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Photosensitive Heterostructures Made of Sulfonamide Zinc Phthalocyanine and Organic Semiconductor

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The photovoltaic properties of thin films and double-layer heterostructures made of sulphonamide-substituted zinc phthalocyanine were studied. The films of phthalocyanine were prepared from a chloroform solution by spin-coating. Top-layer components of heterostructures (pentacene, lead phthalocyanine, perylene derivative) were thermally evaporated on phthalocyanine films. The effect of annealing and aging on the photovoltaic properties of films was examined. The observed reversal of the sign of photovoltage spectra for the films and heterostructures was explained in present paper.

Keywords Heterostructure; reversal of sign in photovoltage spectra; sulphonamide-substituted phthalocyanine

Introduction

Thin film heterostructures (HS) made of organic semiconductors have been promising for optoelectronic and photovoltaic applications [1], especially for the development of organic solar cells [2,3] and light-emitting diodes [4]. Recently, the power conversion efficiency of $(5.0 \pm 0.3)\%$ was achieved for organic solar cells made of thermally deposited HS of copper phthalocyanine and C_{60} fullerene under 1 sun AM1.5 solar illumination [5]. The elaboration of a fabrication technology for HS has been intensively pursuing for last decades due to the emerging prospects of applications of organic solar cells. For example, one seeks for cheap new and more efficient organic materials. From this point of view, one of the possible ways to solve the problem of production of organic solar cells might be to use soluble derivatives of phthalocyanines synthesized in recent years [6,7].

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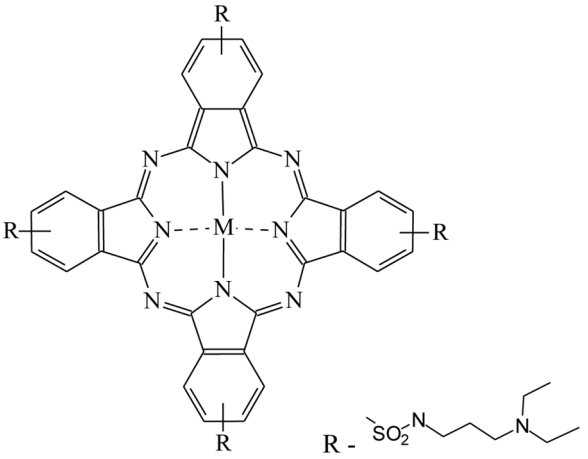
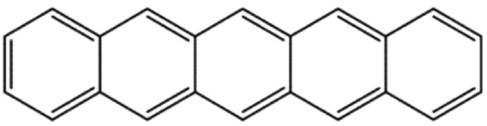
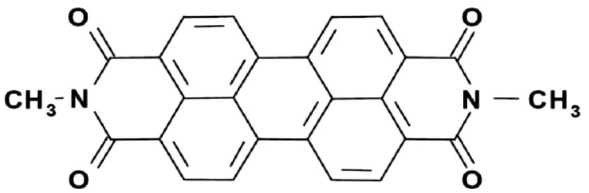


Scheme 1. Formulas of 3-diethylamino-1-propylsulphonamide zinc phthalocyanine (ZnPcSu) – M=Zn, R = 1–2 (a); and lead phthalocyanine (PbPc) – M=Pb, R = 0 (b).

The preliminary studies performed in our group showed [8] that one of the most photosensitive soluble phthalocyanines is 3-diethylamino-1-propylsulphonamide zinc phthalocyanine (ZnPcSu) (Scheme 1). N-type ZnPcSu was the most photosensitive one among the studied zinc phthalocyanines with other substituents [8]. Therefore, ZnPcSu appeared to be a promising material for the development of HS photosensitive in a wide spectral range. For example, the comparison of absorption spectra of thin films of the above-mentioned material and lead phthalocyanine (PbPc), pentacene (Pn), and methyl perylene pigment (MPP) (Schemes 1–3) showed that a double-layer HS made of ZnPcSu has a significant ability to absorb solar light (Fig. 1). The estimation of a potential barrier at the interface of organic semiconductors has been predominantly stipulated by the energy diagram of ionized states [9]. Unfortunately, the parameters of the diagram for ZnPcSu have not been determined up to date.



Scheme 2. Formulae of pentacene (Pn).



Scheme 3. Formulae of N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide (DMe-PTCDI) or methyl perylene derivative (MPP).

