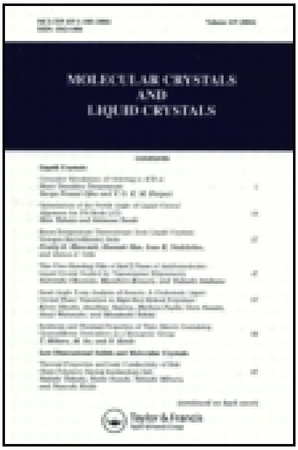

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p-n Type Heterostructures Based on N,N′-Dimethyl Perylene-Tetracarboxylic Acid Diimide

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p-n Type Heterostructures Based on N,N′-Dimethyl Perylene-Tetracarboxylic Acid Diimide

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Photovoltaic properties of new photosensitive p-n type heterostructures based on N,N′-dimethyl perylene-tetracarboxylic acid diimide and organic [pentacene, hexathiopentacene, lead phthalocyanine] and inorganic [CuI] semiconductors are investigated. The basic attention is focused on the influence of energy diagram parameters and substrate temperatures (T_s) during the deposition on the photosensitivity of heterostructures.

The maximal photovoltage, minimal surface recombination rate, and structural homogeneity of layers for the heterostructures were obtained at $T_s = 370\,K$.

The comparison of the obtained results with energy diagram parameters according to the Anderson model (without taking surface states into account) shows a qualitative agreement for two-layered organic p-n heterojunctions.

Keywords: heterostructures; methyl perylene pigment; organic semiconductors; photovoltage

1. INTRODUCTION

Heterostructures (HS) made from organic and inorganic semiconductors are perspective for optoelectronic and photovoltaic applications [1,2], especially for the development of organic solar cells (SC) [3,4] and light-emitting diodes [5]. Now, for double-layer organic SC (thermally deposited in vacuum) from copper phthalocyanine and C_{60} fullerene, the photovoltaic efficiency $(3.6 \pm 0.2)\%$ was achieved under sunlight illumination of $150\,\mathrm{mW/cm^2}$ [6].

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For organic thin-film SC based on methyl perylene pigment, an efficiency of 1.04% was obtained under sunlight illumination of 100 mW/cm^2 [4,7]. This efficiency of photoconversion isn't enough for a practical application, which is mainly caused by both the unbalanced selection of components and the conditions of preparation of organic thin-film HS.

The number of organic semiconductors is much more, than that of inorganic ones, and their properties are less investigated. Therefore, the searches for the methods of both component selection and efficiency increasing for these HS are very topical of the further development of more effective organic SC.

The investigations of the photoelectric properties of organic films (HS components) show that the selection of a substrate temperature (T_s) during the thermal deposition is one of the most effective methods for the photosensitivity increase of the films [8,9]. Therefore, the basic aims of this article were the investigation of both the photovoltaic properties of organic HS with various parameters of the energy diagram and the influence of T_s on the photovoltage of these structures.

2. EXPERIMENTAL

The requirement of the promising HS preparation for photovoltaic conversion of sunlight is the effective absorption of photons in the visible, near IR, and UV spectral ranges ($\sim$1.2–3.2 eV). In contrast to inorganic semiconductors, the majority of photosensitive organic p-type semiconductors weakly absorbs sunlight in the range 2–3 eV. Therefore, for the creation of HS, we used the photosensitive organic n-type semiconductor N,N′-dimethyl perylene-tetracarboxylic acid diimide (methyl perylene pigment–MPP) (see Fig. 1a) which effectively absorbs light in the range 2–3 eV. Initial MPP obtained by vacuum sublimation before deposition was kindly given by Prof. D. Meissner [4].

Pentacene (Pn) – Figure 1b, hexathiopentacene (HTP) – Figure 3c, lead phthalocyanine (PbPc) – Figure 1d, and CuI were used as p-type components of HS with various band gaps and work functions (Table 1).

Experimental parameters for HTP are not measured. But since the molecular structure and absorption spectra in the visible and near IR ranges for HTP and tetrathiotetracene (TTT) films practically coincide, we have assumed that the energy diagram parameters of HTP and TTT will be close (Table 1).

