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Photoelectric Properties of the Mn_2O_3/*n*-InSe Heterojunction

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Photosensitive Mn_2O_3/*n*-InSe heterojunctions were produced by the method of low-temperature spray pyrolysis. An aqueous solution of the appropriate composition was sprayed onto a heated substrate made of a layered *n*-InSe crystal. As a result, a thin film of Mn_2O_3 was formed on its surface. The use of layered semiconductors makes it possible to obtain high-quality interfaces, even with significant differences in the crystal lattice parameters of the contacting materials. The front layer of the wide-gap semiconductor Mn_2O_3 is transparent in the region of maximum light absorption in InSe. This makes it possible to effectively exploit the photovoltaic properties of the latter. The photoelectric and optical properties of the obtained heterojunction were studied, the corresponding graphical dependences were constructed: current-voltage characteristics and differential resistance at different temperatures, temperature dependence of the height of the potential barrier, spectral dependence of the relative quantum efficiency in the photon energy range of 1.2÷3.2 eV. Theoretical models describing the obtained results are proposed. Based on the analysis of the temperature dependences of the direct and reverse branches of the current-voltage characteristics, the energy parameters of the heterojunction were determined. The value of the series and shunt resistances was evaluated. The mechanisms of the formation of forward and reverse currents through the Mn_2O_3/*n*-InSe energy barrier are determined.

Keywords: Indium Selenide, Mn_2O_3, Heterojunction, *I-V* Characteristics, Photosensitivity.

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1. INTRODUCTION

Nowadays, thin films of semiconducting metal oxides are of considerable scientific and practical interest. Most vividly, such films reveal themselves in the field of manufacturing heterostructures of various types. They are able to efficiently absorb light in the region of fundamental absorption and remain transparent at photon energies smaller than the band gap. This determines their potential as materials for the manufacture of solar energy devices and optoelectronics. The development of the physics and technology of semiconductor heterojunctions is one of the main directions of research in the field of modern materials science and semiconductor device engineering [1]. This causes significant and undiminished interest in semiconductor devices based on heterojunctions and the emergence of a significant volume of new scientific material regarding manufacturing methods and research into their electrical and photovoltaic properties. One of the main problems faced by researchers in the manufacture of heterojunctions is the difference in the parameters of the crystal lattices of the starting materials. As a result, mechanical stresses and broken interatomic bonds occur at the interface. The latter can effectively capture charge carriers and/or form additional barriers for carrier movement. In addition, such surface defects create energy levels in the middle of the band gap. They can work as recombination centers or traps, which have a significant effect on the electrical properties of semiconductor devices based on heterojunctions. Quite often, this leads to the fact that the experimenter has two promising materials with suitable energy parameters, and they do not produce a high-quality heterojunction. A possible solution to this problem is the use of layered 2D materials [2, 3]. The peculiarities of their crystal structure make it possible to obtain atomically smooth surfaces that do not contain broken bonds by simple mechanical chipping without the need for further mechanical or chemical processing. In addition, they are not so sensitive to the mismatch of crystal lattice parameters [4], which significantly expands the choice of materials for the manufacture of high-quality heterojunctions.

The layered structure of InSe crystals with a weak van der Waals bond between the layers and a strong ionic-covalent bond in the layers ensures their advantage over classical semiconductors in the manufacture of substrates for heterostructures. Ideal surfaces are obtained by simple mechanical chipping along the layers of the crystal. This allows you to exclude from the technological process such operations as cutting ingots and further mechanical and chemical processing. We also note that the resistance of InSe to radiation expands the scope of its use. The interest of researchers in InSe has grown significantly in recent years, various prototypes of electronic devices have already been manufactured on its basis [5-7].

This work is a continuation of research into the possibilities of constructing heterojunctions based on the contact of the InSe layered semiconductor with other semiconductors. We have already produced photosensitive heterojunctions on FeS_2/InSe [8], $Zn_{0.5}Cd_{0.5}O$/InSe [9], SnS_2/InSe [10] and $CuFeO_2$/InSe [11], which show good straightening properties.

