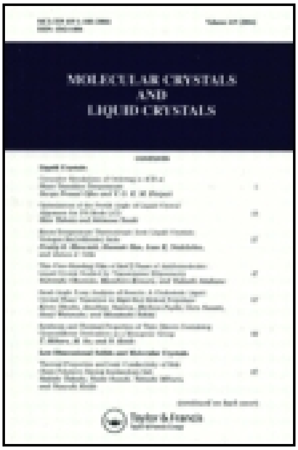

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Organic Iso-Type Double-Layer Heterostructures Based On Pentacene, Hexathiopentacene, and Lead Phthalocyanine

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Organic Iso-Type Double-Layer Heterostructures Based On Pentacene, Hexathiopentacene, and Lead Phthalocyanine

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Photovoltaic properties of double-layer iso-type heterostructures based on pentacene, hexathiopentacene, and lead-phthalocyanine are studied. The heterostructures are prepared by thermal deposition on glass substrates at various substrate temperatures (T_s). Under modulated illumination, the sign reversal is observed in photovoltage spectra of pentacene/lead-phthalocyanine heterostructures deposited at $T_s = 300\,K$. The properties of these structures are well described by the van Opdorp model for inorganic iso-type heterojunctions. No sign reversal has been observed in pentacene/lead-phthalocyanine, pentacene/hexathiopentacene, acene, and hexathiopentacene/lead-phthalocyanine heterostructures deposited at $T_s = 370\,K$, the magnitudes of photovoltage being higher than those in structures prepared at $T_s = 300\,K$.

Keywords: interface; iso-type heterostructures; organic solar cells

INTRODUCTION

Organic solar cells are promising renewable sources of energy, but the efficiencies of these devices are in most cases too low for practical application [1,2], due to a high series resistance and a low efficiency of solar light collection. In inorganic solar cells, the series resistance

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can be significantly lowered using the impurity doping and the formation of p-p$^+$ and/or n-n$^+$ junctions [3]. But, in organic solar cells, this method to decrease the series resistance is inefficient and technologically complicated. To solve this problem, the formation of organic p-p$^+$ or n-n$^+$ junctions using iso-type heterostructures (IHS) was suggested in Ref. [4]. p-p$^+$ or n-n$^+$ IHS can be prepared simultaneously with aniso-type heterostructures using a simple low-cost technology. Moreover, an optimal selection of heterostructure components can extend the spectral range of photosensitivity and increase the efficiency of the collection of charge carriers in solar cells, provided a low concentration of surface states is formed at the interface of the heterostructure.

The photovoltaic properties of organic IHS have been little studied so far. Therefore, the aim of this work was a study of photovoltaic properties of IHS based on photosensitive organic semiconductors. We also plan to consider a possibility to fabricate IHS with a low rate of charge carrier recombination at the interface that can be useful for improving the characteristics of organic solar cells.

METHODS OF EXPERIMENT

The materials under consideration (Fig. 1) were p-p$^+$ IHS based on pentacene (Pn), hexathiopentacene (HTP), and lead-phthalocyanine (PbPc). Pn is a photosensitive organic semiconductor that has been used for the development of organic solar cells [5,6]. Conductivities of HTP and PbPc layers are much higher than that of Pn films

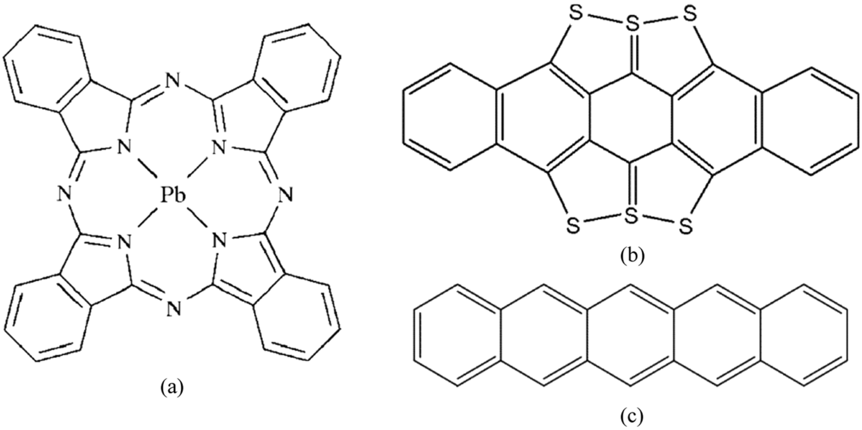

FIGURE 1 Molecular structure of PbPc (a), HTP (b) and Pn (c).