The films (HS components) and HS were prepared by thermal deposition in vacuum ($2 \cdot 10^{-4}$ Pa). The films thickness was controlled during deposition by a quartz sensor of weight and, after preparing, was measured with an atomic force microscope. The thickness of HS components

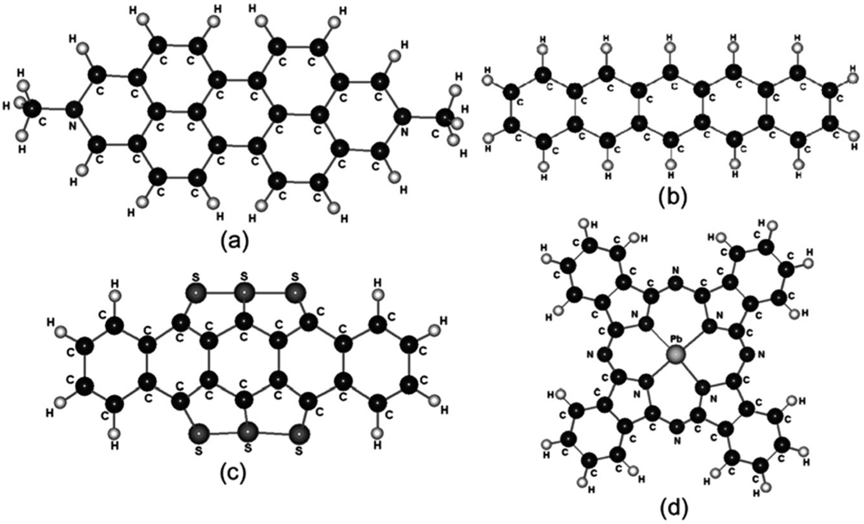

FIGURE 1 Structural formulas of the investigated organic compounds: a) MPP; b) Pn; c) HTP; d) PbPc.

was close to the diffusion length of excitons in these layers [24,25] and was set from 50 to 200 nm. The quartz plates with a conducting transparent indium tin oxide (ITO) layer were used as the substrates. T_s were measured using a copper-constantan thermocouple.

Absorption spectra were measured with a double beam "Hitachi" spectrophotometer.

Photovoltaic properties of HS were investigated by the Bergman-Akimov technique [26] under the modulated illumination of both sides of HS (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 described in refs. [27,28] in detail.

TABLE 1 Parameters of the Energy Diagrams for HS Components (eV)

	I_c, eV	E_g, eV	A_c, eV	E_F, eV
MPP	6.47 [10,11]	2.6 [10,11]	3.87 [10,11]	4.38 [10,11]
PbPc	4.9 [12]	1.6 [13]	3.3 [14]	4.2–4.6 [15]
Pn	5.07 [1,16]	2.2 [1,16]	2.87 [1,16]	4.3–4.8 [16–20]
TTT	4.75 [16]	2.0 [16]	2.75 [16]	4.4 [21,22]
HTP*	4.7–4.8	1.95–2.05	2.7–2.8	4.3–4.5
CuI	6.1 [23]	3.0 [23]	3.1 [23]	6.0 [23]

3. OPTICAL AND PHOTOVOLTAIC PROPERTIES OF HS COMPONENTS

The absorption spectra (absorption coefficient–α) of layers used for the HS preparation at $T_s = 300\,K$ are presented in Figure 2 (curves 1–5). The increase of T_s from 300 up to 370 K results in a small change of the intensity and width of the absorption bands only for MPP, Pn, HTP, and CuI films, but the spectra shapes are kept. Therefore, the absorption spectra of the films deposited on the substrates at $T_s = 370\,K$ aren't considered. However, T_s increasing leads to an essential change of the absorption bands intensities for PbPc films, especially in the range 1.2–1.6 eV (Fig. 2, curve 6). This feature of PbPc films is caused by the formation of 4 polymorphic modifications, and the absorption bands (associated with the formation of charge transfer states) corresponded to each of these modifications [8]. The most stable [29], structurally homogeneous, and photosensitive [30] PbPc films (triclinic modification) were obtained at $T_s \approx 410-430\,K$.

