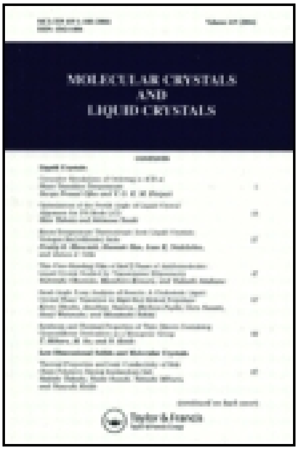

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Effect of Interface Texturing on Optical and Photoelectric Properties of Organic/Inorganic Semiconductor Heterojunctions

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The effect of texturing interfaces on the optical and photoelectric properties of anisotype and isotype organic (OS)/inorganic (IS) semiconductor heterojunctions has been investigated. p-(Pentacene) and n-(methyl perylene pigment, MPP) type organic semiconductor layers were evaporated on n-GaAs and p-InP substrates, respectively, with flat substrates and the substrates textured by chemical anisotropicetching (with a microrelief of the quasigrating type). The spectra of the light reflectance and the short-circuit photocurrent for the Au/OS/IS heterostructure were measured and analyzed to distinguish the contribution of the photocurrent generated in the OS layer. A considerable enhancement of the photocurrent generated in both inorganic and organic semiconductors was found for structures with textured interface.

Keywords: heterojunction; methyl perylene pigment; pentacene; photoelectric characteristics; texturing

1. INTRODUCTION

Organic semiconductors (OS) have attracted a considerable attention both as potential materials for thin film transistors and as the components of barrier heterojunctions with other organic or inorganic semiconductors (IS) for the sensor or photovoltaic application. Therefore, the electronic and recombination properties of the heterostructure interface are of great importance. Their dependence on technological conditions of the formation of the interface for chosen components of

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heterostructures has been intensively studied [1–6]. So, the urgent problem of the photovoltaic application of OS/IS heterostructures is the choice of their components and methods for the control over their photoelectric properties.

With regard for the attained enhancement of the photosensitivity and the solar energy conversion efficiency for metal/IS [7] or *p-n* junction [2,8] heterostructures with micro/nano textured interface, we devoted this work to the investigation of the effect of texturing the organic/inorganic semiconductor interfaces on the optical, photoelectric, and electrical properties of heterostructures. Both isotype and anisotype heterostructures were fabricated by vacuum evaporation of *p*-(pentacene) or *n*-(MPP) type organic semiconductors on flat or chemically textured surfaces of *n*-GaAs and *p*-InP IS single crystals. The subsequent evaporation of a thin continuous semitransparent Au film through the mask was made to obtain photodiode structures. The surface microrelief morphology of both IS substrates and OS films was studied by the atomic force microscopy (AFM) technique, and the spectral dispersion of optical parameters was determined in the range of wavelengths $\lambda = 400 \div 1000$ nm from measurements of the reflectance spectra for *p*- and *s*-polarized light at several angles of incidence. The spectra of the short-circuit photocurrent, as well as the dark and light current-voltage characteristics, were measured for the electrical and photoelectric characterization of the OS/IS heterostructures under study.