[7–9], and the spectral ranges of photosensitivity of HTP and PbPc films are wider than that of Pn films [6,9,10]. A double-layer structure based on these materials absorbs solar light in the visible and near infrared ranges (like CdTe or Si). Such a feature is required for the development of highly efficient organic solar cells.

Thin IHS films were prepared by successive thermal deposition of the layers onto a glass substrate covered with the conductive semitransparent ITO electrode. The substrates were maintained at various temperatures (T_s) during the fabrication of IHS. The thickness of IHS was controlled by changing the frequency of a quartz resonator and, after the deposition, by optical density spectra and an atomic force microscope.

Absorption and photovoltage spectra were measured using a double-beam "Hitachi" spectrophotometer and a laboratory-assembled setup [11,12], respectively. The basic illumination for photovoltage measurements was modulated. The structures were additionally illuminated with an unmodulated beam applied from the back side of IHS. The intensity of the additional illumination was measured by a PPTN-02 radiometer based on a calibrated Si photodiode. The spectra have at least 500 measurement points.

PENTACENE/LEAD-PHTHALOCYANINE (Pn/PbPc) IHS

The photovoltage spectra of Pn/PbPc IHS correlate with the absorption spectra of PbPc films in the range of transparency of the Pn layer (1.2–1.8 eV). In the range of strong absorption of Pn films (1.8–2.5 eV), the photovoltage spectra reverse their sign, i.e., the photovoltage spectra of Pn/PbPc IHS are similar to the difference of the photovoltage spectra of the components [12]. According to the van Opdorp model developed for inorganic IHS [3], the reversal of sign in photovoltage spectra is due to a high concentration of surface states (centers of charge carrier trapping and recombination) at the interface of Pn/PbPc IHS. The charged states at the IHS interface form two depleted layers, and the heterojunction can be described by two oppositely biased Schottky diodes connected in series. The study of the influence of an additional illumination on the photovoltage confirms that our systems can indeed be described by the model of two Schottky diodes. The magnitude of the negative (or positive) component of photovoltage spectra and the potential barrier that corresponds to this photovoltage [13] decreases under the additional illumination in the range of strong absorption of this component (Fig. 2, curves 2 and 3).

The photovoltage spectra of Pn/PbPc IHS deposited at $T_s = 370$ K do not reverse sign (Fig. 3), the magnitude of photovoltage maximum for these IHS being almost twice higher than that for Pn/PbPc IHS

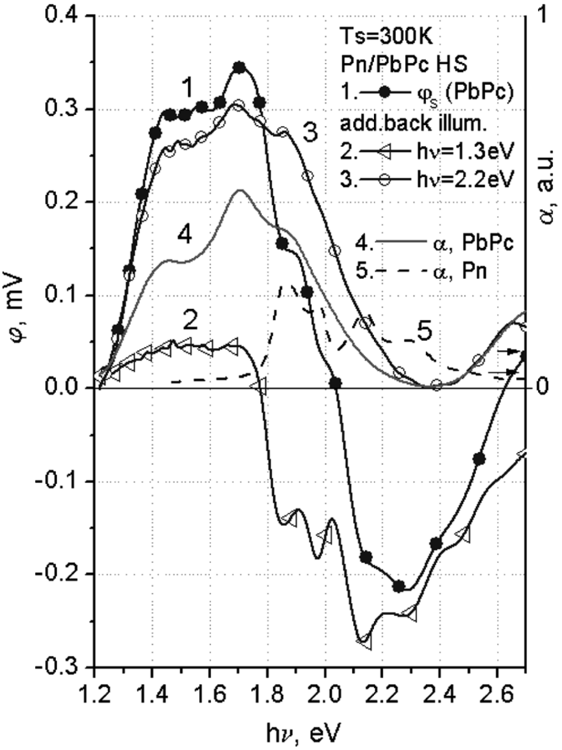

FIGURE 2 Photovoltage spectra of Pn/PbPc IHS under illumination of the PbPc side (1) and under the additional illumination with 1.3 eV light (2), 2.2 eV light (3), and the absorption spectra of PbPc (4) and Pn (5) films. All structures are deposited at $T_s = 300\,\mathrm{K}$.

