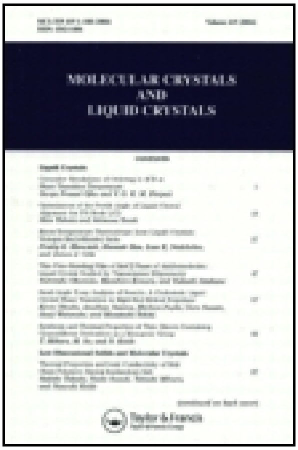

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Photovoltaic Properties of Conducting Polymer-(InSe) Heterostructures

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The investigation of heterojunctions based on conductive polymer PPA or PAN and InSe has been reported. The temperature dependence of the saturation current was carried out to obtain the barrier height of the investigated structures. The barrier height φ_0 has been found to be equal to 0.6 eV and 0.83 eV for InSe-PPA and InSe-PAN, respectively. For the InSe-PPA heterostructure, the higher power conversion efficiency than that for the InSe-PAN heterostructure at a light intensity of $50\,mW/cm^2$ has been obtained.

Keywords: conducting polymer; heterostructure; photovoltaic

INTRODUCTION

Inorganic-organic semiconductor devices have been the subject of investigations during the last few years, because of their low cost and the simplicity of technology. The fabrication of such devices requires a proper combination of materials and processing protocols.

We investigate the systems based on conjugated polymer-semiconductor with a inorganic layered crystal structure of $A^{III}B^{VI}$ type to research their potential use as solar cells. A wide range of

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conducting polymers has been described in the literature [1]. As organic materials, we used the conjugated polymers such as polyaniline (PAN) and polyphenylacetylene (PPA) which are interesting owing to their electrical and optical properties [2]. Such polymers are stable in air, soluble in most organic solvents, and have many interesting properties such as non-linear optical properties and their potential use in semiconductor, photoreceptor, and chemical sensor devices [3,4].

Polyaniline has been studied for the use as a hole injection layer in OLEDs and PLEDs from the early 1990s till now [5–7]. However, there was neither broader scientific research, nor industrial development focused on the topic of using ones on InSe heterostructures. Moreover, in the development of photosensitive heterostructures, polyphenylacetylene which is characterized by a significant photoconductivity [8,9] had a lack of study. The use of PPA in heterojunctions with InSe gives a possibility to widen the spectral sensitivity in the ultra-violet region due to the high photosensitivity of polymer absorption [10] in this spectral range. Besides that, the developed methods of PPA synthesis and doping allow one to significantly change its conductivity [11].

Because of crystal features, semiconductors of $A^{III}B^{VI}$ type don't need a precise mechanical or chemical processing of the surface and are resistive to adsorb strange atoms or molecules. The absence of cut bonds causes a slow recombination process. One of those materials, InSe (the energy gap of 1.2 eV), is highly photosensitive in the visible and infrared ranges [12], which makes it suitable for the creation of solar cells.

The aim of this work is to create heterojunctions based on *p*-InSe-PPA and *p*-InSe-PAN and to investigate their electrical and photoelectrical properties. We have researched the current-voltage characteristics of created heterostructures and their spectral and energetic photosensitive properties for their application as solar cells.

EXPERIMENTAL

In the present work, the isotype "*p*-*p*"-heterojunctions based on a layered single crystal, InSe (:Ag), and a conducting polymer, polyphenylacetylene (PPA) or polyaniline (PAN), are created for the first time. The InSe doping by silver provides the p-type conductivity with the concentration of majority carriers of $2 \times 10^{13}\,\mathrm{cm}^{-3}$ at room temperature. In order to obtain the lower resistance in series at a constant area of photo-cell saving, the sample of InSe (:Ag) was designed in the form of thin rectangular plates (0.2 mm in thickness) of $5 \times 2.5\,\mathrm{mm}^2$ in dimension, whose biggest facets create the (100) shear plane. By the electron-ray process, one side of a single crystal plate was covered by an In film that formed the Ohmic contact with InSe. The layer of conjugated polymer (PPA or PAN) of 0.3–0.4 μm in thickness covered the other side of the plate. On the polymer film, a semitransparent layer of platinum was applied by the magnetron saw procedure.