2. EXPERIMENTAL TECHNIQUE

As OS components of OS/IS heterostructures, we used photosensitive organic semiconductors: of the *p*-type, pentacene (Pn), and of *n*-type, N,N′-dimethyl perylene-tetracarboxylic acid diimide (methyl perylene pigment, MPP), for which the dependences of optical and photoelectric properties on technological conditions are intensively studied [1–4,9]. The OS/IS heterostructures have been fabricated by the evaporation of OS layers in vacuum at $2 \cdot 10^{-4}$ Pa on the preliminarily prepared flat (chemically polished in $1H_2O_2$:$3H_2SO_4$:$1H_2O$) or textured substrates of *n*-GaAs and *p*-InP at room temperature ($\sim$300 K). The quasigrating type of (100) GaAs and InP surface texturing by wet chemical anisotropic etching in a 2HF:$1H_2SO_4$:$1{,}5H_2O_2$ solution (GaAs) or concentrated HCl (InP) [2,7,10] was chosen to provide a necessary diminution of optical losses due to the reflection decrease at the excellent recombination properties of IS surfaces [7,10]. Photodiode structures have been fabricated by evaporation of an Au layer of $\sim$35 nm in thickness onto an OS film as the barrier contact and by evaporation of an In or In:Zn film onto the n-GaAs or p-InP back surface to obtain the ohmic contact. For the comparison, in addition to OS/IS heterojunctions, the Au/IS Schottky diodes were fabricated simultaneously on the same substrates. The thickness of OS layers was chosen to be $\sim$100 nm, which is supposed to be sufficient to exclude the appearance of voids in them [6] even on the textured substrate, i.e. the OS layers were continuous.

The surface micro/nano relief morphology both for textured IS substrates and OS films on the polished (so-called flat) substrates were investigated by the AFM technique using a NanoScope IIIa AFM (Digital Instruments, CA, USA) in the tapping mode regime with a Si_3N_4 tip.

The measurement of the reflectance spectra for OS and Au films on the flat substrates in the spectral range 400–1000 nm at a variable angle of incidence of p- and s-polarized light and their following fitting by theoretical curves calculated within the framework of a one-layer model allowed us to determine the OS layer thickness and the dispersion of its optical parameters [the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$, $\check{n} = n - ik$). So, the spectra of the absorption coefficient, $\alpha = 4\pi k/\lambda$ for OS films and the light transmittance spectra $T(\lambda)$ through the Au and Au/OS layers into photodiode heterostructures were calculated to determine their internal quantum efficiencies Q, i.e. the number of charge carriers per absorbed photon. The spectra of the diffuse reflectance at a normal incidence of light were also measured for heterostructures with flat and textured interfaces to determine the effect of the interface texturing on the total reflectance (specular and diffuse reflectance sum) spectra.

3. RESULTS AND DISCUSSION

Figure 1 demonstrates the AFM images for Pn and MPP films on the flat substrates which testify to the polycrystalline (granular) structure with the shapes and dimensions of crystallites typical of the films obtained at a substrate temperature of $\sim$300 K [1,6,9]. The comparison of the root-mean-square roughness of the OS layer surface ($\delta = 8.7$ nm for Pn and 4.1 nm for MPP) with the thickness of this layer of $\sim$90 nm indicates the continuous topology of the organic semiconductor films under study.

The investigation of optical parameters for Pn and MPP films on various substrates showed the characteristic peculiarities inherent in these thin films, specifically the energy position of peaks for the dependences of n, k, or α on λ [3,9]. At the same time, the values of these peaks depend on the film processing and the substrate used.

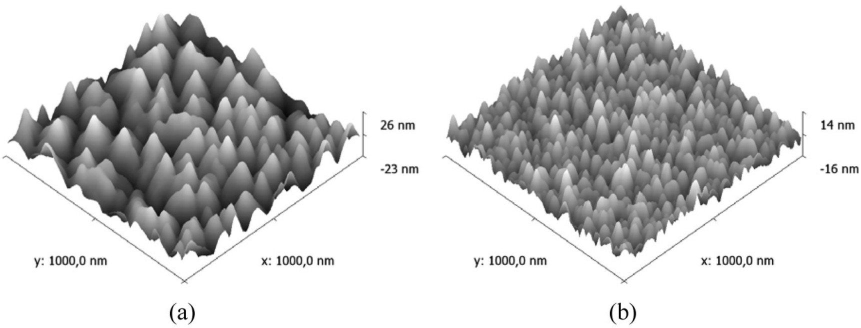

FIGURE 1 AFM images for Pn (a) and MPP (b) films on flat substrates.