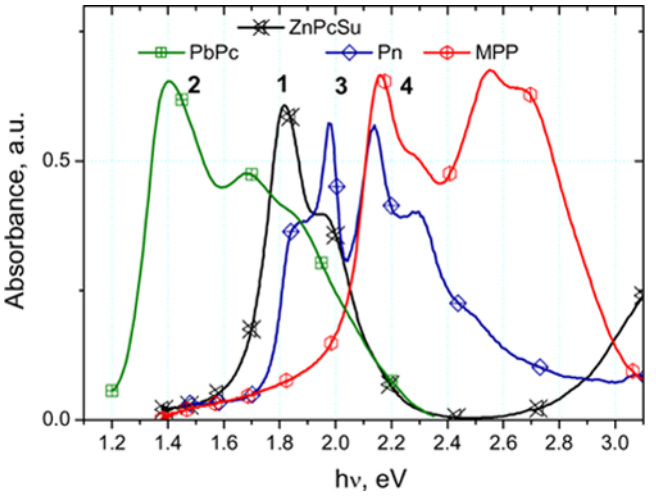


Figure 1. Absorption spectra of ZnPcSu (1), lead phthalocyanine (2), pentacene (3), and MPP (4) films.

We studied the optical and photovoltaic properties of thin films of ZnPcSu and double-layer HS made of bottom ZnPcSu and top PbPc, Pn, or MPP. The aim of the studies was the experimental search for efficient organic photosensitive semiconductors being a components of HS based on ZnPcSu and the ways to improve the photovoltaic parameters, as well as to achieve a photosensitivity in a wide spectral range of solar light.

Experimental

The thin films of ZnPcSu were prepared by the spin coating from a chloroform solution with a concentration of 10 mg/ml. The glass substrates with the conductive and transparent indium tin oxide (ITO) electrode were used. The thin films of MPP, Pn, and PbPc were thermally deposited on the ZnPcSu layers at substrate temperatures of 370 K (MPP, Pn) and 410 K (PbPc) being optimal for photoelectric properties of the materials [10–12]. The thickness of films was ca. 100 nm. The annealing of ZnPcSu films was performed at a temperature of 410 K for 1 h, and the aging lasted for 2 months in ambient atmosphere.

The absorption spectra were measured with a Shimadzu UV 2450 UV-Vis spectrophotometer.

Photovoltaic properties of samples were examined by the Bergman-Akimov technique [13] under the modulated illumination of both sides of samples (the bottom ITO-electrode side and the top free surface side). Photovoltage spectra were measured using an MDR-4 monochromator and a "Unipan-232B" lock-in nanovoltmeter. The photovoltage was recalculated on the same number of incident photons. The used technique was comprehensively described in Refs. [14,15]. The advantage of the Bergman–Akimov technique is in that we have no need to deposit a top ohmic electrode on a thin film or HS, considering that the parameters of the deposition have not been specified for new materials.

Results and Discussion

Optical and Photovoltaic Properties of ZnPcSu Films

The comparison of the absorption spectra of a ZnPcSu solution in chloroform (Fig. 2a, curve 1) and thin films (Fig. 2a, curves 2–4) shows that a change of the aggregate state, the transition from a solution to the solid state, results in both a significant drop of the intensity of the lower electronic transition with maximum at 1.82 eV and a widening of spectral bands. The minimum changes of the absorption spectra were observed at $h\nu > 1.9$ eV in the range of intramolecular vibrations. The annealing and the aging of films resulted in a moderate (ca. 20%) decrease of the spectral band peaked at 1.82 eV. The spectral bands of films became a little wider due to the annealing (Fig. 2a, curve 3). The broadening was less pronounced after the aging of films (Fig. 2a, curve 4). The effect of broadening appears to be more evident in differential absorption spectra (Fig. 2b), by showing the explicit increase of the optical density after the annealing and the aging in the interval of a low absorption of films. This behavior can be explained by a rise of the concentration of structural defects due to the annealing of films. A similar change of the absorption spectra is observed for Pn films [16] evidencing the formation of partially oriented crystalline grains in ZnPcSu films. However, a shift of the electronic transition maximum at a change of the aggregate state was insignificant for ZnPcSu in comparison with, for example, Pn, vindicating the weakness of the intermolecular interaction of ZnPcSu molecules in a film due to the repulsion of molecules with substitution.