The double-layer HS based on MPP and Pn, HTP, PbPc films are seen to well absorb the significant part of sunlight that increases in the line: MPP/Pn⟶MPP/HTP⟶MPP/PbPc (Fig. 1). Therefore, these double-layer structures can be perspective for the development of organic SC. Since MPP/CuI HS absorbs a small part of sunlight,

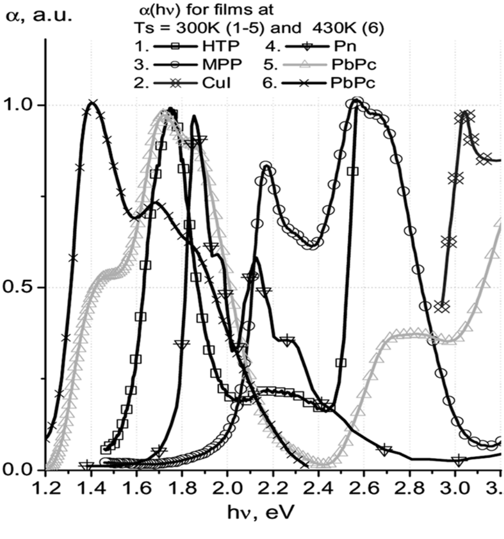

FIGURE 2 Absorption spectra of thin films (HS components) at $T_s = 300\,K$ (curves 1–5) and at $T_s = 430\,K$ (curve 6).

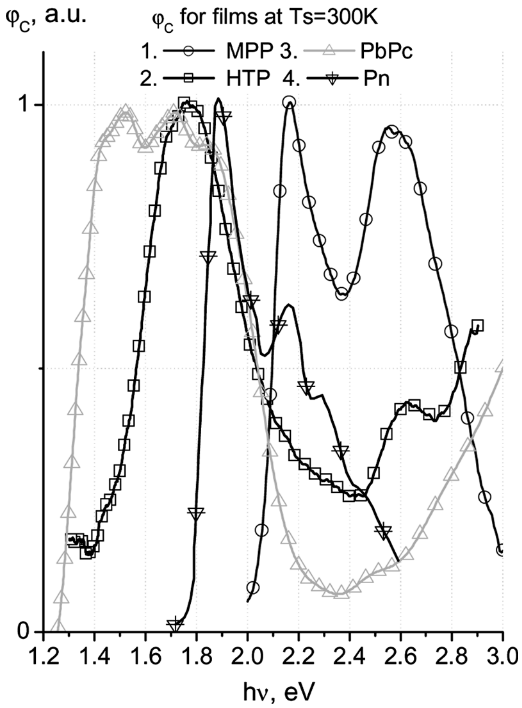

FIGURE 3 Photovoltage spectra of HS components at illumination of the ITO contact (φ_c) at $T_s = 300\,K$.

this HS is practically unsuitable for the SC development. But MPP/CuI HS can be a modeling structure for the research of interface photoprocesses, because the Fermi level ($E_F = 6.00 \pm 0.02\,eV$ [23]) for CuI films practically doesn't depend on preparing conditions.

It is very important that the sunlight absorption in the researched organic layers results in the effective formation of non-equilibrium charge carriers due to a built-in potential at the interface (secondary requirements for effective SC). The measurements of the photovoltage spectra (Fig. 3) for these films confirm this requirement. We have established that the increase in T_s (or annealing temperatures) to 370 K, despite a small change of the absorption spectra, results in the essential increase in the photovoltage for MPP [9], HTP [24], Pn [25] films. This photovoltage increasing is caused mainly by increasing the diffusion length of non-equilibrium charge carriers as a consequence of the structural ordering improvement in the films at T_s increasing up to 370 K. At the further increase in T_s, the films structure becomes worse (the number of structural defects grows), which results in a reduction of both the diffusion length of charge carriers and the photosensitivity of the layers.