So, the accurate measurements and the analysis of optical properties for each OS film preceded to the calculation of the light transmittance (into the photoactive region of a heterostructure) spectra and the quantative analysis of the photoelectric properties for Au/OS/IS heterostructures. An example of the spectral dependences of n and k for an MPP layer on GaAs and InP substrates is shown in Figure 2. The corresponding absorption spectra and their approximation with the sum of the one-oscillator Gaussian functions F_{G} are presented in Figure 3 and Table 1,

$$F_G(x, x_i, A_i, w_i) = \frac{A_i}{w_i\sqrt{\frac{\pi}{2}}} e^{\frac{2(x-x_i)^2}{w_i^2}}, \tag{1}$$

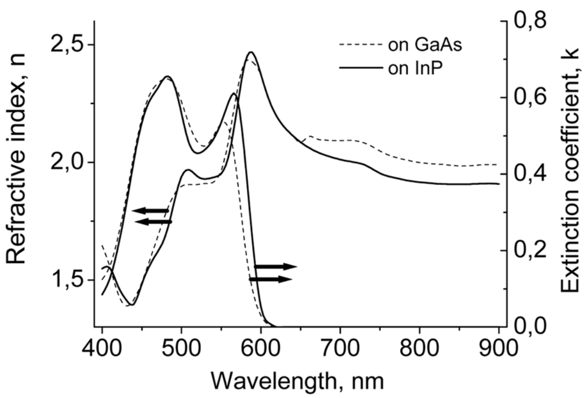

FIGURE 2 Dispersion of optical parameters (n, k) for MPP films on GaAs and InP substrates.

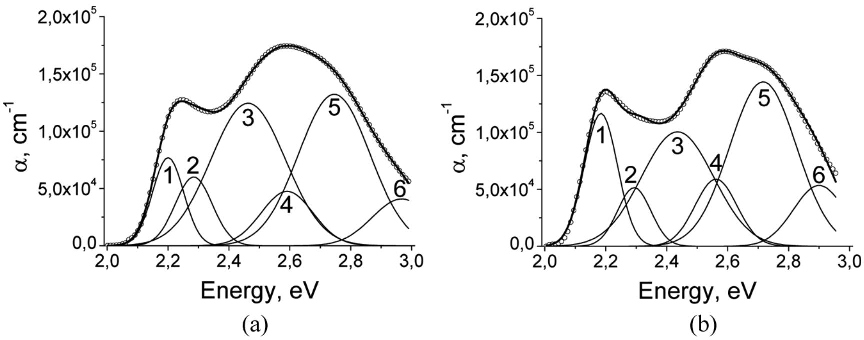

FIGURE 3 Fitting the absorption spectra for MPP on GaAs (a) and InP (b) substrates with a sum of several Gaussian functions.

where A_i is the total area under the i-oscillator curve, x_i is the center position of a peak, and w_i is approximately 0.849 of the half-height width of the peak.

The energy positions of absorption bands for an MPP thin film known from [9,11] are given in Table 1 as well. The difference in the corresponding values of peaks for the layers deposited on GaAs and InP substrates can be caused by peculiarities of the MPP crystal structure believed to have two types of arrangements of organic molecules (in-plane and in-stack aggregates [9]) and two corresponding types of interactions (intralayer and interlayer ones).

The light transmittance spectra through the Au film $T_1(\lambda)$ and Au/Os layers $T_2(\lambda)$ for the analyzed Au/OS/IS heterostructures, which are calculated with regard for the above-determined optical parameters of Au and OS layers, are shown in Figure 4. It is seen that

TABLE 1 The Parameters of Gaussian Functions (x_i, A_i), Obtained from the Fitting of the Absorption Spectra for MPP on GaAs and InP Substrates

Band	on InP		on GaAs		Data of [7]
	x_i, eV	A_i, 10^4eV/cm	x_i, eV	A_i, 10^4eV/cm	x_i, eV
1	2.18	1.59	2.20	0.99	2.16
2	2.29	0.70	2.28	0.91	2.29
3	2.44	2.98	2.46	3.81	2.42
4	2.56	1.01	2.59	1.01	2.54
5	2.72	3.97	2.75	3.89	2.70
6	2.90	1.12	2.97	0.99	2.85

