Thin dye layers – vacuum deposition and structure

To cite this article: D Dimov et al 2012 J. Phys.: Conf. Ser. 356 012037

View the article online for updates and enhancements.

Related content

- Ion – beam assisted process in the physical deposition of organic thin layers
  D Dimov, A Georgiev, E Spassova et al.

- Room temperature humidity sensors based on co-evaporated TeO₂ and Sn
  B Georgieva, I Podolesheva and G Spasov

- Optical characterization of Zn coatings deposited on low carbon steel substrates
  G Bodurov, N Boshkov, L Lutov et al.
Thin dye layers – vacuum deposition and structure

D Dimov\textsuperscript{1,3}, J Assa\textsuperscript{1}, A Georgiev\textsuperscript{2}, R Kazakov\textsuperscript{1}, D Karashanova\textsuperscript{1}, G Danev\textsuperscript{1} and E Spassova\textsuperscript{1}

\textsuperscript{1} Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 109, 1113 Sofia, Bulgaria
\textsuperscript{2} University of Chemical Technology and Metallurgy, 8, St. Kl. Ohridski Blvd., 1756 Sofia, Bulgaria

E-mail: dean@clf.bas.bg

Abstract. Vacuum-deposited layers of zinc phthalocyanine and perylene-3,4,9,10-tetracarboxylic dianhydride were obtained with regard to the development of converters of solar radiation into electricity, namely, organic solar cells. It was shown that there were no differences in the composition of the initial dyes and the deposited ones, which is a proof of their thermal stability and a prerequisite for the reproducibility of the composition of the single and mixed layers under study. The results obtained are interpreted in view of the possible applicability of the layers studied for the fabrication of organic solar cells in which the processes of creation, the lifetime and the diffusion paths of the current carriers depend significantly on the film composition and the defects formed at the time of deposition of the active dye layers.

1. Introduction

In recent decades, the progress related to the utilization of renewable energy sources, such as organic (OSC) or inorganic solar cells, wind parks, the heat of the earth, etc., has been substantial [1]. The major drawback of the OSCs is their comparatively low (up to 5-6 \%) efficiency [2] with a predicted limit for some experimental donor-acceptor pairs of 11 \% [3]. The growth of each vacuum deposited (VD) layer in an OSC affects the characteristics of the films deposited subsequently – roughness, defectlessness and granularity, thus determining to a large extent the efficiency of the OSCs.

The best parameters of a thin-layer OSC were reported by the group of Forest [2,4]. This group used copper phthalocyanine (CuPhTc) as a donor and 3,4,9,10-perylenetetracarboxylic bis-benzimidazol (PTCBI) or fullerene (C_{60}) as an acceptor. The efficiency reached was in the range of 3-5 \% per 1 cm\textsuperscript{2}. [2,4]. Obviously, these parameters are considerably lower than those of the inorganic SC [5], which, together with their lower stability, are the reasons why the OSCs will not replace the SCs based on silicon in the near future.

As a result from the absorption of solar light in an OSC, a predominant formation of bound electrons and holes (photogenerated excitons) takes place [5]. The excitons are destroyed in the comparatively strong electrical field between the electrodes to charge carriers – electrons and holes. Their transformation is influenced by the presence of defects in the volume of the layers, their microstructure and the existence of traps. The latter are to a large extent a consequence of the

\textsuperscript{3} To whom any correspondence should be addressed.

Published under licence by IOP Publishing Ltd
fabrication conditions – purity of the initial substances, reproducibility of the composition and structure of the active layers, etc. This is why the aim of the present study was to investigate the impact of the parameters for preparing films of VD “small molecules” organic substances on the composition and structure of the deposited layers with regard to their utilization as active layers in OSCs.

2. Experimental
Most of the experiments were carried out with VD films consisting of successive or mixed condensed ZnPhTc or PTCDA. The substrate used was a flexible polymer band – polyethylene-terephtalate (PET) covered by electroconductive films – 30 Ω/sq or 60 Ω/sq – of indium tin oxide (ITO). Al films of thickness 10-12 nm were used as upper electrodes. The ZnPhTc and PTCDA were thermally evaporated from specially designed sources. The latter allow one to heat carefully the organic dyes thus overcoming the problems of their low thermal conductivity and insufficient thermal stability. The deposition rates were 0.1 – 0.4 nm/sec at 550°C for ZnPhTc and 430-460°C for PTCDA at a basic pressure of 4×10⁻² Pa. The rates and the final thicknesses were strictly controlled by quartz oscillators (Rate-thickness Monitor Inficon SQM 160, USA). The VD layers on a KBr substrate were characterized by Fourier transform infrared spectroscopy (FTIR). The FTIR absorbance spectra were recorded on a Bruker Tensor 27 spectrometer in the range of 4400 - 450 cm⁻¹. The surface morphology of the layers was investigated using Philips 515 SEM, and the microstructure, by means of a high-resolution transmission electron microscope (HRTEM JEOL 2100).

3. Results and discussion
3.1. FTIR investigations
The results from the FTIR investigations are presented in figures 1, 2. The spectra are normalized with respect to band 720 cm⁻¹. Figure 1 shows the FTIR spectra of the initial ZnPhTc dispersed in a KBr pill. The spectra of the VD layers of ZnPhTc – as deposited and after thermal treatment for 1 h at 200 °C, are compared in figure 2. The peaks at 720 cm⁻¹, 1120 cm⁻¹, 1165 cm⁻¹ and 1333-1335 cm⁻¹ in figures 1 and 2 are typical for the existence of ZnPhTc [6]. The band at 720 cm⁻¹ is typical of an α-polymorphic modification which is characteristic of a thermally untreated material. The bands at 1287 cm⁻¹, 1070-1170 cm⁻¹ and 720-770 cm⁻¹ correspond to the existence of different polymorphic modifications. The important results from our study are that a constant composition is preserved upon

![Figure 1](image1.png)  
**Figure 1.** FTIR of initial ZnPhTc in KBr pill.

