

Surface Topology of p -InSe and n -SnS_{2-x}Se_x ($0 \leq x \leq 1$) Layered Crystals and Heterojunctions on Their Basis

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The surfaces of the grown p -InSe and n -SnS_{2-x}Se_x layered crystals were studied by means of atomic force microscopy. By the method of optical contact we have created p -InSe – n -SnS_{2-x}Se_x heterojunctions and investigated their spectral and current-voltage characteristics.

Keywords: Atomic force microscopy, Layered crystals, Heterojunctions, Spectral characteristics, Current-voltage characteristics.

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1. INTRODUCTION

Solid solutions based on porous SnS₂ – SnSe₂ crystals [1] allow to smoothly change the band gap during the transition from one compound to another, and, so, photosensitivity band on their basis can be changed within a wide range. To this end, SnS_{2-x}Se_x ($0 \leq x \leq 1$, x defines the composition of SnS₂ – SnSe₂ solid solutions) crystals were grown, and n -SnS_{2-x}Se_x – p -InSe heterojunctions were produced by the optical contact method [2]. The effect of “window” and concentration of depletion region in basic InSe provide the maximum current due to gathering of photogenerated carriers by heterojunction. This is because of the fact that in comparison with InSe, solid solutions have lower resistivity and wider band gap.

2. EXPERIMENTAL TECHNIQUE

SnS_{2-x}Se_x ($0 \leq x \leq 1$) single crystals were grown by the method of chemical transition reactions in quartz ampoules. The product was grown in the form of chaotically oriented along ampoule plates of different sizes and thickness. All plates had mirror surface. Based on the Hall effect, it is established that at $x=0$ samples had the n -type conduction with concentration of the majority charge carriers $n \sim 10^{16}$ - 10^{17} cm⁻³ and mobility $\mu_{\perp c} \sim 20$ cm²/(V·s), where C is the crystallographic axis which coincides with the normal to the layer plane.

InSe crystals of the p -type conduction were grown by the vertical Bridgman method. Ingots of crystals had 16-18 mm in diameter, and the length was equal to 6-10 cm. Because of the porous structure, thin plates of these ingots were cut using a razor blade. Additional detachment of layers by adhesive tape allowed to obtain the samples with mirror surface without scratches and other damages. Since specially non-doped crystals always have the n -type conduction, then in order to change it they were doped by cadmium impurity with 0,1-0,5 wt.%. The Hall measurements allowed to determine that concentration of the majority charge carriers is equal to $p \sim 5 \cdot 10^{14}$ - 10^{15} cm⁻³, and their mobility is $\mu_{\perp c} \sim 80$ -100 cm²/(V·s).

Freshly cleaved SnS_{2-x}Se_x and InSe plates were placed into intimate mechanical contact. Confinement of

these dissimilar plates is the same as the connection of layers in each porous crystal which is provided by the Van der Waals forces. For the wide band-gap frontal semiconductor, thin (20-30 μm) SnS_{2-x}Se_x plates of the thickness of 200-400 μm were used as of basic p -InSe. Pure indium was used for current contacts. The area of the produced samples was equal to 0,08-0,12 cm².

Photosensitivity spectra of the produced heterojunctions were studied using the monochromator MDR-3 with the resolution of 2,6 nm/mm. All spectra were normalized relative to the number of incident photons.

Current-voltage characteristics (CVC) of heterojunctions were investigated on the plant “Schlumberger SI 1255” with computer interface.

Surfaces of InSe, SnS₂, and SnSSe layered crystals were studied using the atomic force microscopy (Nanoscope IIIa Dimension 3000 SPM (Digital Instruments, USA)). For InSe surface in the plane (001) the mean-square value of its roughness is equal to $\sim 0,053$ nm. This value implies high quality of the crystal cleavage (see Fig. 1a).