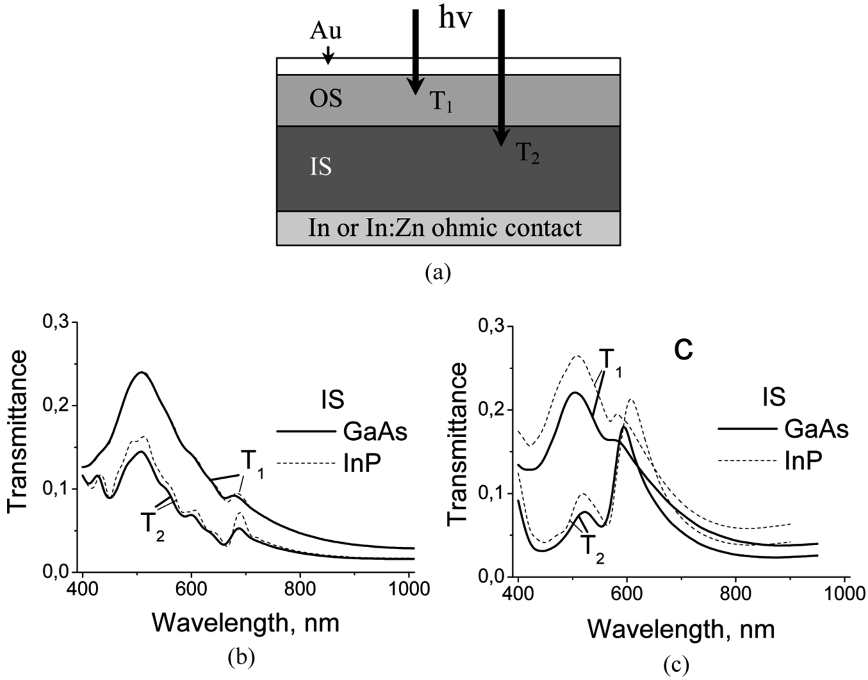

FIGURE 4 Scheme of the investigated layer structure (a) and the calculated light transmittance spectra for Au/OS structures, T_1, and Au/OS/IS structures, T_2. (b – Pn, c – MPP).

both $T_1(\lambda)$ and $T_2(\lambda)$ are small due to the great thickness of Au and OS layers and the great reflectance of light for Au/OS/IS structures.

The corresponding reflectance spectra for such flat structure and for one with a textured interface are shown in Figure 5. They demonstrate a decrease of the total reflection of light for the Au/OS/IS structures with textured (of the quasigrating type) interface with respect to that for the flat one in spite of an increase of the diffuse reflection.

The spectrum of the corresponding increase of the light transmittance through an Au layer caused by a decrease of the reflectance from the textured surface, i.e. $(1\text{-}R_{gr})/(1\text{-}R_{fl})$, is shown in Figure 6. The spectrum of the ratio of the short-circuit photocurrent i_{ph}^{gr} for the Au/n-GaAs structure with textured interface to i_{ph}^{fl} for the flat one is shown there as well. The similarity of these spectra is seen, but the increase of i_{ph}^{gr} is greater. This is mainly caused by some increase of the Au layer transmittance for a non-flat interface, though the changes of the series resistance and the edge planar photoeffect [7] also influence.

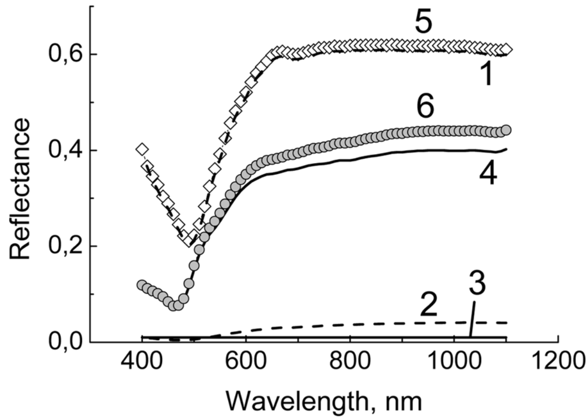

FIGURE 5 Specular (1,2), diffuse (3,4), and total (5,6) reflection spectra for the Au/Pn/GaAs heterostructures with flat (1,3,5) and textured (quasigrating) (2,4,6) interfaces.