deposited at $T_s = 300\,\mathrm{K}$ and ten times higher than that for ITO/PbPc structures (Fig. 3). This shows that the potential barrier height increases and the concentration of surface states decreases at the interface of Pn/PbPc IHS upon increasing T_s up to 370 K. The photovoltage spectra of these IHS are similar to the absorption and photovoltage spectra of PbPc films (Fig. 3). But, in the range of strong absorption of Pn films (1.85 eV), the relative photovoltage of Pn/PbPc IHS is 30% higher than that for PbPc films, pointing to a contribution of charge carriers photogenerated in the Pn layer. The magnitude of photovoltage at 1.85 eV is higher than that at 1.4 eV under the additional illumination with 1.3 eV light, absorbed by PbPc only (Fig. 3). The additional illumination decreases the contribution of PbPc to the photovoltage spectra, and we can assess the contribution of Pn to the photovoltage spectra of Pn/PbPc IHS.

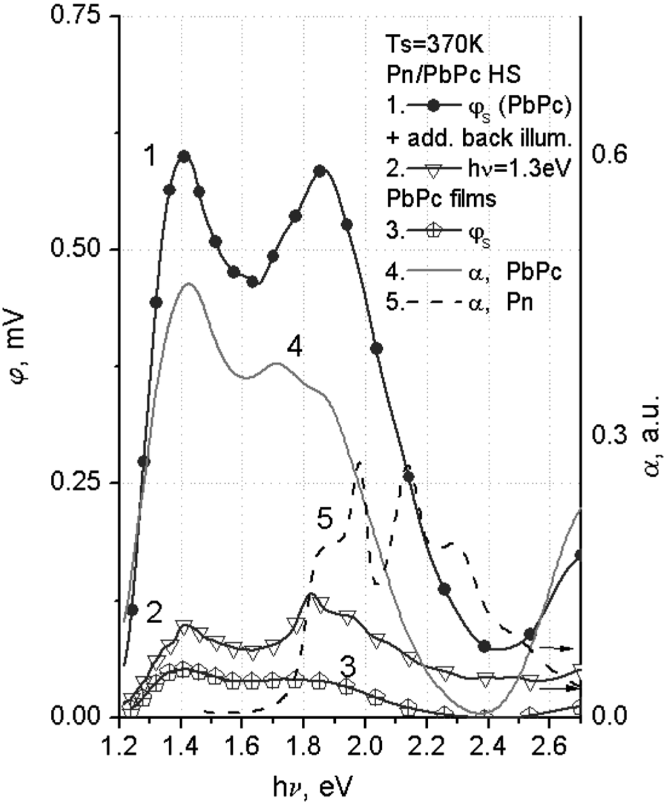

FIGURE 3 Photovoltage spectra of Pn/PbPc IHS under illumination of the PbPc side (1) and under the additional illumination with 1.3 eV light (2); the photovoltage spectrum of a PbPc film (3), and the absorption spectra of PbPc (4) and Pn (5) films. All structures are deposited at $T_s = 370\,\text{K}$.