2. EXPERIMENTAL

Mn_2O_3/*n*-InSe heterojunctions were produced by the method of low-temperature spray pyrolysis. The advantage of this technology is simplicity and cheapness.

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An aqueous solution of the appropriate composition was sprayed onto the InSe substrate, which was placed on the heater. The substrate was made of single-crystal n-InSe grown by the Bridgman method. From the InSe crystal ingot, plane-parallel plates were chipped along the cleavage plane, which were then cut to a size of $5 \times 5 \times 1$ mm^3. Chipping was carried out in the air. The substrates had perfect mirror surfaces.

The surface temperature of the substrate during pyrolysis was maintained at $T_S = 350$ °C. Spray pyrolysis took place under atmospheric pressure conditions. A solution with a concentration of 0.1 M of manganese dichloride $MnCl_2 \cdot 4H_2O$ in distilled water was used to create a finely dispersed aerosol over the substrates. As a result of the process of pyrolysis of $MnCl_2$ salt during interaction with atmospheric oxygen, a film of the binary bixbite compound α-Mn_2O_3 with n-type electrical conductivity and resistivity $\rho \approx 10^7$ Ω·cm at room temperature is grown on the surface of the substrates. The band gap $E_g \approx 2.12$ eV of the obtained films is in good agreement with the values of E_g given in the literature sources $E_g = 2.02$ eV [12], $E_g = 2.2 \div 2.4$ eV [13]. The n-Mn_2O_3 films grown by the spray-pyrolysis method have a high resistivity and a small electron diffusion coefficient $D_n = 5 \cdot 10^{-3}$ cm^2/s [14]. The concentration of charge carriers in them is $n \approx 1.1 \cdot 10^{12}$ cm^{-3}. The thickness of the Mn_2O_3 films was ≈ 0.5 μm. It was determined by the displacement of the interference lines at the film-substrate interface using the Linnyk MII-4 multi-beam microinterferometer.

Contacts to the InSe base material and to the n-Mn_2O_3 film were formed using silver-based conductive paste. The current-voltage characteristics of the Mn_2O_3/n-InSe heterostructures were studied on a Solartron 1255 measuring complex (265÷321 K). The photosensitivity spectra were measured at room temperature on an MDR-3 monochromator with a resolution of 2.6 nm/mm. The spectra were normalized with respect to the photon flux.

3. RESULTS AND DISCUSSION

Fig. 1 shows the straight lines of the *I-V* characteristics of the Mn_2O_3/n-InSe heterojunction, measured at different temperatures. To analyze the obtained graphs, we will use a well-known formula that takes into account the influence of series and shunt resistances [15]:

$$I = I_s\left[\exp\left(\frac{e(V - IR_s)}{nkT}\right) - 1\right] + \frac{V - IR_s}{R_{sh}}, \qquad (1)$$

where I_s is the saturation current, n is the imperfection coefficient, R_s is the series resistance, R_{sh} is the shunt resistance. Solid curves in Fig. 1 represent the results of approximation using formula (1). The value of the differential resistance of the heterojunction (R_{diff}) (see Fig. 2) was taken as the initial values of R_s and R_{sh} at high voltages V in the saturation region and at $V \approx 0$ V, respectively. A good match between experimental data and theoretical calculations confirms the validity of the selected model and allows us to evaluate the characteristics of the heterojunction n, R_s and R_{sh}. The found values of the fitting parameters are given in the Table 1.

