

## PHYSICAL PROCESSES IN ENERGY CONVERTERS ON THE BASE OF InSe-GaSe<sub>1-x</sub>S<sub>x</sub> HETEROJUNCTIONS

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The InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions were prepared by the method of the optical contact. These structures have the pronounced diode characteristics ( $k \sim 10^3$  for  $x=0.2$  at  $U=2$  V) and photosensitivity in the region 490-1040 nm. The efficiency changes between 2.36% (GaSe) and 1.62% (GaS).

### 1. Introduction.

It is known that compounds GaSe and GaS crystallize in a layer structure and form a continuous series of solid solutions. Wide-band monocrystals of solid solutions GaSe<sub>1-x</sub>S<sub>x</sub> possess the high photosensitivity and are perspective materials for creation of sources and receivers of a radiation in the visible spectral region. At the same time it is known that the photosensitivity of diode structures is much more than the photosensitivity of one and the same material. Therefore, making of photosensitive diode structures on the basis of given crystals is necessary for extension of possibilities of their practical applications. However, it is known that making of usual p-n junctions on the basis of solid solutions GaSe<sub>1-x</sub>S<sub>x</sub> is impossible in practice, because they possess, as a rule, by the conductivity of the p-type and it is not possible to change the type of the conductivity of these crystals by means of the doping. Therefore, the creation of heterojunctions (HJ) or rectifying contacts metal-semiconductor on their base is the only one way of making diode structures. However, as far as we know, there is no information on receipt and investigation of similar structures. Works [1,2] are the only exceptions which advise on receipt and investigation of HJ in the system GaSe<sub>1-x</sub>S<sub>x</sub>-InSe by the method of fusion of the low-temperature component InSe on high-temperature components GaSe<sub>0.4</sub>S<sub>0.6</sub> [1] and in the system GaSe<sub>0.6</sub>S<sub>0.4</sub>-InSe by the method of optical contact [2]. The error of the lattice constant of single crystals InSe and GaSe<sub>1-x</sub>S<sub>x</sub> (in particular at  $x=0.6$ ) is 10%. Therefore, we can expect that HJ, manufactured by the fusion method, possesses the large concentration of boundary states and their properties, in the main, are determined by a state of the interface. For removal of this problem, we made (as in [2]) HJ in the system InSe-GaSe<sub>1-x</sub>S<sub>x</sub> by the method of the optical contact [3-5], when matching of lattice parameters and thermal coefficients of contacting materials is not necessary.

Present work devotes to results of investigations of some electrical and photoelectrical properties of HJ in the system InSe-GaSe<sub>1-x</sub>S<sub>x</sub> manufactured by the method of the optical contact.

### 2. Experimental method.

For making of HJ, single crystals n-InSe and p-GaSe<sub>1-x</sub>S<sub>x</sub> ( $x=0; 0.2; 0.4; 0.6; 0.8; 1.0$ ) were used, which were obtained by the method of slow cooling at the constant gradient of temperatures. Concentration of charge carriers at 300 K was  $n=10^{14}-10^{15}$  cm<sup>-3</sup> in used crystals of InSe and  $p=10^{10}-10^{14}$  cm<sup>-3</sup> in crystals of GaSe<sub>1-x</sub>S<sub>x</sub>.

HJ were manufactured by the following method. At first, plane-parallel layers of InSe with a thickness 100-200 μm and GaSe<sub>1-x</sub>S<sub>x</sub> with thickness 50-100 μm were made by means of spalling from big ingots.

Then cuted surfaces of given layers were in the close contact. The structure is kept between two plane layers under the pressure of the order of 10 kG/cm<sup>2</sup> during few hours for receipt of the durable contact. Then surfaces of contacted crystals are coalesced because of intermolecular forces. Strength of such contact does not yield the volume strength of layer crystals.

Ohmic contacts to layers InSe and GaSe<sub>1-x</sub>S<sub>x</sub> were manufactured by fusion of the indium. Ohmage of contacts was preliminary controlled of volt-ampere characteristic (VAC) symmetric structures In-InSe-In and In-GaSe<sub>1-x</sub>S<sub>x</sub>-In. Surface sizes of manufactured HJ were of the order of 3x3 mm<sup>2</sup>. Surface of contacting crystals preliminary was not undergone by any chemical treatment.

