

CURRENT-VOLTAGE CHARACTERISTICS, RELAXATION PROPERTIES, AND PHOTSENSITIVITY OF POLYTHIOPENTACENE FILMS

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The hysteresis of dark current-voltage characteristics (JVC) has been observed for the first time for polythiopentacene (PTP) films 1540 nm in thickness in sandwich-like ITO(PTP)Ag cells at room temperature and in the range of applied voltages V from 0 to 10 V. At the negative polarity of the ITO electrode, the dark current density J was found to diminish to a stationary value with the time constants $\tau_1 = 10$ s and $\tau_2 = 150$ s. If the polarity of this electrode was positive, the current-density reduction with $\tau_1 = 10$ s was followed by the current-density increase with $\tau_2 = 150$ s. The time dependences of J , the densities of the short circuit current, J_{sc} , and photocurrent, J_{ph} , and, hence, the algebraic sum $J_{sc} + J_{ph}$ were found to be governed by relaxation changes in the magnitudes of near-electrode space charges. The photosensitivity S_0 of PTP films at their illumination with monochromatic light with a quantum energy of 1.51 eV (photogeneration in the bulk) turned out five times as high as that, when the light quantum energy was 1.77 eV (photogeneration near the electrode). The near-electrode photogeneration is characterized by the presence of horizontal and linearly increasing sections in the dependence $S_0(V)$, which are associated with linear and quadratic, respectively, variations of the sum $J_{sc} + J_{ph}$ with the changing voltage V . For photogeneration in the bulk, this sum depends linearly on V .

1. Introduction

Thioderivatives of linear acenes were synthesized for the first time by Marshalk [1, 2]. A scientific interest in studying the properties of chalcogene derivatives of linear acenes is connected with a rather low, as for organic substances, electric resistance ($\rho(300\text{ K}) = 100\ \Omega \times \text{m}$) of tetrathiotetracene (TTT), tetraselenetetracene (TST), and hexathiopentacene (HTP) [3, 4].

The absorption spectra of chalcogene derivatives of acenes are shifted toward long waves (the bathochromic effect) in comparison with those for nonsubstituted molecules, which is a consequence of the conjugation between the valence electrons of chalcogene heteroatoms (S, Se, and Te) and π -systems of acene rings [5].

In the reaction between pentacene and sulfur, there emerges PTP, a mixture of thioderivatives with various numbers of S atoms. The most probable components

of PTP are tetrathiopentacene (TTP) and hexathiopentacene (HTP), which can be identified by the peak intensities and the positions of maxima in their long-wave absorption bands [6].

Every elementary cell of HTP crystals contains two molecules. Translationally equivalent molecules combine into stacks with an intermolecular distance of 0.354 nm. The distances S–S between neighbor translationally nonequivalent molecules are even shorter at that and amount to 0.337–0.341 nm, which is shorter than the van der Waals distance for S atoms (0.370 nm). This evidences a strong overlapping between the orbitals of S atoms, which favors the electric charge transfer between molecules both along the stack axes and between the stacks [7].

The photovoltage of the free surface of PTP films PTC is determined by the Demer, V_D , and surface-barrier, V_b , photovoltages, which are opposite to each other by the polarity [6, 8]. Photovoltaic properties of HTP-based thin-film heterostructures were studied in work [9].

In work [7], the characteristics of transistors on the basis of HTP films were reported: the hole mobility $\mu_p = 0.01\ \text{cm}^2/(\text{V} \times \text{s})$ and the large ratio $I_1/I_2 = 10^7$ between the magnitudes of currents at a switched-on, I_1 , or switched-off, I_2 , gate electrode and a low threshold voltage of this electrode. Those researches were continued in work [10], and a report was made concerning a capability of creating field-effect transistors with the use of HTP-based crystalline nanowires ($\mu_p = 0.27\ \text{cm}^2/(\text{V} \times \text{s})$ and $I_1/I_2 > 10^3$) and nanofibrils ($\mu_p = 0.057\ \text{cm}^2/(\text{V} \times \text{s})$ and $I_1/I_2 = 10^4$). In this case, HTP nanofibrils can be formed on flexible substrates and used for the manufacturing of rather cheap displays, integrated circuits, solar cells, and memory cells. The μ_p -values obtained in work [10] for HTP crystalline nanowires turned out close to those for field-effect transistors on the basis of pentacene films [11].

Therefore, the properties of pentacene and its thio derivatives are intensively studied today with the purpose of using those materials as active elements in field-

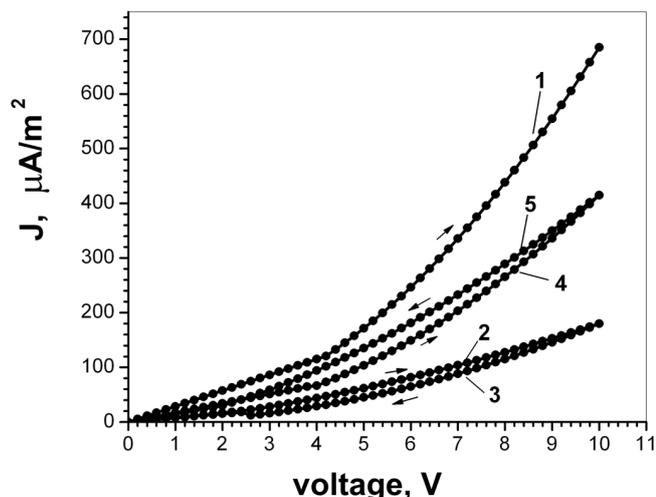


Fig. 1. Current-voltage characteristics of a dark current through sandwich-like ITO(PTP)Ag cells with PTP films 1540 nm in thickness. The arrows directed to the right and to the left indicate an increase of the applied voltage from zero to the maximum value (10 V) and a voltage reduction from the maximum to the zero value, respectively. Curves 1, 4, and 5 were recorded at the positive polarity at the ITO electrode, and curves 2 and 3 at the negative polarity of this electrode. The order of JVC records is defined by the curve number

effect transistors. However, in spite of all that, the near-electrode processes in HTP and PTP films, which can substantially affect the efficiency and the stability of electronic devices constructed on their basis, have not been studied enough. Those processes formed a subject of investigation in our work.