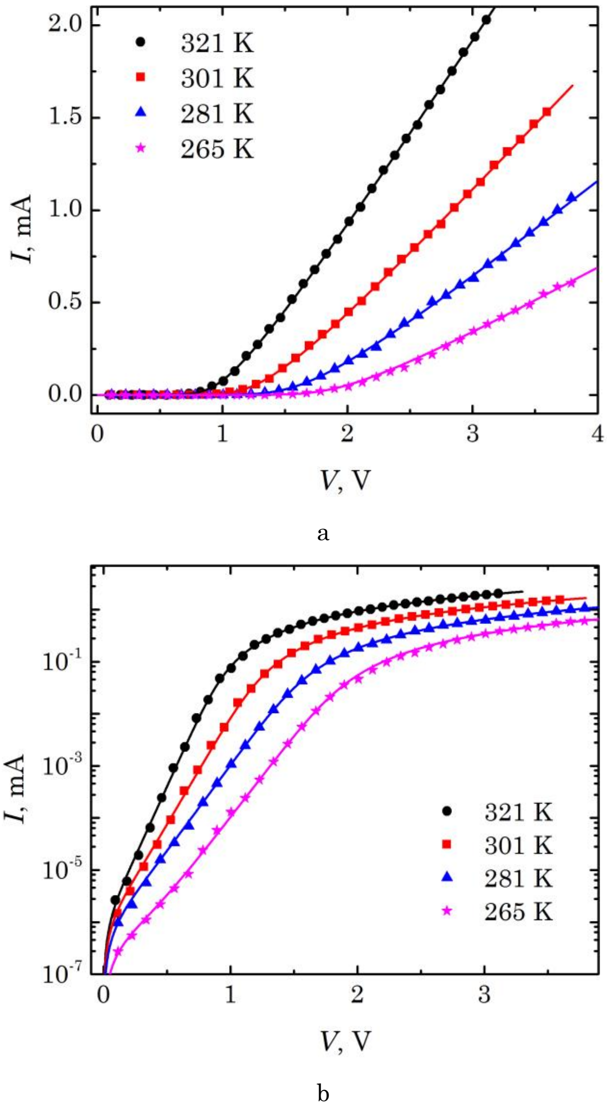

Fig. 1 – Forward *I-V* characteristics of Mn_2O_3/n-InSe heterojunction at different temperatures (points are experimental data, curves are approximation by formula (1))

Table 1 – Fitting parameters

T, K	I_s, 10^{-10} A	n	R_s, Ohm	R_{sh}, 10^8 Ohm
265	0.7	6	2600	7
281	5	5.4	1800	4
301	6	6	1350	2
321	8	2.9	950	0.5

The large value of the shunt resistance indicates that our technology allows to grow high-quality heterojunctions, in which there is no shorting on the sides or through conduction channels in the interface area.

The R_s value in Mn_2O_3/n-InSe heterostructures is determined by the resistance of the thick InSe base region.

In InSe in the region of the investigated temperatures, the electron concentration increases with T due to electron transitions from a deep uncompensated donor level, and the mobility is determined by optical phonon scattering: $n \sim T^{3/4} \cdot \exp(-E_d/2kT)$, $\mu \sim T^{-3/2}$ [16]. Taking this into account, the temperature dependence of electrical conductivity is described by the expression

$\sigma(T) \sim T^{-3/4} \cdot \exp(-E_d/2kT)$. Using this formula, it is possible to estimate the depth of the donor level E_d by the slope of the graphical dependence $\ln(\sigma \cdot T^{3/4})$ on $1/T$ (see Fig. 3): $E_d = 0.3$ eV.

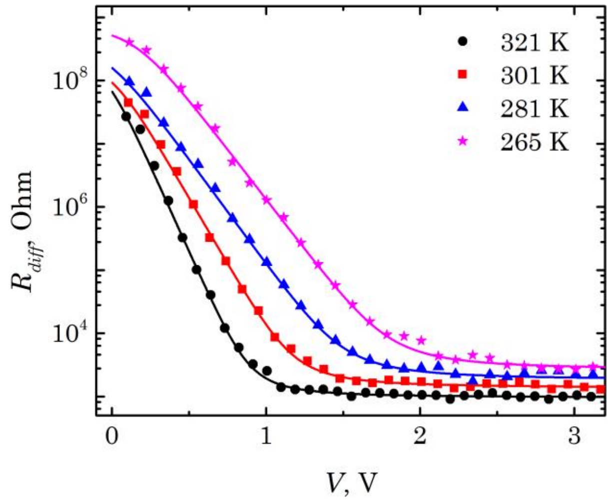

Fig. 2 – Dependence of differential resistance of Mn_2O_3/n-InSe heterojunction on voltage at different temperatures

