity of about 1000 mW cm⁻² was controlled by an RR2000

calibrated reference silicon cell (ReRa Solutions BV; Nijmegen, Netherlands). The current-voltage characteristics were measured by a Keithley 2601B electrometer (Keithley Instruments Inc., Cleveland, OH, USA).

Thin films for optical characterization were deposited on soda-lime-silica glass. The absorption spectra of the layers were measured in the range of 300 – 800 nm by a Varian Cary-50 UV-VIS spectrophotometer. The morphology of the as-cast and the SVA films was investigated by a Philips 515 scanning electron microscope (SEM) at an accelerating voltage of 25 kV. The samples for SEM characterization were deposited on microscope glasses. Before the SEM study, the sample surface was covered consecutively by carbon and palladium/gold films. The thickness of the layers was measured by a Decktak XT profilometer.

3. Results and discussion

3.1. Surface morphology study

Figure 1 presents SEM images of as-cast (a) and SVA in THF vapors for 20 s (b) vacuum-deposited DPP(TBFu)₂:C₆₀ composite thin films. In both cases, uniform films without visible pinholes are seen. The freshly-deposited film exhibits a relatively rough surface with a grain size of about 300 – 500 nm.

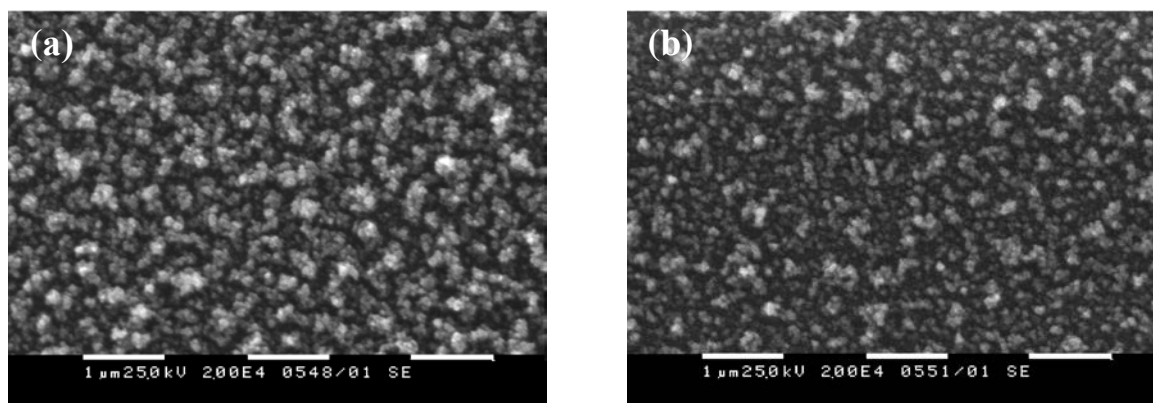


Figure 1. SEM images of vacuum-deposited DPP(TBFu)₂:C₆₀ composite thin films (a) as-cast; (b) annealed in THF vapors for 20 s.

The film treated for 20 s in THF vapors demonstrates a similar morphology, but apparently a smoother surface. The predominant grain size is about 100 – 200 nm. It could be assumed that the treatment by THF vapors partially dissolves the soluble DPP(TBFu)₂ clusters leading to a flatter film surface. A partial segregation of the composite could also be expected with a predominant appearance of the C₆₀ material on the film surface [9].

3.2. UV-VIS spectroscopy

In figure 2, optical absorption spectra of pure DPP(TBFu)₂ and C₆₀ films are presented. Curve (a) shows typical DPP(TBFu)₂ spectra [10] consisting of a broad doublet (500 – 750 nm) and a relatively narrow peak positioned at about 350 nm. This characteristic spectrum shows that no apparent destruction of the material is taking place. Curve (b) presents also a typical C₆₀ spectrum [11]. Comparing the two spectra in figure 2, it could be expected that preparing DPP(TBFu)₂:C₆₀ composite will combine the spectra in a way extending the light absorption to the UV-VIS region.

In figure 4, curve (a) is a typical spectrum of an as-cast DPP(TBFu)₂:C₆₀ composite film. As expected, increased absorption is observed, especially around the 350-nm peak. This effect should be related to the absorption by C₆₀.

Treatment in THF vapors for 20 s (figure 3, curve (b)) causes a decrease of the strength of the “red” positioned peak in the doublet and a remarkable increase of the peak strength around 350 nm. Thus,

the impact of solvent annealing by THF on the samples' optical spectra is similar to that of thermal annealing.

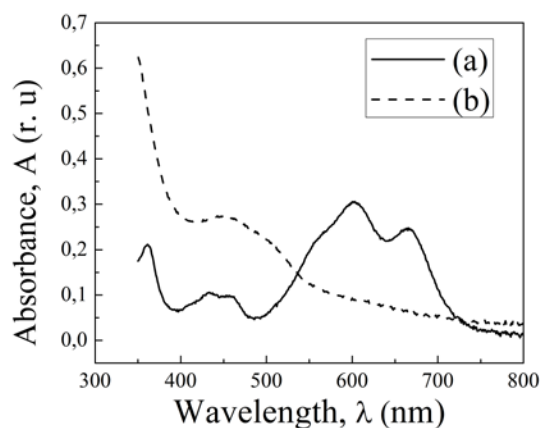


Figure 2. Optical spectra of (a) DPP(TBFu)₂ and (b) C₆₀ vacuum deposited films.

