PROPERTIES OF HETEROJUNCTIONS BASED ON INORGANIC AND ORGANIC SEMICONDUCTORS: POLYPHENYLACETYLENE—InSe:Ag HETEROSTRUCTURE

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The electrical and photovoltaic properties of heterojunctions based on InSe—PPA(polyphenylacetylene) are studied. The spectra of photosensitivity and volt-farad characteristics are investigated. The height of the potential barrier obtained from the volt-ampere and volt-farad properties is equal to 0.61 eV. It is found that the optical properties of the heterostructure are caused mainly by processes in InSe. The energy diagram of the InSe—PPA heterojunction is build.

For the last decade, the photosensitive conjugated polymers have a wide practical application as base materials for solar cells, detectors of different types of radiation, and light emissive devices [1—3]. These polymers exhibit a semiconductor property [4]; the reason for that is the existence of conjugated π-electron bonds. Under the overlap of p_z-orbitals of a carbon atom, the π-band is splitted into two, π and π^*, bands. Since each band can hold two electrons per atom with spin up and spin down, the difference between the energies of the higher occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is the energy of the π—π^* transition, which may be associated with the band gap energy E_g [4]. For most polymer semiconductors, E_g is in the range of 1.5—3 eV [1, 4], which provides their perspective for the use in optical devices operating in the visible range of the spectrum.

At the excitement of a conjugated polymer, an exciton appears. To convert the optical energy to the electric one, the process of separation of an exciton to an electron and a hole should occur. The possible mechanism of such a separation can be related to the existence of a potential barrier at the polymer—metal electrode interface. A conventional device consists of a polymer with two electrodes on both sides with different work functions. Excitons decay on the potential barrier, and electrons and holes move in the opposite directions: electrons move to the electrode with a lower work function, and holes move to that with a higher work function.

Unfortunately, the separation of charges in such devices at the polymer—electrode interface is low-effective because of a high density of admixtures that act as exciton traps [1].

We investigate the systems based on conjugated polymer—semiconductor with layered crystal structure of the $\mathrm{A^{III}B^{VI}}$ type to research their potentiality to be used as solar cells. Because of the crystal structure features, these materials don't need the precise mechanical and chemical processing of the surface and resist to adsorb extraneous atoms or molecules. The absence of cut bonds on the surface ensures a low rate of recombination. One of those materials, InSe (the energy gap is equal to 1.2 eV), is highly photosensitive in the visible and infrared ranges [5], which make it perspective for the creation of solar cells.

As polymer materials suitable to the photo-power generation in heterostructures, the functionalized polyphenylenevinylene, polythiophene, polyaniline and polypyrrole [1—4] are intensively studied. However, in the development of photosensitive heterostructures, a small attention is given to polyacetylene polymers, particularly, to PPA, which is characterized by a significant photoconductivity [6, 7]. The use of PPA in heterojunctions with InSe can widen the spectral sensitivity in the ultra-violet region due to the high photosensitivity of the polymer [6] in this spectral range. In addition, the developed methods of synthesis and doping of PPA allow one to significantly change its conductivity [7, 8]. The aim of this work is to create heterojunctions based on p-InSe—PPA and to investigate their electrical and photoelectrical properties. So we have researched the current-voltage and volt-farad characteristics (accordingly VAC and

