



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrsol



On photovoltaic effect in hybrid heterojunction formed from palladium phthalocyanine and titanium dioxide layers

R. Signerski *, G. Jarosz, B. Kościelska

Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul.G.Narutowicza 11/12, 80-952 Gdansk, Poland

ARTICLE INFO

Article history:
Available online xxxxx

PACS:
72.80.Le
73.40.Lq
73.50.Pz

Keyword:
Heterojunctions

ABSTRACT

The results of the research on the photovoltaic properties of a system formed from tin oxide, titanium dioxide, palladium phthalocyanine and gold (SnO₂:F/TiO₂/PdPc/Au) are presented. Films of TiO₂ were deposited using a sol-gel method, then PdPc and Au layers were subsequently evaporated under a high vacuum. The system exhibits a strong rectification effect in the dark, while an effective photogeneration of charge carriers within the TiO₂/PdPc junction is observed under illumination. The experimental relations of a short-circuit current and an open-circuit voltage against the light intensity suggest that trap states participate in recombination processes.

© 2009 Published by Elsevier B.V.

1. Introduction

Hybrid devices formed from titanium dioxide (TiO₂) and polymers [1–5] or low molecular weight organic compounds [6–16] exhibit interesting photovoltaic properties. In these devices, TiO₂ constitutes an n-type semiconductor with a high light transmission and good chemical and thermal stability, whereas the organic material should exhibit the ability to transport of holes and strong light absorption. The desired optical and electrical properties are attributes of some conjugated polymers [1,2,15], porphyrins and phthalocyanines [16–18]. In particular, zinc phthalocyanine (ZnPc) [11,14], copper phthalocyanine (CuPc) [8,12] and bromophosphorus phthalocyanine (PBrPc) [13] films have been often used in TiO₂/organic solid-state heterostructures. In all the systems mentioned here, the charge carrier photogeneration process results basically from a dissociation of the excited state of the organic material at the TiO₂/organic interface which leads to the electron transfer to the TiO₂ conduction band and a positive charge is transported through the organic material.

The photovoltaic properties of a heterojunction formed from a TiO₂ and palladium phthalocyanine (PdPc) layer are considered in this work. Such a junction has not been investigated yet. Photoelectric and electric properties of PdPc thin films have been discussed only in a few works. The photoelectric response of n-ZnO:Al/PdPc/p-CuIn₃Se₅ and n-ZnO:Al/PdPc/p-Si has been presented in the works [19,20]. As is shown in [21], PdPc films exhibit

a p-type conductivity with a hole mobility equal to $2.5 \times 10^{-5} \text{ cm}^2/(\text{Vs})$. Our own investigations performed on PdPc layers provided with different electrodes (ITO, Au, Al, In) also prove that the electric conductivity of PdPc for the samples exposed to air is determined by holes. Therefore, PdPc, similarly as CuPc or ZnPc, can be treated as a p-type semiconductor due to doping by oxygen [16].

Fig. 1 shows a sandwich structure of the device considered in this work which hereinafter will be referred to as SnO₂/TiO₂/PdPc/Au. The layers of SnO₂ and Au act as electrodes. A diagram of energy levels of all the materials used in the investigated device is presented also in Fig. 1. In the case of PdPc we have assumed the same energy values of electron- or hole-transporting levels as for PdPc – Langmuir–Blodgett films [22]. It should be noticed that these energy values are similar to the values obtained for CuPc and ZnPc [12,16,23,24]. For the other materials, the energy levels have been taken from the literature [1,12,25,26]. However, although such an energy-level diagram can be useful while estimating the barriers limiting the charge carrier transport in a system, it is worth bearing in mind that the inaccuracy of energy levels for organic materials can be as big as several tenths eV.

The aim of this work is to present the results of the research on photoelectric properties of the SnO₂/TiO₂/PdPc/Au system. Particular attention is paid to the recombination processes occurring within the heterojunction region.

2. Experimental details

The devices (Fig. 1) were prepared on glass substrates covered in half by transparent conducting oxide (SnO₂:F, 10Ω/square,

* Corresponding author.
E-mail address: ryszard@mif.pg.gda.pl (R. Signerski).