4. MPP/CuI HS

Photovoltage spectra of ITO/MPP structures prepared at $T_s = 300$ and 370 K, before and after the CuI layer deposition under illumination of the MPP free surface or the CuI layer side are given in Figure 4. Photovoltage under illumination of the free surface (φ_s) for ITO/MPP structures is shown to increase approximately twice at T_s increases from 300 up to 370 K. The further increase in T_s results in a reduction of φ_s. The deposition of a CuI layer on the MPP surface, i.e., the HS

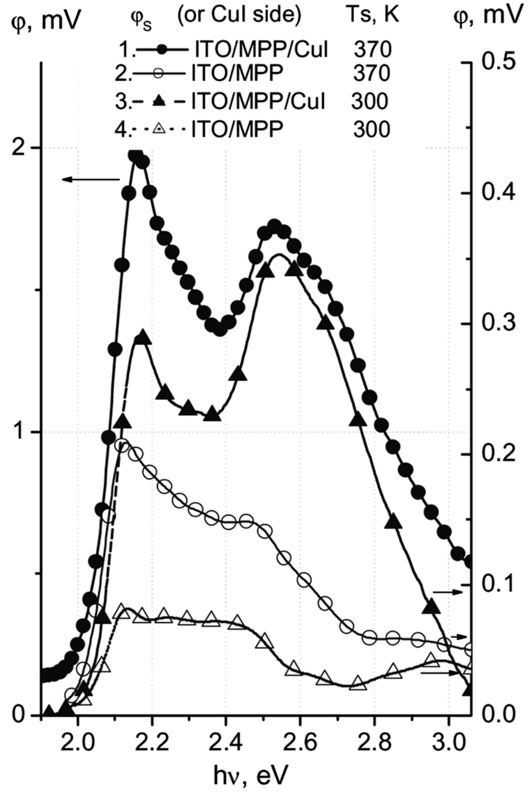

FIGURE 4 Photovoltage spectra of ITO/MPP/CuI (1,3) and ITO/MPP (2,4) structures prepared at $T_s = 370\,\mathrm{K}$ (1,2) and $T_s = 300\,\mathrm{K}$ (3,4) under illumination of the CuI side (1,3) and the free surface of MPP (2,4).

formation, results in a significant increase in the photovoltage (φ). φ_s grows from 6 to 10 times at $T_s = 300\,K$ and from 10 to 15 times at $T_s = 370\,K$, which is associated with the structure improvement of MPP and CuI layers as T_s increases from 300 to 370 K. The photovoltage increase can be caused by the bend of bands increasing at the MPP/CuI interface and a reduction of the surface recombination rate of charge carriers.

The dependence of φ on α under weak illumination should be linear in the absence of the charge carriers recombination, and the inclination of the line is proportional to the bend of bands at the interface of the structure. The dependence $\varphi(\alpha)$ becomes nonlinear and tends to the saturation at an increase in the surface recombination rate of charge carriers [31,32].

The dependences $\varphi_s(\alpha)$ and $\varphi(\alpha)$ in the range 2.00–2.15 eV are presented in Figure 5. The deviation from linearity and the tend to the saturation is observed on the $\varphi_s(\alpha)$ dependence for MPP films (Fig. 5, curves 2 and 4). This indicates that the surface recombination rate of excitons and charge carriers is great at the free surface of MPP films (in air). After the deposition of a CuI layer, the dependence $\varphi(\alpha)$ becomes practically linear and the inclination of $\varphi(\alpha)$ increases (Fig. 5, curves 1 and 3). Consequently, the deposition of a thin CuI film on the MPP surface results in a significant increase in the bend of bands at the interface and in a significant reduction of the surface recombination for excitons and charge carriers. This can testify that the concentration of the surface centers of trapping and recombination for charge carriers strongly decreases at the evacuation of air molecules adsorbed on the MPP surface (before the deposition of a CuI layer). As a result, the blocking bend of bands is formed at the interface of MPP (n-type) and CuI (p-type) layers with the insignificant rate of surface recombination of excitons and charge carriers.

5. Pn/MPP HS

Photovoltage spectra of MPP/Pn HS are shown in Figure 6 (curve 1). The Pn layer deposition on the MPP surface at $T_s = 370\,K$ results in a significant increase of the photovoltage in comparison with φ_s (from 20 up to 90 times depending on the quantum energy and the illumination side). This photovoltage increase indicates the formation of a great bend of bands at the interface of MPP/Pn HS that improves the photogeneration of charge carriers in MPP and Pn layers.