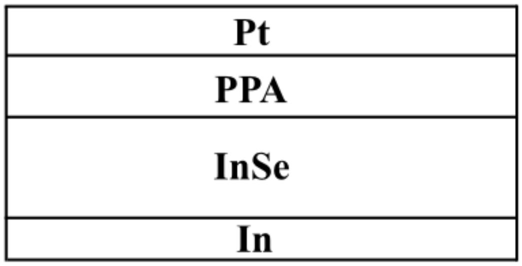

Fig.1. Side view of a heterojunction based on the InSe—PPA heterostructure

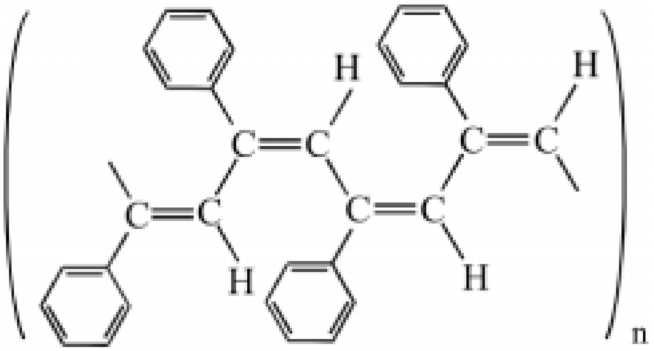

Fig. 2. Chemical structure of *trans*-polyphenylacetylene

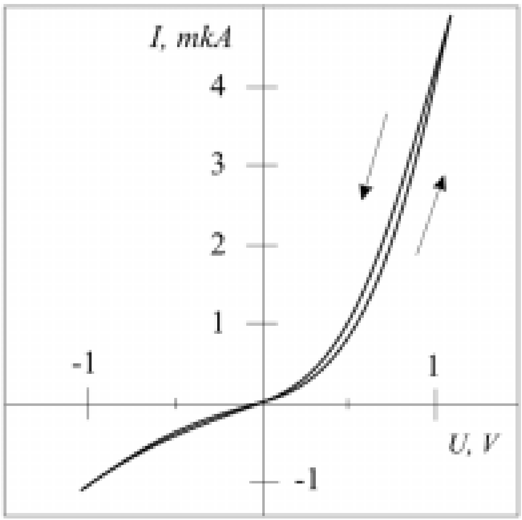

Fig. 3. Current-voltage characteristics of PPA—InSe heterostructure at the temperature $T = 293$ K

VFC) of the created heterostructures, as well as their spectral and energetic photosensitive properties.

The scheme of the researched heterojunction based on the InSe—PPA structure is presented in Fig. 1. The base for it is a InSe single-crystal plate of 5×5 mm in size and $300 - 400$ μm in thickness. The single crystal was grown up by the Bridgman—Stockbarger method, and then was split into plates. The plates were doped by silver to provide the p-type of conductivity. The density of major charge carriers of InSe at room temperature is $2 \cdot 10^{13}$ cm^{-3}. By the electron-ray process, one side of a single crystal plate was covered by indium to create the contact electrode. On the another side, a layer of conducting polymer by 0.3—0.4 μm in thickness was coated.

The conducting polymer PPA, was obtained in an acetonitrile solution by the method of electrochemical polymerization of phenylacetylene [9]. The film was formed on the (InSe:Ag) single-crystal surface by the solution evaporation at room temperature under dynamic vacuum conditions. The conducting polymer was prepared in the form of p-doped trans-polyphenylacetylene [7, 8] as shown in Fig. 2. The energy gap of PPA is 2.5 eV [6, 7]. The PPA surface was covered by a semitransparent layer of platinum by the magnetron saw procedure. As a result, an isotype heterojunction of the p—p-type has been fabricated. The VAC and VFC of the heterojunction have been obtained with the use of an AUTOLAB equipment with GPES and FRA computer programs. In measuring VAC, the voltage change rate was 0.03 V/s. For the forward line of VAC, the negative and positive potentials were applied, respectively, to the platinum and In electrodes. The backward line of VAC was measured with the inverse potentials. A scanning was carried out from the zero voltage to the maximum positive value and then in the opposite direction to the maximum negative value and again to zero. To obtain VFC, the impedance of the InSe—PPA device was measured at the frequency $f = 5$ kHz. The capacity was obtained from the imaginary part of the impedance Z'' by the formula

$$C = \frac{1}{2\pi f Z''}.$$

The current photosensitivity was measured with light force from 5 to 120 W/m^2. To obtain the photosensitivity spectrum, we illuminated a heterojunction from the side of the semitransparent platinum film by a modulated light of a deuterium lamp DDS-30 at a modulation frequency of 300 Hz.