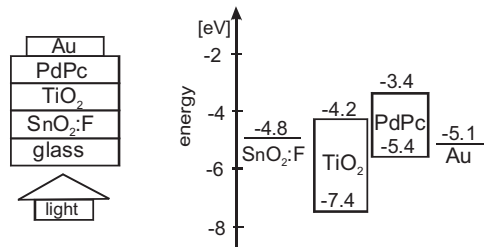


Fig. 1. Device structure and energy-level diagram of the materials used. Fermi levels of electrodes and hole-transporting and electron-transporting levels are given with the respect to vacuum level.

Analyzing the shape of curve 1 in Fig. 2 it can be noticed that this curve is quite complex and it cannot be described by a simple heterojunction model. For instance, its forward bias part ($U < 0$) can be approximated to the typical relation [16,30]:

$$j = j_0 \exp\left(-\frac{eU}{nkT}\right), \quad (1)$$

only when the diode quality factor n is higher than 2 and varies with voltage. Namely, it can be estimated as $n = 4.2$ for $0.2 \text{ V} < |U| < 0.5 \text{ V}$, $n = 6.6$ for $0.5 \text{ V} < |U| < 0.9 \text{ V}$, $n = 7.9$ for $|U| > 0.9 \text{ V}$.

Additionally, we have performed investigations on a system without PdPc, i.e. $\text{SnO}_2\text{:F}/\text{TiO}_2/\text{Au}$. The current-voltage relationship of this system was ohmic, without a rectification effect, and the current intensity values (including also conductivity) were several order of magnitude higher than in the case of the system with PdPc. It means that the shape of curve 1 in Fig. 1 can be determined by the TiO_2/PdPc junction properties and by the charge transport through the PdPc layer or the Au/PdPc contact.

Curves 2 and 3 presented in Fig. 2 were obtained on the sample under illumination through an $\text{SnO}_2\text{:F}$ electrode with monochromatic light (curve 2) or a white light of $20 \text{ mW}/\text{cm}^2$ (curve 3). The photovoltaic effect is explicitly noticeable and its basic parameters were estimated as follows: a short-circuit current as $j_{sc} = 0.3 \text{ } \mu\text{A}/\text{cm}^2$, an open-circuit voltage as $U_{oc} = 0.35 \text{ V}$, a fill factor as $FF = 0.39$ and a power conversion efficiency as $\eta = 0.013\%$ for curve 2, and $j_{sc} = 30 \text{ } \mu\text{A}/\text{cm}^2$, $U_{oc} = 0.46 \text{ V}$, $FF = 0.35$ and $\eta = 0.025\%$ for curve 3. The higher power conversion efficiency observed for curve 3 is related to photogeneration of charge carriers in TiO_2 caused by a light of $\lambda < 400 \text{ nm}$ included in the white light. It is worth adding at this point that the investigated system has not been optimized with regard to the photovoltaic parameters. However, the photovoltaic effect parameters for our system take values comparable with the values obtained on other bilayer systems with homogeneous TiO_2 [3,8,13].

The short-circuit current spectrum $j_{sc}(\lambda)$ obtained under illumination through $\text{SnO}_2\text{:F}$ as well as the absorption spectra of TiO_2 and PdPc are presented in Fig. 3. It is noticeable that the shape of $j_{sc}(\lambda)$ directly reflects the PdPc absorption shape. This relation between the spectrum of j_{sc} and the absorption spectrum of PdPc explicitly proves that photogeneration of charge carriers results from dissociation of excitons excited in PdPc at the TiO_2/PdPc interface. The photogeneration in TiO_2 (band to band excitation) can occur only when the wavelength is shorter than 400 nm . According to the above mentioned conclusion that conductivity of a TiO_2 layer is much higher than the conductivity of a PdPc layer, it can be assumed that the energy-level diagram of our device in a short-cir-

Solaronix). First, the homogeneous 300 nm -thick TiO_2 films were deposited using a sol-gel method. The detailed procedure is described in our previous work [13]. Then, the systems of $\text{glass}/\text{SnO}_2/\text{TiO}_2$ were placed under a high vacuum ($3 \times 10^{-4} \text{ Pa}$) and the following layers were subsequently evaporated with an average rate equal to $0.2 \text{ } \text{Å}/\text{s}$: 60 nm -thick PdPc and 30 nm -thick Au. The palladium phthalocyanine was provided by Kempa, who had synthesized it in accordance with the procedure described in [27]. The active surface of electrodes of a single sample yielded 6 mm^2 . The white light source consisted of an Xe lamp and AMO filter (Oriol). The apparatus used in the electric and photoelectric measurements is described in detail in our previous work [13]. All measurements were performed under ambient air at room temperature.

