

# Photoelectrochemical processes at electrolyte–multinary layered semiconductor interfaces

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## Abstract

The electric and photoelectric properties of the electrolyte–semiconductor interface in the chains formed by metal auxiliary electrode–electrolyte–multinary layered semiconductors have been investigated. The dependencies of flatband potential  $\varphi_{fb}$  and contact potential  $\varphi_c$  at the electrolyte–semiconductor interface on the concentration of  $S^{2-}/S_2^{2-}$  ions and the value of pH of the electrolyte were studied. The values of the photopotential up to 0.6 V and the short circuit current up to 1 mA/cm<sup>2</sup> have been obtained. It was shown that the photoelectrode corrosion is practically absent. An energetic diagram for the investigated system is proposed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrochemical cells; Multinary semiconductors; Photoelectric properties

## 1. Introduction

The problem of utilization of ecologically pure solar energy becomes more and more topical because of progressive exhaustion of fossil fuel reserves and the environment pollution. Besides solid state converters of solar energy into electric one, the operation which is based on electric charges separated by the electrostatic field in homojunctions, heterojunctions or Schottky diodes is intensively studied. The conversion by means of photoelectrochemical reactions in special devices containing electrodes from semiconductor materials is also intensively studied later [1–5].

The main distinction of such converters consists of the fact that the light generated carriers transmit their energy to chemical substances which are found in electrolyte. To improve the technical characteristics of the photoelectrochemical converters, it is necessary to know the energetic diagram of the electrolyte–semiconductor interface. The construction of the energetic diagram requires the knowledge of the energetic flatband  $\varphi_{fb}$  value and sign as well as  $\varphi_{fb}$  dependence on different factors.

From our viewpoint the multinary layered sulphides and sulphoselenides as photoelectrodes and electrolyte containing sulphides and sulphoselenides redox pair are perspective for the investigation and for the creation of photoelectrochemical solar cells. The results of the study of electrical and photoelectric properties of photoelectrochemical cells

on the base of such photoelectrodes and electrolyte are described in this paper.

## 2. Experimental

The layered multinary semiconductor crystals ZnIn<sub>2</sub>S<sub>4</sub>, Zn<sub>2</sub>In<sub>2</sub>S<sub>4</sub>, Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>, Zn<sub>3</sub>InGaS<sub>6</sub> and CuIn<sub>5</sub>S<sub>3</sub>Se<sub>5</sub> were used as photoelectrodes. These crystals have been obtained by chemical transport reactions method using iodine as the transport agent [6,7]. They are stable in atmosphere, irrespective of its humidity degree on acidic intensity and alkaline solutions at temperatures up to 500 K. For the conversion of the solar energy into an electric one while using photoelectrochemical solar cells, we can simultaneously use every crystal as photoelectrode from the multinary layered sulphides and sulphoselenides in combination with the electrolyte containing the sulphides and sulphoselenides redox pair.

The n-type ZnIn<sub>2</sub>S<sub>4</sub> semiconductor, as well as other studied crystals of this type, have a stratified structure. The cleavage plane is perpendicular to the C (0001) crystallographic axes, the electron concentration is 10<sup>12</sup>–10<sup>14</sup> cm<sup>-3</sup> [6]. The cleaved surface of the ZnIn<sub>2</sub>S<sub>4</sub> crystals contains a monoatomic layer of sulphur with a perfect structure which ensures a small velocity of surface recombination.

The main parameters of layered multinary semiconductor crystals which have been used as photoelectrodes are shown in Table 1. The resistivity was measured with the

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Table 1  
Parameters of layered multinary semiconductors

Semiconductor	Band gap (eV)	Permittivity	Resistivity ( $\Omega$ cm)
ZnIn <sub>2</sub> S <sub>4</sub>	2.8	8.90	$5 \times 10^7$
Zn <sub>2</sub> In <sub>2</sub> S <sub>5</sub>	3.0	8.63	$2 \times 10^8$
Zn <sub>3</sub> In <sub>2</sub> S <sub>6</sub>	3.1	8.46	$6 \times 10^8$
Zn <sub>3</sub> InGaS <sub>6</sub>	3.26	7.83	$3 \times 10^9$
CuIn <sub>5</sub> S <sub>3</sub> Se <sub>5</sub>	1.5	–	$1 \times 10^5$

help of terraometer on the samples with plate electrodes from indium deposited in vacuum.

