

OPTICAL AND PHOTOELECTRIC PROPERTIES OF PROPOLIS-LAYERED SEMICONDUCTOR (p-InSe) HETEROJUNCTION

S. I. Drapak*, A. P. Bakhtinov, I. T. Drapak^a, Z. D. Kovalyuk, M. V. Tovarnitsky

Frantsevich Institute of Material Sciences Problems, the National Academy of Sciences of Ukraine, Chernivtsi Department, 5, Iryna Vilde Str., 58001 Chernivtsi, Ukraine

^aChernivtsi National University, Physical Department, 2, Kotsyubinski Str., 58012 Chernivtsi, Ukraine

The spectra of optical absorption, photoluminescence in the spectral range 0.2 to 10 μm for thin propolis (an organic entity of biological nature) layers deposited onto various substrates, and spectral distribution of photosensitivity of propolis-p-InSe heterocontacts are investigated. In the optical absorption spectra measured at room temperature we have found an abrupt optical absorption edge (3.0÷3.25 eV) in the short-wavelength range and some typical absorption bands in the near IR range. In the room temperature photoluminescence spectra a maximum at 2.88÷2.96 eV was observed. It is shown that some of these structures have photosensitivity in the infrared region of the electromagnetic spectrum at $h\nu \leq 1.2$ eV.

(Received June 6, 2004; accepted March 23, 2005)

Keywords: InSe, Intrinsic oxide, Heterojunction, Photoelectrical properties

1. Introduction

Recently much attention was paid to heterocontacts (HCs) of semiconductors with organic substances of biological nature [1-3]. In such structures a biological layer acts as a wide-gap component which, like electrolytes, is used for formation of an energy barrier in semiconductor. Photogeneration of non-equilibrium carriers in such structures takes place at heterocontact interface or in bulk semiconductor, i.e. at the energy of incident photons $h\nu \geq E_g$, where E_g is the energy gap of a semiconductor. In [4,5] we have demonstrated the possibility to prepare heterocontacts between layered semiconductor p-InSe and propolis (P), an organic substance (produced by bees), with a room temperature photosensitivity at $h\nu \leq E_g$.

In this paper we present investigations of spectral distribution of photosensitivity for p-InSe/P HCs with thin P layers prepared in different ways as well as the results for optical absorption and photoluminescence of these layers.

2. Experimental procedure

Heterostructures were prepared on electrically homogeneous layered Cd-doped p-InSe single crystals ($p=10^{14} \text{ cm}^{-3}$ at 300 K) cleaved along the plane (0001). Because of the fact that the interlayer forces have molecular nature, mainly Van der Waals type, such layers have nearly perfect surfaces with a low density of dangling bonds can form heterocontacts with other semiconductors with low density of surface states at the interface [6]. HCs were prepared by deposition of P layers from an alcohol solution or melt onto fresh-cleaved InSe substrates with previously deposited ohmic Ag contacts. In order to receive homogeneously thick P films ($d < 30 \mu\text{m}$) a centrifugal procedure was applied. A heterocontact between p-InSe and a P alcohol solution was realized in a special vessel.

* Corresponding author: chimsp@unicom.cv.ua

Investigations of the optical absorption spectra of thin P films on substrates of BaF₂, sapphire, and high-resistive p-InSe have been carried out in the spectral range 0.3 - 10 μm .

The photoluminescence (PL) spectra were measured at excitation of the film structures with a nitrogen laser ($h\nu = 3.69$ eV).

The spectral distribution of photosensitivity of the HCs was measured in the spectral range 0.3 - 10 μm at illumination with a non-polarized monochromatic light directed on both the frontal P layer and InSe substrate. All the measurements were performed at $T=300$ K.

3. Results and discussion

Earlier, we established [5] that the equilibrium current-voltage characteristics of InSe/P heterocontacts show a well-defined rectification effect and at the contact with the semiconductor the biological entity (P) behaves as a material of p-type conductivity.

The spectral dependences of the photoconversion relative quantum efficiency normalized to the amount of incident photons are shown in Fig. 1 for the heterocontacts between p-InSe and 96 % ethyl alcohol (a), p-InSe and a 10 % alcohol solution of P (b), p-InSe and a solid film of P deposited from an alcohol solution (c), and p-InSe and a film of P deposited from a melt (d).