A typical static VAC of the InSe—PPA isotype heterojunction at the temperature $T = 293$ K is shown in Fig. 3. As seen, the device behaves itself as a conventional diode. The forward line of VAC corresponds to the positive potential on PPA. The presence of a small hysteresis of the forward line of VAC may be connected with the considerable influence of the

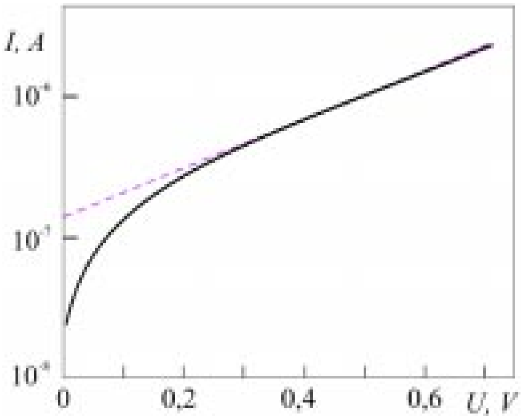

Fig. 4. Logarithmic dependence of the current across a PPA—InSe heterostructure on the forward bias voltage

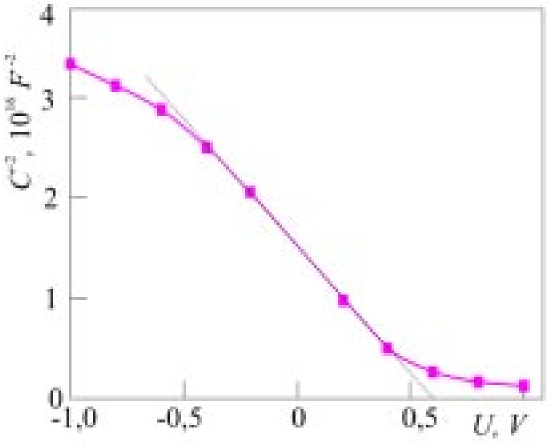

Fig. 5. FC of a PPA—InSe heterojunction obtained at a frequency of 5 kHz at a temperature of 293 K

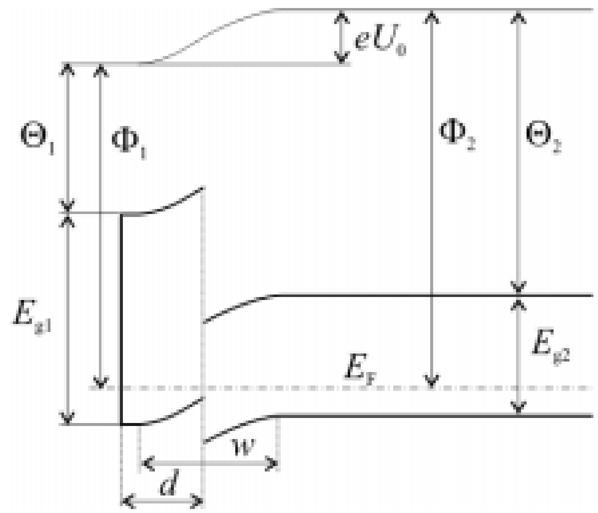

Fig. 6. Energy band diagram of an isotype heterojunction PPA—InSe:Ag

polarization and reorganization processes in the PPA polymer matrix under the action of an external field on the kinetics of rising and falling of the current in the cojugated polymer [10, 11]. For the forward bias at relatively low voltages, the VAC is well described by the thermoemission mechanism of charge transport (Fig.4):

$$I = I_0 \exp\left(\frac{eU}{\beta kT}\right),$$

where the coefficient $b \approx 10$ and $I_0 = 1.39 \cdot 10^{-7}$A. For relatively high voltages (above 0.7 V), the linear section is observed. It is found that the voltage of the cutoff current is $U_0^{(I)} = 0.63$ V.