The investigation of the electric properties of the electrochemical chain In–carbon–H<sub>2</sub>O(S<sup>2-</sup>/S<sub>2</sub><sup>2-</sup>)-layered multinary semiconductor crystal–In, where the redox pairs in the electrolyte are the ions S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup>, was carried out in an organic glass cell with thin walls of 1 mm thickness (see Fig. 1).

The design of this cell permits an easy change of the photoelectrodes, with semiconductor plates of 80–100  $\mu$ m thickness. The photoelectrode was stuck to the external part of the cell wall, while the contact with the electrolyte was provided through an orifice in the wall. Two third of the cell volume was filled with an aqueous solution of the mixture of sodium sulphide and disulphide in the proportion 1:1. Al, Zn, In, Sn, Cu, Ag, Pt and C were used as auxiliary electrodes. The electrical properties were measured in the darkness at  $T = 300$  K. Photoelectrical measurements were performed by irradiating the photoelectrode through the electrolyte.

The  $\varphi_{fb}$  potential has been determined for different concentrations  $C_{Na_2S}$  of sodium sulphide and for different values of pH in electrolyte. The value of  $\varphi_{fb}$  was found by means of the establishment of the zero value of the surface conductivity when changing the electric field which is in between the photoelectrode and carbon auxiliary one [8]. At the same time current–voltage characteristics have been measured for different concentrations  $C_{Na_2S}$  and different values of pH. The values of the contact potential  $\varphi_c$  have

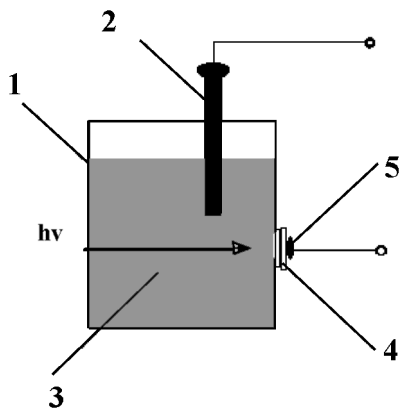


Fig. 1. The photoelectrochemical cell: (1) cell, (2) carbon auxiliary electrode, (3) aqueous solution of the mixture (Na<sub>2</sub>S–Na<sub>2</sub>S<sub>2</sub>), (4) single crystalline photoelectrode and (5) ohmic contact.

been found out extrapolating the linear part of the forward branch of the current–voltage characteristics.

The semiconductor compound ZnIn<sub>2</sub>S<sub>4</sub> was used as a certain type material when the mentioned measurements were provided. The results, obtained by implementing as photoelectrodes of other materials of this class, which are shown in Table 1, demonstrate generally the same regularities.

### 3. Results

For a qualitative description of the electric charge transport mechanism at the ZnIn<sub>2</sub>S<sub>4</sub>–H<sub>2</sub>O(S<sup>2-</sup>/S<sub>2</sub><sup>2-</sup>) interface it is necessary to underline the following. The polar structure of the water molecules (the permittivity  $\epsilon = 78$ ) determines the exothermic dissociation of these molecules in H<sup>+</sup> and OH<sup>-</sup> ions of the same concentration:  $C_{H^+} = C_{OH^-} = 10^{-7}$  gram – ion/l. At the same time there occurs exothermic dissociation of the sodium sulphide in Na<sup>+</sup> and S<sup>2-</sup> ions, which are partially or completely hydrated. The electrical conductivity of the electrolyte is determined only by the concentration and the mobility of ions which persist there. The electric neutral equilibrium state of the electrolyte is maintained by the following reactions:



The presence of the last reaction is confirmed by a specific smell of H<sub>2</sub>S especially when Na<sub>2</sub>S begins to dissolve in water. So, H<sup>+</sup>, OH<sup>-</sup>, Na<sup>+</sup>, S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> are present in the electrolyte.