To determine the participation of OS layers in the formation of photocurrents of the heterostructures, the internal quantum efficiencies have been calculated from the experimental photocurrent (i_{ph}) spectra presented as the external quantum efficiencies (Fig. 7), with

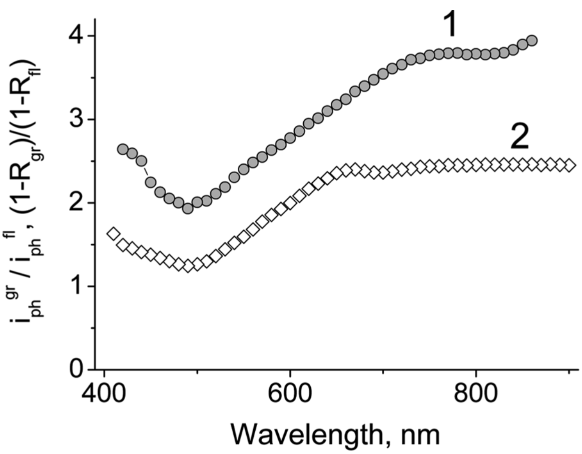

FIGURE 6 Spectra of the ratio of the short-circuit photocurrent $i_{ph}{}^{gr}$ for the Au/n-GaAs structure with textured interface to $i_{ph}{}^{fl}$ for the structure with the flat one ($i_{ph}{}^{gr}/i_{ph}{}^{fl}$) (1) and (1-$R_{gr}$)/(1-$R_{fl}$)–(2), where R_{gr} (R_{fl}) is the total reflectance for Au/Pn/n-GaAs with relief (flat) interface.

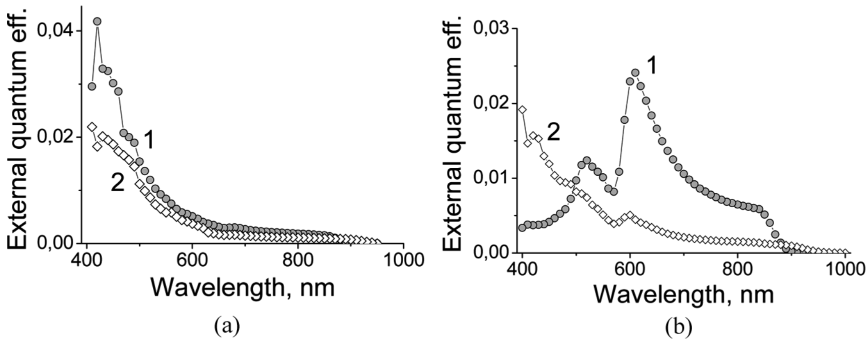

FIGURE 7 Spectra of external quantum efficiencies for Au/Pn/IS (a) and Au/MPP/IS, (b) on GaAs (1) and InP (2) substrates with flat interfaces.

taking the calculated transmittances (T_1 and T_2) spectra from Figure 4 into account.

An example of the spectra of internal quantum efficiencies for the Au/Pn/n-GaAs and Au/MPP/n-GaAs heterostructures calculated as $i_{\mathrm{ph}}/T_1$is shown in Figure 8.

