

ABOUT THE OPPORTUNITY OF CREATION WIDEBAND SOLAR PHOTOCELLS ON THE BASIS OF GALLIUM SELENIDE DOPED BY RARE EARTHS ELEMENTS

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ABSTRACT

In this paper with the purpose of revealing an opportunity of creation of photoelectric solar energy converters the p-GaSe<RE>/n-InSe anizotypic heterojunctions based on p-GaSe monocrystals are created by the method of landing to optical contact. Their electric, capacitance and photoelectric characteristics are investigated. It is shown, that on the basis of p-GaSe<RE> crystals, where RE - is the rare earth element such as Gd, Ho and Dy, with percentage of entered impurity $N_{RE}=10^{-2}$ - 10^{-1} at.%, one can to create photoelectric converters with stable electric and photoelectric parameters in $(0.50 \leq \lambda \leq 1.35 \text{ } \mu\text{m})$ m spectrum region.

Keywords: solar, photocell, monocrystal, gallium selenide, energy converter.

I. INTRODUCTION

Application of semiconductor heterojunctions besides optoelectronics is opened the large prospects also for solar energetics. It is possible to create highly effective photoelectric converters of solar energy to electric. The fact that monocrystals of some A_3B_6 compounds, in particular gallium selenide (p-GaSe) and indium selenide (n-InSe) are easily chopped off on thin layers with various $(0.05 \leq d \leq 5.00 \text{ mm})$ thickness and atomically smooth surface, therefore the last years opportunity of application of these materials for creation of heterojunctions is revealed by direct planting to optical contact [1, 2]. This way allows overcoming the problems connected to distinction of lattice constant, mechanical and metallophysical properties of contacting materials at creation of heterojunctions by the traditional ways, in particular by alloying. On the other hand, significant photosensitivity of these semiconductors (p-GaSe) in a wide range of temperature (up to $\sim 400 \text{ K}$) and almost in all the visible and near infrared regions of spectrum $(0.30 \leq \lambda \leq 0.70 \text{ } \mu\text{m}$ and $0.30 \div 1.30 \text{ } \mu\text{m}$ for p-GaSe and n-InSe, respectively) allows to recommend them as a suitable material for solar energetics (for creation of highly effective solar photocells). Earlier us it was informed on an

opportunity of creation of solar converters on the basis of InSe monocrystals doped by rare earth elements.

In the given work the results obtained by us at complex investigation of electric and photoelectric properties of heterojunctions on the basis of gallium selenide monocrystals doped by rare earth elements (p-GaSe<RE>) as gadolinium (Gd), holmium (Ho) and dysprosium (Dy) are stated depending on the chemical nature and percentage of the entered impurity with the purpose of revealing an opportunity of stabilization of key parameters and characteristics of these structures for the further practical application in solar energetic.

II. EXPERIMENTAL TECHNIQUE

As the base semiconductor we use p-GaSe<RE> and n-InSe monocrystals at various percentage ($N_{RE} \approx 0; 10^{-5}; 10^{-4}; 10^{-3}; 10^{-2}; 10^{-1}$ at.%) of the entered impurity grown by the methods of Bridjemenne and slow cooling at a constant gradient of temperature along an ingot. The crystals were electrically homogeneous with concentration and mobility of free carriers $p \approx 10^{14} \text{ cm}^{-3}$ и $\mu_p \approx 5 \div 100 \text{ cm}^2/\text{V}\cdot\text{s}$ (at 300 K) accordingly. Thus, value of p and μ_p under various conditions and various structures of samples were determined by results of VAC measurements in a regime of the currents limited by volumetric charge (VLC) [3]. It was found, that the value of p does not depend on the doping, and μ_p - varies depending on the N_{RE} . Thus, dependence of μ_p on the chemical nature of the entered impurity is not observed.

The anizotypic heterojunctions were created by planting to optical contact thin ($d \leq 200 \text{ } \mu\text{m}$) p-GaSe<RE> and n-InSe, or n-InSe<RE> layers. Both layers were chopped off from large ingots along the plane of (001), "C" axes of crystal were perpendicularly to natural layers.

As ohmic contacts we use In, Sn, Ga, and also Ag paste and dag. Contacts were created by soldering (in the case of In, Sn, Ga) and drawing of paste (in the case of Ag and dag) in air. It is shown that the best results (good ohmic

contacts) are provided at In contacts. Therefore, characteristic measurements by us were made on structures with In contacts.