The reactions (1)–(3) cause the decrease of H<sup>+</sup> in electrolyte; thus, pH decreases either. Further, electrolyte gains more alcalynic properties. The interchange of electrons in between the semiconductor and the electrolyte takes place at the ZnIn<sub>2</sub>S<sub>4</sub>–electrolyte interface. The rate of this interchange is much greater than the rate of ions interchange which is stopped by the sulphur monoatomic layer on the crystal surface. The positive space charge region due to ionized donor centres appears in the semiconductor at the interface [1,2]. In this region the energetic bands are deflected and a Schottky-type potential barrier is formed. The value of the energetic band deflection determines the flat-band potential which depends considerably on the S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> ions concentration in the electrolyte. The current which flows through the electrolyte–semiconductor interface is determined mainly by the presence of the Schottky barrier in ZnIn<sub>2</sub>S<sub>4</sub>. The direction of the reverse current corresponds to the electron flow from the interface to the semiconductor volume and their value is limited by the discharge velocity of S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> ions as in reaction (1). The analysed processes at the electrolyte layered semiconductor interface are consequently confirmed by the results of the electric and photoelectric measurements.

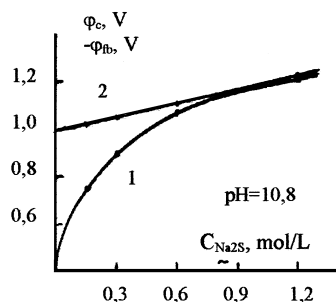


Fig. 2. The dependencies of the flatband potential  $\varphi_{fb}$  (1) and the contact potential  $\varphi_c$  (2) on the  $\text{Na}_2\text{S}$  concentration in the electrolyte  $T = 300\text{ K}$ ,  $\text{pH} = 10.8$ .

The dependence of both flatband potential  $\varphi_{fb}$  and contact potential  $\varphi_c$  on the concentration  $C_{\text{Na}_2\text{S}}$  value in the electrolyte as well as the pH value of the electrolyte at the interface electrolyte– $\text{ZnIn}_2\text{S}_4$  was investigated. The characteristics of  $\varphi_{fb}$  and  $\varphi_c$  are often used for the quantitative description of:

- the double electric layer of the semiconductor–electrolyte interface,
- the space charge region in the semiconductor near the interface,
- the potential drops in the double electric layer and in the space charge region, etc.

These potential drops in the dark thermodynamic equilibrium have the major influence on the electrical and photovoltaic properties at the semiconductor–electrolyte interface.

In Fig. 2 the dependencies of the flatband potential  $\varphi_{fb}$  and contact potential  $\varphi_c$  at the interface electrolyte– $\text{ZnIn}_2\text{S}_4$  for C as auxiliary electrode on the concentration  $C_{\text{Na}_2\text{S}}$ , using the AgCl reference electrode, are shown. The values of  $\varphi_{fb}$  are negative and they grow exponentially on the concentration up to 1.2 mol/l. These values were obtained at temperature 300 K in the dark. The values of  $\varphi_c$  grow linearly from 1.0 V at  $C_{\text{Na}_2\text{S}} = 0.15\text{ mol/l}$  up to 1.23 V at  $C_{\text{Na}_2\text{S}} = 1.2\text{ mol/l}$ . One can see in Fig. 2 that for  $C_{\text{Na}_2\text{S}}$ , which is greater than 0.8 mol/l, the values of  $\varphi_c$  and  $\varphi_{fb}$  and their dependencies on the concentration are similar.

The dependencies of  $\varphi_{fb}$  and  $\varphi_c$  on the value of pH at 300 K and  $C_{\text{Na}_2\text{S}} = 0.3\text{ mol/l}$  are shown in Fig. 3.

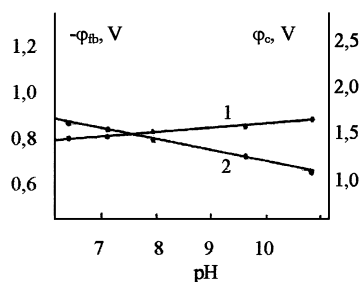


Fig. 3. The dependencies of the flatband potential  $\varphi_{fb}$  (1) and the contact potential  $\varphi_c$  (2) on the pH value of the electrolyte.

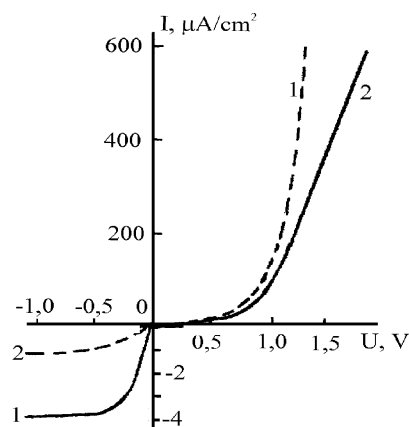


Fig. 4. The dark current–voltage characteristics of the contact  $\text{H}_2\text{O}(\text{S}^{2-}/\text{S}_2^{2-})\text{-ZnIn}_2\text{S}_4$  for the different values of the  $\text{Na}_2\text{S}$  concentration in the electrolyte  $T = 300\text{ K}$ ,  $\text{pH} = 10.8$ : (1)  $C = 0.15\text{ mol/l}$ ; (2)  $C = 1.2\text{ mol/l}$ .