The aim of the capacity measurements was to define the transition character and determine a zone warping in the transition. In Fig. 5, we present the VFC of the investigated structure for the reverse bias at a temperature of 293 K. On the VFC, the section of a linear dependence, $C^{-2} = f(U_r)$, which indicates a sharp character of transitions is observed. It is established that the capacity cutoff voltage found by the extrapolation of the linear plot to zero capacity is $U_0^{(C)} = 0.61$ V and defines a total zone warping in the heterojunction area. This value is close to the cutoff current voltage, which indicates a small density of states at the heterojunction interface.

We have built the energy zone diagram for an isotype heterojunction based on InSe(:Ag)—PPA (Fig. 6). To build this diagram, a data on the electron affinities of PPA ($\Theta_1 = 2.6$ eV [6]) and InSe ($\Theta_2 = 4.6$ eV [5]), PPA and InSe energy gaps ($E_{g1} = 2.5$ eV [6, 7]) ($E_{g2} = 1.2$ eV [5]), and work function for PPA $\Phi_1 = 4.9$ eV were used [6]. The Fermi level position in InSe:Ag ($E_{\mathbf{F}} = 0.3$ eV) was estimated by using the known density of holes and the relation for the density of carriers in a nondegenerated semiconductor:

$$p = 2\left(\frac{m_p kT}{2\pi h^2}\right) \exp\left(-\frac{E_{\mathrm{F2}}}{kT}\right),$$

where the effective mass of holes is $m_p = 0.73 m_0$ [5]. The total warping of zones found from the energy zone diagram of the heterojunction is 0.61 eV that is supported by experimental data.

Because of the absence of the reliable data on the effective mass of holes and permittivity of PPA, we cannot exactly calculate a bulk charge distribution for

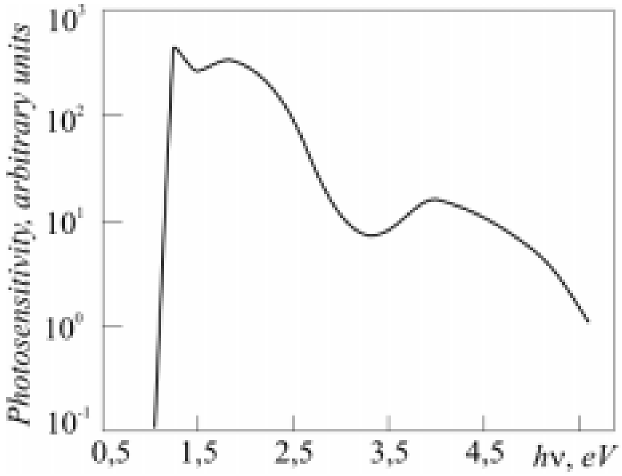

Fig. 7. Photosensitivity spectrum of a PPA—InSe heterostructure in the photovoltaic regime at room temperature

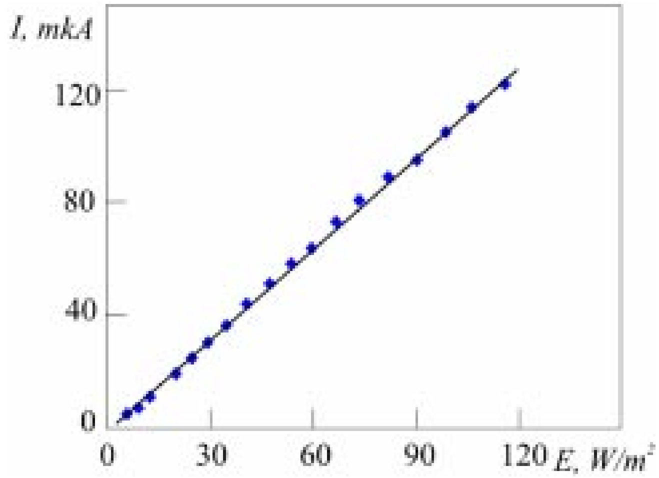

Fig. 8. Short-circuit current dependence in a PPA—InSe heterostructure on the lighting with white light

both components of the heterojunction. But the estimation of the total thickness for the bulk charge area gives a value of order of 5 μm. Since the thickness of the PPA layer isn't more than 0.5 μm, we can assert that the bulk charge area in PPA occupies its whole thickness.