3. Results and discussion

The current-voltage curves are presented in Fig. 2. The positive voltage refers to the case when a higher potential is applied to the $\text{SnO}_2\text{:F}$ electrode. The curve obtained in the dark (curve 1) exhibits a strong current rectification effect. The rectification ratio exceeds 270 at $U = 1.3 \text{ V}$. Taking into account the height of the barriers existing between the layers of the device (see Fig. 1), it can be assumed that the forward current (i.e. when $U < 0$) is determined mainly by a recombination of charge carriers within the TiO_2/PdPc junction region. This process can operate when electrons are injected from $\text{SnO}_2\text{:F}$ into TiO_2 and holes are injected from Au into PdPc. For a reverse case (i.e. when $U > 0$) the current can result from a thermal generation of the charge carriers within the TiO_2/PdPc junction: the electrons from the valence band of PdPc can be thermally excited into a conduction band of TiO_2 (the barrier yields about 1.2 eV , Fig. 1).

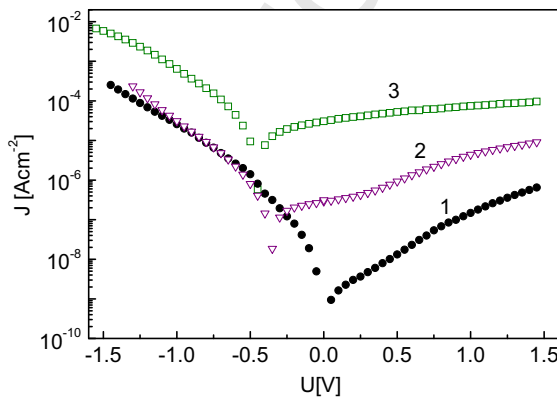


Fig. 2. Current density against the applied voltage in the dark (1) and illuminated with a monochromatic light of 600 nm and $I_0 = 10^{15} \text{ photons}/(\text{cm}^2 \text{ s})$ (2) or with a white light of $20 \text{ mW}/\text{cm}^2$ (3).

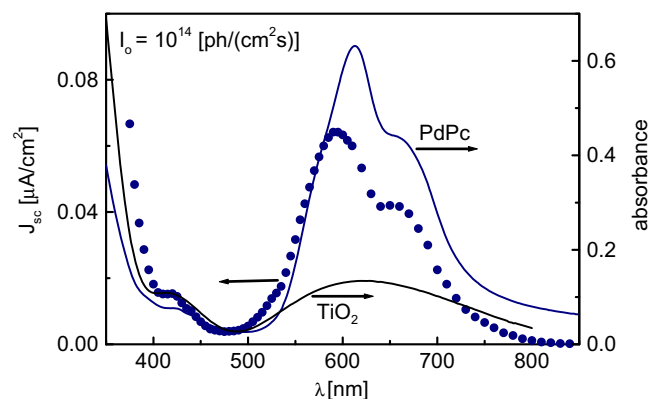


Fig. 3. Spectrum of short-circuit current and absorption spectrum of PdPc and TiO_2 layers.