The photovoltage spectra at the illumination of the ITO-electrode side, as well as the illumination of the free surface side, correlate with absorption spectra (Fig. 3) in the range of strong absorption, 1.6–2.2 eV, revealing a low charge carrier

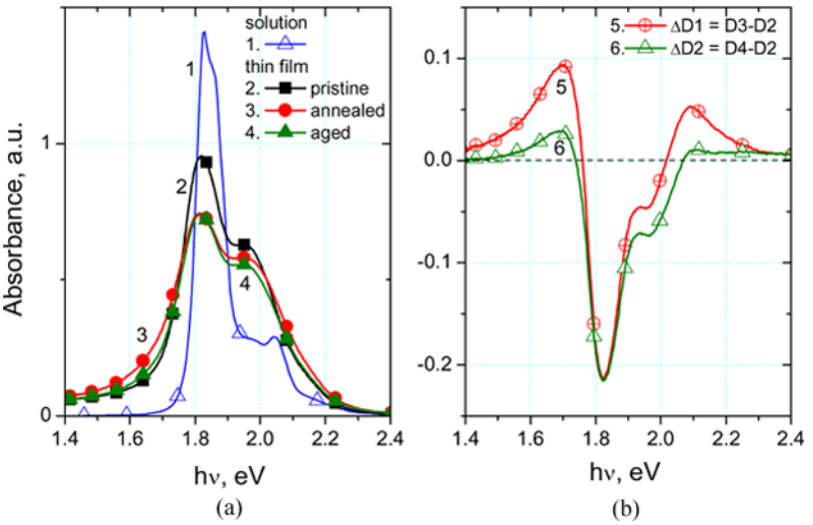


Figure 2. (a) Absorption spectra of ZnPcSu solution (1) and thin films (2–4) before annealing – pristine (2 – D2), annealed (3 – D3), and aged (4 – D4) samples. (b) Difference of absorption spectra of ZnPcSu films before and after the annealing (5), $\triangle D1 = D3 - D2$, as well as after the aging (6), $\triangle D2 = D4 - D2$.

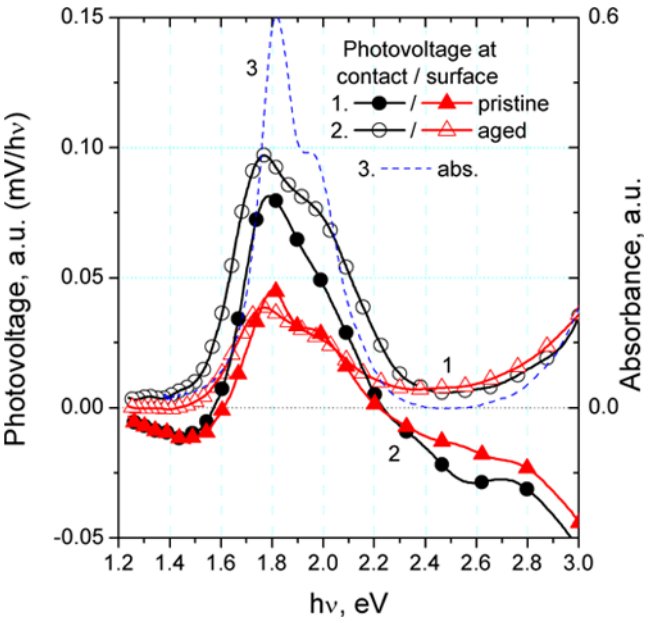


Figure 3. Photovoltage spectra of pristine (1, filled) and aged (2, open) ZnPcSu films at the illumination on the sides of the ITO electrode (circles) and the free surface (triangles). Absorption spectra of ZnPcSu film (3, dashed line).

recombination in ZnPcSu films. The photovoltage under the illumination on the ITO side was higher than that under the illumination on the free surface side (Fig. 3) evidencing the difference of barriers and charge carrier recombination rates at the both sides of films. The reversal of the sign in photovoltage spectra of pristine films was observed in the range of low absorption (Fig. 3). The magnitude of negative photovoltage slightly shrank at the annealing of films (Fig. 4) and became positive in the process of aging (Fig. 3). The observed reversal of the sign of photovoltage spectra in the region of low absorption was explained within a simple model of two oppositely directed barriers formed at the ITO electrode and the free surface. The potential barriers form the space charge regions separated by a quasineutral area. The thickness of space charge regions should be in the interval 20–40 nm, being typical of phthalocyanines [17]. The radiation in the range of strong absorption, 1.65–2.10 eV, was absorbed predominantly near the illuminated barrier forming one photovoltage component at the barrier. Light in the region of low absorption was absorbed in space charge regions on both sides of the film, and the photovoltage can be determined as the difference of photovoltage components originated at both barriers leading to the sign reversal. Thus, the negative photovoltage (Figs. 3 and 4) is determined mainly by the difference of potential barrier heights being influenced by the rate of charge carrier recombination commonly different at both sides of the film.