As layers of p-GaSe<RE> and n-InSe with thickness of $d \leq 200 \mu\text{m}$ possess the good plasticity, providing optical contact even rather big roughness of a surface of the second component of contacting pairs, makes possible achievement of good electric characteristics.

Heterojunctions are prepared by a uniform mechanical pressing of p-GaSe<RE> and n-InSe plates to each other in special holder (fig. 1).

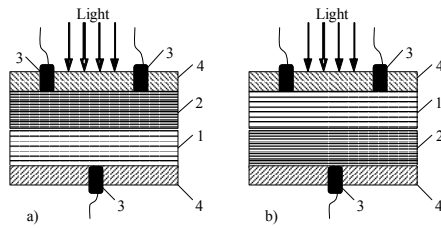


Fig. 1. The schematic image of investigated heterojunctions.
1- n-InSe, 2 - p-GaSe<RE>, 3 - ohmic contact, 4- plate of the holder

Dark VAC in direct and reverse directions, spectral dependence of photosensitivity in photovoltaic regime, their dependence on the N_{RE} and temperatures at illumination of investigated structures from various side (from the side of p-GaSe<RE> and other contacting semiconductor - fig. 1, a and 1, b, respectively). For definition of junction type are measured also their volt - capacitance characteristics. Measurements were carried out in the temperature $77 \div 400\text{K}$, wavelength $\lambda = 0.30 \div 3.50 \mu\text{m}$, light $F \leq 10^2 \text{Lx}$ and electrical $E \leq 10^3 \text{V/cm}$ intensity intervals by the installation KSVU-12.

III. EXPERIMENTAL RESULTS AND DISCUSSION

It is established, that VAC of the investigated crystals have diode character with rectification factor $\sim 4 \div 8$ at $\sim 5\text{V}$ (fig.2, curves 1-5). The pass direction corresponds to positive polarity of an external voltage on the p-GaSe<RE> wide-gap crystals.

It is established, that forward branches of VAC of the investigated heterojunctions at all considered by us temperatures (measurements were carried out by us in the temperature range of 77 - 400 K through everyone $\sim 50 \div 60$ degrees) at low voltage due to dependence of

$$I = I_0 \{ \exp(A(V - IR_0)) - 1 \} \quad (1)$$

Where R_0 - is the resistance of high-ohmic layer (p-GaSe<RE>) and its value is determined from linear region of the VAC, which is about $\sim 105 \div 106 \text{Om}$ at 300K for various samples depending on the N_{RE} . With decreasing T up to 77K, R_0 strongly increases. Therefore it was impossible sometimes (at thicker layers) to carry out the dark VAC measurements. The reverse branch VAC of the

investigated structures is due to $I \sim U^k$, where k- at rather low U_{sam} is about $\sim 0.5 \div 0.8$ and increases almost up to 2 with the further increasing of the voltage. At direct voltages of $U \geq 1.5 \div 2.0 \text{V}$, the dark VAC of these structures are described by expression of

$$V \approx V_{oc} + R_0 I,$$

i.e. is due to almost linear law. Here V_{oc} - is the cutoff voltage. The value of V_{oc} corresponds to potential barrier height $e\phi_0 \approx eV_{oc}$ for investigated structures and at 300K is about $\sim 1.2\text{eV}$.

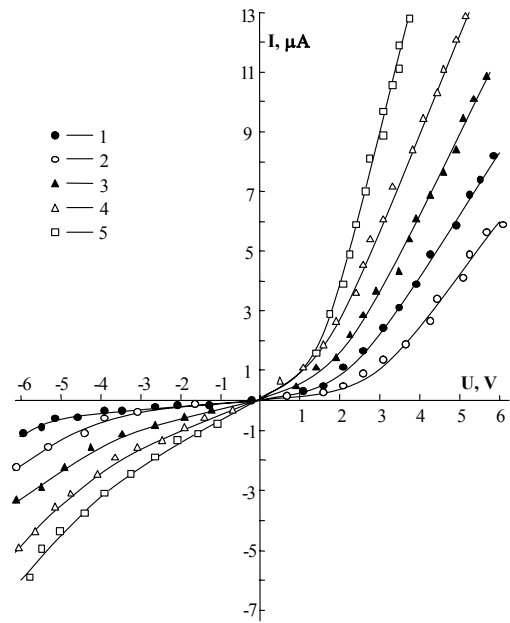


Fig. 2. Volt-ampere characteristics of the p-GaSe<RE>/n-InSe (curves 1-4) and p-GaSe<RE>/n-InSe <RE> structures at various percentage of the entered impurity.
 N_{RE} , at. %: 1 - 0; 2 - 10^{-4} ; 3 - 10^{-3} ; 4, 5 - 10^{-1} . T=300 K