2. Experimental Technique

Sandwich-like ITO(PTP)Ag cells were fabricated by carrying out the consecutive thermal sputtering of a PTP layer and an upper metallic electrode in a vacuum of 0.67 mPa onto a quartz substrate covered with an ITO electrode. The design of those cells allowed the resistance of electrodes to be monitored. While measuring the JVC and the time dependences of the dark current, the cells were connected to a stabilized voltage source of the P1405 type and an U5-9 dc amplifier with a digital voltmeter or a recorder at the output. At modulated illumination, the time dependences of the photocurrent J_{ph} and the short circuit current J_{sc} were measured making use of an UPI-1 ac amplifier, inserted into the electric circuit instead of the U5-9 amplifier. The cells were illuminated with light produced by a halogen incandescent lamp and passed through an SPM-2 monochromator or filters. The power of stabilized or modulated light inci-

dent onto the cell was measured using an RTN-20 thermopile or a pyroelectric radiation sensor with a sensitivity of 0.83 or 250 V/W, respectively.

An aluminum disk with symmetric sector cuts was used as a light modulator. The disk rotation allowed us to obtain rectangular light pulses 7 ms in length and a leading edge duration of 20 μ s.

3. Experimental Results

Dark JVC measured for sandwich-like ITO(PTP)Ag cells are depicted in Fig. 1. The arrows specify the variation directions of the voltage V applied to the electrodes (from zero to a certain value and backward). Let us denote the current density and the applied voltage at the positive and negative ITO-electrode polarities as J_+ , V_+ and J_- , V_- , respectively. The initial JVC for J_+ (curve 1) was registered, when V was growing from 0 to 10 V. Then, the V -polarity was changed, and the JVC for J_- was measured at V growing from 0 to 10 V, with the corresponding curve 2 going below curve 1 (J_+). If V_- was reduced (by the absolute value) from 10 to 0 V, the corresponding curve 3 passed below curve 2. Afterward, the V -polarity was changed, and the JVC for J_+ was firstly measured at V growing from 0 to 10 V (curve 4) and, then, at V decreasing from 10 to 0 V (curve 5). Hence, when the voltage V was cyclically varied (curves 2 to 5), a hysteresis of dark JVC was observed. It is worth noting that curve 4 is located below curve 1, i.e. the sandwich-like ITO(PTP)Ag cell does not restore its initial characteristics. After this cell having been kept in the dark for a week, the process of JVC recording (curves 1 to 5) can be repeated.

On the log-log scale, the initial JVC (curve 1) is described by two straight lines with different slopes k 's. In particular, $k_1 = 1.0$ at $0 < V_+ \leq 4$ V (the ohmic section), and $k_2 = 2.0$ at $4 < V_+ \leq 10$ V (the quadratic section). For curve 2, the voltage of transition from the ohmic section to the superlinear one with $k_2 = 1.54$ is equal to $V_- = 2.4$ V. Curves 3, 4, and 5 also consist of two sections each, one of the sections being ohmic (at low V). The transition voltage for them equals 4.6, 3.8, and 2.0 V, respectively, and the slope $k_2 = 2.00$, 2.00, and 1.62, respectively.

The time dependences $J(t)$ obtained for sandwich ITO(PTP)Ag cells are exhibited in Fig. 2. The magnitude of J_- decreased in time at all V_- 's in the range $0 < V_- \leq 10$ V (Figs. 2, b and d). The variation kinetics consisted of the fast and slow components. In this voltage range, a quick reduction of J_+ to the minimum value was observed firstly, and then this quantity slowly

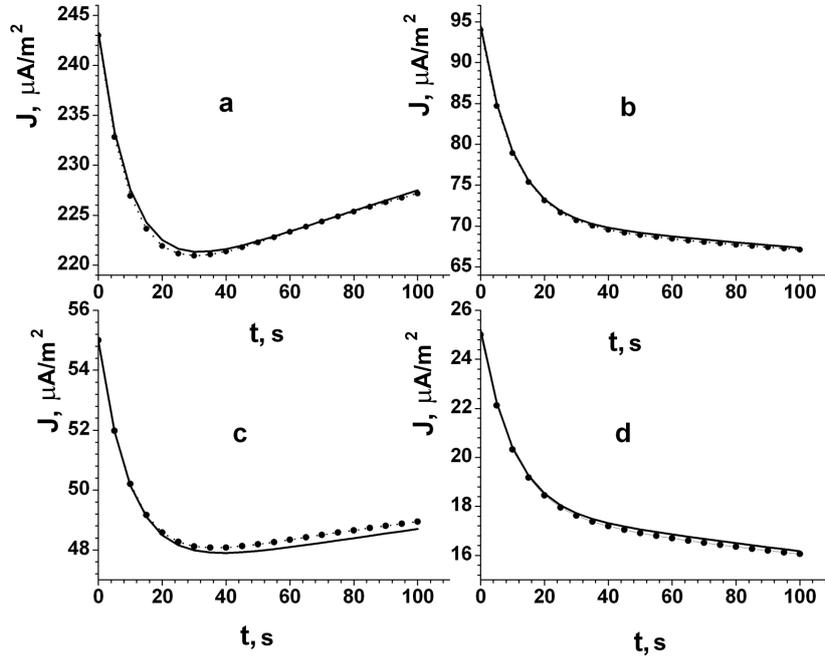


Fig. 2. Time dependences of the dark current through sandwich-like ITO(PTP)Ag cells at various voltages at the ITO electrode: +7.5 (a), +3.0 (b), -3.0 (c), and -7.5 V (d)