The model of two opposite directed barriers clarifies also the absence of the sign reversal in photovoltage spectra of aged ZnPcSu films. During the aging process, the films adsorb active gases from air, and dopants on the surface become centers of recombination. Therefore, the aging results in a decrease of the photovoltage component formed at the surface due to the enhanced recombination. In this case, the photovoltage component at the ITO electrode barrier becomes much more intense

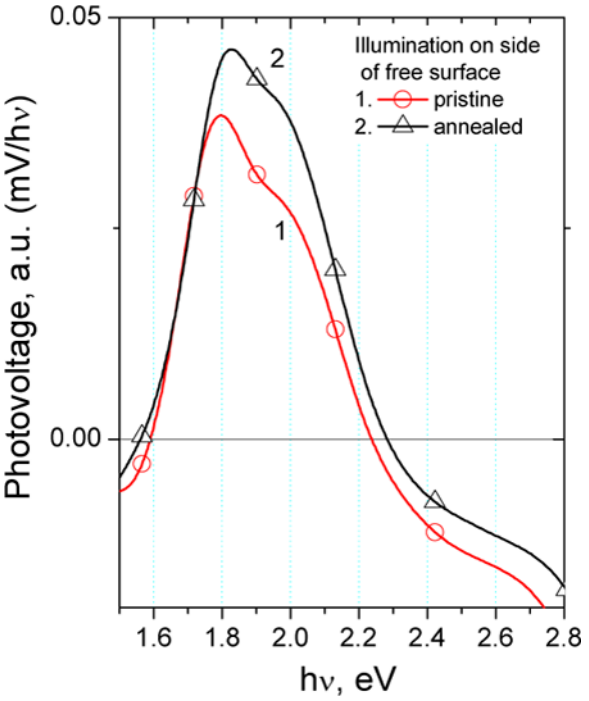


Figure 4. Photovoltage spectra of pristine (1) and annealed (2) ZnPcSu films under the illumination of the films on the free surface side.

than that at the free surface barrier, so the difference of photovoltage components results only in the one-sign spectrum. An increase in the rate of surface recombination of charge carriers, S, was confirmed by the dependence of the photovoltage on the optical density (Fig. 5). According to the literature [18–20], the dependence of the photovoltage on the absorbance tends to be linear for low S and to saturate for high S. Figure 5 shows that S at the free surface is substantially higher for the aged films.

The vanishing of the negative photovoltage is also explained by a schematic representation of photovoltage components forming the spectrum (Fig. 6). Two components (positive and negative) and their sum are drawn on the left and right sides of Fig. 6, respectively. The photovoltage components are schematically shown with the use of Gauss curves, which correlates with the absorbance. The positive component, V_c, characterized by low S, and the negative component, V_s, appears with a local maximum due to significant S, S_1 and S_2, where $S_2 > S_1$. The maximum is characterized by a decrease of the photovoltage with increase in the absorbance at high S [18–20]. The sum of V_c and V_s gives the sign reversal for low S, S_1, like for pristine ZnPcSu films, while one-sign (without the sign reversal) spectra were obtained for high S, S_2, mimicking the case of aged ZnPcSu films.

HS Made of ZnPcSu and Organic Semiconductors

The organic semiconductors were thermally deposited on wet-prepared ZnPcSu films, being treated (annealing, aging) in different ways. The treatment performed

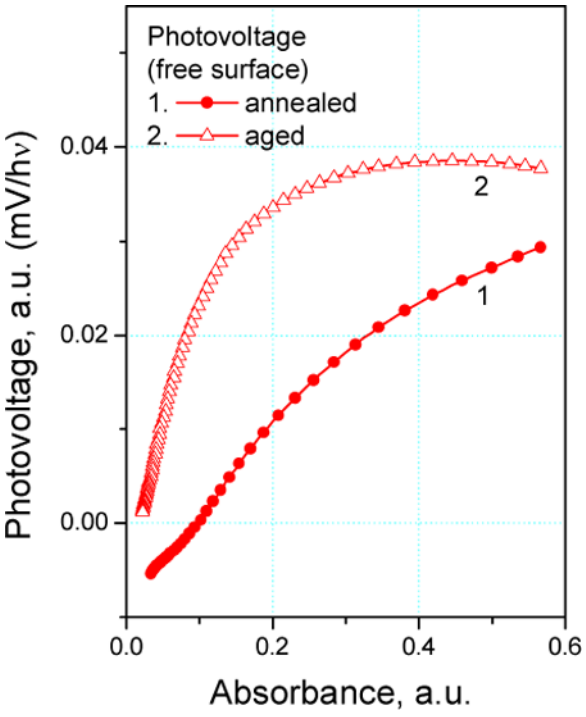


Figure 5. Photovoltage vs. the absorbance for annealed (1) and aged (2) ZnPcSu films in the interval 1.5 – 1.8 eV.