Conducting polymer PPA in the form of *p*-doped trans-polyphenylacetylene (the energy gap of 2.5 eV [8,9]) was obtained in an acetonitrile solution by the method of electrochemical polymerization of phenylacetylene according to [11].

Other conducting polymer PAN was used in the nondoped form of emeraldine base, which provides the maximal photosensitivity of this polymer [12]. PAN (base) was dissolved in DMF to obtain the saturated solution.

The polymer films were cast on the (InSe:Ag) single crystal surface by the solution evaporation at room temperature under dynamic vacuum conditions.

The view of the researched heterojunction based on the InSe conductive polymer structure is presented in Figure 1.

In the present work, the mechanisms of charge transport in the heterostructures InSe(:Ag)-conducting polymers were studied. These mechanisms are essentially defined by a value of heterostructure dynamic series resistance which depends on the fabrication technology, resistivity of conducting polymers, and doping method. The conductivity of polymers is defined by the concentration of charge carriers and their mobility [6,7]. It depends on the length of conjugation and the type and level of doping, which provides a significant charge delocalization. Specific bulk conductivities in the films of conducting polymers in the present work were $\sigma_1 = 3.5 \times 10^{-6}\,\mathrm{Sm/m}$ (PPA), $\sigma_2 = 4.7 \times 10^{-9}\,\mathrm{Sm/m}$ (PAN base). The use of two conducting polymers

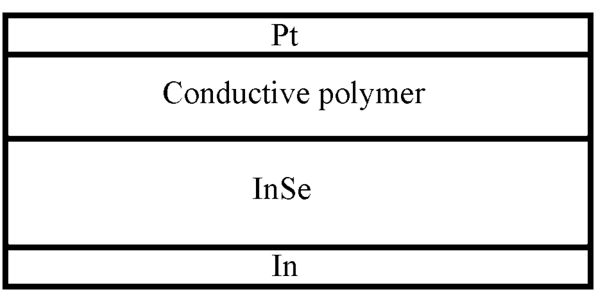

FIGURE 1 Side view of a heterojunction based on InSe-PPA (PAN) heterostructure.

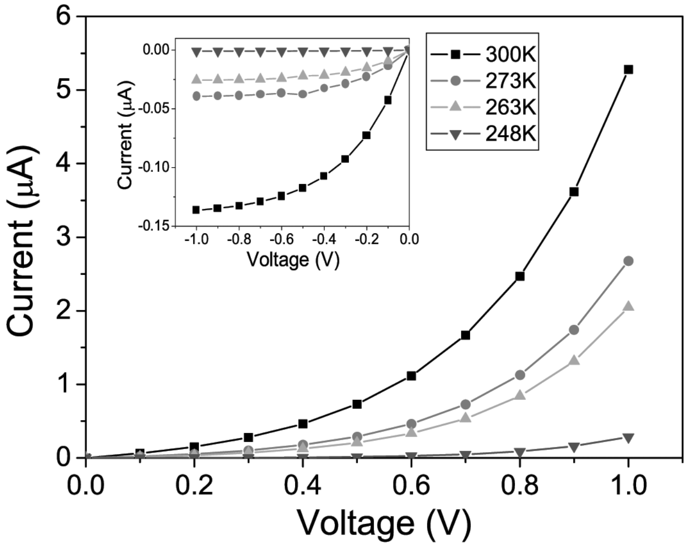

FIGURE 2 Current–voltage (I–V) dark characteristics of InSe-PPA structures under forward bias (reverse bias on the frame).

by different chemical structures and types of charge carriers (solitons in PPA and polarons in PAN) can give a new information about charge transport processes in heterojunctions based on organic and inorganic semiconductors.