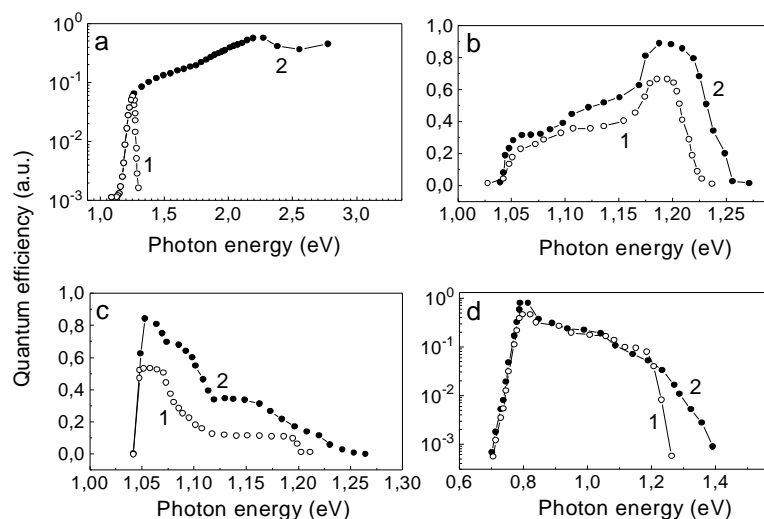


Fig. 1. Room temperature photocurrent quantum efficiency spectra for the heterocontacts p-InSe - 96 % ethyl alcohol (a), p-InSe - 10 % alcohol solution of P (b), p-InSe - solid propolis film deposited from an alcohol solution (c) and p-InSe - a P film deposited from a melt (d) at illumination directed at the back p-InSe side (1) and the frontal layer (2).

For the heterocontacts between p-InSe and ethyl alcohol, when the light beam is directed to the alcohol film, we have found the “window effect” typical for a semiconductor – electrolyte contact and the long-wavelength edge $h\nu \sim 1.2$ eV is in agreement with the value of E_g for InSe (curve 2 in Fig.1a). When the semiconductor side is illuminated, there appears a narrow peak with an abrupt short-wavelength edge (curve 1 in Fig.1a) caused by the increase of the optical absorption in the range of InSe direct band-to-band transitions at $h\nu > 1.2$ eV. For the p-InSe/P heterostructures some photosensitivity is observed at the energy of incident photons $h\nu < E_g$. Its spectral distribution and magnitude depend on the way of preparing the frontal layer, i.e. the state of aggregation of P films (Figs. 1b-1d). For the heterocontacts of p-InSe with solid state P films the long-wavelength edge and photosensitivity maximum are shifted to the low-energy range and for the heterocontact between p-InSe and a solid state P film deposited from alcohol solution (Fig. 1c) photosensitivity takes a value of 10^4 V/W. The shape of the spectral characteristics (Fig. 1d) and their coincidence at $h\nu < 1.2$ eV at illumination both the P and InSe sides indicate that photoexcitation occurs in the organic layer. The existence of such essential photosensitivity in this spectral range cannot be caused

by photogeneration from impurity states in the energy gap of p-InSe which have a small cross-section of optical absorption.

Fig. 2 shows the spectral dependences of the optical transmission of solid state P films deposited onto sapphire substrates from alcohol solution (curve 1) and melt (curve 2).

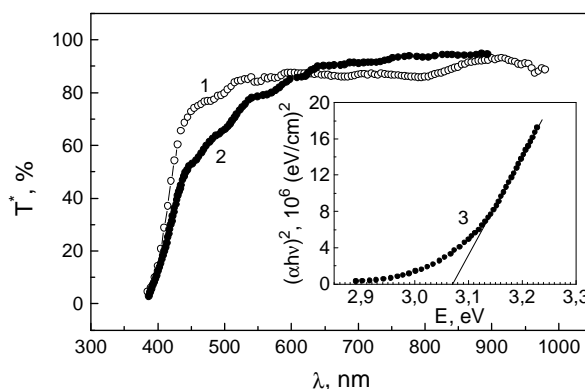


Fig. 2. Spectral dependences of optical transmission coefficient T^* for propolis films deposited from alcohol solution (1) and melt (2). In insert - extrapolation to zero of the curve representing the function $(\alpha h\nu)^2 = f(h\nu)$ (3). $T = 300$ K.

In the short-wavelength spectral range, corresponding to the electron transitions we have found an abrupt change of the absorption coefficient – the intrinsic absorption edge typical for organic semiconductors. From the absorption edge, the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LOMO) gap (corresponding to the band gap in semiconductor) was evaluated to be $E_g^{\text{opt}} \sim 3.07$ eV (Fig. 3, curve 3) by using a simple analysis with the assumption of a direct band gap, that is from the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) plot, where α is the absorbance.

From the measurements of conductivity of P films it is established that their dark conductivity is low and at $T=300$ K varies between 10^{-4} and 10^{-7} $\text{Ohm}^{-1}\text{cm}^{-1}$ depending on the state of aggregation. The temperature dependence of conductivity has an activated behaviour and in the temperature range 280 – 300 K is described by an activation energy of about 2.9 eV close to E_g^{opt} .

In the spectral range $0.5 < \lambda < 10$ μm the propolis films are transparent with a transmission coefficient $T^* \sim 90$ % at $d < 30$ μm . The wide absorption bands typical for vibrational spectra of condensed molecular media were observed in the spectral range $\Delta\lambda = 2.8 - 3.6$ μm .