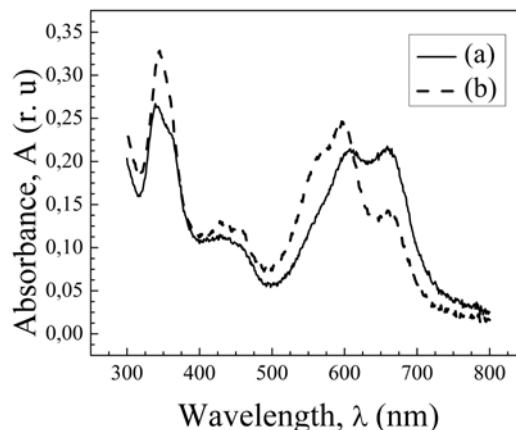


Figure 3. Optical spectra of (a) as-deposited DPP(TBFu)₂:C₆₀ composite film and (b) after exposure to THF vapors for 20 s.

3.3. Solar cell measurements

3.3.1. Current voltage characteristics. The parameters of ITO|PEDOT:PSS|DPP(TBFu)₂:C₆₀|Al solar cell samples were calculated from the *I-V* characteristics measured in dark and under light exposure. The results are presented in table 1.

Table 1. Parameters* of the solar cell samples calculated from *I-V* measurements.

Sample	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
As-cast	1.0±0.03	695±2	22±0.5	0.20±0.01
SVA	6.5±0.04	730±3	50±0.7	2.2±0.05

* J_{sc} stands for current density; V_{oc} , for open-circuit voltage; FF , for fill factor; η , for efficiency.

It is clearly seen that the SVA improves the solar cell parameters. In particular, the efficiency is increased more than tenfold. This effect could be related to the more homogenized structure of the DPP(TBFu)₂:C₆₀ SVA composite film, as observed by SEM. The increased UV-VIS absorption, especially around the peak positioned near 350 nm, also contributed to the better SVA solar cell performance.

The improvement of the solar cell parameters could also be related to a partial segregation of the DPP(TBFu)₂:C₆₀ SVA composite film. This effect has been discussed with respect to similar measurements of DPP(TBFu)₂:PC₆₀BM composite solar cells [12]. The SVA influence on vacuum deposited DPP(TBFu)₂:C₆₀ composite solar cell samples seems to be similar. This phenomenon needs more extensive investigations.

3.3.2. Dependence on the light intensity. The dependence of the photocurrent density on the light intensity is plotted in a log-log scale in figure 4. It is clearly seen that the graph follows a linear dependence. The linear regression performed shows a slope (γ) of 1.0 ± 0.017 . The dependence $J = I^\gamma$, where γ is close to 1 indicates a typical monomolecular mechanism of charge carrier generation under light exposure.

Figure 5 is a plot of the open-circuit voltage (V_{oc}) as a function of the light intensity. The graph follows a nonlinear dependence. This phenomenon could not be connected with the predominant influence of the shunt or serial resistance. This nonlinearity is more probably connected to the

nonlinear changes in the electric field in the sample as a result of the changed conditions for charge carrier generation and recombination under the influence of the light.

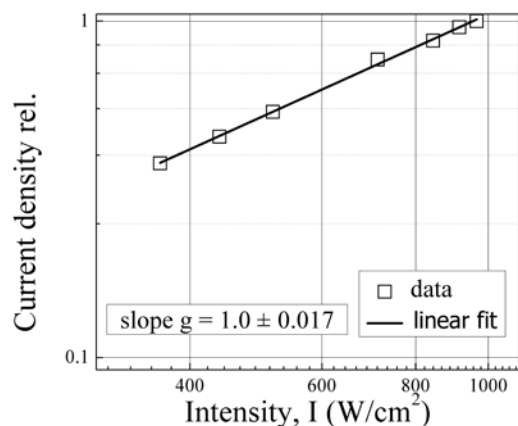


Figure 4. Dependence of the photocurrent density on the light intensity measured in ITO|PEDOT:PSS|DPP(TBFu)₂:C₆₀|Al samples.

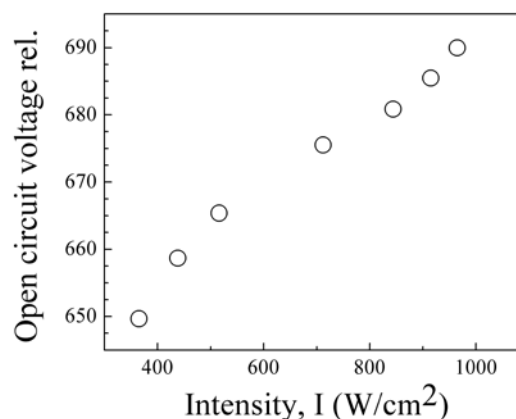


Figure 5. Dependence of the open-circuit voltage on the light intensity in ITO|PEDOT:PSS|DPP(TBFu)₂:C₆₀|Al samples.

4. Conclusions

Solvent annealing by THF vapors of vacuum-deposited DPP(TBFu)₂:C₆₀ composite films improves the solar cell parameters of ITO|PEDOT:PSS|DPP(TBFu)₂:C₆₀|Al samples. In particular, the efficiency is increased more than tenfold. This effect could be related to the more homogenized structure of the DPP(TBFu)₂:C₆₀ SVA composite film, as observed by SEM.

The increased light absorption, as shown by UV-VIS spectroscopy, around the peak positioned near 350 nm also contributed to the better SVA solar cell performance.

The photogeneration in the samples follows a monomolecular mechanism.

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