### 3. Experimental results and their discussion.

Volt-ampere characteristic of all manufactured HJ possesses by the obvious diode character (Fig.1). Rectification coefficient is  $k \sim 10^3$  or  $x=0.2$  at  $U=2$ V and smoothly decrease, with the increasing of  $x$ . It is connected with the increase of the volume resistance of the layer GaSe<sub>1-x</sub>S<sub>x</sub> with the increasing of  $x$  that restricts the current in the forward direction. Analysis of VAC at different temperatures shows that at forward bias are described by the exponential dependence at relatively low voltages

$$I = I_0 (e^{A(u-IR)} - 1)$$

where  $IR$  is the voltage drop in the volume resistance of samples, which may be determined from the linear section of VAC.

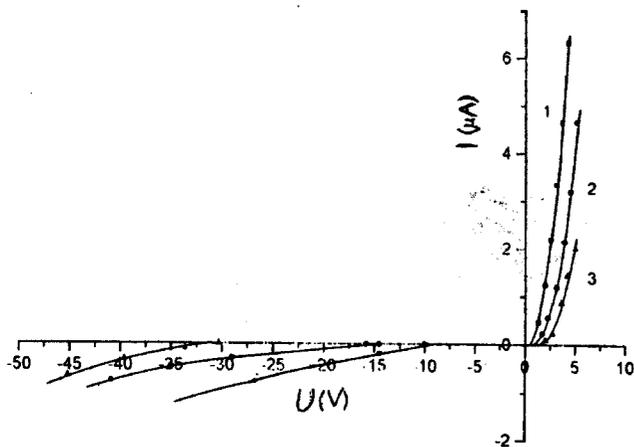


Fig. 1. The current-voltage characteristic of InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunction for different  $x$ : 1-0.2, 2-0.6, 3-1.0.

Observed direct bias of VAC for the system InSe-GaSe<sub>0.6</sub>S<sub>0.4</sub> at different temperatures shows that forward currents mainly correspond to the recombination-tunnel mechanism [6]. Tunnelling of holes with participation of acceptors centres in GaSe<sub>0.6</sub>S<sub>0.4</sub> with the position depth  $\Delta E = 0.4\text{eV}$  is the weak point in the process of the tunnelling. This position depth was determined from the temperature dependence of the parameter  $I_0$ . Dependence of the type  $I \sim U^n$  (where  $n \geq 2$ ) are observed at relatively high voltages. It may be explained by the injection of charge carriers in GaSe<sub>1-x</sub>S<sub>x</sub>. Reverse bias of VAC correspond to the exponential dependence at relatively high voltages

$$I \sim (V_d - U) e^{B/(V_d - U)^{1/2}}$$

where  $V_{cb}$  is the contact potential difference,  $B$  is some constant.

According to [6], this fact testifies on the tunnel mechanism of a transfer of charge carriers through HJ.

It is known that photoelectrical properties of HJ are determined by peculiarities of an energetic zone diagram. However, it is necessary to know values of the contact potential difference (CPD) for construction of such diagram for HJ under study. As monocrystals GaSe<sub>1-x</sub>S<sub>x</sub> have a relatively large volume resistance, then definition of CPD on a value of the current voltage of the cut-off is not accurate. Therefore, we have determined the CPD on a saturation of photo-emf at the irradiation of the structure by a flash of the pulsed lamp with the duration  $\sim 3 \cdot 10^{-6}$  s. In this case, the relaxation of the photo-emf corresponds to the exponential dependence with one constant on time of the order of  $10^{-4}$ - $10^{-5}$  s.

Positions of Fermi levels were estimated from investigation of the temperature dependence of the conductivity of contacting materials. Energetic zone diagram was created on the basis of the Anderson model [7]. Values of zones breaks also were determined in the conduction band ( $\Delta E_c$ ) and in the valence band ( $\Delta E_v$ ) (Table). This table also presents values ( $\Delta E_c$ ) and ( $\Delta E_v$ ), calculated on the basis of quantities of electron affinities and widths of forbidden zones of monocrystals