The current–voltage (I–V) dark characteristics of the InSe-PPA and InSe-PAN structures are shown in Figures 2 and 3.

Depending on the nature of contacts, a number of mechanisms can effect the current–voltage characteristics of the proposed heterojunctions. For a semiconductor device with one Ohmic and one Schottky contact, the current–voltage characteristics may be described by the Shockley equation [13]

$$I = I_s \exp\left(\frac{q}{nkT}(V - IR_s)\right), \tag{1}$$

where n is the ideality factor, I_s – the saturation current, k – Boltzmann's constant, e the charge of an electron, R_s – serial resistance, and T – the absolute temperature.

So, the dynamic resistance of the structure is expressed as

$$r = \frac{dV}{dI} = \frac{nkT}{qI} + R_s. \tag{2}$$

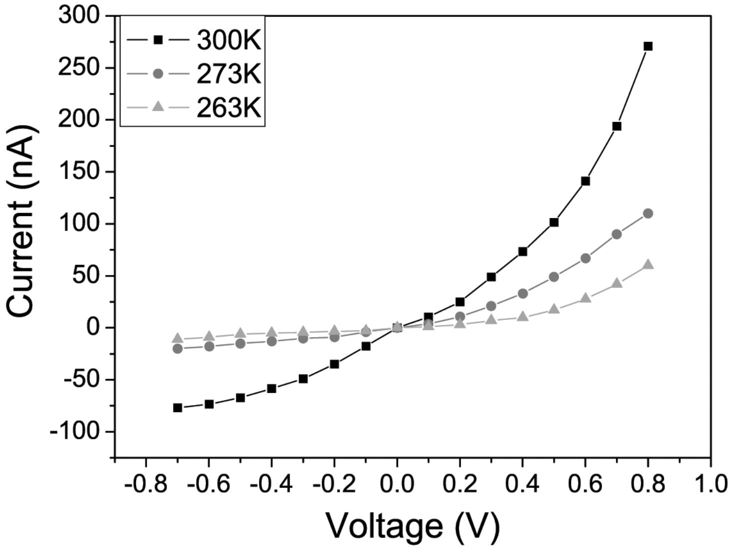

FIGURE 3 Current–voltage (I–V) dark characteristics of InSe-PAN structures.

The saturation current I_s can be defined as

$$I_s = AT^2 \exp\left(-\frac{\varphi_0}{kT}\right), \tag{3}$$

where φ_0 is the barrier height and A is a constant.

The temperature dependence of the saturation current gives a possibility to obtain the barrier height of the investigated structures, $\varphi_0 = 0.6\,\text{eV}$ for InSe-PPA and $\varphi_0 = 0.83\,\text{eV}$ for InSe-PAN, which corresponds to barrier heights found from capacitive measurements. The serial resistance R_s for the InSe-PPA heterojunction is essentially larger than that for the InSe-PAN heterojunction, both being calculated from the current–voltage characteristics.

We have built an energetic zone diagram for the isotype heterojunction based on the InSe(:Ag)-conductive polymer (Fig. 4). To build this diagram, the data on electron affinities of PPA ($\Theta_1 = 2.6\,\text{eV}$ [8]) and InSe ($\Theta_2 = 4.6\,\text{eV}$ [12]), PPA, PAN, and InSe energy gaps [$E_{g1} = 2.5\,\text{eV}$ (PPA), $E_{g1} = 2.4\,\text{eV}$ (PAN) [6,7], $E_{g2} = 1.2\,\text{eV}$ (InSe) [12]], and work functions for PPA and PAN [$\Phi_1 = 4.9\,\text{eV}$ (PPA) and $\Phi_1 = 4.8\,\text{eV}$ (PAN) [8]] were used. The estimation of a Fermi level position in InSe:Ag ($E_F = 0.3\,\text{eV}$) was made using the known