It is well seen in Fig. 1b that SnS₂ surface consists of the bands of substance stratifications which have a stepwise character with the step of about $\sim 0,345$ nm. Such picture of the surface is conditioned by the growth of the crystals themselves – by the method of chemical transition reactions. This implies that formation of the crystal of separate SnS₂ molecules during the growth does not have a planar behavior. Surface of SnSSe crystals is quite similar to the surface of SnS₂, but, in the given case, the step is equal to $\sim 0,539$ nm.

3. INVESTIGATION RESULTS AND DISCUSSION

Spectral dependences of the quantum efficiency of photocurrent of the studied heterojunctions are shown in Fig. 2.

Photosensitivity band of the heterojunction is determined by the light absorption in the corresponding semiconductors. The long-wave side of the spectrum of different heterojunctions in all cases is conditioned by the light absorption in InSe, whose band gap E_g at the room temperature is equal to 1,2 eV [7].

Wide band-gap frontal semiconductor does not prevent light transmission until quantum energy $h\nu$ does

not reach the value of E_g of $\text{SnS}_{2-x}\text{Se}_x$. In this case, light is absorbed in the near-surface region, does not reach the heterojunction boundary, and distribution of the photogenerated carriers is stopped. We note that band gap of solid solution can be changed from 0,97 eV for SnSe_2 to 2,07 eV for SnS_2 [8]. In Fig. 3 we represent the dependence of the value of photosensitivity band ΔE on the composition x of $\text{SnS}_{2-x}\text{Se}_x$ solid solution.

It is well seen that changing x , one can create selective photodetectors of different photosensitivity bands.

Photoelectric parameters of $\text{SnS}_{2-x}\text{Se}_x - \text{InSe}$ heterojunctions are presented in Table 1.

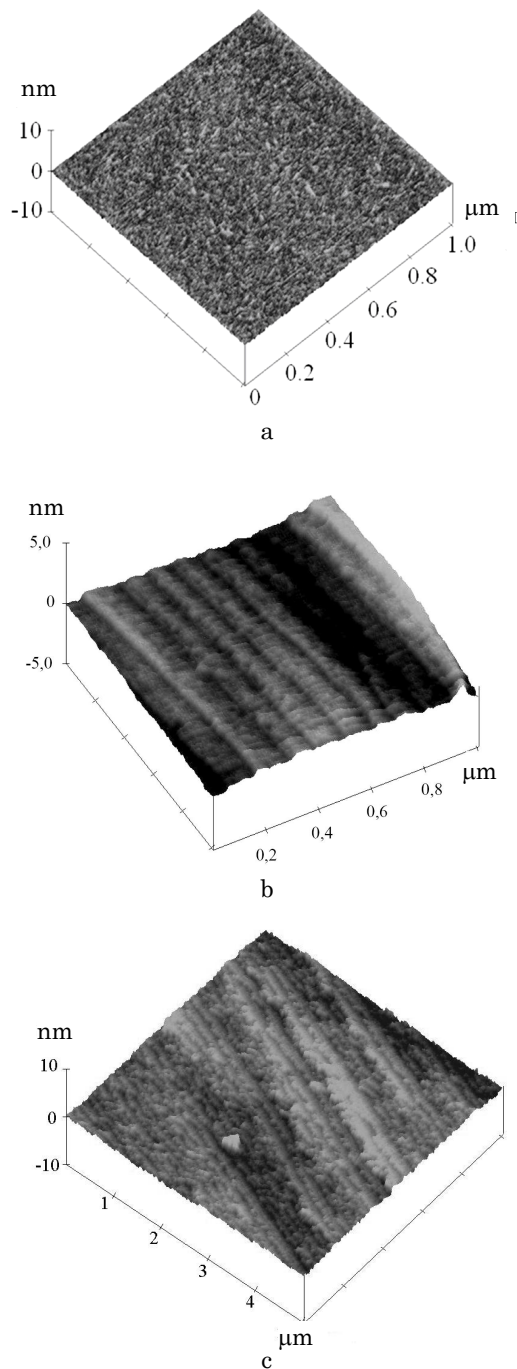


Fig. 1 – AFM-images of the surface fragments of the crystals: InSe (a), SnS_2 (b), SnSSe (c)