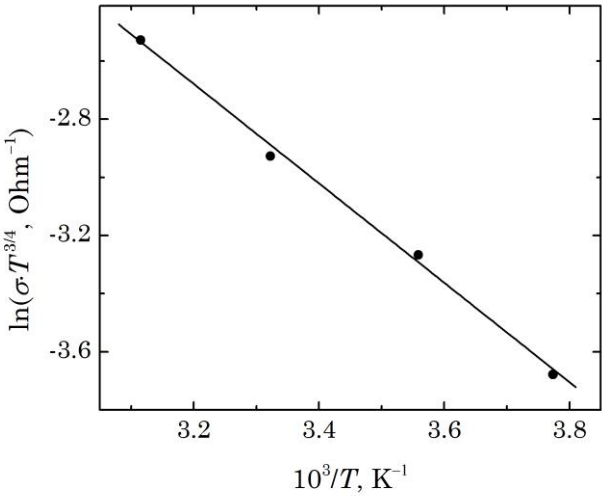

Fig. 3 – Dependence of $\ln(\sigma \cdot T^{3/4})$ of Mn_2O_3/n-InSe heterojunction on $10^3/T$

The value of the energy barrier of the heterojunction φ_0 is an approximation of the linear section of the *I-V* characteristic to the intersection with the abscissa axis. Its temperature dependence (see Fig. 4) is linear:

$$\varphi_0(T) = \varphi_0(0) - \beta_\varphi T , \qquad (2)$$

where $\beta_\varphi = 0.016$ eV·K^{-1} is the temperature coefficient of the height of the potential barrier, and $\varphi_0(0) = 6.1$ eV is the height of the potential barrier at $T = 0$ K.

Straight branches of the current-voltage characteristics of the heterojunction in semi-logarithmic coordinates at different temperatures are shown in Fig. 1. As can be seen from the figure, straight sections are observed in the area of direct displacements $V > 3kT/e$.

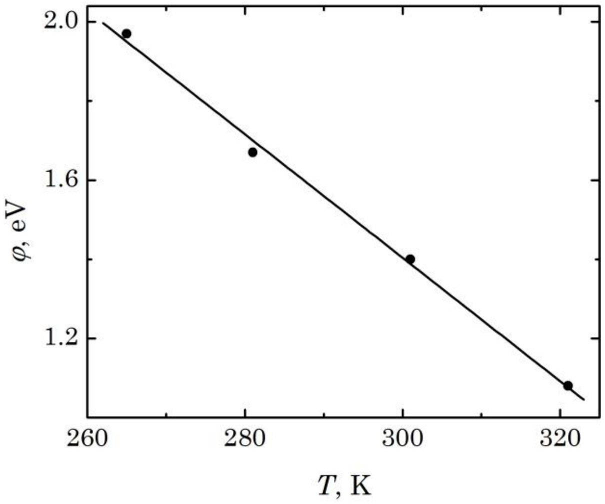

Fig. 4 – Temperature dependence of the height of the potential barrier of Mn_2O_3/n-InSe heterojunction