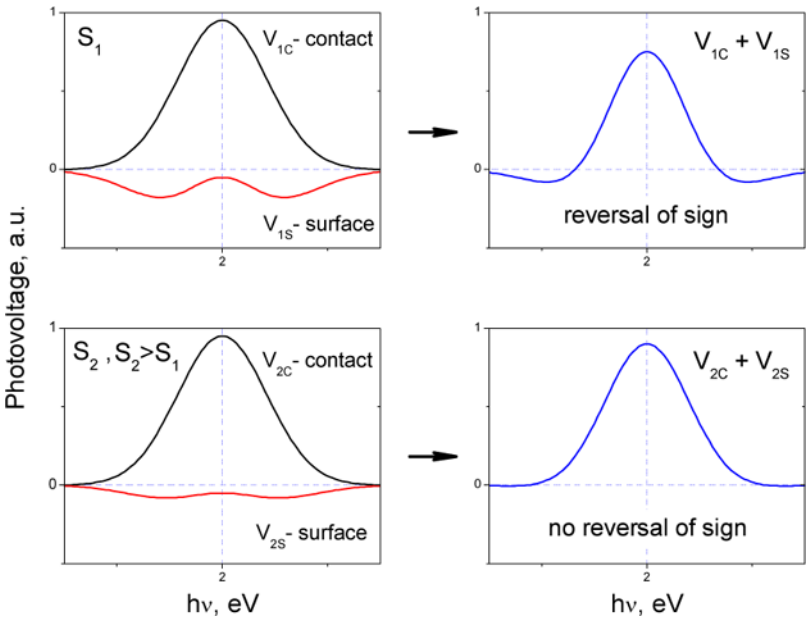


Figure 6. Schematic drawing of the mechanism of sign reversal in the photovoltage spectrum appearing due to the formation of positive and negative photovoltage components (left) and the sum of the components (right).

can alter the properties of HS. In fact, the partial degassing and the annealing in vacuum occur during the placing of a substrate with ITO/ZnPcSu structure in a vacuum chamber for the thermal deposition of a top layer. The annealing took place due to the heating of the substrate to a temperature of 370 K or 410 K, being optimal for the fabrication of thin films of organic semiconductors [10–12]. To elucidate the impact of the treatment of ZnPcSu, the organic semiconductors were deposited on pristine, annealed, and aged ZnPcSu films.

The photovoltage spectra of HS show a photosensitivity of HS in the almost whole visible spectral range evidencing the contribution of photogenerated charge carriers from both components of HS. The sign reversal in photovoltage spectra was also observed for HS made of organic semiconductors on pristine ZnPcSu films (Figs. 7–9). Whereas the positive photovoltage is in the range of strong absorption of ZnPcSu, the negative one appears in the range of strong absorption of an organic semiconductor regardless of the type (*p*- or *n*-type) of a semiconductor (Figs. 7 and 8). The typical behavior is shown in Fig. 7 for aniso-type (*n*-*p*-type) ZnPcSu/PbPc HS and in Fig. 8 for iso-type (*n*-*n* + -type) ZnPcSu/MPP HS. The sign reversal vindicates the formation of recombination centers at a high concentration at the interface of HS. The HS is described by an equivalent circuit with two oppositely biased Schottky diodes connected in series, being considered in our previous studies of Pn/PbPc HS [21].

The photovoltage of all studied HS is higher than that of ZnPcSu films. The rise of the photovoltage indicates the formation of a potential barrier much higher than that for ZnPcSu films. The photovoltage of ZnPcSu/PbPc HS (Fig. 7) in the range of strong absorption of PbPc was a few times higher than the photovoltage in the range of strong absorption of ZnPcSu evidencing a higher efficiency of the photogeneration in a PbPc layer than that in a ZnPcSu one. The similar behavior was observed for ZnPcSu/Pn HS; however, the photogeneration efficiencies for ZnPcSu/MPP HS are comparable in both layers of HS.