At higher values of applied voltage the switching effect which is characteristic for GaSe and InSe[4, 5] is observed both in direct, and in the reverse direction. It is established, that though at doping of p-GaSe with RE such as Gd, Ho and Dy diode character of investigated structures is kept, however value of separate parameters - cutoff voltage, residual resistance, and rectification factor, switching voltage vary (fig. 2, curves 1-5). The obtained results testify to no monotonic change of resistance of the p-GaSe<RE> depending on the N_{RE} . In particular, with increasing of N_{RE} (at $N_{RE} \leq 10^{-3}$ at. %) at first the resistance of this material increases in time order of magnitude, and further (at $N_{RE} > 10^{-3}$ at. %) decreases and at $N_{RE} \approx 10^{-1}$ at. % becomes even less than initial. The degree of stability of electric parameters of the investigated structures varies also with changing of the N_{RE} . Not dependence of parameter A in expression of (1) on the temperature allows telling, that

the tunnel mechanism dominates over the investigated junctions. However thus the role existing of local centers in the forbidden zone of p-GaSe<RE> and n-InSe [3], which causes tunnel-recombination mechanism, through the junctions is not excluded also. The increase of reverse current under other identical conditions with increasing of N_{RE} (fig.2, curves 1 and 3-5) testifies that ions of considered RE type enter to p-GaSe as the shallow α -centers. Thus it is necessary to take into account also dependence of disarray degree of p-GaSe crystals on the N_{RE} . For the benefit of it testifies also the results obtained by us at investigation of VLC [3], at creation of investigated junctions on the base of p-GaSe<RE> monocrystals. It is necessary to note, that according to the experimental results obtained by us electric properties of p-GaSe<RE>/n-InSe heterojunctions on the chemical nature of entered RE impurity does not depend almost, and it is determined only by the N_{RE} . It is established, that the parameter of I_0 in (1) varies with temperature by law $I_0 \sim \exp(-\Delta\varepsilon/kT)$ and value of $\Delta\varepsilon$ determined from this dependence is about ~ 0.40 eV. This value of $\Delta\varepsilon$ well coincides with occurrence depth of the \square -centers in p-GaSe<RE>, determined based on VLC measurements [3]. In addition, it is established, that thus $\Delta\varepsilon$ does not depend both on the N_{RE} , and on the chemical nature of the entered impurity. It was found, that at $N_{RE} \approx 10^{-1}$ at.% heterojunctions on their basis from the practical point of view become more favorable and at 77K because of decrease of resistance of the p-GaSe<RE> layer.

At 300K dependence of capacitance (C) of the investigated heterojunctions on the external voltage (U) is investigated also. It is established, that under the conditions considered by us irrespective of N_{RE} and the chemical nature of entered RE impurity the experimental points well follow dependence of $1/C^2 \sim U$ for all investigated junctions (fig. 3.). This result unequivocally testifies that structures investigated by us are sharp. The total bend of zones is about ~ 0.5 eV determined from $1/C^2 \sim U$ dependence. The results obtained at capacitance investigation, testify also to insignificance of conditions density on junction region of the heterojunctions created on the basis of p-GaSe<RE> crystals. Following already known works of other authors [2] and experimental results [8, 9] the energetic diagram of investigated structures (fig. 4) is constructed. Thus, as well as in the structures created on the basis of not alloyed specially p-GaSe crystals in both zones there are big energetic breaks ($\Delta\varepsilon_c \approx 1.20$ eV и $\Delta\varepsilon_v \approx 0.45$ eV in conductivity and valence zones accordingly). This fact also testifies to domination of tunnel-recombination, instead of thermo-emission mechanism through the investigated junctions.