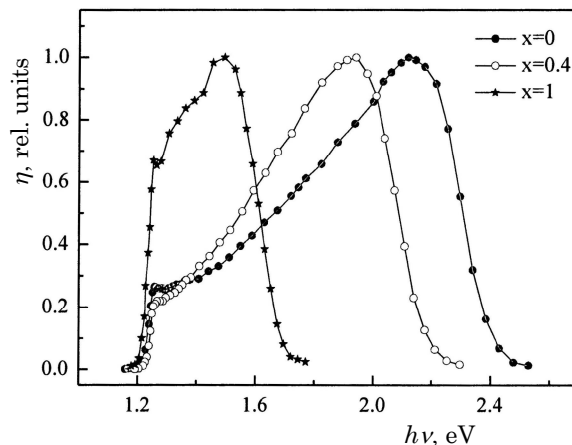


Fig. 2 – Spectrum of the quantum efficiency of photocurrent of $\text{SnS}_{2-x}\text{Se}_x - \text{InSe}$ ($x = 0; 0,4; 1$) heterojunction. $T = 293$ K

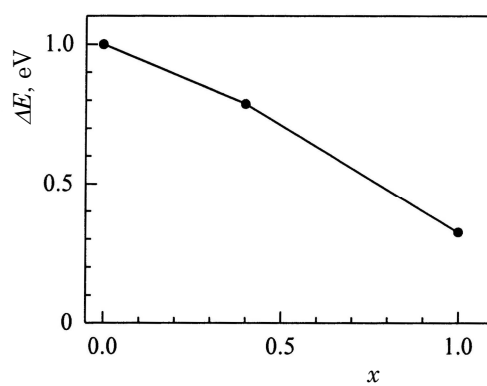


Fig. 3 – Dependence of the photosensitivity band width on the value of x

Table 1 – Photoelectric parameters of $\text{SnS}_{2-x}\text{Se}_x - \text{InSe}$ heterojunctions. $T = 293$ K

x	U_{xx}, V	$J_{sc}, \text{mA/cm}^2$	φ_b, eV	$\Delta E, \text{eV}$
0	0,5	6,8	0,75	1
0,4	0,33-0,35	1,25	0,35	0,8
0,5	0,3-0,35	1,0	0,35	–
1	0,34-0,4	0,33	0,4	0,32

Measurement results of the capacity-voltage characteristics (CapVC) of heterojunctions have shown that in coordinates $1/C^2$ versus U they have a linear behavior. This indicates a sharp type of all produced $p-n$ -heterojunctions. The value of the potential barrier height φ_b obtained from the CapVC allowed to qualitatively analyze the energy diagram of heterojunction. The values of φ_b are given in Table 1. Because of the difference in the concentrations of the semiconductor carriers, depletion region and a whole fold of energy bands take place for more high-resistance InSe. $\varphi_b < E_g/2$ at $x > 0$ (Table 1) in all cases of the studied heterojunctions. However, for $x = 0$, inversely, $\varphi_b > E_g/2$. In this case, we have the appearance of the inversion layer near the interphase boundary of heterojunction and shift of the $p-n$ -junction in depth of InSe. Detailed characteristics of heterojunctions with high potential barrier are considered in the work [9]. Obtained values of φ_b agree well with the measurements of saturation photo-electromotive force of heterojunctions which are also represented in Table 1.

Quality of the produced heterojunctions was tested based on the temperature measurements of their CVC. As an example, the CVC of SnS_{2-x}Se_x – InSe heterojunction at $x = 1$ are represented in Fig. 4.