According to the van Opdorp model for IHS [3], at a high concentration of charge carrier recombination centers at the interface, the photovoltage can be described as

$$\varphi = \varphi_1 \cdot \ln\left(1 + \frac{I_{R1}}{I_{S1}}\right) - \varphi_2 \cdot \ln\left(1 + \frac{I_{R2}}{I_{S2}}\right) = \varphi_1 \cdot \ln(1 + \gamma_1 \cdot P) - \varphi_2 \cdot \ln(1 + \gamma_2 \cdot P), \tag{1}$$

where ϕ_1, ϕ_2, γ_1, and γ_2 are the coefficients independent of the intensity of illumination (P) of the IHS, I_{R1} and I_{R2} are the photocurrent densities (I_{R1} and I_{R2} are proportional to P), and I_{S1} and I_{S2} are the densities of dark saturation currents for various components of IHS and the corresponding

Schottky diodes, respectively. In our case, the PbPc component of the photovoltage is positive and corresponds to the term with index 1, whereas the Pn component of the photovoltage is negative and corresponds to the term with index 2. If the illumination is absorbed in the PbPc layer, then the $\phi(P)$ dependence will be fitted by one term of the equation only. If, however, the illumination is absorbed in both layers, then both terms of the equation will contribute, and $\phi(P)$ can reverse the sign. If the contribution of one term is neutralized by an additional illumination, then the basic contribution will be given by the other term.

The validity of this model for IHS under investigation was checked by measurements of the $\phi(P)$ dependence in the spectral range where both components of IHS contribute to the photovoltage, without and with additional illumination (Fig. 4). It is seen that the infrared

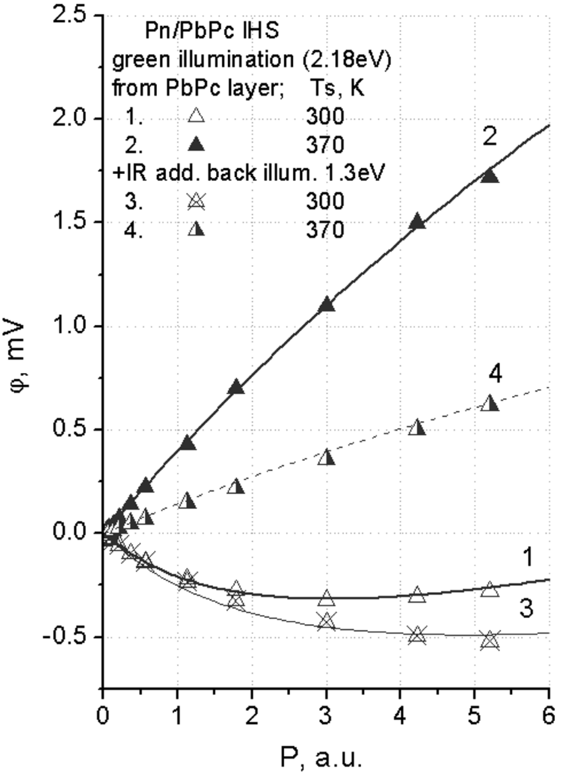

FIGURE 4 Dependence of the photovoltage of Pn/PbPc IHS deposited at $T_s = 300\,\mathrm{K}$ (1,3) and $370\,\mathrm{K}$ (2,4) on the intensity of illumination (with 2.18 eV light) from the side of a PbPc layer without (1,2) and with (3,4) the additional illumination with 1.3 eV light.

additional illumination which decreases a potential barrier in only the PbPc layer results in increasing the negative component of the photovoltage for Pn/PbPc IHS deposited at $T_s = 300\,\mathrm{K}$ (Fig. 4, curves 1 and 3). In other words, the components of the photovoltage spectrum of this IHS have two various polarity.

It can be described using the equivalent scheme of two oppositely biased Schottky diodes connected in series. The photovoltage of Pn/PbPc IHS deposited at $T_s = 370\,\mathrm{K}$ under the additional illumination with $h\nu = 1.3\,\mathrm{eV}$ decreases (Fig. 4, curves 2 and 4). The photovoltage components have the same sign that corresponds to the scheme of two identically biased Schottky diodes, connected in series [3]. The experimental dependences of $\phi(P)$ are fitted by Eq. (1), hence confirming the applicability of the van Opdorp model to organic IHS (Fig. 4).