Photovoltage spectra of MPP/Pn HS very well correlate with the absorption spectra of the components even in the range of strong

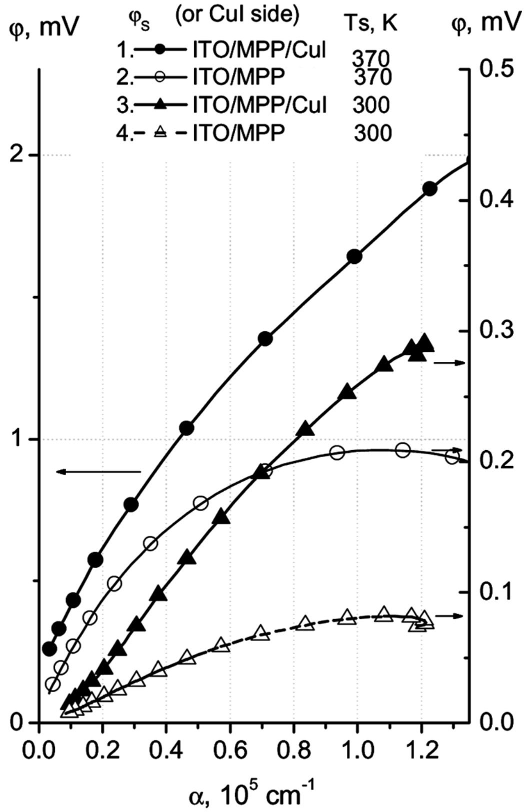

FIGURE 5 Dependences of the photovoltage on the absorption coefficient for ITO/MPP/CuI (1,3) and ITO/MPP (2,4) structures prepared at $T_s = 370\,\text{K}$ (1,2) and $T_s = 300\,\text{K}$ (3,4) under illumination of the CuI side (1,3) and the free surface of MPP (2,4).

absorption. This testifies that the rate of surface recombination for excitons and charge carriers is very small at the interface of MPP and Pn layers.

In the range of strong absorption of the Pn layer (1.8–2.1 eV), the HS photovoltage is more under illumination through the MPP layer, than that under illumination through the Pn layer. This is associated with fact that the greater part of photons is absorbed in the range of the strong potential field of the barrier in the Pn layer under illumination through the MPP layer, than that under illumination through the Pn layer. This results in a more effective separation of charge carriers.

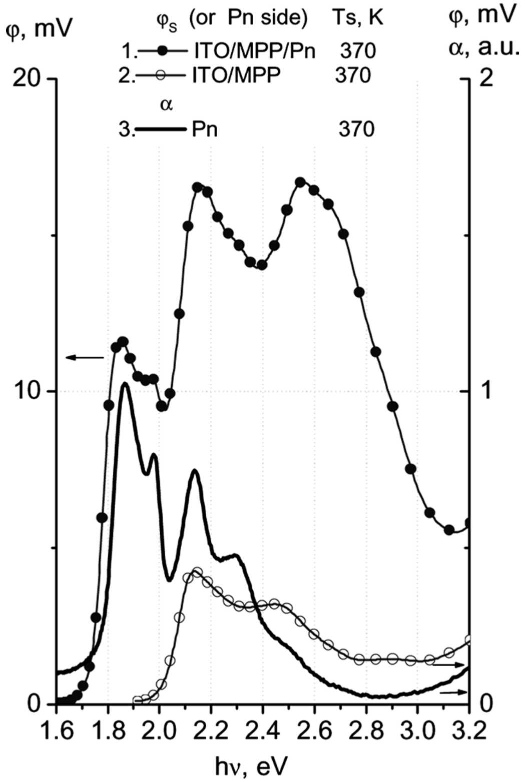

FIGURE 6 Photovoltage spectra of ITO/Pn/MPP HS under the MPP side illumination (1), ITO/MPP structures under the free surface illumination (2) and the absorption coefficient of Pn film (3). All structures prepared at $T_s = 370\,K$.

6. MPP/PbPc HS

Photovoltage spectra of PbPc/MPP HS are presented in Figure 7 (curves 1 and 2). At the deposition of a MPP layer on PbPc (at the ITO/PbPc/MPP HS formation), the photovoltage increases from 10 up to 30 times in comparison with φ_s for MPP and PbPc layers. This testifies to the formation of a great blocking potential barrier on the PbPc/MPP interface, which promotes a photosensitivity increase of the structures.