In general, i_{ph} is the sum of photocurrents generated in OS and IS layers which are determined by the light transmittances T_1 and T_2 and by the internal quantum efficiencies Q_{OS} and Q_{IS}, respectively:

$$i_{ph} = i_{OS} + i_{IS} = Q_{OS}T_1 + Q_{IS}T_2. \qquad (2)$$

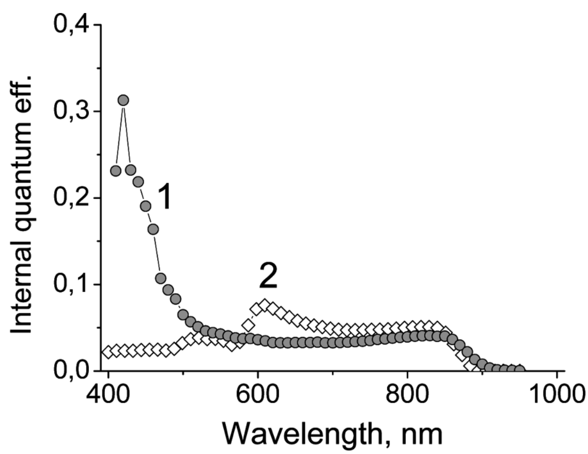

FIGURE 8 Spectra of internal quantum efficiencies (i_{ph}/T_1) for Au/Pn/ n-GaAs (1) and Au/MPP/n-GaAs (2) heterostructures.

We took into account that the absorption in OS layers takes place at $\lambda < \lambda^*$, where

$$\lambda^* = \begin{cases} 750\,\text{nm for Pn layer} \\ 600\,\text{nm for MPP layer} \end{cases}$$

So, for $\lambda > \lambda^*$, the photocurrent is generated in the IS component of a heterostructure only, $Q_{\rm IS}$. As seen from Figure 9, its spectrum practically coincides with the $Q_{\rm IS}$ spectrum for an Au/IS Schottky diode:

$$\lambda > \lambda^*, Q_{OS} = 0, \qquad \frac{i_{ph}}{T_2} = Q_{IS} \approx Q_{Au/IS}. \tag{3}$$

So, the last relation can be used for the calculation of the $Q_{\rm IS}(\lambda)$ spectrum for the Au/OS/IS structure in the $\lambda < \lambda^*$ region. The quantity $Q_{\rm OS}$ is determined as the difference of $i_{\rm ph}/T_1$ and the calculated $Q_{\rm IS}{\cdot}T_2/T_1$:

$$\lambda < \lambda^*, \qquad \frac{i_{ph}}{T_1} = Q_{OS} + Q_{IS}\frac{T_2}{T_1} \tag{4}$$

$$Q_{IS} = \frac{Q_{Au/IS}}{m}, \; m = \frac{T_1}{T_2} \tag{5}$$

$$Q_{OS} = \frac{i_{ph}}{T_1} - \frac{Q_{Au/IS}}{m} \tag{6}$$

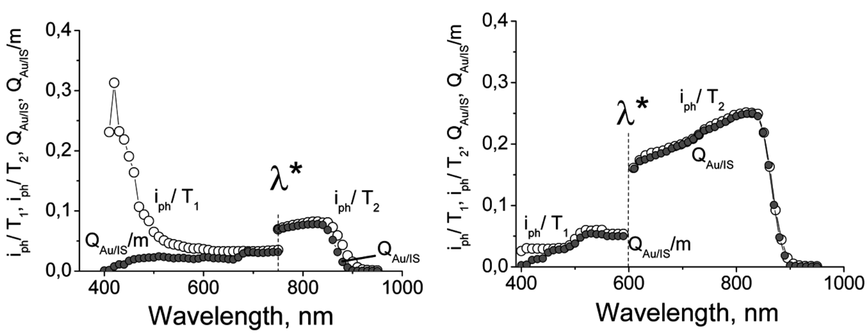

FIGURE 9 Spectra of internal quantum efficiencies for the Au/Pn/GaAs (a) and Au/MPP/GaAs (b) heterostructures (open circles): $i_{\rm ph}/T_1$ in the spectral range $\lambda < \lambda^*$ and $i_{\rm ph}/T_2$ for $\lambda > \lambda^*$. Spectra of internal quantum efficiency for an Au/n-GaAs Schottky diode (filled circles): $Q_{\rm Au/IS}$ at $\lambda > \lambda^*$ and $Q_{\rm Au/IS}/m$ at $\lambda < \lambda^*$.