The additional illumination decreases the potential barrier (a band bending) predominantly in the component that absorbs this additional illumination [13]. The efficiency of the photovoltage decrease will be higher in that component of IHS, in which the potential barrier is higher. Therefore, the space charge distribution can be estimated at the interface of IHS components using the influence of the additional illumination on the photovoltage. The additional illumination with $h\nu = 1.3\,\mathrm{eV}$ is absorbed in the PbPc layer only, and the one with $h\nu = 2.18\,\mathrm{eV}$ is absorbed predominantly in the Pn layer. It is shown in Figure 5 that the additional illumination with $h\nu = 1.3\,\mathrm{eV}$ more strongly affects the photovoltage of Pn/PbPc IHS than that with $h\nu = 2.18\,\mathrm{eV}$. However, it should be noted that both additional illuminations affect the photovoltage more strongly in IHS deposited at 370 K. According to the above results, the space charge is basically localized in the PbPc layer for both types of structures, the band bending at the interface of IHS being higher for structures deposited at 370 K.

Pentacene/hexathiopentacene (Pn/HTP) IHS

As was shown above, the concentration of recombination centers at the interface of Pn/PbPc IHS significantly decreases with increase in T_s from 300 to 370 K during the deposition of the structures. To check this effect for other structures, the Pn/HTP IHS were fabricated. The photovoltage spectra of Pn/HTP IHS deposited at $T_s = 370\,\mathrm{K}$ (Fig. 6) do not reverse the sign. The comparison of the photovoltage spectra of Pn/HTP IHS and ITO/HTP structures deposited at $T_s = 370\,\mathrm{K}$ (Fig. 6) shows that the photovoltage of IHS in the range of strong absorption of HTP films (1.4–1.8 eV) is almost twice higher than that of ITO/HTP. This feature seems to result from a low concentration of

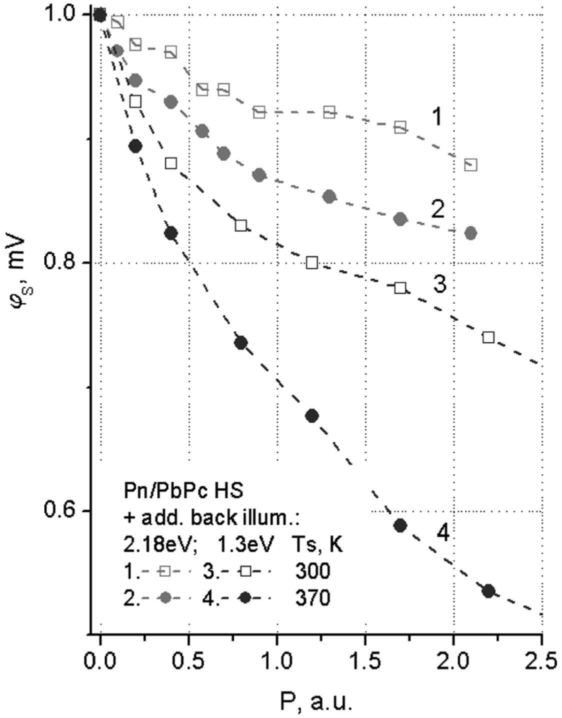

FIGURE 5 Dependence of the photovoltage of Pn/PbPc IHS deposited at $T_s = 300\,\mathrm{K}$ (1,3) and 370 K (2,4) under illumination with 1.45 eV light from the side of a PbPc layer on the intensity of the additional illumination with 2.18 eV light (1,2) and 1.3 eV light (3,4).

charge carrier recombination centers at the interface of IHS on heating the substrate up to 370 K and the top layer deposition. It should be noted that HTP films at $T_s = 370\,\mathrm{K}$ have lower roughness and higher photovoltage, than those at $T_s = 300\,\mathrm{K}$. In the range of strong absorption of the Pn layer (1.8–2.4 eV), the photovoltage of IHS is three times higher than that of ITO/HTP (Fig. 6). The largest increase of the photovoltage occurs in the range of Pn film absorption at $h\nu = 2.10$–$2.15\,\mathrm{eV}$, pointing to a contribution of the charge carriers photogeneration to both HTP and Pn components of the heterostructure.