grew to a stationary value (Figs. 2,a and c). The analytic expressions for J_+ and J_- are the algebraic sums of a constant component J_0 and two exponential ones,

$$J = J_0 + J_1 e^{-\frac{t}{\tau_1}} + J_2 e^{-\frac{t}{\tau_2}}, \quad (1)$$

where the time t was measured in seconds. The time constants are $\tau_1 = 10$ s and $\tau_2 = 150$ s. The values for parameters J_0 , J_1 , and J_2 are given in Table 1.

After the voltage V_+ or V_- had been switched-off, the discharge currents flowed through short-circuited cells. The directions of those currents were opposite to those of J_+ and J_- , and the current magnitudes vanished as the time grows. The initial values of those currents depended on the value of switched-off voltage and increased with the growth of V_+ or V_- .

After the dark current J had saturated, monochromatic light was switched-on, and the maximum of photo-

current J_{ph} was measured at a constant voltage V . For J_{ph} , we observed only a slow reduction of this quantity in time, with the time constant being equal to $\tau_2 = 150$ s.

Modulated monochromatic light with a photon energy of 1.51 or 1.77 eV was used, while measuring the time dependences of J_{sc} and the algebraic sum $J_{sc} + J_{ph}$, when the applied voltage was switched-off and switched-on, respectively. In all cases, the time dependences were described by the relation

$$X = A + B e^{-\frac{t}{\tau_3}} \quad (2)$$

where X stands for either J_{sc} or $J_{sc} + J_{ph}$, the coefficients A and B are constants, and $\tau_3 = \tau_2 = 150$ s are the time constants.

The values of coefficients A and B for J_{sc} and $J_{sc} + J_{ph}$ are quoted in Tables 2 and 3, respectively. Row 1 in Table 2 includes the values of A and B for the initial current, $J_{sc}(V = 0)$, and rows 2 to 5 include the corresponding values for J_{sc} after switching-off the negative ($V < 0$) and positive ($V > 0$) bias potentials of 0.17, 0.34, 0.68, and 1.36 V, respectively, at the ITO electrode. The signs of bias potentials at this electrode are also shown in Table 3. The plots for the time dependences of J_{sc} and $J_{sc} + J_{ph}$ at the illumination of the cell with monochromatic light with $E_{ph} = 1.77$ eV (the

Table 1. Values for J_0 , J_1 , J_2 , ΔQ_1 , and ΔQ_- quantities

N	B - ITO-electrode bias, V	J_0 $\mu\text{A}/\text{m}^2$	J_1 $\mu\text{A}/\text{m}^2$	J_2 $\mu\text{A}/\text{m}^2$	ΔQ_1 $\mu\text{C}/\text{m}^2$	ΔQ_- $\mu\text{C}/\text{m}^2$
1	+7.5	240	28	-25	280	-3750
2	-7.5	63	23	+8	230	+1200
3	+3.0	51	8	-4	80	-600
4	-3.0	14	7	+4	70	+600

Table 2. *A* and *B* values for J_{sc} after various voltages *V*

curve No	$J_{sc}, A/m^2$							
	$V < 0$				$V \geq 0$			
	$E_{ph} = 1.51 \text{ eV}$		$E_{ph} = 1.77 \text{ eV}$		$E_{ph} = 1.51 \text{ eV}$		$E_{ph} = 1.77 \text{ eV}$	
	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
	$\mu A/m^2$	$\mu A/m^2$						
1	2.00	0.00	2.59	0.00	-0.99	0.00	1.80	0.00
2	1.47	-3.39	2.49	-0.13	0.30	3.12	1.90	0.14
3	0.58	-5.54	2.40	-0.30	1.44	4.69	2.12	0.24
4	-0.50	-13.75	2.27	-0.57	2.42	10.54	2.32	0.39
5	-1.57	-19.49	1.85	-1.45	5.70	19.52	2.54	1.17

Table 3. *A* and *B* values for $J_{sc} + J_{ph}$ at various voltages *V*

curve No	<i>V</i>	$(J_{sc} + J_{ph}), \mu A/m^2$							
		$V < 0$				$V > 0$			
		$E_{ph} = 1.51 \text{ eV}$		$E_{ph} = 1.77 \text{ eV}$		$E_{ph} = 1.51 \text{ eV}$		$E_{ph} = 1.77 \text{ eV}$	
		<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$	$\mu A/m^2$
1*	0.17	2.61	4.36	2.72	0.13	-0.99	-1.86	1.60	-0.13
2*	0.34	3.43	6.62	2.81	0.18	-1.42	-3.55	1.49	-0.49
3*	0.68	4.22	11.66	2.92	0.31	-1.99	-7.97	1.38	-0.69
4*	1.36	5.36	28.64	3.02	0.59	-2.85	-16.93	1.26	-0.96