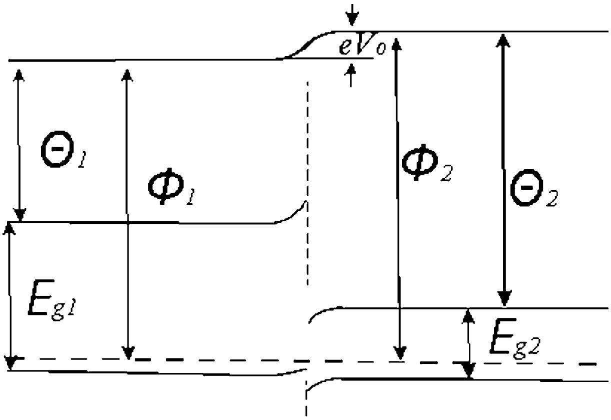

FIGURE 4 Energetic band diagram of isotype heterojunction conducting polymer InSe:Ag.

relation for the densities of holes and carriers for a nondegenerate semiconductor:

$$p = 2\left(\frac{m_p \mathrm{k}T}{2\pi\hbar^2}\right)^{3/2} exp\left(-\frac{E_{\mathrm{F2}}}{\mathrm{k}T}\right).$$

Here, the effective mass of holes is $m_p = 0.73\, m_0$ [14]. The total warpings of zones found from the diagram of energetic zones at the boundary of a heterojunction are $\varphi_0 = 0.6\,\mathrm{eV}$ for InSe-PPA and $\varphi_0 = 0.83\,\mathrm{eV}$ for InSe-PAN, which is supported by experimental data.

As was shown, the I–V dependences under illumination, current density I_{s0}, and open circuit voltage U_{xx} for the InSe-PPA structure essentially differ from similar parameters for the InSe-PAN structure. The I_{s0} and U_{xx} dependences on light intensity can be described as [14]

$$I_{so} = gP^m, \tag{4}$$

$$U_{xx} = \frac{nkT}{q}\ln\left(const\frac{P}{I_s}\right), \tag{5}$$

where P is the light intensity, g is a constant proportional to the absorption of light in the material.

The dark saturation current I_s is defined by the charge transport mechanism. As seen from Figure 5 (2), the current density as a function of white light intensity for the InSe-PPA heterojunction has a linear character. Thus, $m = 1$, and the linear generation of nonequilibrium charge carriers takes place. But, for the InSe-PAN heterojunction, the current density as a function of white light intensity has

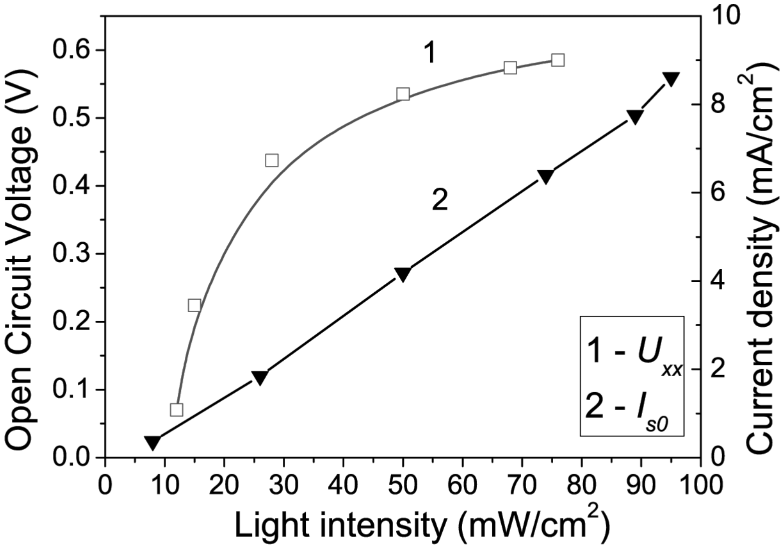

FIGURE 5 Open circuit voltage (1) and current density (2) as functions of white light intensity for the InSe-PPA heterojunction.