The heterojunction photosensitivity spectrum in the photovoltaic regime at room temperature obtained at the lighting of the heterostructure from the side of PPA is shown in Fig. 7. The spectrum covers a wide interval of photon energies (from 1 to 5.5 eV). In the spectrum, three well-pronounced maxima connected with the light absorption by both PPA and InSe layers are present. The low-energy edge of the photosensitivity is restricted by the InSe energy gap. The high-energy part of the spectrum is determined by the photosensitivity of PPA, whose spectral dependence is correlated with the absorption spectra of this material [6, 7]. In this part of spectrum, two maxima are present. One maximum is consistent with the PPA energy gap, and second one is in agreement with a rapid increase in the absorption at photon energies higher than 4 eV. The reason for this may be in that the heterojunction lode depth from the side of PPA is small (it is determined by the PPA layer thickness) as compared to the diffusion length of charge carriers in this direction. So, the bulk charge distribution covers the whole thickness of the PPA layer. In Fig. 8, the dependence of the photocurrent (in the short-circuit regime) on the lighting of an InSe—PPA heterojunction by white light is present. As seen from the plot, the photocurrent exhibits a linear dependence on the light intensity in contrast to other organic photoreceivers characterized by a nonlinear behavior [12]. This allows us to suggest that the photosensitivity of the investigated heterostructure is mainly caused by nonequilibrium processes runnung in InSe (:Ag). This assumption is confirmed by the spectral distribution of the photosensitivity (see Fig. 7), because the highest photosensitivity is observed in the spectral range corresponding to the generation of nonequilibrium charge carriers namely in InSe. It is obvious that, in this case, the separation of nonequilibrium charge carriers generated in InSe occurs at the expense of the recombination of nonequilibrium electrons collected at the peak of the InSe conduction band near the boundary of a heterojunction with holes at the peak of the valence band of PPA through the interface local levels in the band gap. In [13], that the enhancement of the photosensitivity of an isotype p—p-heterojunction based on GaSe—InSe was observed as the result of a similar mechanism.

Thus, for the first time, an isotype p—p heterojunction based on polyphenylacetylene–InSe(:Ag) has been created and investigated. The values of the potential barrier of such a structure, which were obtained from the volt-ampere and volt-farad characteristics, coincide and are equal to the rated value of 0.61 eV. The photosensitivity spectra of the heterojunction covers a vast range (from the ultraviolet to near infrared region), which makes it perspective for the development of solar cells.

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ВЛАСТИВОСТІ ГЕТЕРОПЕРЕХОДІВ НА ОСНОВІ НЕОРГАНІЧНИХ ТА ОРГАНІЧНИХ НАПІВПРОВІДНИКІВ: ГЕТЕРОСТРУКТУРА ПОЛІФЕНІЛАЦЕТИЛЕН — InSe:Ag

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Резюме

Розглянуто електричні і фотоелектричні властивості гетеропереходів на основі поліфенілацетилену(ПФА)—InSe:Ag. Знайдено величину потенціального бар'єра, отримано спектр фоточутливості, досліджено вольт-фарадні властивості зразків. Отримані на основі вольт-амперних (ВАХ) і вольт-фарадних (ВФХ) характеристик величини потенціального бар'єра такої структури узгоджуються між собою і збігаються з розрахованим значенням 0,61 еВ. Знайдено, що оптичні властивості гетероструктури визначаються в основному процесами у InSe. Побудовано енергетичну зонну діаграму ізотипного гетеропереходу ПФА—InSe:Ag.