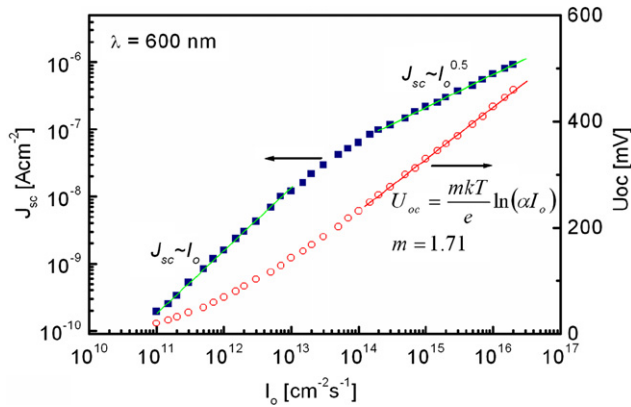


Fig. 4. Short-circuit current and open-circuit voltage against light intensity for the device illuminated through SnO₂:F with a monochromatic light of wavelength 600 nm.

cuit mode is similar to the diagram proposed by Coakley and McGehee [2]: horizontal bands in TiO₂ (no electric field in TiO₂) and oblique bands (inner electric field) in PdPc. It indicates that the electron current in the TiO₂ layer is only a diffusion current, while the hole current in PdPc can have both parts, diffusion and drift.

Moreover, we have recorded a spectrum of open-circuit voltage $U_{oc}(\lambda)$ and also this spectrum exhibits the same shape as $j_{sc}(\lambda)$ therefore it is not presented here.

Fig. 4 shows both the short-circuit current and open-circuit voltage against a photon flux when the device is illuminated through SnO₂:F with a monochromatic light of a wavelength of 600 nm. It can be noticed that the short-circuit current is directly proportional to the light intensity: $j_{sc} \sim I_0$, up to $I_0 = 10^{13}$ photons/(cm² s). When $I_0 > 10^{14}$ photons/(cm² s), the relation can be approximated as $j_{sc} \sim \sqrt{I_0}$ which can be interpreted as a result of a bimolecular recombination of the charge carriers in a heterojunction. A free charge carrier-free charge carrier or free charge carrier-trapped charge carrier recombination can be taken into account. Generally, the presence of a charge carrier recombination leads to the power relation of the short-circuit current against the light intensity, $j_{sc} \sim I_0^n$, with the exponent n decreasing from 1 to 0.5 with the increasing light intensity [28,29].

The relation between the open-circuit voltage and light intensity can be also applied in studies of recombination processes in a heterojunction. For instance, if this relation in a certain range of light intensity is approximated as [16,30]

$$U_{oc} = \frac{m k T}{e} \ln(\alpha I_0), \quad (2)$$

where kT/e is the thermal potential, the m and α parameters depend on the heterojunction model, then the recombination via trapping states leads to $m > 1$ [31,32]. In our case Eq. (2) is fulfilled for the curve $U_{oc}(I_0)$ presented in Fig. 4, when $I_0 > 10^{14}$ photons/(cm² s) with $\alpha = 2.18 \times 10^{-12}$ cm²/s and $m = 1.71$. Therefore, we come to the conclusion that states trapping charge carriers operate in our heterojunction.

4. Conclusions

Our researches on photovoltaic properties of the SnO₂/TiO₂/PdPc/Au system enable us to come to the following conclusions:

- The investigated system exhibits a strong rectification effect in the dark, resulting from the presence of the TiO₂/PdPc junction.
- Illumination of the system leads to a photovoltaic effect. The spectral dependence of the short-circuit current suggests that it results from an exciton dissociation at the TiO₂/PdPc interface.
- For $I_0 > 10^{14}$ photons/(cm² s), both relations, $U_{oc}(I_0)$ and $j_{sc}(I_0)$, indicate that a recombination of charge carriers occurs within the TiO₂/PdPc junction. Additionally, the $U_{oc}(I_0)$ relation suggests the occurrence of a free charge carrier-trapped charge carrier recombination.

Acknowledgment

This work has been supported by Polish Ministry of Science and Higher Education with a grant for 2006–2009 under Program No. 3T11B06530.