sublinear character [Fig. 6 (2)]. In this case, $m = 0.67$, which can be explained by the generation of non-equilibrium charge carriers in the space-charge region and in bulk of InSe, which has high photoconductivity. This fact caused the dependence of the serial resistance on light intensity. A shift of the experimental dependence of the open circuit voltage $U_{xx}(P)$ on light intensity is caused by the serial resistance influence and the recombination process that is defined by n which is, in our case, nearly 2 [Figs. 5 and 6 (1)].

As seen from the plot, the photocurrent at low light intensities exhibits a linear dependence on light intensity in contrast to other organic photoreceivers characterized by a nonlinear behavior [14].

It gives the grounds to suggest that the photosensitivity of the investigated heterostructures is mainly caused by a non-equilibrium process in InSe (:Ag). It is obvious that, in this case, the separation of non-equilibrium charge carriers, generated in InSe, proceeds by the recombination of non-equilibrium electrons collected at a peak of the InSe conduction band near the boundary of the heterojunction with holes at a peak of the valence band of PPA or PAN through the interface local levels in the band gap.

The power conversion efficiencies of the proposed heterostructures were calculated at a light intensity of $50\,\mathrm{mW/cm^2}$ and are 2.2% and 0.7% for the InSe-PPA and InSe-PAN heterostructures, respectively.

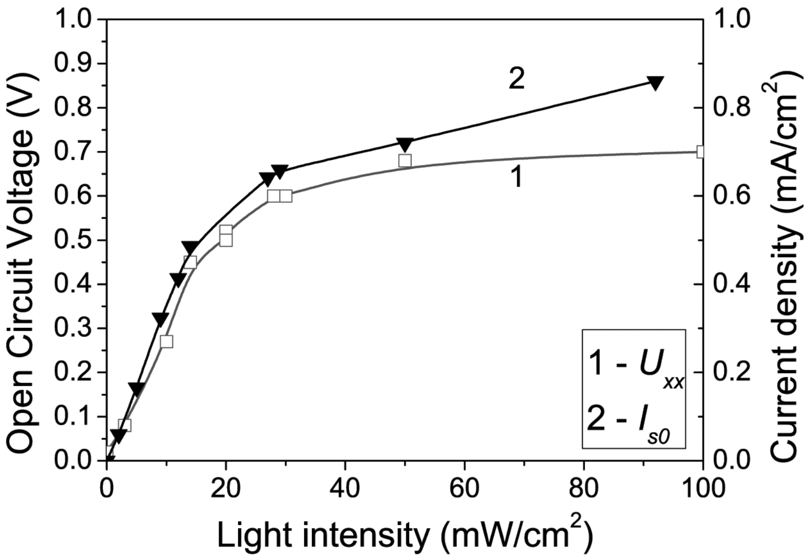

FIGURE 6 Open circuit voltage (1) and current density (2) as functions of white light intensity for the InSe-PAN heterojunction.

CONCLUSION

The development of a conducting polymer based on the PPA or PAN – InSe heterojunction has been reported. The stable reproducibility of electrical and photovoltaic characteristics has been detected. The barrier height φ_0 of the investigated structures has been found to be equal to 0.6 eV and 0.83 eV for InSe-PPA and InSe-PAN, respectively, which agrees well with our recent results from capacitive measurements. The linear behaviour of the current density vs. white light intensity has been found for InSe-PPA, whereas this dependence for the InSe-PAN heterojunction has been found to be sublinear ($m = 0.67$). It is concluded that superlinearity might be associated with the generation of non-equilibrium charge carriers in the space-charge region and bulk InSe.

For the InSe-PPA heterostructure, we have obtained the higher power conversion efficiency than that for the InSe-PAN heterostructure at a light intensity of $50\,\mathrm{mW/cm^2}$.

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