InSe ( $\chi = 4.6\text{eV}$ ,  $E_g = 1.2\text{eV}$ ) and GaSe<sub>1-x</sub>S<sub>x</sub>. There are not values of electron affinities for crystals GaSe<sub>1-x</sub>S<sub>x</sub> in literature. Therefore, we determined these values on the basis of known electron affinities of monocrystals GaSe ( $\chi = 3.4\text{eV}$ ) and GaS ( $\chi = 4.0\text{eV}$ ) [8], taking into consideration that positions of zones boundaries linearly change with the increasing of  $x$ . According to the table, the experimental and calculated values ( $\Delta E_c$ ) and ( $\Delta E_v$ ) are in a good conformity. Thus, the boundary of manufactured HJ is sufficiently perfect and their zone diagrams satisfactorily correspond to the ideal Anderson model (Fig. 2). It is interesting to note that  $\Delta E_v = 0$  at  $x = 0.3$ . The height of the barrier for holes is less than for electrons one for all values  $x$ . Therefore, we can suppose that monocrystals GaSe<sub>1-x</sub>S<sub>x</sub> effectively inject holes in InSe and transfer of minority carriers occurs from InSe in GaSe<sub>1-x</sub>S<sub>x</sub> at  $x > 0.3$  by means of tunnelling through the "spike" in the valence zone.

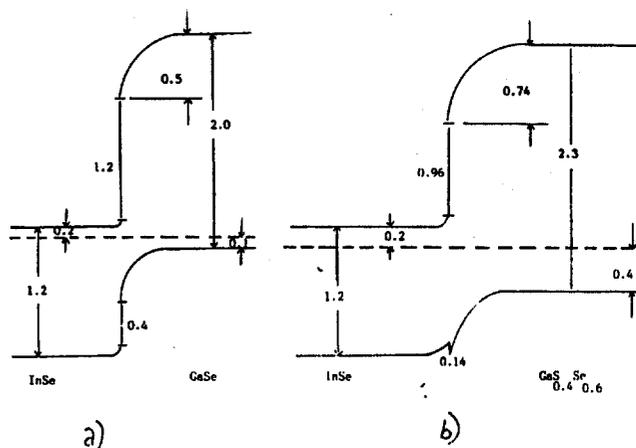


Fig. 2. The energy band diagram of InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions a)  $x=0$ , b)  $x=0.4$ .

According to presented diagrams, at  $x < 0.3$  structures of energetic zones of the interface of HJ promote to an effective separation of non-equilibrium carriers at absorption of a light both by monocrystals InSe and GaSe<sub>1-x</sub>S<sub>x</sub>. However, the appearance of the energetic "spike" in the valence zone at  $x > 0.3$  hampers processes of transition of minority holes in GaSe<sub>1-x</sub>S<sub>x</sub> at light absorption by monocrystals InSe. Therefore, according to experimental observations, photosensitivity decreases with the increasing of  $x$  in indicated systems in the absorption region of InSe. For example, Fig. 3 presents spectral distributions of photosensitivity of investigated HJ at the irradiation from GaSe<sub>1-x</sub>S<sub>x</sub>.

Table

$x$	Calculated Values		Experimental Values		$\Delta\lambda, (\text{nm})$
	$\Delta E_c, (\text{eV})$	$\Delta E_v, (\text{eV})$	$\Delta E_c, (\text{eV})$	$\Delta E_v, (\text{eV})$	
0	1.20	-0.40	1.20	-0.40	600-1060
0.2	1.08	-0.13	1.10	-0.15	560-1060
0.4	0.96	0.14	1.0	0.10	520-1060
0.6	0.84	0.50	0.80	0.53	480-1060
1.0	0.60	0.90	0.65	0.85	450-1060

$$1/C^2 = 2(V_d - V) / S^2 q \epsilon \epsilon_0 N_I$$

where  $S$  is the junction area,  $q$  is the fundamental unit charge and  $\epsilon_0$ ,  $\epsilon$  are the permittivity of free space and semiconductor material, respectively.

The variations of  $1/C^2$  versus  $V$  for InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions are given in Fig.4. From the plot of figure, we find  $V_d$  (0,5; 0,75; 1) and  $N_I$  ( $8,5 \cdot 10^{13} \text{ cm}^{-3}$ ;  $7,2 \cdot 10^{13} \text{ cm}^{-3}$ ;  $6,2 \cdot 10^{13} \text{ cm}^{-3}$ ) for  $x=0; 0,4; 0,6$ , respectively.

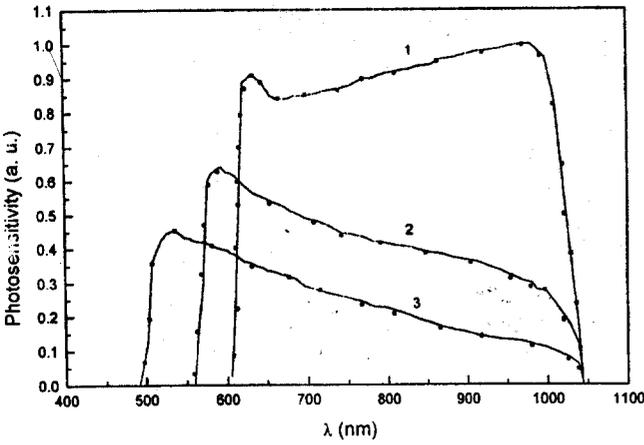


Fig.3. The dependence between the photoelectric voltage and the wavelength light in InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions for different  $x$ : 1-0, 2-0.2, 3-0.6.