The dark current–voltage characteristics of contact  $\text{H}_2\text{O}(\text{S}^{2-}/\text{S}_2^{2-})\text{-ZnIn}_2\text{S}_4$  for the concentration of  $C_{\text{Na}_2\text{S}}^1 = 0.15\text{ mol/l}$  and  $C_{\text{Na}_2\text{S}}^2 = 1.2\text{ mol/l}$  are demonstrated in Fig. 4. Here we can observe that the current flow through the electrolyte– $\text{ZnIn}_2\text{S}_4$  contact is determined by the potential barrier which is formed at the interface. The increase of the concentration  $C_{\text{Na}_2\text{S}}$  leads to the growth of the forward current and simultaneously decreases the reverse one.

A double electric layer with a strong internal electric field is formed at the electrolyte–semiconductor interface, here comes the separation of electron hole pairs generated by the light in the photoelectrode. The minority non-equilibrium carriers, holes in our case, enters into the electrode reaction at the semiconductor–electrolyte interface. The majority carriers pushed into the ohmic contact pass through the external circuit towards the auxiliary electrode, where they participate in the reaction in the opposite direction. It should be especially noted, that the direction of the photopotential gradient depends on the nature of the auxiliary electrode. The photoelectrode (C, Al, Zn, In, Sn, Cu, Ag and Pt) is negative for all the auxiliary electrodes except Zn.

As the photoelectrode was irradiated through the electrolyte (see Fig. 1) there was a necessity to know the spectral distribution of their transmittance  $T$ . It was found that in the wave band range  $\lambda = 320\text{--}990\text{ nm}$ ,  $T$  is practically independent of  $\lambda$  with the exception of wavelengths in the range of 380–400 nm, where a decreasing of  $T$  is observed. This linear decrease depends on the concentration of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_2$  in the electrolyte (Fig. 5). The thickness of the electrolyte is equal to 1 cm.

The spectral distribution of the open circuit photopotential ( $U$ ) and the photoconductivity ( $I$ ) of the photoelectrode semiconductor materials are shown in Fig. 6. It is seen from this figure that the photocurrent maximum for all photoelectrode materials is situated at longer wavelengths. We suppose that it happened due to the influence of the negative value of the semiconductor electron affinity at the

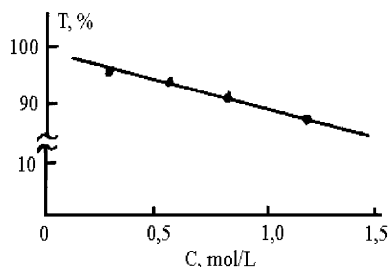


Fig. 5. The dependence of the electrolyte transmittance  $T$  on the concentration  $C$  of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_2$  in the solution at room temperature.

photoelectrode–electrolyte interface as a result of the polarizational interaction of the emitted carriers in the polar medium (aqueous solution of  $\text{Na}_2\text{S}$  +  $\text{Na}_2\text{S}_2$ ) and also due to the additional potential jumps at the interface which may be stipulated, by the adsorption of uncontrolled impurities in the solution.

The load current–voltage characteristics for different values of the illumination intensity and electrolyte concentration are obviously seen in Fig. 7. The growth of illumination intensity leads to an increase of the current in comparison with the voltage.

The photoelectrical parameters of the investigated photoelectrochemical cells are included in Table 2.