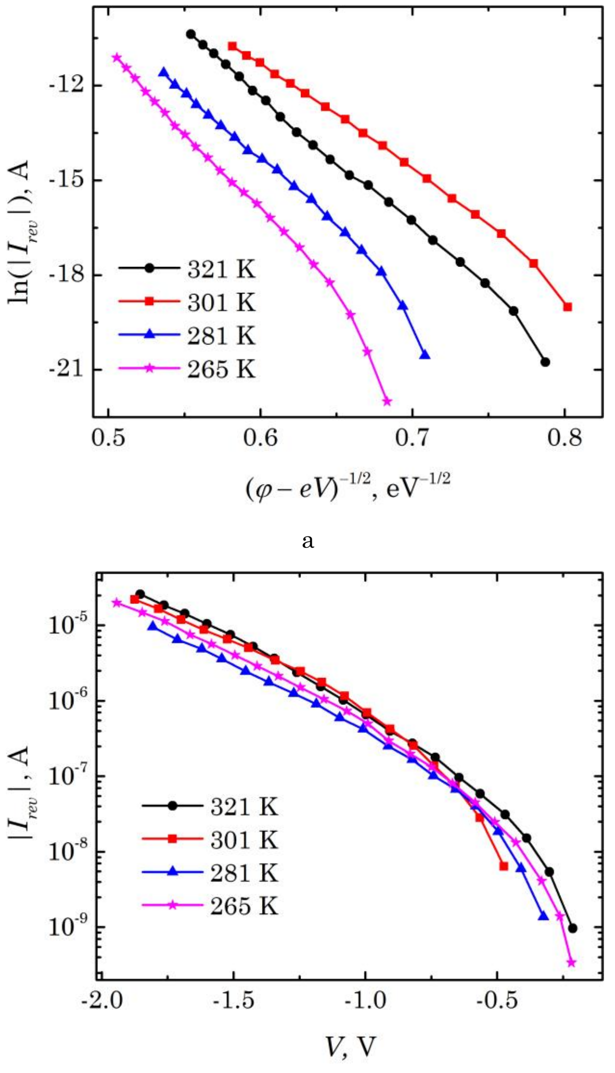

Fig. 5 – Reverse *I-V* characteristics of Mn_2O_3/n-InSe heterojunction at different temperatures

The analysis of the straight branches of the *I-V* characteristics of the Mn_2O_3/*n*-InSe heterostructures built on a semi-logarithmic scale showed that the dependence $\ln I = f(V)$ consists of two straight sections, which indicates the exponential dependence of the current on the voltage. The calculated by formula $\Delta\ln I/\Delta V = e/nkT$ values of the non-ideality coefficient are $n \approx 3.5$ ($V < 1$ V) and $n \approx 7$ ($V > 1$ V). A large value n and a weak slope of the dependences $\ln I = f(V)$ at high voltages is evidence of the tunneling nature of the current transfer mechanism.

The expression for the tunnel current with reverse bias in the case of a sharp heterointerfaces has the form [1]:

$$I_{rev}^{t} \approx a_0 \exp\left(\frac{b_0}{\sqrt{\varphi_0(T) - eV}}\right), \qquad (3)$$

where a_0 and b_0 are voltage-independent parameters.

The fact that the reverse branches of the *I-V* characteristics in Fig. 5 are straight lines in the coordinates $\ln I_{rev} = f(\varphi_0 - eV)^{-1/2}$, according to equation (3), confirms the dominance of the tunnel mechanism of current transfer in the region of reverse displacements $|V| > 3kT/e$.