Figure 9 demonstrates the spectra of internal quantum efficiencies for the Au/Pn/GaAs and Au/MPP/GaAs heterostructures determined by the above-described method: $Q_{IS}(\lambda)$ and $Q_{IS}(\lambda)$ are shown in the spectral range $\lambda > \lambda^*$. The spectral dependences of i_{ph}/T_1 and $Q_{Au/IS}/m$ are presented in the $\lambda < \lambda^*$ range. So, $Q_{OS}(\lambda)$ is determined as the difference of the last curves in the spectral range of the light absorption in an OS layer.

The comparison of the spectra of Q_{OS} and α, both for Pn and MPP, indicates that, for the flat Au/IS/OS structures with the used OS layer thickness, the OS layers contribute to the photocurrent in the spectral range of the band-to-band photogeneration only: $h\nu > E_g$, where $E_g = 2.2\,eV$ for Pn and 2.6 eV for MPP approximately.

The spectra of the photocurrent enhancement due to the textured interface for the Au/OS/IS heterostructures are shown in Figure 10. The increase of the short-circuit photocurrent for the Pn(MPP)/*n*-GaAs structures due to texturing interfaces is much greater than that for the Au/*n*-GaAs structure (Fig. 6). This can be caused by an additional increase of the light absorption in the OS layer due to the multiple internal reflection of light from a textured interface or by an increase of the light transmittance into *n*-GaAs, in particular, in the spectral range, where the absorption in the OS layer is absent.

The considerable increase of i_{ph} for the Au/Pn/IS structure with textured interface is mainly caused by the increase of transmittance and photogeneration in the IS layer and also by some decrease of the series resistance (see Table 2). In addition to the increase of i_{ph} for the Au/MPP/IS structure with textured interface due to the IS layer, the increase of the photocurrent generated in the OS layer is

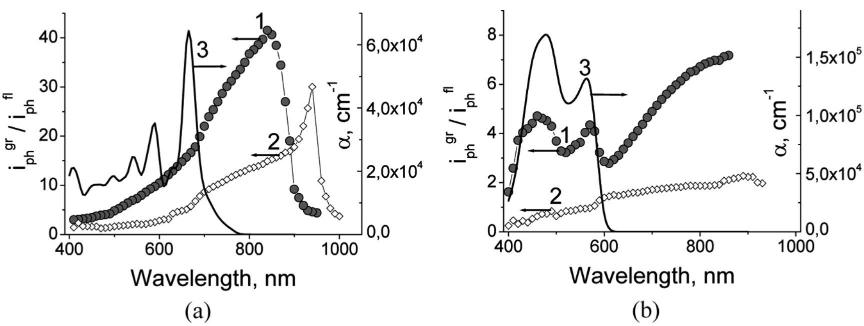

FIGURE 10 Spectra of the i_{ph}^{gr}/i_{ph}^{fl} ratio for the Au/Pn/IS (a) and Au/MPP/IS (b) heterostructures on GaAs (1) or InP (2), and the absorption coefficient spectrum for the Pn or MPP layer (3).

TABLE 2 Photoelectric Parameters of the Au/OS/IS Structures Under Illumination with Light from a Lamp with Tungsten Incandescent Filament