#### 4. Energetic diagram of semiconductor–electrolyte interface

The method of calculation of the energetic diagram of  $\text{H}_2\text{O}(\text{S}^{2-}/\text{S}_2^{2-})\text{-ZnIn}_2\text{S}_4$  interface under thermodynamic

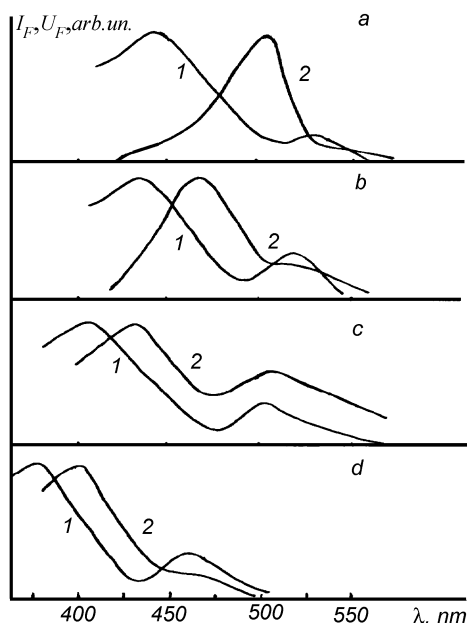


Fig. 6. The spectral distribution (300) of photoconductivity (1) and of the photoelectrochemical cells open circuit voltage (2): a —  $\text{ZnIn}_2\text{S}_4$ ; b —  $\text{Zn}_2\text{In}_2\text{S}_5$ , c —  $\text{Zn}_3\text{In}_2\text{S}_6$ , and d —  $\text{Zn}_3\text{InGaS}_6$ .

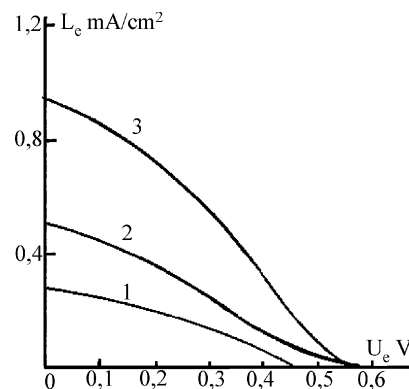


Fig. 7. The load current–voltage characteristics of the cell  $\text{In-C-H}_2\text{O}(\text{S}^{2-}/\text{S}_2^{2-})\text{-ZnIn}_2\text{S}_4\text{-In}$  at different illuminations  $E$  and concentrations  $C$ : (1)  $E = 40 \text{ mW/cm}^2$ ,  $C = 1.2 \text{ mol/l}$ ; (2)  $E = 100 \text{ mW/cm}^2$ ,  $C = 0.6 \text{ mol/l}$ ; (3)  $E = 100 \text{ mW/cm}^2$ ,  $C = 1.2 \text{ mol/l}$ .

conditions in darkness and under illumination is described below as an example for all materials used as photoelectrodes [2].

The magnitude of energetic flat band potential  $\varphi_{\text{fb}}$  at  $\text{Na}_2\text{S}$  concentration in electrolyte, which is more than  $1.2 \text{ mol/l}$  as compared with standard reference electrode of  $\text{AlCl}_3$  is  $\varphi_{\text{fb}}^{\text{AlCl}_3} = -1.2 \text{ V}$  (Fig. 2), but in the case of the reference electrode of hydrogen  $\varphi_{\text{fb}}^{\text{H}} = -1.0 \text{ V}$ .

The Fermi level  $F_{\text{sc}}$  in  $\text{ZnIn}_2\text{S}_4$  and in the auxiliary electrode material (carbon) is the same as the level of potential  $\varphi_{\text{fb}}^{\text{H}} = -1.0 \text{ V}$ . On the physical energetic scale for  $\varphi_{\text{fb}}^{\text{H}} = -1.0 \text{ V}$  the  $E_{\text{sc}} = -3.5 \text{ eV}$ . For free carriers concentration in  $\text{ZnIn}_2\text{S}_4$   $n_0 = 10^{14} \text{ cm}^{-3}$  [6], effective density of energetic states in conductivity band  $N_c = 2.5 \times 10^{19} \text{ cm}^{-3}$  and its edge  $E_c = -2.55 \text{ eV}$ . As  $E_g = 2.8 \text{ eV}$  [4] the valence band edge will be  $E_v = -5.35 \text{ eV}$  (Fig. 8a).

At thermodynamic equilibrium in the electrolyte takes place the reaction  $\text{S}_2^{2-} + 2e \rightleftharpoons 2\text{S}^{2-}$  and the electrons exchange with  $\text{ZnIn}_2\text{S}_4$ , which obtain the potential of redox pairs  $\text{S}^{2-}/\text{S}_2^{2-}$ . So, the potential in  $\text{ZnIn}_2\text{S}_4$   $\varphi_{\text{redox}} = \varphi_{\text{fb}}^{\text{H}} = -1.0 \text{ V}$  or  $F_{\text{sc}} = F_{\text{redox}} = -3.5 \text{ eV}$  (Fig. 8a).