The maxima of the photovoltage spectra for PbPc/MPP HS are precisely shown at 1.4 and 1.7 eV that correspond to the absorption bands of PbPc films, and at 2.2 and 2.4 eV corresponded to the MPP layers

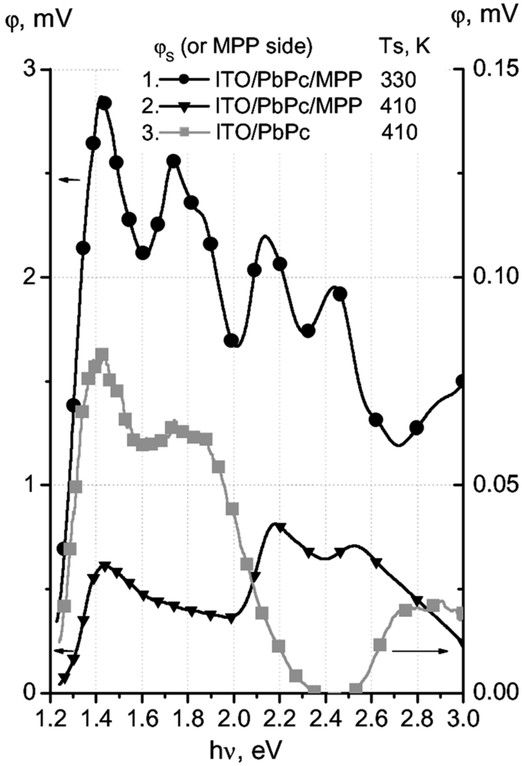

FIGURE 7 Photovoltage spectra of ITO/PbPc/MPP HS prepared at $T_s = 330\,\mathrm{K}$ under illumination of the MPP side (1) and at $T_s = 410\,\mathrm{K}$ under illumination of the PbPc side (2) and PbPc film under illumination of the free surface (3).

absorption. This confirms that the surface recombination rate of excitons and charge carriers at the PbPc/MPP interface is small and the increase in φ occurs mainly due to an increase in the potential barrier height.

The structure of PbPc and MPP layers strongly influences the spectra of PbPc/MPP HS (whereas, in our case, the surface structure of bottom PbPc layer influences the structure of the top MPP layer). Therefore, we need the additional investigation of the influence of a polymorphic modification for PbPc films on the structure of the top organic layer. It is a topical problem, because the double-layer PbPc/MPP HS more effectively absorbs sunlight than the most photosensitive Pn/MPP HS.

7. INFLUENCE OF PARAMETERS OF THE ENERGY DIAGRAMS ON HS PROPERTIES

The selection of components for the successful development of effective organic SC is a very topical problem. The purpose is to select components for preparing the more effective SC. At least two requirements should be satisfied for this purpose. The double-layer structure should absorb the most part of sunlight in the range 1.4–3.0 eV, and this absorption should result in the effective formation of charge carriers; i.e., both components should be photosensitive in the visible and near-IR spectral ranges. But it isn't enough. The third important requirement is the formation of a significant ($\geq$0.5 eV) barrier (a bend of bands) with a small surface recombination rate of charge carriers on the interface of two components. To check the possibility of this requirement, we have decided to use the energy diagram for HS according to the Anderson model (without taking surface states into account) [2]. This approach is valid for many organic semiconductors, because the breaks of covalent bonds are absent on their surface. According to the obtained results, the surface recombination rate is insignificant on the interface of the considered HS.

To construct the energy diagrams according to the Anderson model, the experimental values of the corresponding parameters (ionization potential $-I_c$, band gap $-E_g$, electron affinity $-\chi$, work function or Fermi level $-E_F$) were used for the materials under consideration (Table 1). The examples of the energy diagrams for Pn/MPP and CuI/MPP HS are displayed in Figure 8.