range of strong absorption in the PTP film) are presented in Figs. 3, *a* and *b*. For different V_+ -values, the sum $J_{sc} + J_{ph}$ increases (curves 1* to 4* in Fig. 3, *a*), and the current J_{sc} decreases (curves 1 to 5 in Fig. 3, *a*) in time to reach the corresponding stationary value. At the same time, the initial and stationary values for J_{sc} increase, and the corresponding values for $J_{sc} + J_{ph}$ decrease as the voltage V_+ grows. For different V_- -values, the sum $J_{sc} + J_{ph}$ decreases (curves 1* to 4* in Fig. 3, *b*), and the current J_{sc} increases (curves 1 to 5 in Fig. 3, *b*) in time to reach the corresponding stationary value. The initial and stationary values for J_{sc} decrease, and the corresponding values for $J_{sc} + J_{ph}$ increase as the voltage V_- grows.

For monochromatic light with $E_{ph} = 1.51 \text{ eV}$ (the range of weak absorption in the PTP film), the time dependences of $J_{sc} + J_{ph}$ and J_{sc} (Fig. 4) are the same as for light with $E_{ph} = 1.77 \text{ eV}$ (the range of strong absorption in the PTP film). The difference consists in that, when the monochromatic illumination with $E_{ph} = 1.51 \text{ eV}$ is carried out, the direction of the current J_{sc} changes (curves 2 to 5 in Figs. 4, *a* and *b*), and the ratios between the initial and stationary values of both $J_{sc} + J_{ph}$ and J_{sc} are much more larger than the corresponding ratios obtained for light with $E_{ph} = 1.77 \text{ eV}$.

The photosensitivity of PTP films was determined using the formula

$$S_0 = \frac{J_{ph}}{P \times V}, \quad (3)$$

where J_{ph} is the photocurrent density, P the specific power measured in the W/m^2 units, and V the applied voltage. The dependences of S_0 and the ratio J_{ph}/J on V are depicted in Fig. 5. The S_0 -values (the solid curves) are reckoned along the left and the J_{ph}/J -ones (the dashes curves) along the right ordinate axis. In the case of light with $E_{ph} = 1.56 \text{ eV}$ (the range of weak absorption in the PTP film), the quantity S_0 did not depend on V_+ (straight line 2). The ratio J_{ph}/J decreased with growing V at that (curve 2*). If the polarity of the ITO electrode was negative, both S_0 and J_{ph}/J were V_- -independent (straight lines 1 and 1*, respectively).

For the light quantum energy $E_{ph} = 1.77 \text{ eV}$ (the range of strong absorption in the PTP film), two sections of variation were observed for S_0 and J_{ph}/J . At $0 < V \leq 1 \text{ V}$, both those characteristics did not depend on V_+ (straight lines 3 and 3*, respectively) and V_- (straight lines 4 and 4*, respectively). In the voltage range $1 < V \leq 4 \text{ V}$, the quantity S_0 increased with the growth of V for both polarities of the ITO electrode (straight lines 3 and 4, respectively). In this case, the ratio J_{ph}/J slightly decreased as V_+ grew (straight line 3*)

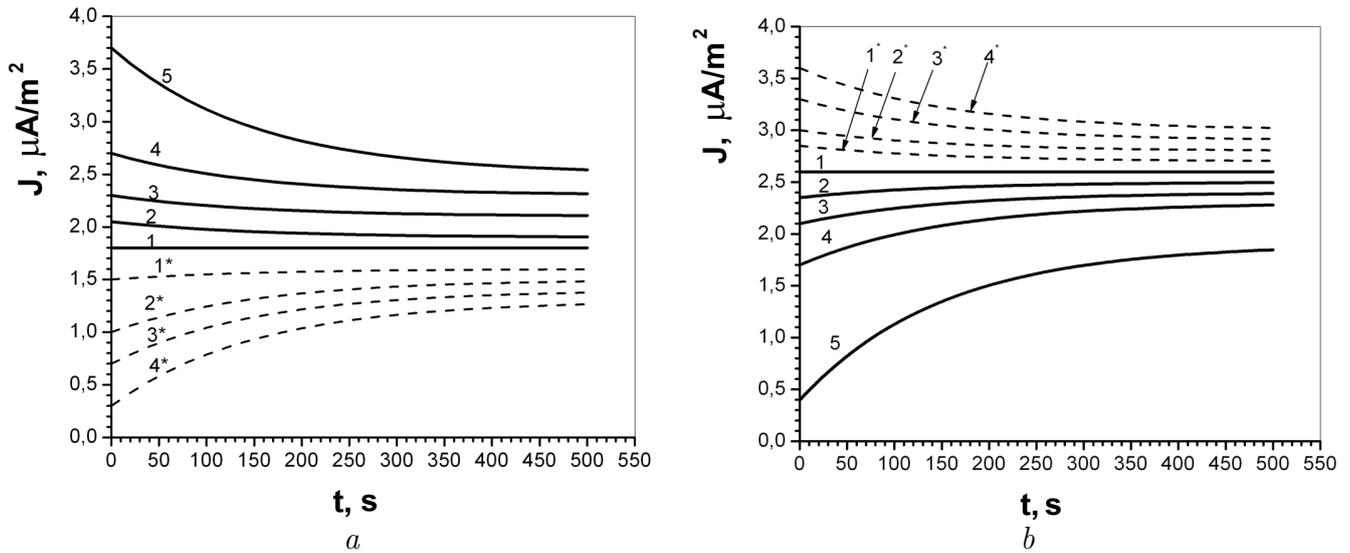


Fig. 3. (a) Time dependences of the initial short circuit current J_{sc} (curve 1), J_{sc} after the voltage has been switched-off (curves 2 to 5) and the sum $J_{sc} + J_{ph}$ (curves 1* to 4*) at positive voltages of 0.17, 0.34, 0.68, and 1.36 V at the ITO electrode. All curves were measured, when illuminating the cell with light modulated with a frequency of 72 Hz, and characterized by the light quantum energy $E_{ph} = 1.77$ eV. (b) The same as in panel a, but for the negative polarity of the ITO electrode