![Figure 2](image2.png)  
**Figure 2.** FTIR spectra of thin vacuum deposited ZnPhTc layers: dotted line – as deposited; solid line – after thermal treatment for 1 h at 200°C.
vacuum deposition of the ZnPhTc and negligible changes take place after thermal treatment at 200 °C of the condensed films whose structural defects can be reduced by annealing. Based on the spectra obtained and in accordance with the data in the scientific literature [6], we established a full correspondence between the initial substances and the composition of the VD layers prepared.

3.2. SEM and TEM investigations

Figure 3 presents electron microscope images of the surface morphology of ZnPhTc of thickness 63 nm and 190 nm.

![Figure 3](image1)

**Figure 3.** Dependence of the surface morphology of ZnPhTc films on the thickness: a) d = 63 nm b) d = 190 nm; PET/ITO substrate 60 Ω/sq.

![Figure 4](image2)

**Figure 4.** SEM of profile of consecutively deposited ZnPhTc/PTCDA, d ≈ 1.2 μm.

![Figure 5](image3)

**Figure 5.** TEM of the different films with thicknesses in the range of 200 nm. Magn. 100k.

The PET/ITO (60Ω/sq) flexible substrate proved to be the most suitable one with regard to the smoothness of the surface, fine surface morphology and defectlessness of the active layer – figure 3. The thin ZnPhTc layers (d = 63 nm) are more sensitive to the type and structure of the substrate and replicate their defects. The thickness of the VD layer is also important. In the case of thicknesses of over 100 nm, no substrate-related effects were registered. In summary, the condensation of ZnPhTc on the substrates with conductivity 60Ω/sq determines the possibility of preparing dye layers (≥ 80 nm) with uniform fine structure and an almost defectless surface, which was one of the aims of the work.

In contrast to the typical crystalline films, in the ones studied by us (figure 4), column-like growth is only slightly marked, but the results observed are not sufficient for a final conclusion. It is important to note the absence of a phase boundary in the consecutive deposition of both dyes – ZnPhTc and PTCDA – figure 4. The results from the microscopy studies – figures 3, 4, as well as for fullerene – figure 5, show that the films obtained, similarly to the copper phthalocyanine ones [7], have an even surface, fine microstructure and lack considerable defects. This is an important prerequisite for a foreseeable structure of the active films in the multi-layer or tandem OSCs.
3.3. Electrical measurements

The structures ITO/ZnPhTc:PTCDA/PTCDA/Al show a typical diode behavior. The $I/U$ curves – figure 6, cross the ordinate below the origin, which is a promising result for their applicability as a SC. The current increase in daylight and upon illumination by a lamp (60 W) is clearly discernible (approximately by one order of magnitude). In spite of the weak response – around pA to nA, registered as a photovoltaic effect, a low $J_{sc}$ is measurable.

![Figure 6. a) Volt-ampere curves of ITO/ZnPhTc:PTCDA/PTCDA/Al layers depending on the type of exposition, b) zoom of the square area in figure 6 a).](image)

Conclusions

The experimental conditions are established for preparation of VD semiconductor “small molecules” organic films, consisting of pure or mixed dye layers in view of their application as active elements in OSCs. The analyses of the FTIR spectra of initial and VD materials show that they remain unchanged, which is a confirmation of the presence of ZnPhTc in the layers deposited. The results from the microscopy studies show that the films obtained have an even surface without considerable defects. This is an important prerequisite for the growth of the upper layers in the formation of multi-layered or tandem OSCs. Because of the relatively low resolution of the SEM Philips 515, confirming the presence of column-like growth needs additional experimental studies. The initial electrical measurements give us grounds to expect registering a better response to illumination by light similar to the solar light after the improvement of the experimental set-up.

Acknowledgements

This work was supported by the Bulgarian National Science Fund at the Ministry of Education, Youth and Science under contracts BY-TH- 205/06 and DO 02-254/18.12.2008 are gratefully acknowledged.

References

[1] Riede M, Mueller T, Tress W, Schueppel R and Leo K 2008 Small-molecule solar cells-status and Perspectives Nanotechnol. 19 424001

[2] Xue J, Uchida S, Rand B and Forrest S 2004 Asymmetric tandem organic photovoltaic cells with hybrid planar-mixed molecular heterojunctions Appl. Phys. Lett. 84 3013-5 98 5757-9

[3] Schuppel R, Schmidt K, Uhrich C, Schulze K, Wynands D, Bredas J, Maennig B, Pfeiffer M, Leo K, Brier E 2007 Tailored heterojunctions for efficient thin-film organic solar cells: a photoinduced absorption study Proc. SPIE 6656 66560G1-11

[4] Peumans P and Forrest S 2001 Very-high-efficiency double-heterostructure copper phthalocyanine / C60 photovoltaic cells Appl. Phys. Lett. 79 126

[5] Hoppe H and Sariciftci N 2004 Organic solar cells; An overview J. Mater. Res. 19/7 1924-45

[6] Szybowicz M, Runka T, Drozdowski M, Baia W, Wojdyia M, Grodzicki A, Piszczek P and
Bratkowski A 2007 Temperature study of Raman, FTIR and photoluminescence spectra of ZnPc thin layers on Si substrate J. Molec. Struct. 830 14–20

[7] Zhivkov I, Spassova E, Danev G, Andreev S and Ivanov Tz 1998 Vacuum deposited copper phthalocyanine thin films – structure and surface morphology Vacuum 51 2 189-92