To estimate the distribution of space charge at the interface of Pn/HTP IHS, we also studied the influence of the additional illumination with $h\nu = 1.9$ and 2.18 eV on the photovoltage spectra of IHS. The photovoltage spectra of Pn/HTP IHS without and with additional illumination are compared in Fig. 7. Upon the additional illumination

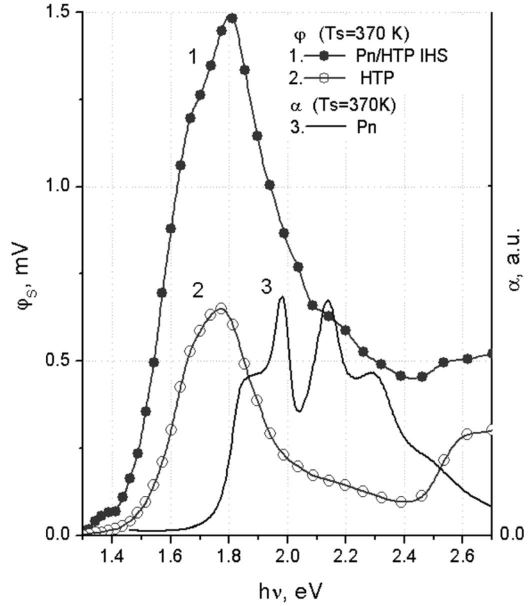

FIGURE 6 Photovoltage spectra of both Pn/HTP IHS under illumination of the HTP side (1) and a HTP film under illumination of the free surface (2), and the absorption spectrum of Pn films (3). All structures are deposited at $T_s = 370\,\mathrm{K}$.

with $h\nu = 1.9\,\mathrm{eV}$ (absorbed by both components of Pn/HTP IHS), the photovoltage decreases in the spectral range 1.4–2.3 eV (Fig. 7), confirming the space charge formation at the interface in both components of Pn/HTP IHS. It should be noted that the efficiency of the additional illumination with $h\nu = 2.18\,\mathrm{eV}$ (in the range of strong absorption of the Pn layer) is much lower than that with $h\nu = 1.9\,\mathrm{eV}$ (in the range of strong absorption of both the HTP and Pn films). This shows that the space charge at the interface of Pn/HTP IHS is localized predominantly in the HTP layer.

Hexathiopentacene/lead-phthalocyanine (HTP/PbPc) IHS

The photovoltage spectra of HTP/PbPc IHS deposited at $T_s = 300\,\mathrm{K}$ (Fig. 8, curve 1) do not reverse the sign. The magnitude and shape of HTP/PbPc IHS photovoltage spectra are close to those of Pn/PbPc IHS deposited at $T_s = 370\,\mathrm{K}$. Two maxima (1.4 and 1.9 eV) are observed in the photovoltage spectra of HTP/PbPc IHS corresponding to the absorption and photogeneration in PbPc, and the minimum at

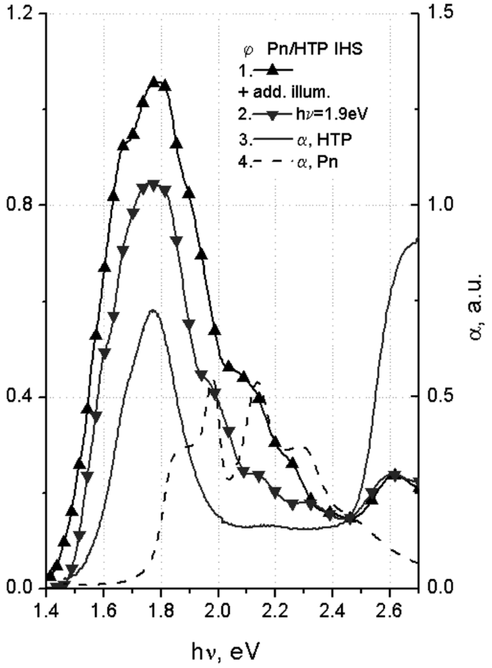

FIGURE 7 Photovoltage spectra of Pn/HTP IHS under illumination of the HTP side without (1) and with (2) the additional illumination with 1.9 eV light, and the absorption spectra of HTP (3) and Pn (4) films. All structures are deposited at $T_s = 370\,\mathrm{K}$.