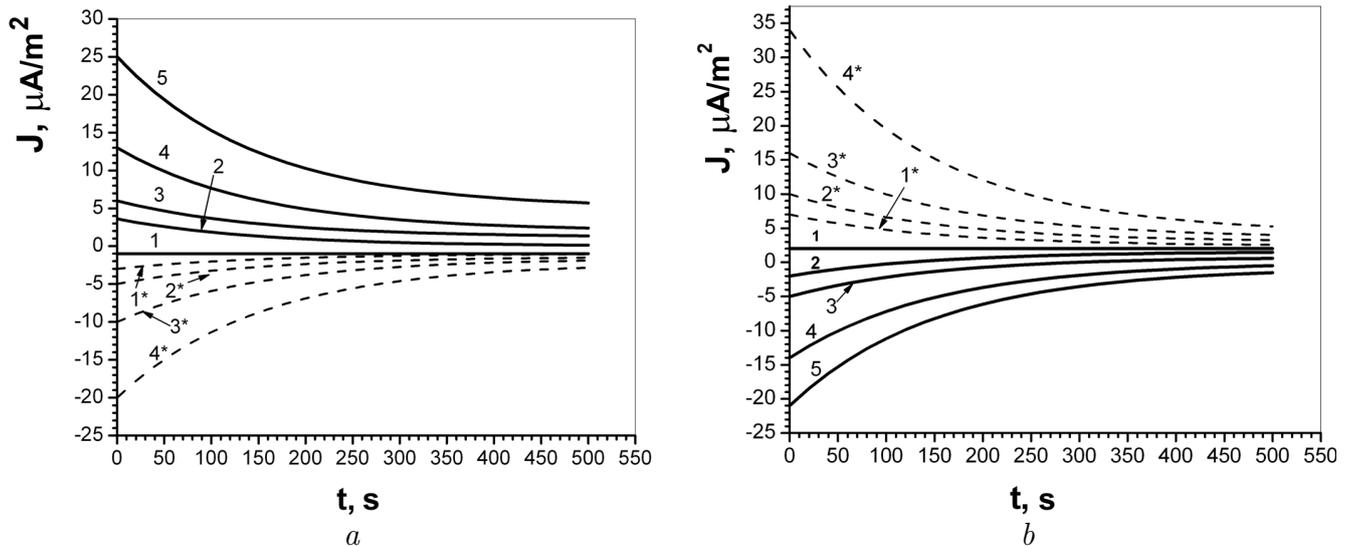


Fig. 4. The same as in Fig. 3, but for the light quantum energy $E_{ph} = 1.51$ eV

and increased if V_- became larger (straight line 4*). The comparison between the corresponding S_0 -values showed that PTP films are more sensitive to light with $E_{ph} = 1.51$ eV.

4. Discussion of Experimental Data

The structural formulas of HTP and TTP molecules are given in work [6]. The core of those molecules is formed

by five linearly connected benzene rings. Chemically active points of the core (carbon atoms, C, located at the vertices of internal benzene rings) are connected with six (HTP) or four (TTP) sulfur atoms, S. PTP was identified as a mixture of HTP and TTP molecules on the basis of their characteristic bands at 1.70 and 1.76 eV, respectively [12]. Those bands appear as a result of contributing by the external electrons of S atoms to the π -system of pentacene core. Those electrons are localized

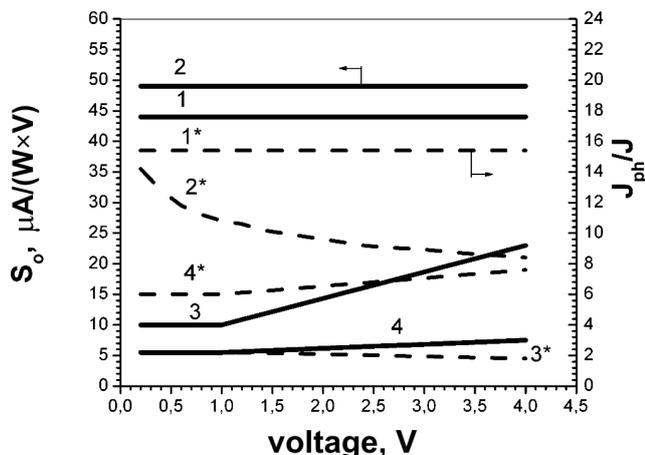


Fig. 5. Dependences of the photosensitivity S_0 (solid curves, the left ordinate axis) and the ratio J_{ph}/J (dashed curves, the right ordinate axis) on the applied voltage at the illumination of a cell with a constant intensity and a light quantum energy of 1.51 eV (curves 1, 1* and 2, 2*, respectively) and 1.77 eV (curves 3, 3* and 4, 4*, respectively)

at $3p_z$ orbitals, the dimensions of which considerably exceed the external $2p_z$ orbitals of C atoms and which are easily polarized under the action of electric fields produced by ions. As a result, the electric dipoles emerge in HTP and TTP molecules, which changes the constant electric dipoles along C–S bonds [13].