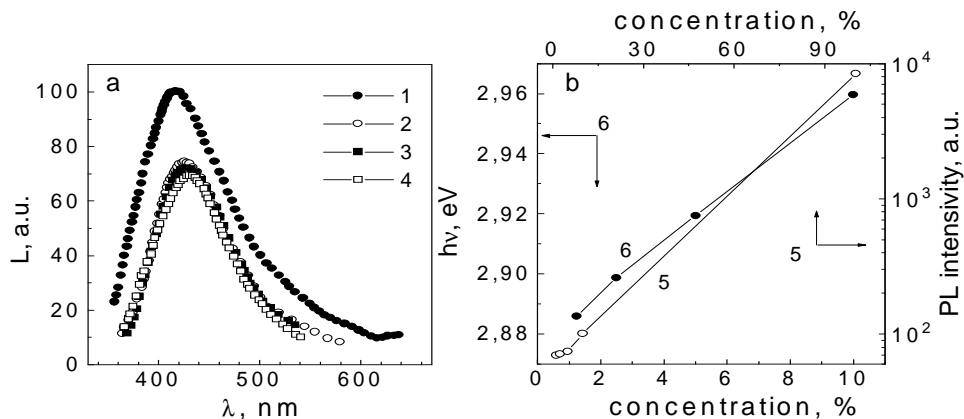


Fig. 3. Spectral distribution of photoluminescence (a) of propolis alcohol solution at different concentration of P, %: 1-10, 2-5, 3-2.5, 4-1.25 as well as PL intensity L (5) and maximum of PL peak location (6) vs propolis concentration in solution. $T = 300$ K.

The spectral dependences of photoluminescence of different propolis alcohol solutions are shown in Fig. 3a (curve 1 – 4). The concentration dependences of PL intensity L and PL peak location are shown in Fig. 3b (curves 5 and 6, respectively). As follows from the figure, the PL intensity increases with increasing propolis concentration and is the highest for the films deposited from alcohol solution (Fig. 3b, curve 5) with the largest concentration of P. For the amorphous samples of propolis being applied as the initial material at preparing P films (Fig. 4, curve 2) and for the P films deposited from alcohol solution (Fig. 4, curve 1) the PL maxima coincide. The solution concentration dependence of PL peak location (Fig. 3) can be caused by a field induced by the solvent molecules on the molecules of P components.

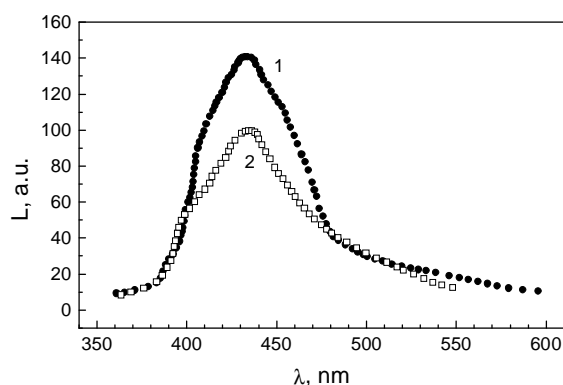


Fig. 4. Photoluminescence spectral distribution for initial composition of P (2) and films deposited from alcohol solution (1). $T = 300$ K.

4. Conclusions

From the measurements of electrical, optical, and photoelectric properties of p-InSe/propolis heterocontacts it is established that propolis, a molecular organic substance of biological nature, behaves itself in these structures as a p-type semiconductor with the energy gap $E_g \approx 3.0 - 3.1$ eV at $T = 300$ K.

Photogeneration in amorphous or quasi-crystalline films of propolis occurs because of the absorption of light by its molecules, formation of molecular Frenkel excitons and their subsequent dissipation at structural defects and impurity centers. Additionally, the direct photoionization of the impurity centers located in the energy gap is possible. The local trap levels in the energy gap of organic molecular systems have a structural origin. Therefore, the observed spectral distribution of the photoconductivity at $h\nu \leq 1.2$ eV depends on biological nature of propolis as well as method of preparing heterocontacts.

References

- [1] V. Yu. Rud', Yu. V. Rud', V. Kh. Shpunt, *Semiconductors* **31**, 129 (1997).
- [2] V. Yu. Rud', Yu. V. Rud', A. A. Vaipolin, I. V. Bodnar, N. Fernelins, *Semiconductors* **37**, 1321 (2003).
- [3] S. I. Drapak, Z. D. Kovalyuk, *Tech. Phys. Lett.* **30**, 73 (2004).
- [4] S. I. Drapak, A. P. Bakhtinov, V. B. Orletskii, Z. D. Kovalyuk, V. V. Netyaga, *Proc. 2-nd Internat. Workshop on Quantum Well Infrared Photodetectors – QWIP*, Turin, Italy, September 13-17, 2002, P. 58.
- [5] S. I. Drapak, V. B. Orletskii, Z. D. Kovalyuk, V. V. Netyaga, *Tech. Phys. Lett.* **29**, 867 (2003).
- [6] A. M. Goodman, *J. Appl. Phys.* **34**, 329 (1963).