1.67 eV is close to the spectral position of the absorption maximum of HTP layer. The comparison of the photovoltage spectra of HTP/PbPc IHS and PbPc films shows that the deposition of a HTP layer leads to an increase of the photovoltage in the range of strong absorption of the PbPc layer and to a decrease in the range of strong absorption of the HTP layer. The basic contribution to the potential barrier formation at the interface of HTP/PbPc IHS comes from the PbPc layer. The contribution of the HTP layer is low and can be negative in comparison with the PbPc photovoltage. This results in the formation of the minimum in the photovoltage spectrum of HTP/PbPc IHS at 1.67 eV.

The increase of T_s from 300 to 370 K for HTP/PbPc IHS leads to a significant increase of the photovoltage in the range of 1.2–1.5 eV (the range of low and strong absorption of the PbPc film). This behavior points to an increase of the potential barrier height and a decrease of the rate of charge carrier recombination in the PbPc layer at the interface of IHS. The photovoltage and the poterntial barrier of

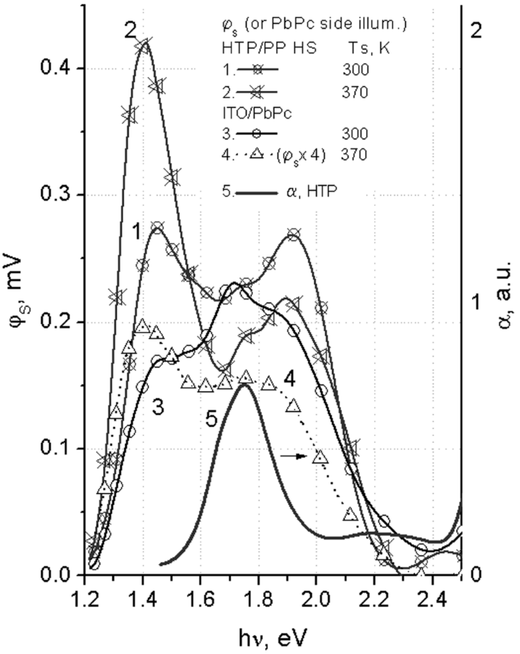

FIGURE 8 Photovoltage spectra of HTP/PbPc IHS under illumination of the PbPc side (1,2) and ITO/PbPc under illumination of the free suface (3,4), and the absorption spectrum of a HTP film (5). The structures are deposited at 300 (1,3) and 370 (2,4,5) K.

HTP/PbPc IHS are higher than those of a free surface of PbPc layers. Also the contribution of the negative photovoltage component increases in the range of strong absorption of the HTP layer (1.6–1.9 eV) at increasing T_s from 300 to 370 K.

The photovoltage of HTP/PbPc IHS deposited at $T_s = 370$ K in the range of the 1.4 eV peak is higher than that in the range of the 1.7 eV peak (Fig. 8, curves 1,2). It can be explained assuming the dominant formation of the triclinic modification of PbPc [14].

The influence of the additional illumination with $h\nu = 1.3$ eV (in the range of strong absorption of the PbPc layer) confirms the presence of the negative component of the photovoltage (potential barrier). This additional illumination can decrease only the potential barrier in the PbPc layer. The photovoltage spectra of HTP/PbPc IHS with the additional illumination at $h\nu = 1.3$ eV reverse the sign in the range of strong absorption of the HTP layer with peak at ca. 1.7 eV (Fig. 9,

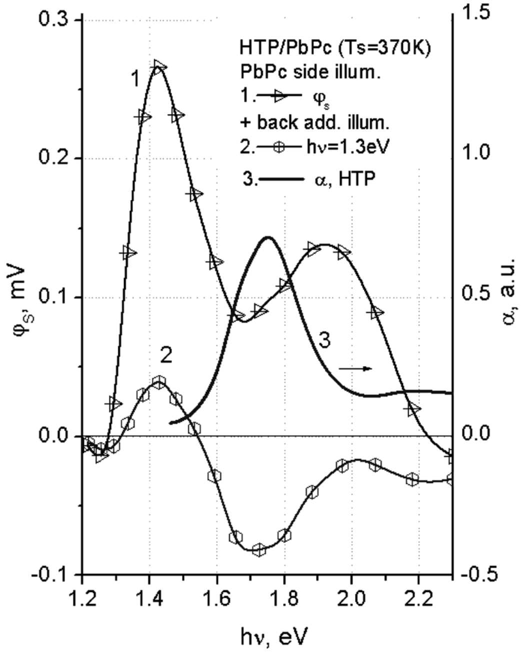

FIGURE 9 Photovoltage spectra of HTP/PbPc IHS under illumination of the PbPc side without (1) and with (2) additional back illumination with 1.3 eV light, and the absorption spectrum of a HTP film (3). The structures are deposited at 370 K.