Let the electron work function φ for PTP be approximately equal to that for TTT and amount to 4.47 eV [14]. The validity of this assumption is confirmed by the fact that, for this class of compounds, the work function is governed by the valence electrons of sulfur atoms. For ITO and Ag, this parameter equals 5.15 and 4.30 eV, respectively [15]. The electroconductivity in PTP was found to be of the hole type [6, 8]. Since $\varphi(\text{ITO}) > \varphi(\text{PTP}) > \varphi(\text{Ag})$, the band bending in PTP in a vicinity of the ITO and Ag electrodes for holes is, in the band approximation, antibarrier and barrier, respectively. In this case, a positive space charge is formed in the PTP film near the ITO electrode, and a negative one in a vicinity of the Ag electrode. The presence of a potential barrier for holes near the Ag electrode is confirmed by the asymmetry of dark JVC (Fig. 1).

The estimation of the specific resistance ρ for a PTP film in its ohmic JVC section brought us to a value of $10^{10} \Omega \times \text{m}$, i.e. PTP is a high-resistance organic semiconductor. The JVC sections with $k = 2$ testify that the current in PTP films can be restricted to the bulk charge. To confirm this assumption, it is necessary to measure JVC for PTP films of various thicknesses and at $V > 10$ V.

The fast component of $J(t)$ decaying with the time constant $\tau = 10$ s was observed at all V 's and for both bias polarities at the ITO electrode (Fig. 2). The same τ characterized a reduction of the discharge currents. Such changes in $J(t)$ evidence the variation of space charges near the electrodes. The magnitude of those changes, ΔQ_1 (see Table 1), was estimated by integrating the fast component of $J(t)$ with the time constant $\tau = 10$ s. It turned out to depend on the strength of the external electric field.

The character of the slow component of $J(t)$ with $\tau = 150$ s is determined by the direction of the external electric field. If a positive bias potential is applied to the ITO electrode, electron-hole pairs, which were thermally generated in this electrode, are separated by the external electric field, and the electrons transit to the external section of the electric circuit, whereas holes drift to the negatively charged Ag electrode. At the same time, in a vicinity of the Ag electrode, electrons that form the negative space charge Q_- and belong to the conduction band of PTP drift to the ITO electrode. As a result, the height of the potential barrier for holes decreases owing to a reduction of Q_- with the time constant $\tau = 150$ s. Therefore, more holes can penetrate into the Ag electrode to be neutralized by electrons in the external section of the circuit, which is responsible for the growth of J_+ in time (Figs. 2, a and c).

The negatively charged ITO electrode injects electrons into the PTP film. The electrons drift to the positively charged Ag electrode and increase the magnitude of Q_- with the time constant $\tau = 150$ s, which governs the slow decay kinetics for J_- (Figs. 2, b and d). In this case, holes are generated in the Ag electrode. High-energy holes overcome the potential barrier and, driven by the external electric field, drift toward the negatively charged ITO electrode to be neutralized by electrons in the external section of the electric circuit.

The dependence $J(t)$ considered above lies in the basis of the phenomenon observed for dark JVC (Fig. 1). The change of ΔQ_- near the Ag electrode is quoted in Table 1. It was evaluated by integrating the slow component of the $J(t)$ dependence with the time constant $\tau = 150$ s.

If the sandwich-like structures are illuminated with light, the following processes can take place in the PTP film bulk and in a vicinity of the electrodes:

1. The photo-induced generation of electron-hole pairs owing to the absorption of photons with $E_{ph} > E_g$, where E_g is the energy gap width, by electrons in the valence band.

2. The photo-induced excitation of holes in the valence band. This process is equivalent to the transition of an electron from the valence band onto a neutral or positively charged acceptor level in a vicinity of this band.
3. The appearance of electrons in the conduction band at their photoexcitation from donor levels.

Let $E_g = 2.0$ eV for PTP (the threshold value for the characteristic photoconductivity in TTT [16]). Then, to explain the photoconductivity in PTP films, processes 2 and 3 are suitable, because $E_{ph} > E_g$.

To estimate the width W of the photo-induced generation region for charge carriers in PTP film, we used the Lambert–Beer law

$$I = I_0 e^{-\alpha d}, \quad (4)$$

where I_0 and I are the intensities of light incident on the film and passed through it, respectively; α is the absorption coefficient; and d is the PTP film thickness. Under the term “the width of photo-induced generation”, W , we understand the distance between the illuminated surface and a plane parallel to it, for which the transmission coefficient $T = I/I_0 = 0.1$. Substituting the equalities $d = W$ and $T = 0.1$ into Eq. (4) and carrying out transformations, we arrive at the expression

$$W = \frac{2.3}{\alpha}. \quad (5)$$

For $\alpha = 6.7 \times 10^4 \text{ cm}^{-1}$ (strong absorption in PTP, $E_{ph} = 1.77$ eV), we obtain $W = 373$ nm. It is much less than the film thickness $d = 1540$ nm, and the photogeneration region is concentrated near the ITO electrode in this case. It was found [8] that $V_D < V_b$ near this electrode. Nonequilibrium holes drift to the surface of the ITO electrode under the action of a near-electrode electric field, then they are neutralized by electrons from the external section of the electric circuit. In addition, nonequilibrium electrons in the conduction band of PTP may appear near the ITO electrode as a result of their photoexcitation from donor levels. Driven by the near-electrode field, these electrons drift toward the Ag electrode and transit to the external section of the circuit. The fluxes of nonequilibrium charge carriers create the current J_{sc} , the magnitude of which is governed by the concentration of the charge carriers concerned and the effective strength of the electric field near the ITO electrode.