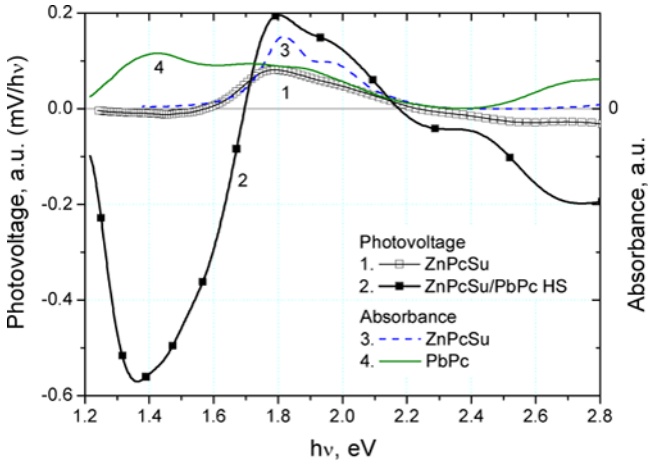


Figure 7. Photovoltage spectra of a pristine ZnPcSu film at the illumination on the ITO electrode side (1) and ZnPcSu/PbPc HS under the illumination on the ZnPcSu layer side (2). Absorption spectra of ZnPcSu (3) and PbPc (4) films. HS was deposited on a pristine ZnPcSu film.

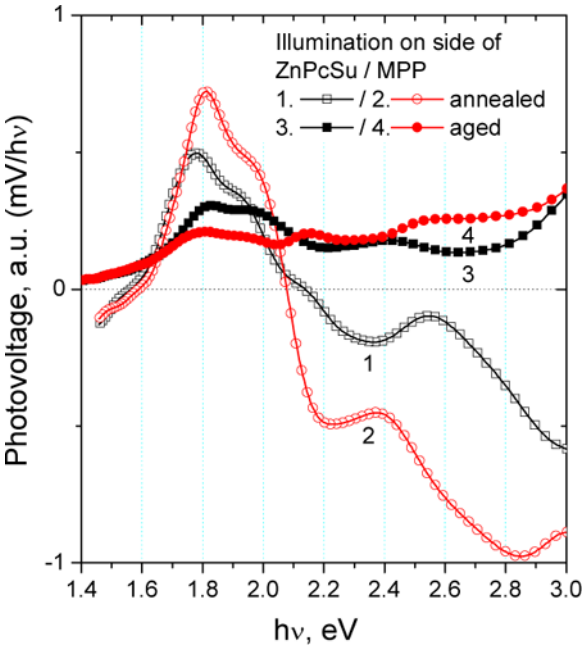


Figure 8. Photovoltage spectra of annealed (1,2) and aged (3,4) ZnPcSu/MPP HS at the illumination on the sides of ZnPcSu (1,3) and a MPP (2,4) layer.

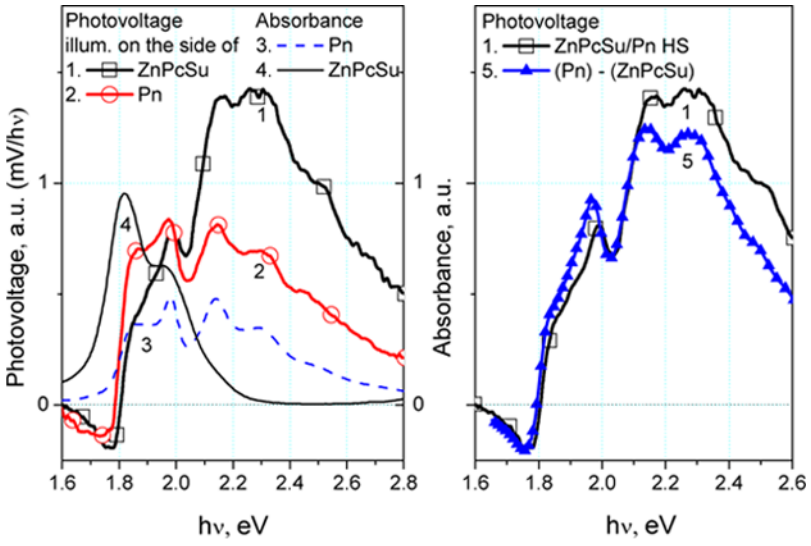


Figure 9. Photovoltage spectra of the ZnPcSu/Pn heterostructure at the illumination on the sides of ZnPcSu (1) and Pn (2). Absorption spectra of Pn (3) and ZnPcSu (4) films. The normalized sum of the positive photovoltage spectrum of a Pn film and the negative photovoltage spectrum of a ZnPcSu film (5).