References

- [1] P.A. Lane, Z.H. Kafafi, in: S.-S. Sun, N.S. Sariciftci (Eds.), Organic Photovoltaics, Taylor & Francis, 2005, pp. 49–104.
- [2] K.M. Coakley, M.D. McGehee, in: S.-S. Sun, N.S. Sariciftci (Eds.), Organic Photovoltaics, Taylor & Francis, 2005, pp. 299–312.
- [3] P. Ravirajan, S.A. Haque, J.R. Durrant, D.D.C. Bradley, J. Nelson, Adv. Funct. Mater. 15 (2005) 609.
- [4] E. Itoh, Y. Takamizawa, K. Miyairi, Jpn. J. Appl. Phys. 47 (2008) 509.
- [5] T. Ishwara, D.D.C. Bradley, J. Nelson, P. Ravirayan, I. Vanseveren, T. Cleij, D. Vanderzande, L. Lutsen, S. Tierney, M. Heeney, I. McCulloch, Appl. Phys. Lett. 92 (2008) 053308.
- [6] J. Wienke, T.J. Schaafsma, A. Goossens, J. Phys. Chem. B103 (1999) 2702.
- [7] J.E. Kroeze, T.J. Savenije, J.M. Warman, Adv. Mater. 14 (2002) 1760.
- [8] E. Itoh, Y. Ohmori, K. Miyairi, Jpn. J. Appl. Phys. 43 (2004) 817.
- [9] A. Huijser, T.J. Savenije, L.D.A. Siebbeles, Thin Solid Films 511–512 (2006) 208.
- [10] Y. Ohmori, E. Itoh, K. Miyairi, Thin Solid Films 499 (2006) 369.
- [11] K. Kajihara, K. Tanaka, K. Hirao, N. Soga, Jpn. J. Appl. Phys. 35 (1996) 6110.
- [12] M. Thelakkat, C. Schmitz, H.W. Schmidt, Adv. Mater. 14 (2002) 577.
- [13] R. Signerski, B. Kościeliska, Opt. Mater. 27 (2005) 1480.
- [14] D. Ino, K. Watanabe, N. Takagi, Y. Matsumoto, J. Phys. Chem. B109 (2005) 18018.
- [15] J. Sworakowski, J. Ulański, Annu. Rep. Prog. Chem. Sect. C 99 (2003) 87.
- [16] J. Simon, J.-J. André, Molecular Semiconductors, Springer, Berlin, 1985.
- [17] C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, VCH Pub, New York, 1989.
- [18] D. Wróbel, A. Dudkowiak, Mol. Cryst. Liq. Cryst. 448 (2006) 15.
- [19] I.V. Bodnar, E.S. Dmitrieva, S.E. Nikitin, V.Y. Rud, Y.V. Rud, E.I. Terukov, Semiconductors 39 (2005) 402.
- [20] G.A. Il'chuk, S.E. Nikitin, Y.A. Nikolaev, V.Y. Rud, Y.V. Rud, E.I. Terukov, Semiconductors 39 (2005) 409.
- [21] N. Karl, K.-H. Kraft, J. Marktanner, M. Münch, F. Schatz, R. Stehle, H.-M. Uhde, J. Vac. Sci. Technol. A17 (1999) 2318.
- [22] E. Itoh, M. Iwamoto, M. Burghard, S. Roth, Jpn. J. Appl. Phys. 39 (2000) 5146.
- [23] G. Hill, A. Kahn, Z.G. Soos, R.A. Pascal Jr., Chem. Phys. Lett. 327 (2000) 181.
- [24] S.M. Tadayyon, H.M. Grandin, K. Griffiths, L.L. Coatsworth, P.R. Norton, H. Aziz, Z.D. Popovic, Org. Electron. 5 (2004) 199.
- [25] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
- [26] M. Eschle, E. Moons, M. Grätzel, Opt. Mater. 9 (1998) 138.
- [27] Kempa, J. Dobrowolski, Can. J. Chem. 669 (1988) 2553.
- [28] L.J.A. Koster, V.D. Mihailetchi, P.W.M. Blom, Appl. Phys. Lett. 88 (2006) 052104.
- [29] R. Signerski, J. Non-Cryst. Solids 354 (2008) 4465.
- [30] S.M. Sze, Physics of Semiconductors Devices, Wiley, New York, 1981.
- [31] R. Signerski, J. Non-Cryst. Solids 352 (2006) 4319.
- [32] D. Cheyins, J. Poortmans, P. Heremans, C. Deibel, S. Verlaak, B.P. Rand, J. Genoe, Phys. Rev. B77 (2008) 165332.