Based on the parameters of the energy diagrams, we have determined the intervals for magnitudes of a potential barrier (V_D). According to the Anderson model, V_D is equal to the difference of E_F of p- and n-type layers: $V_D = E_{F(p)} - E_{F(n)}$ [2]. The dispersion of V_D is basically caused by different experimental data for E_F in different works and possible experimental errors. Thus, it is necessary to take into account that E_F can be shifted depending on the conditions of both preparing and illumination of structures. Also the conduction band ($\Delta E_C = \chi_{(n)} - \chi_{(p)}$) and valence band ($\Delta E_v = I_{(n)} - I_{(p)}$) offsets for HS based on MPP were determined (Table 2).

The results on the photovoltage spectra of the researched HS are given in Figure 9. We have also determined the integral magnitude of HS photovoltage (φ_i) by integration of the photovoltage spectra of the researched HS in the range 1.2–3.26 eV (Table 2). Based on the comparison of these results, we come to conclusion that the most effective SC should be prepared on the base of MPP/Pn HS (Fig. 9 and Table 2). However, by the further optimization of the preparing technology

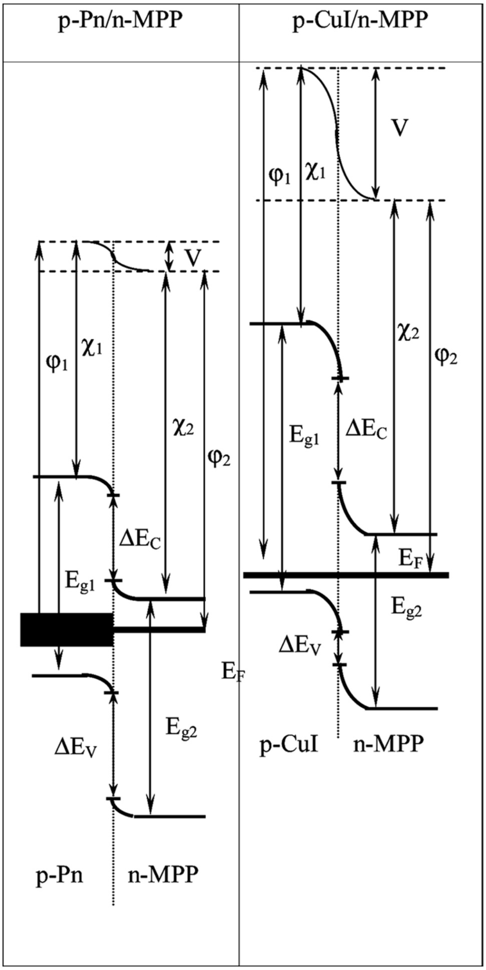

FIGURE 8 Energy diagrams for p-n HS under equilibrium conditions (indices 1 and 2 are associated with p- and n-type semiconductors, accordingly). The case of maximal barriers is shown.

(a polymorphic modification of thin-film structures), more perspective HS can be obtained based on PbPc layers that have smaller ΔE_C and effectively absorb sunlight with the formation of non-equilibrium charge carriers in a wider spectral range, than that for other considered HS.

The experimentally obtained φ_i for the researched MPP/Pn, PbPc/MPP, and HTP/MPP [10] HS well agree with V_D values (Table 2). To

TABLE 2 Parameters of the Energy Diagram for HS Based on MPP (eV)

P/n	Pn/MPP	PbPc/MPP	HTP/MPP	CuI/MPP
ΔE_c	1.0	0.57	0.87–1.17	0.77
ΔE_v	1.4	1.57	1.47–1.87	0.37
V_D	(−0.10)–0.45	(−0.2)–0.25	(−0.1)–0.15	1.6–1.64
V_D	0.175 ± 0.275	0.025 ± 0.225	0.025 ± 0.125	1.62 ± 0.02
φ_i, a.u.	17.8	3.6	1.3	1.5

check the correlation between the photovoltage and V_D for organic HS, the dependence of the maximal photovoltage (φ_m) and φ_i on V_D are shown in Figure 10. The linear dependence of the average value of V_D on φ_m (or φ_i) can be plotted (Fig. 10) for the organic HS under consideration.

However, the obtained φ_m and φ_i values for MPP/CuI HS (Fig. 9, Table 2) are much less than those predicted with the Anderson model.