A positive voltage bias of 0.17 V at the ITO electrode creates an external electric field of the strength $E \approx 1 \times 10^5$ V/m, which reduces the strengths of both

near-electrode fields. In this case, the algebraic sum $J_{sc} + J_{ph}$ (curve 1^* in Fig. 3,*a*) is smaller than J_{sc1} (straight line 1 in Fig. 3,*a*) by the magnitude of J_{ph1} , the latter being connected with a drift flux of nonequilibrium holes in the bulk of a PTP film under the action of the external electric field. The amplitude of this sum increases in time. After a stationary value of $J_{sc} + J_{ph}$ had been established, $J_{sc} + J_{ph} < J_{sc1}$, the external electric field was switched-off, and the current J_{sc2} was measured (curve 2 in Fig. 3,*a*). The latter turned out larger than J_{sc1} , i.e. the specimen did not restore its initial characteristics.

For external electric fields with the strength $E \geq 1 \times 10^5$ V/m, the growth of $J_{sc} + J_{ph}$ (curves 1^* to 4^* in Fig. 3,*a*) and the reduction of J_{sc} (curves 2 to 5 in Fig. 3,*a*) in time to the corresponding stationary values can be explained as a result of changes of the positive space charge, Q_+ , in a vicinity of the ITO electrode. If a positive bias is applied to the ITO electrode, the drift fluxes of nonequilibrium holes and electrons arise in the near-electrode region. Those fluxes are oppositely directed, and they form two components of the current, J_{sc} and J_{ph} . The fluxes of nonequilibrium electrons in the bulk of the PTP film and nonequilibrium holes toward the ITO electrode dominate. The magnitude of Q_+ increases owing to a noncompensated charge of ionized donors, which gives rise to an enhancement of the band bending and, hence, to the growing of J_{sc} . The equilibrium value of the current $J_{sc} + J_{ph}$ is established at an increased Q_+ . The time constant for those processes equals 150 s. At the initial moment, just after the external electric field has been switched-off, the band bending is large enough, whereas the barrier thickness is small. This fact favors the tunneling of electrons, which were photogenerated in the ITO electrode, into the PTP film bulk. Those electrons are captured by ionized donors, which results in a reduction of Q_+ and J_{sc} with a time constant of 150 s.

If the bias at the ITO electrode is negative, the band bending becomes larger near both electrodes. In this case, the currents J_{sc} and J_{ph} are codirectional. A certain number of electrons injected from the ITO electrode become captured by ionized electron donors, which is responsible for a reduction of Q_+ with a time constant of 150 s (curves 1^* to 4^* in Fig. 3,*b*). After the electric field has been switched-off, the magnitude of Q_+ grows owing to the donor photoionization and the drift of nonequilibrium electrons toward the Ag electrode (curves 1 to 5 in Fig. 3,*b*).

For light with the quantum energy $E_{\text{ph}} = 1.51$ eV, which is weakly absorbed by the PTP film, $\alpha = 1.5 \times 10^4$ cm⁻¹, and, according to Eq. (5), $W = 1540$ nm, i.e., it is equal to the PTP film thickness. This means that nonequilibrium holes and electrons are photogenerated near both electrodes and in the PTP film bulk. The large initial values for J_{sc} and J_{ph} in comparison with those for light with $E_{\text{ph}} = 1.77$ eV are associated with the growth in the concentrations of nonequilibrium charge carriers due to the bulk photogeneration. In addition, the current J_{sc} changes its initial direction. This phenomenon is related to the fact that, when the illumination is carried out through the ITO electrode, the resulting photovoltage is formed by the diffusion, V_D , and drift, V_b , components, which are opposite to each other by polarity [6, 8]. If $V_D > V_b$, then $J_{\text{sc}} < 0$ (straight line 1 in Fig. 4,a), i.e., the diffusion flux of nonequilibrium holes dominates in the PTP film bulk. At $V_D < V_b$, $J_{\text{sc}} > 0$ (straight line 1 in Fig. 4,b), and the drift component, which is directed to the ITO electrode, becomes more intensive. Since the quantities V_D and V_b do not differ substantially by their absolute values, the variations of the band bending near the electrodes change the polarity of the resulting photovoltage and, therefore, the initial direction of J_{sc} . The time dependences of J_{sc} and $J_{\text{sc}} + J_{\text{ph}}$ at $E_{\text{ph}} = 1.51$ eV (Fig. 4) are described by the same mechanisms considered above for light with $E_{\text{ph}} = 1.77$ eV.

The analysis of time dependences for the quantities J , J_{sc} , J_{ph} , and $J_{\text{sc}} + J_{\text{ph}}$ carried out above demonstrates that they are governed by the changes of space charges near the electrodes under the action of the external electric field and the illumination. We may suppose that the origin of those changes lies in the processes of interaction of holes and injected electrons with corresponding traps and sticking levels in the forbidden gap of PTP. Moreover, a contribution to those processes can be given by dipoles induced along the C–S bonds in TTP and HTP molecules by the external electric field. The elucidation of the nature of those mechanisms will be a subject of our following researches.