The bending of the conductivity band  $\varphi_c^{\text{H}} = -3.0 \text{ V}$  (Fig. 8b) leads to  $\varphi_c^{\text{H}} = -3.0 \text{ V} < \varphi_{\text{redox}}^{\text{H}} = -1.0 \text{ V}$ .

During the illumination, due to the appearance of photopotential which is equal to  $0.6 \text{ V}$  (Table 2) gradual diminishing of energetic bands bending is already seen in Fig. 8c.

Table 2  
Photoelectrical parameters of the photoelectrochemical cells

Photoelectrode material	$\lambda_{\text{max}}$ of the $V_{\text{oc}}$ , (nm)	Open circuit voltage $V_{\text{oc}}$ , (V)	Short circuit current $I_{\text{sc}}$ , ( $\text{mA/cm}^2$ )
$\text{ZnIn}_2\text{S}_4$	510	0.60	1.2
$\text{Zn}_2\text{In}_2\text{S}_5$	470	0.65	0.75
$\text{Zn}_3\text{In}_2\text{S}_6$	430	0.70	0.40
$\text{Zn}_3\text{InGaS}_6$	410	0.80	0.15
$\text{CuIn}_5\text{S}_3\text{Se}_5$	–	0.43	8.00

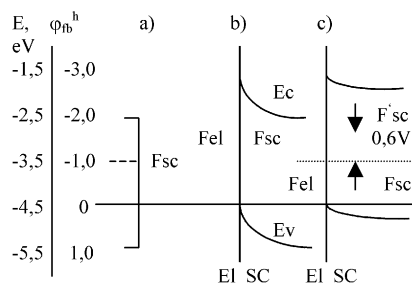


Fig. 8. The energetic diagram of electrolyte–semiconductor interface: (a) energetic diagram of semiconductor; (b) energetic diagram of electrolyte–semiconductor interface in the dark; (c) energetic diagram of electrolyte–semiconductor interface under illumination.

## 5. Conclusions

The photoelectric properties of the electrolyte–semiconductor interface in the chains formed by metal auxiliary electrodes (Al, Zn, In, Sn, Cu, Ag, Pt, and C), aqueous solution of the mixture ( $\text{Na}_2\text{S}$ – $\text{Na}_2\text{S}_2$ ) and layered multinary semiconductors crystals have been investigated. The following results were found in the investigation:

1. The values of the flatband potential  $\varphi_{fb}$  in the range of  $\text{Na}_2\text{S}$  concentration in electrolyte up to 1.2 mol/l are negative and grow almost exponentially on this concentration. The value of the contact potential  $\varphi_c$  linearly depends on the  $\text{Na}_2\text{S}$  concentration. At  $C_{\text{Na}_2\text{S}}$  1.2 mol/l the values of  $\varphi_{fb}$  and  $\varphi_c$  coincide.
2. The values of  $\varphi_{fb}$  depend fractionally on pH of the electrolyte. Such a dependence confirms the small growth of free electrons flow from  $\text{ZnIn}_2\text{S}_4$  in the electrolyte, necessary to maintain the reactions (1) and (2), respectively.
3. The current–voltage characteristics of the electrolyte– $\text{ZnIn}_2\text{S}_4$  interface are determined by the potential barrier which is formed in the semiconductor at the interface.

4. The height of the potential barrier increases with the growth of  $\text{Na}_2\text{S}$  concentration in the electrolyte, although the current–voltage characteristics become more asymmetric. The interface layered semiconductor–electrolyte, which contains  $\text{S}^{2-}/\text{S}_2^{2-}$  redox pairs is photosensitive in the visible spectrum ranging from ultraviolet to blue-green part. The open circuit voltage reaches the value of 0.6 V.
5. The presence of the monoatomic layer of sulphur or selenium on the surface of the photoelectrode when it comes into contact with the electrolyte, containing sulphides and sulphoselenides redox pairs, leads to the essential decrease of the photoelectrode corrosion, diminishing the life time of the photoelectrochemical cells.
6. The energetic diagram of interface  $\text{H}_2\text{O}(\text{S}^{2-}/\text{S}_2^{2-})$ – $\text{ZnIn}_2\text{S}_4$  was proposed.

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