We have also tested the effect of the use of aged ZnPcSu films as a component of HS. The photovoltage spectra without sign reversal were obtained for ZnPcSu/MPP HS (Fig. 8), where MPP was deposited on aged ZnPcSu films, by showing a low concentration of recombination centers at the interface. On the other hand, the sign reversal with a minimum at 1.78 eV, regardless of the side of illumination, remains for ZnPcSu/Pn HS made of aged ZnPcSu layer (Fig. 9). The negative photovoltage for ZnPcSu/Pn HS might be related to the formation of complexes between Pn and ZnPcSu molecules or a high concentration of recombination centers at the interface. As was mentioned above and elaborated in Ref. [21], HS with a high concentration of recombination centers at the interface behaves itself like two diodes connected oppositely. The last case conforms to the results for HS made of pristine ZnPcSu films. A difference of the photovoltage spectra of Pn and ZnPcSu films is another proof of the high concentration of recombination centers at the interface of ZnPcSu/Pn HS. We can compare a sum of the positive photovoltage spectrum of a Pn film and the negative photovoltage spectrum of a ZnPcSu film with the photovoltage spectrum of ZnPcSu/Pn HS (see Fig. 9, curve 5). The spectral features of the sum correlate with those of the photovoltage spectrum of ZnPcSu/Pn HS testifying to the model of two oppositely connected diodes in HS under study.

We expected a lowering of the concentration of recombination centers at the interface of HS and an increase of the photovoltage for HS, where organic semiconductors were deposited on previously annealed ZnPcSu films. The experimental studies of HS with various temperatures of the annealing of ZnPcSu did not confirm the expectations in an unambiguous way. For example, ZnPcSu/MPP HS with MPP

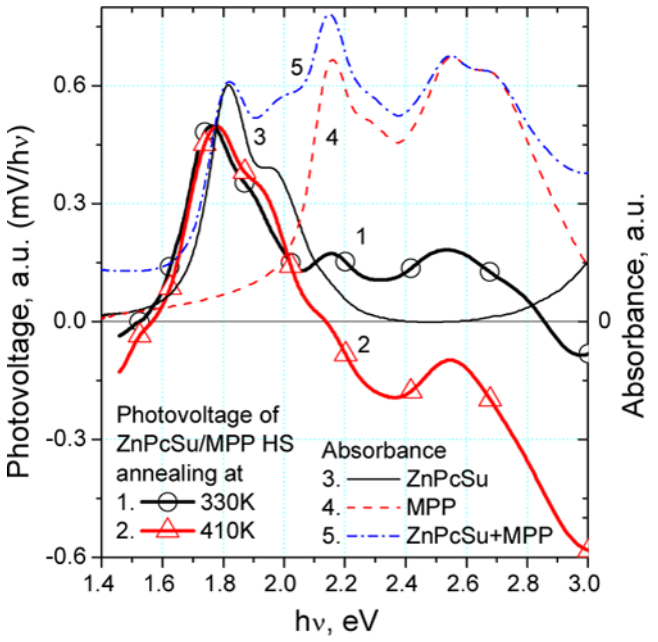


Figure 10. Photovoltage spectra of ZnPcSu/MPP HS at the illumination on the side of ZnPcSu. The HS made of ZnPcSu films annealed at 330 K (1) and 410 K (2). Absorption spectra of ZnPcSu films (3), MPP films, and ZnPcSu/MPP HS (5).

deposited on both pristine (unannealed) film and a ZnPcSu film annealed at low temperatures (330 K) undergoes the sign reversal only in the ranges of $h\nu < 1.5$ eV and $h\nu > 2.9$ eV (Fig. 10). However, ZnPcSu/MPP HS made of a ZnPcSu film annealed at high temperatures (410 K) undergoes the sign reversal at $h\nu < 1.5$ eV and in the region of strong absorption of MPP ($h\nu > 2.1$ eV). Nevertheless, the annealing at high temperatures (410 K) slightly improved the photovoltage of ZnPcSu films (Fig. 4). On the other hand, some structural defects form the recombination centers for charge carriers at this temperature, by widening the range of reversed photovoltages in HS. The appearance of structural defects in the annealing process was argued above by an increase in the absorbance in the interval 1.5–1.7 eV (Fig. 2, curves 3,5).

Summary

The studies of optical and photovoltaic properties of ZnPcSu films and HS made of ZnPcSu have clarified the following important points:

i. The sign reversal observed in photovoltage spectra of pristine ZnPcSu films can be interpreted in terms of two differently directed barriers at the free surface and at the ITO contact. The absence of the sign reversal caused by the aging of films was accompanied by an increase of the rate of recombination of charge carriers at the free surface of films due to the adsorption of active gases from air.
ii. HS made of solution-processed ZnPcSu and thermally deposited organic semiconductors (Pn, MPP, PbPc) had the photovoltage much higher than ZnPcSu films, by evidencing in favor of the formation of a much higher barrier at the interface of HS than that in ZnPcSu films. The sign reversal in photovoltage spectra of HS is explained by the formation of the centers of charge carrier recombination at a high concentration at the interface which is like two oppositely connected Schottky diodes. In fact, pristine ZnPcSu and the organic semiconductor contribute to the photovoltage of HS with different signs, by forming the sign reversal in photovoltage spectra of HS. HS made of aged ZnPcSu and MPP layers had no sign reversal revealing a low concentration of the centers of charge carrier recombination at the interface of HS. A feasibility of the fabrication of HS made of ZnPcSu films photosensitive in a wide spectral range is shown experimentally.