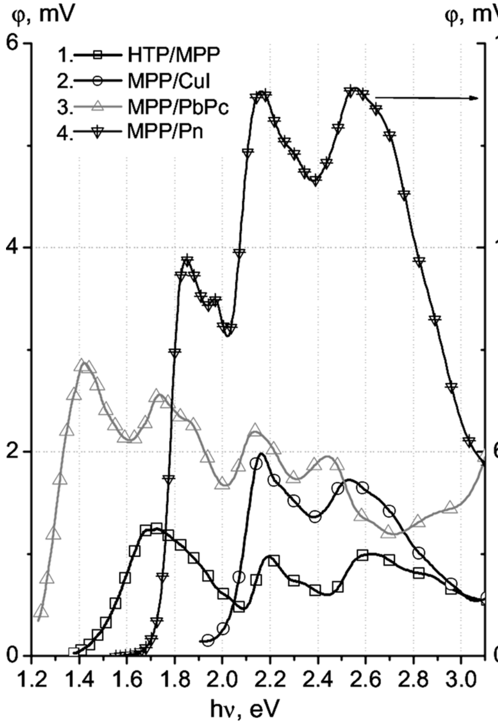

FIGURE 9 Photovoltage spectra of ITO/HTP/MPP (1), ITO/MPP/CuI (2), ITO/PbPc/MPP (3), ITO/MPP/Pn (4) HS, under illumination of the MPP side.

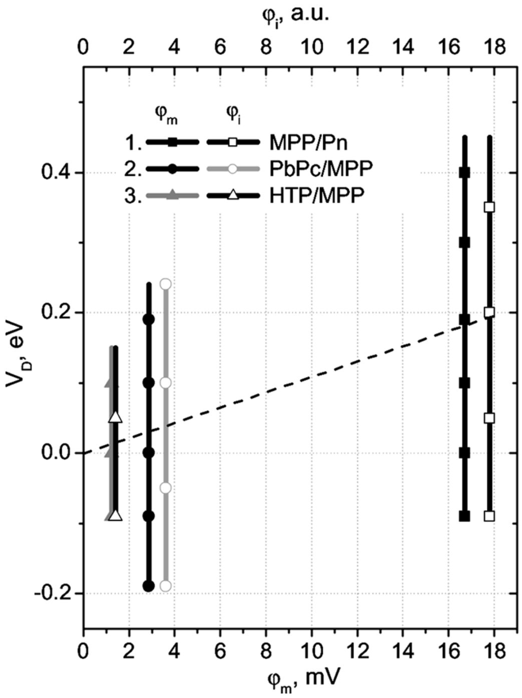

FIGURE 10 Dependence of maximal (φ_m) and integral (φ_i) values of the photovoltage on the potential barrier height (V_D).

This deviation of the results from the parameters of the energy diagram for HS with a CuI layer can be caused by the diffusion of iodine in organic layer. Consequently, the Anderson model (without taking surface states into account) shows the qualitative agreement for double-layer organic p-n-type HS.

CONCLUSIONS

The maximal and integral photovoltage for heterostructures based on N,N′-dimethyl perylene-tetracarboxylic acid diimide (n-type) and CuI, pentacene, lead phthalocyanine (p-type) layers increases (by several times) with the substrate temperature up to 370 K at preparing the structures. The annealing of the layers and heterostructures (at the same temperature that substrate temperature) weakly effects on the photovoltage.

The obtained results for double-layer organic heterostructures qualitatively agree with parameters of the energy diagram according to the Anderson model (without taking surface states into account). The observed deviation of our results from the parameters of the energy diagram in heterostructures with CuI was explained by the iodine diffusion in an organic layer.

The maximal photovoltage was observed for heterostructures based on N,N′-dimethyl perylene-tetracarboxylic acid diimide (n-type) and pentacene (p-type) layers prepared at a substrate temperature of 370 K. However, the heterostructures with lead phthalocyanine (p-type) layer should be expected to be perspective at the subsequent optimization of the processing method (a polymorphous modification of structures), since these hopeful heterostructures have a less conduction band offset (Table 2) and effectively absorb sunlight (Fig. 1) with the formation of non-equilibrium charge carriers (Fig. 2) in a wide spectral range.

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