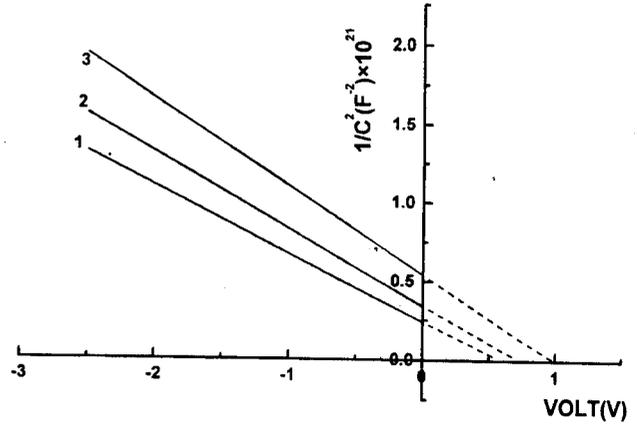


Fig.4.  $1/C^2$  versus  $V$  plot for abrupt InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions for different  $x$ : 1-0, 2-0.4, 3-0.6.

The variation of current density versus the applied voltage under illumination power density  $P=100 \text{ mW/cm}^2$  for a InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterojunctions show that by the variation of the value of  $x$  from  $x=0$  to  $x=1$  the efficiency changes from 2,36 % to 1,62 %.

The photoelectric parameters of these heterojunctions exhibit the high stability under illumination.

Regions of the spectral sensitivity  $\Delta\lambda$  at different values  $x$  are presented in the table. We can see that the long-wave boundary of the spectrum corresponds to the width of the forbidden zone of monocrystal InSe for all values  $x$ . At the same time, short-wave boundaries of spectra are restricted by the region of the strong absorption of monocrystals GaSe<sub>1-x</sub>S<sub>x</sub>. In this case, the light is absorbed in surface region of monocrystals GaSe<sub>1-x</sub>S<sub>x</sub>. Thus, minority carriers do not reach the region of HJ, because of a small diffusion length of given carriers in layer crystals. Therefore, separation of photocarriers does not occur between phases.

Measurement of the junction capacitance ( $C$ ) as a function of reverse bias ( $V$ ) can be used to determine the built-in voltage ( $V_d$ ) and the effective doped concentration ( $N_I$ ) near the junction. This relation can be written as [9]:

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### InSe-GaSe<sub>1-x</sub>S<sub>x</sub> HETEROKEÇİDLƏRİ ƏSASINDA ENERJİ ÇEVİRİCİLƏRİNDƏ FİZİKİ PROSESLƏR

Optik kontakt üsulu ilə InSe-GaSe<sub>1-x</sub>S<sub>x</sub> heterokeçidləri hazırlanmışdır. Hazırlanmış heterokeçidlər yaxşı ifadə olunmuş diod xarakteristikalarına ( $x=0,2$  tərkibi üçün  $U=2V$  olduqda  $k \sim 10^3$ ) və geniş intervalda (490-1040 nm) fotohəssaslığa malikdir. Faydalı iş əmsali 2,36 % (GaSe) və 1,62 % (GaS) intervalında dəyişir.

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**ФИЗИЧЕСКИЕ ПРОЦЕССЫ В ПРЕОБРАЗОВАТЕЛЯХ ЭНЕРГИИ НА ОСНОВЕ  
ГЕТЕРОПЕРЕХОДОВ InSe- GaSe<sub>1-x</sub>S<sub>x</sub>.**

Методом оптического контакта были изготовлены гетеропереходы InSe-GaSe<sub>1-x</sub>S<sub>x</sub>. Изготовленные структуры обладают ярко выраженными диодными характеристиками ( $k \sim 10^3$  при  $U=2$ В для состава  $x=0,2$ ) и фоточувствительностью в широком диапазоне 490-1040 нм. Коэффициент полезного действия меняется в интервале 2,36 % (GaSe) и 1,62 % (GaS).

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