The photosensitivities S_0 of the PTP film illuminated with light that is weakly absorbed by the PTP film are close by magnitude for both polarities of the ITO electrode (straight lines 1 and 2 in Fig. 5). At the same time, they are five times as high as the photosensitivities for light that is strongly absorbed by the PTP film (straight lines 3 and 4 in Fig. 5). This fact testifies that the bulk photogeneration of nonequilibrium charge carriers is more effective in comparison with the near-electrode one. Two sections in the dependence $S_0(V)$ are typical

of the latter. They follow from the linear (the horizontal section in $S_0(V)$) and quadratic (the sloped section in $S_0(V)$) dependences of the algebraic sum $J_{\text{sc}} + J_{\text{ph}}$ on the applied voltage. For light that is strongly absorbed by the PTP film, this sum depends linearly on V at $0 < V < 4$ V.

5. Conclusions

A hysteresis in the dark JVC for PTP films has been observed for the first time. The time dependences of the current J_{sc} and the sum $J_{\text{sc}} + J_{\text{ph}}$ are associated with changes of the space charge near the ITO electrode, if the light absorption by the PTP film is strong ($E_{\text{ph}} = 1.77$ eV), and the space charges near the ITO and Ag electrodes, if the absorption by this film is weak ($E_{\text{ph}} = 1.51$ eV), as well as by the relation between the quantities V_D and V_b . The photosensitivity S_0 of PTP films at their illumination with monochromatic light with a photon energy of 1.51 eV (photogeneration in the bulk) is five times as high as that for light with a photon energy of 1.73 eV (photogeneration near the electrode). The near-electrode photogeneration is characterized by the horizontal and linearly growing sections in the dependence $S_0(V)$, which are associated with the linear and quadratic, respectively, dependences of the algebraic sum $J_{\text{sc}} + J_{\text{ph}}$ on the applied voltage V . For the photogeneration in the bulk, this sum depends linearly on V .

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1. C. Marshalk, Bull. Soc. Chim. France **6**, 1122 (1939).
2. C. Marshalk and C. Stumm, Bull. Soc. Chim. France **15**, 418 (1948).
3. Y. Matsunaga, J. Chem. Phys. **42**, 2248 (1965).
4. E.P. Goodings, D.A. Mitchard, and G. Owen, J. Chem. Phys. Perkin Trans. **1**, 1310 (1972).
5. M.P. Gorishnyi, Ukr. Fiz. Zh. **47**, 711 (2002).
6. M.P. Gorishny, Ukr. Fiz. Zh. **51**, 339 (2006).
7. A.L. Briseno, Q. Miao, M.-M. Ling, C. Reese, H. Meng, Zh. Bao, and F. Wudl, J. Am. Chem. Soc. **128**, 15576 (2006).
8. M.P. Gorishnyi, Ukr. Fiz. Zh. **52**, 1154 (2007).

9. P. Lutsyk and Ya. Vertsimakha, *Mol. Cryst. Liq. Cryst.* **426**, 253 (2005).
10. A.L. Briseno, S.C.B. Mannsfeld X. Lu, Y. Xiong, S.A. Jenekhe, Zh. Bao, and Y. Xia, *Nano Lett.* **7**, 668 (2007).
11. V.D. Park, J.Ah. Lim, H.S. Lee, and K. Cho, *Materials Today* **10**, N 3, 46 (2007).
12. M.P. Gorishnyi, M.V. Kurik, and L. Libera, *Ukr. Fiz. Zh.* **32**, 1013 (1987).
13. M.P. Gorishnyi and P.A. Kondratenko, *Ukr. Fiz. Zh.* **34**, 839 (1989).
14. E.A. Silinsh, *Organic Molecular Crystals: Their Electronic States* (Springer, Berlin, 1980).
15. V.S. Fomenko, *Emission Properties of Materials* (Naukova Dumka, Kyiv, 1981) (in Russian).
16. E.A. Silinsh, M.V. Kurik, and V. Capek, *Electronic Processes in Organic Molecular Crystals. Localization and Polarization Phenomena* (Zinatne, Riga, 1988) (in Russian).

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ВОЛЬТ-АМПЕРНІ ХАРАКТЕРИСТИКИ, РЕЛАКСАЦІЙНІ ВЛАСТИВОСТІ І ФОТОЧУТЛИВІСТЬ ПЛІВОК ПОЛІТІОПЕНТАЦЕНУ

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Резюме

Вперше спостерігали гістерезис темнових вольт-амперних характеристик (ВАХ) плівок політіопентацену (ПТП), товщиною 1540 нм у сендвічних комірках ІТО(ПТП)Аg при кімнатній температурі і напругах 0–10 В. Встановили, що при негативній полярності ІТО-електрода густина темнового струму J зменшується до стаціонарного значення із сталими часу $\tau_1 = 10$ с і $\tau_2 = 150$ с. При позитивній полярності цього електрода після спаду J з $\tau_1 = 10$ с спостерігається його зростання з $\tau_2 = 150$ с. Часові залежності J , густини струму короткого замикання J_{sc} , фотоструму J_{ph} і алгебраїчної суми $J_{sc} + J_{ph}$ зумовлені релаксаційними змінами величини просторових приелектродних зарядів. Фоточутливість S_0 плівок ПТП при освітленні монохроматичним світлом 1,51 еВ (об'ємна фотогенерація) у п'ять разів більша від такої для світла 1,77 еВ (приелектродна фотогенерація). Приелектродна фотогенерація характеризується горизонтальною і лінійно зростаючою ділянками залежності $S_0(V)$, що зумовлені, відповідно, лінійною і квадратичною змінами $J_{sc} + J_{ph}$ від напруги V . Для об'ємної фотогенерації ця сума зв'язана із V лінійною залежністю.