	Flat			Quasigrating			Quasigrating/Flat ratio		
	Au/IS	Au/MPP/IS	Au/Pn/IS	Au/IS	Au/MPP/IS	Au/Pn/IS	Au/IS	Au/MPP/IS	Au/Pn/IS
n-GaAs									
J, mA/cm^2	2.02	0.48	0.023	7.97	5.34	2.06	3.95	11.13	89.57
V_{oc}, V	0.56	0.61	0.50	0.61	0.57	0.58	1.09	0.93	1.16
R_s, kΩ	1.1	24	850	0.22	0.94	22	0.20	0.04	0.03
p-InP									
J, mA/cm^2	0.53	$5.2 \cdot 10^{-3}$	$4.6 \cdot 10^{-2}$	0.67	$7.7 \cdot 10^{-2}$	0.22	1.26	14.81	4.78
V_{oc}, V	0.051	0.057	0.145	0.039	0.184	0.161	0.76	3.23	1.11
R_s, kΩ	1.5	340	74	0.89	57	29	0.85	0.17	0.39

seen to be considerable, and its spectrum correlates with the absorption spectrum of the MPP layer even in the range of exciton absorption.

CONCLUSIONS

The investigation of optical and photoelectric properties of the anisotype and isotype OS/IS heterostructures on the basis of Pn, MPP, GaAs, InP semiconductors and the analysis of their internal quantum efficiencies by the proposed method allowed us to distinguish the contribution of the organic semiconductor layer to the generation of the total photocurrent.

The main value and sign of the photocurrent for the investigated OS/IS structures are determined by a type of inorganic semiconductor (GaAs, InP) and by the available depletion layer caused by the surface states at the OS/IS interface. The contribution of the OS layer enhances the photocurrent generated in the IS layer in all the structures under study. This may indicate a small surface recombination rate on the IS/OS interface.

Photosensitivity and efficiency of the isotype MPP/*n*-GaAs, Pn/*p*-InP heterostructures are shown to be greater than those of the anisotype Pn/*n*-GaAs and MPP/*p*-InP structures. This is not a common situation in the case of inorganic semiconductor heterojunctions. So, such isotype heterostructures can be perspective for the photovoltaic application of organic semiconductors after the optimization of their parameters.

Texturing the OS/IS heterostructure interface by wet chemical anisotropic etching of the IS single crystal substrate resulted in a considerable increase of the photocurrent for all the investigated structures. So, the developed modification in the OS/IS heterostructures interfaces is shown to be promising for photovoltaic and optoelectronic applications.

REFERENCES

[1] Vertsimakha, Ya. I. (2001). *Mol. Cryst. Liq. Cryst.*, *355*, 275.
[2] Dmitruk, N. L., Mamontova, I. B., Borkovskaya, O. Yu., & Vertsimakha, Ya. I. (2002). *Mol. Cryst. Liq. Cryst.*, *384*, 49.
[3] Faltermeier, D., Gomof, B., Dressel, M., Tripathi, A. K., & Pflaum, J. (2006). *Phys. Rev. B*, *74*, 125416.
[4] Kim, S. S., Park, S. P., Kim, J. H., & Im, S. (2002). *Thin Solid Films.*, *420–421*, 19.
[5] Schon, J. H. (2001). *Appl. Phys. Lett.*, *25*, 4163.
[6] Yang, J. & Nquyen, T.-Q. (2007). *Org. Electr.*, doi: 10.1016, orgel. 2007.04.005.

[7] Dmitruk, N. L., Borkovskaya, O. Yu., Mamontova, I. B., & Mamykin, S. V. (2000). *Sol. Energy Mater. Solar Cells.*, *60*, 379.
[8] Borkovskaya, O. Yu., Dmitruk, N. L., Horvath, Zs. J., Mamontova, I. B., & Sukach, A. V. (2007). *Phys. Stat. Sol.* (*C*), *4*, 1523.
[9] Vertsimakha, Ya., Lutsyk, P., Palewska, K., Sworakowski, J., & Lytvyn, O. (2007). *Thin Solid Films*, *515*, 7950.
[10] Dmitruk, N. L., Borkovskaya, O. Yu., Mayeva, O. I., & Mamontova, I. B. (2003). *Phys. Stat. Sol.* (*C*), *3*, 944.
[11] Lifshitz, E., Kaplan, A., Ehrenfreund, E., & Meissner, D. (1998). *Opt. Mater.*, *9*, 295.