Acknowledgment

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References

[1] Brabec, Ch., Dyakonov, V., & Scherf, U. (Eds.) (2009). *Organic Photovoltaics*, Wiley-VCH: Weinheim.
[2] Tang, C. W. (1986). *Appl. Phys. Lett.*, *48*, 183.
[3] Rostalski, J., & Meissner, D. (2000). *Solar Energy Materials & Solar Cells*, *61*, 87.
[4] Levermore, P. A., Adamovich, V., Rajan, K., Yeager, W., Lin, Ch., Xia, S., Weaver, M. S., Kwong, R., Ma, R., Hack, M., & Brown, Ju. J. (2010). *Proc. SPIE Conference on*

Light-Emitting Diodes: Materials, Devices, and Applications for Solid State Lighting XIV, January 26, 2010, San Francisco, California, USA; 7617, 761704.
[5] Xue, J., Rand, B. P., Uchida, S., & Forrest, S. R. (2005). *Adv. Mater.*, *17*, 66.
[6] Nešpůrek, S., Chaidogiannos, G., Glezos, N., Wang, G., Böhm, S., Rakušan, J., & Karásková, M. (2007). *Mol. Cryst. Liq. Cryst.*, *468*, 355.
[7] Kadish, K. M., Smith, K. M., & Guilard, R. (2009). *The Porphyrin Handbook: Phthalocyanines: Properties and Materials*, Academic Press: San Diego.
[8] Syromyatnikov, V., Pomaz, I., Perminov, R., Verbitsky, A., Vertsimakha, Ya., Nespurek, S., & Pocheraylov, S. (2009). *Book of abstracts of International Conference 'HighMatTech-2009', October 19–23, 2009*, Kyiv, Ukraine, p. 310.
[9] Pope, M., Swenberg, Ch. E., & Swenberg, Ch. E. (1999). *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press: Oxford.
[10] Vertsimakha, Ya., Lutsyk, P., Palewska, K., Sworakowski, J., & Lytvyn, O. (2007). *Thin Solid Films*, *515*, 7950.
[11] Vertsimakha, Ya., & Verbitsky, A. (2000). *Synthetic Metals*, *109*, 291.
[12] Verzimacha, Ja. I., Kovalschuk, A. V., & Kurik, M. V. (1984). *Physica Status Solidi A*, *82*, K111.
[13] Akimov, I. A., & Meshkov, A. M. (1965). *Dokl. Acad. Nauk SSSR*, *162*, 306.
[14] Verbitsky, A. B., Vertsimakha, Ya. I., Lutsyk, P. N., Studzinsky, S. L., Bereznev, S., & Kois, J. (2006). *Semiconductors*, *40*, 197.
[15] Lutsyk, P., Misiewicz, J., Podhorodecki, A., & Vertsimakha, Ya. (2007). *Solar Energy Mater. Solar Cells*, *91*, 47.
[16] Vertsimakha, Ya. I., Kuryk, M. V., Silinsh, E. A., & Taure, L. F. (1977). *Izv. Akad. Nauk Latviiskoi SSR, Seria Fiz. Tekh. Nauk.*, *2*, 47.
[17] Simon, J., & Andre, J. J. (1985). *Molecular Semiconductors*, Springer: Berlin.
[18] Dmitruk, N. L., Kryuchenko, Yu. V., Litovchenko, V. G., & Popov, V. G. (1986). *Poverkhnost': Fizika, Khimia, Mekhanika*, *5*, 56.
[19] Dmitruk, N. L., Kryuchenko, Yu. V., Litovchenko, V. G., Popov, V. G., & Stepanova, M. A. (1991). *Phys. Stat. Sol. (a)*, *124*, 183.
[20] Lutsyk, P., & Vertsimakha, Ya. (2005). *Mol. Cryst. Liq. Cryst.*, *426*, 265.
[21] Lutsyk, P., & Vertsimakha, Ya. (2008). *Mol. Cryst. Liq. Cryst.*, *496*, 138.