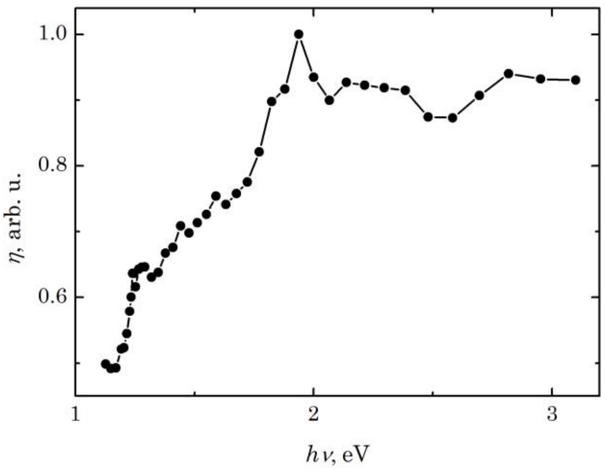

Fig. 6 – Spectral characteristics of the Mn_2O_3/*n*-InSe heterostructure

Fig. 6 shows the spectral dependence of the quantum efficiency of the Mn_2O_3/*n*-InSe heterostructure irradiated from the side of the Mn_2O_3 film in the photon energy range of 1.2÷3.2 eV with a maximum at 1.95 eV. The long-wavelength edge of photosensitivity at $h\nu = 1.2$ eV is caused by the fundamental absorption edge in *n*-InSe. Mn_2O_3 thin films are polycrystalline, as a result of which the fundamental absorption edge is blurred due to partial absorption at grain boundaries compared to monocrystalline materials. At energies $h\nu < E_g = 2.4$ eV, part of the radiation is absorbed at the grain boundaries. At the same time, the light that can be absorbed in *n*-InSe does not penetrate into the base region due to absorption in Mn_2O_3. After the peak value of 1.95 eV, a slight drop is observed in the spectral characteristic, after which it reaches saturation. The full width of the spectrum of the relative quantum efficiency at half-height $\delta_{1/2}$ is ≈ 1.88.

4. CONCLUSION

Photoelectric parameters of Mn_2O_3/*n*-InSe heterojunctions produced by low-temperature spray pyrolysis of Mn_2O_3 thin films on *n*-InSe crystalline substrates were studied. The heterojunctions shows rectifying properties and photosensitivity. Based on the analysis of the *I-V* characteristics, the values of the coefficient of non-ideality, series and shunt resistances were determined. The high value of the shunt resistance confirms the quality of the grown heterostructures. It is shown that the dependence of the height of the energy barrier on *T* is linear in the region of the investigated temperatures. The mechanisms of the formation of forward and reverse currents through the Mn_2O_3/*n*-InSe energy barrier has tunneling nature. The spectral dependence of the quantum efficiency of the Mn_2O_3/*n*-InSe heterostructure irradiated from the side of the Mn_2O_3 film shows the heterostructure is photosensitivity in the range of photon energies of 1.2÷3.2 eV with a maximum at 1.95 eV. The long-wavelength edge of photosensitivity at $h\nu = 1.2$ eV is caused by the fundamental absorption edge in *n*-InSe. Mn_2O_3 thin films are polycrystalline, as a result of which the fundamental absorption edge is blurred due to partial absorption at grain boundaries compared to monocrystalline materials.

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Фотоелектричні властивості гетеропереходу Mn_2O_3/*n*-InSe

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Методом низькотемпературного спрей-піролізу виготовлено фоточутливі гетеропереходи Mn_2O_3/*n*-InSe. На нагріту підкладку з шаруватого кристалу *n*-InSe розпилювався водний розчин відповідного складу. В результаті чого на його поверхі утворювалась тонка плівка Mn_2O_3. Використання шаруватих напівпровідників дозволяє отримувати якісні інтерфейси, навіть при значній розбіжності параметрів кристалічних граток контактуючих матеріалів. Фронтальний шар з широкозонного напівпровідника Mn_2O_3 є прозорим в області максимального поглинання світла у InSe. Це дозволяє ефективно експлуатувати фотоелектричні властивості останнього. Проведено дослідження фотоелектричних та оптичних властивостей отриманого гетеропереходу, побудовано відповідні графічні залежності: вольт-амперні характеристики та диференційний опір при різних температурах, температурна залежність висоти потенційного бар'еру, спектральна залежність відносної квантової ефективності в інтервалі енергій фотонів 1.2÷3.2 eV. Запропоновано теоретичні моделі, що описують отримані результати. На основі аналізу температурних залежностей прямих і зворотних гілок вольт-амперних характеристик визначено енергетичні параметри гетеропереходу. Проведено оцінку величини послідовного та шунтуючого опорів. Визначені механізми формування прямого та зворотного струмів крізь енергетичний бар'ер Mn_2O_3/*n*-InSe.

Ключові слова: Селенід Індію, Mn_2O_3, Гетероструктури, Вольт-амперні характеристики, Фоточутливість.