curve 2). The negative component of the potential barrier increases with T_s. The highest negative contribution to the photovoltage (due to the HTP layer) is three times lower than that of the positive component (in the PbPc layer). This shows that the efficiency of charge carrier photogeneration (and space charge) at the interface of the HTP/PbPc IHS is higher in the PbPc layer than in the HTP one.

A comparison of photovoltage spectra of a Pn film with Pn/PbPc, HTP/PbPc, Pn/HTP IHS (Fig. 10) thermally deposited at $T_s = 370\,\mathrm{K}$ shows that the photosensitivity spectra of IHS are wider by 0.5 and 0.3 eV, respectively, in the low-energy range. The integral photovoltage (obtained by integration of the photovoltage spectra in the range 1.2–3.1 eV) for Pn/HTP IHS is higher than that for another studied IHS. This agrees with the energy diagrams of heterojunctions, in which the potential barrier height (obtained by subtraction of the work functions of two components of IHS using data in [6,15,16]) for Pn/HTP IHS is higher than that for another studied IHS.

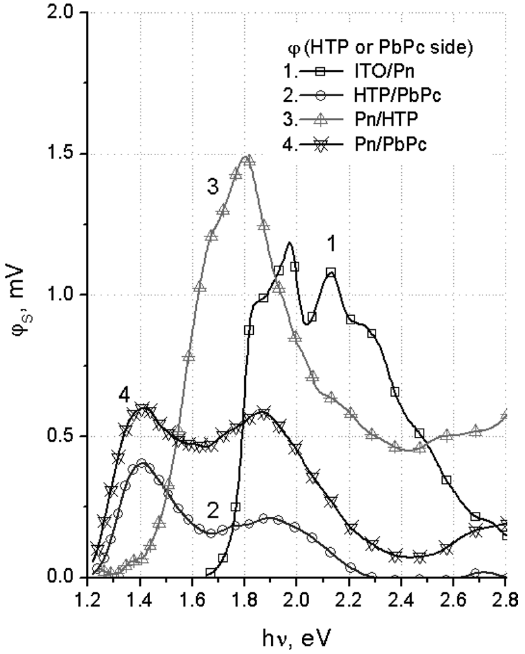

FIGURE 10 Photovoltage spectra of ITO/Pn (1), HTP/PbPc (2), Pn/HTP (3), and Pn/PbPc (4) IHS deposited at $T_s = 370\,\mathrm{K}$.

CONCLUSIONS

The photovoltage spectra of Pn/PbPc IHS prepared by thermal deposition at $T_s = 300\,\mathrm{K}$ reverse the sign and can be described by the model of two oppositely biased Schottky diodes connected in series. This indicates that a high concentration of the centers of charge carrier recombination is formed at the interface of Pn/PbPc IHS. The sign reversal is not observed for Pn/HTP and HTP/PP IHS because of a low potential barrier height for one of the IHS components leading to a low negative photovoltage contribution.

In Pn/PbPc, Pn/HTP, and HTP/PbPc IHS deposited at $T_s = 370\,\mathrm{K}$, there is no sign reversal of photovoltage spectra, and the photovoltage is higher than that in the IHS deposited at 300 K, due to a lowering of the surface states concentration and an increase of the potential barrier height at the interface of these IHS as T_s increases from 300 to 370 K.

The range of the photosensitivity of IHS (in particular, Pn/PbPc IHS) deposited at $T_s = 370\,\mathrm{K}$ is significantly wider than that of the Pn layer. These IHS can improve the solar light collection and the charge carrier photogeneration in multilayer organic solar cells.

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