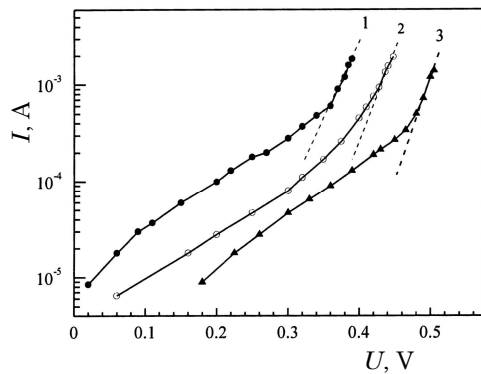


Fig. 4 – Temperature dependences of the CVC of SnS_{2-x}Se_x – InSe heterojunction for $x = 1$: 1 – 300; 2 – 270; 3 – 240 K

As seen from Fig. 4, there are two linear regions on the dependences $I(U)$ in semi-logarithmic coordinates. The first of them, extended one, is characterized by the diode coefficient of CVC n which considerably exceeds 1. This region of heterojunction CVC is usually connected with loss currents [10], since low values of the current correspond to this region, and CVC slope, which defines the values of n , depends on the carefulness of sample production. For the second, short, CVC region, experimental points are compared with theoretically calculated CVC of perfect diodes (dashed line), for which $n = 1$

REFERENCES

1. D.I. Bletzcan, *Kristallicheskie i stekloobraznye khal'kogennidy Si, Ge, Sn i splavy na ih osnove* (Uzhgorod: Zakarpattya: 2004).
2. V.L. Bakumenko, V.F. Chishko, *Semiconductors* **11** No10, 2000 (1977), (in Russian).
3. A. Milnes, D. Feucht, *Geteroperehody i perehody metall-poluprovodnik* (M.: Mir: 1975).
4. V.N. Katerinchuk, M.Z. Kovalyuk, A.D. Ogorodnik, *Neorg. Materialy* **32** No8, 937 (1996).
5. V.N. Katerinchuk, M.Z. Kovalyuk, *Tech. Phys. Lett.* **25** No1, 54 (1999).
6. V.N. Katerinchuk, M.Z. Kovalyuk, M.V. Tovarnitskii, *Ukr. J. Phys.* **45** No1, 87 (2000).
7. Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology. New Ser. Group III: Crystal and Solid State Physics. V.17* (Ed. by O. Madelung) (Berlin e.a.: Springer: 1983).
8. G. Domingo, R.S. Itoga, C.R. Kannewurf, *Phys. Rev* **143** No2, 536 (1966).
9. V.N. Katerinchuk, M.Z. Kovalyuk, *J. Optoelectron. Adv. Mat.* **4** No1, 40 (1997).
10. V.A. Manasson, A.M. Malik, V.B. Baranyuk, *Tech. Phys. Lett.* **7** No9, 549 (1999), (in Russian).
11. S. Zi, *Fizika poluprovodnikovyh priborov*. V 2 kn. Kn. 2, (M.: Mir: 1984).

[11]. Qualitative coincidence of these curves is well seen. This allows to conclude that starting from a certain voltage, direct diffusion current through heterojunction exceeds drain currents because of different exponential dependence of these currents. Therefore, the diffusion current flow should be considered as the main mechanism through SnSSe – InSe heterojunction. The same CVC are typical for SnS_{2-x}Se_x – InSe heterojunctions with other values of x .

4. CONCLUSIONS

Investigation of the AFM-image of the InSe surface in the plane (001) has shown that its roughness is equal to $\sim 0,053$ nm. This implies a high quality of the InSe cleavage. Surfaces of SnS₂ and SnSSe crystals are similar and consist of the bands of substance stratification which have a stepwise character with the step of about $\sim 0,345$ nm and $\sim 0,539$ nm, respectively.

SnS_{2-x}Se_x – InSe heterojunctions are produced by the method of optical contact of semiconductors. SnS₂ – SnSe₂ solid solutions promote the production of crystals with different band gaps: from 1,48 to 2,12 eV at $0 \leq x \leq 1$. If use them as a wide band gap window of heterojunction, they change its photoresponse to the necessary photosensitivity band width. Analysis of the electrical properties of the obtained heterojunctions implies that they correspond to the diodes with perfect characteristics: p - n -transition has a sharp behavior, and the exponential dependence of the current on the voltage is described by the diode coefficient $n = 1$ at $U > 0,35$ V.