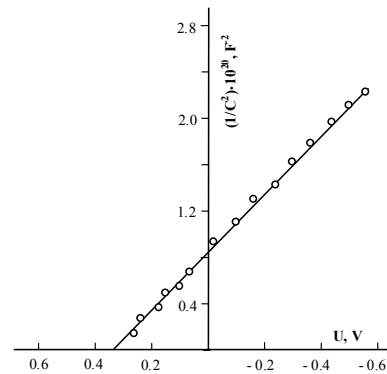


Fig. 3. Volt - capacitance characteristic of the p-GaSe<RE>/n-InSe structures. $T=300$ K; $N_{RE}= 10^{-2}$ at. %

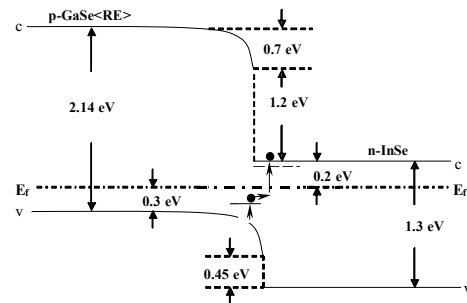


Fig. 4. The energetic diagram of the p-GaSe<RE>/n-InSe structures.

At illumination of investigated junctions by photoactive light arises significant photovoltage (fig. 5). The open circuit photovoltage, short circuit photocurrent density for heterojunctions were $V_{ocn} = 0.34$ V, $J_{scn} = 32$ μ A/cm². At all cases considered by us the p-GaSe<RE> is charged negative concerning the second contacting component (n-InSe and n-InSe<RE>). Under other identical conditions, the maximal value of photovoltage is observed at illumination of investigated structures from the side of p-GaSe<RE>. When illumination is carried out from the side of narrow-gap semiconductor character of photosensitivity spectrum almost completely determined by absorption in narrow-gap component and it appears similar to a spectrum of the photoresistor, created on the basis of this semiconductor with that only differences, that on short-wave region of spectrum (at $\lambda \leq 0.50$ μ m) is observed which first of all can be caused by that in the considered samples thickness of layer is more, than diffusion length of carriers. At illumination of investigated junctions from the side of wide-gap semiconductor (p-GaSe <RE>) two regions in photovoltage spectrum was observed (fig.5, curves 2-6). The first (short -wave region) region is due to absorption of light on narrow-gap component, and the second (long-wave region) - with absorption of light on n-InSe.

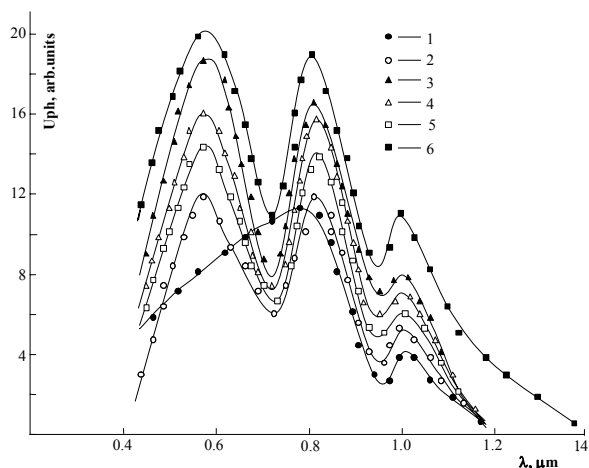


Fig. 5. Photosensitivity spectrum of the p-GaSe<RE>/n-InSe (curves 1-5) and p-GaSe<RE>/n-InSe<RE> (curve 6) structures at various percentage of the entered impurity. N_{RE} , at.‰: 1 - 0; 2, 3 - 10^{-4} ; 4 - 10^{-3} ; 5, 6 - 10^{-1} . $T=300$ K. Curves 2-6 - at illumination from the side of p-GaSe<RE> layer. Curve 1 - at illumination from the side of n-InSe.

IV. CONCLUSION

The obtained results allow to tell, that the heterojunctions on the basis of p-GaSe<RE> crystals created by method of optical contact landings can be used at creation highly effective broadband ($0.50 \leq \lambda \leq 1.35 \mu\text{m}$) photoelectric converters of sunlight energy from $0.35 \leq \lambda \leq 1.25 \mu\text{m}$ to electric, which spectrum and stability

degree of photoelectric and electric parameters can be controlled by the percentage of the entered impurity. The best (optimum) results ($V_{ocn} = 0.34$ V, $J_{scn} = 32 \mu\text{A}/\text{cm}^2$) thus is provided at doping by Dy with $N_{RE} \approx 10^{-2} \div 10^{-1}$ at.‰.

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