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REGULAR ARTICLE

Fe_2O_3/*p*-InSe Heterostructures Produced by Spray Pyrolysis Method

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The method of producing Fe_2O_3 films on *p*-InSe substrates by spray-pyrolysis method at 703 K for the formation and investigation of *n*-Fe_2O_3/*p*-InSe anisotype heterojunctions was studied. The advantage of this method is simplicity and cheapness. It does not require complex technological equipment or ultra-clean environments. The electrical and photoelectric parameters of the heterojunctions were investigated. The effect of temperature is studied, and the regularity of the change in the energy barrier of the heterojunction with increasing temperature is given. Based on the analysis of the *I-V* characteristics, the nature of the currents flowing in the heterojunction was established. To explain the obtained experimental results, an energy diagram of the heterojunction is constructed, which is based on the known numerical values of the energy parameters of the materials from which the heterostructure is made. The experimental data and the proposed energy diagram agree well with each other. The spectral quantum photosensitivity of the heterojunction was measured and analyzed. It was established that *n*-Fe_2O_3/*p*-InSe heterojunctions are photosensitive in the energy range of 1.2÷2.8 eV.

Keywords: Indium selenide, Hematite, Heterostructures, Spray pyrolysis, *I-V* characteristics, Photosensitivity.

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1. INTRODUCTION

In recent years, III-V layered crystals have increasingly attracted attention as promising materials for photoelectronics. The interest of researchers in these materials is due to the possibilities of their application in nonlinear optics, solar energy converters, highly sensitive optical sensors of the near-infrared and visible spectrum [1-3]. This class of the materials also includes indium monoselenide (InSe), which has a number of interesting physical properties (high electron mobility $> 1200\ cm^2/V\cdot s$, photosensitivity, dependence of the band gap on thickness etc. [4]) and a specific chemical structure. According to the value of the band gap $E_g \approx 1.2$ eV, InSe belongs to materials that are able to efficiently convert solar energy into electrical energy [5, 6]. InSe crystals are characterized by a significant anisotropy of properties due to their layered structure, where strong covalent bonds between atoms are within the layers, while the interaction between the layers is weak van der Waals. The crystals are easily chipped parallel to the layers and, as a result, the resulting surface is mirror-like and almost free of broken bonds. Accordingly, such a surface is inactive for the adsorption of foreign atoms, which allows it to be effectively used as a substrate for the purpose of fabricating of a heterojunctions.

In turn, an equally important role in the creation of a high-quality heterojunction is played by the thin film of the frontal layer, which must form a defect-free interface when in contact with the substrate. It is the optimal choice of chemical components and the film sputtering technique that allow creating heterostructures with the necessary electrical and photovoltaic parameters [7, 8]. In this work, the choice was made on Fe_2O_3 films. This inexpensive material is widely distributed in the natural environment, non-toxic and resistant to corrosion. Fe_2O_3 thin films have stable physicochemical parameters, with a band gap of 2.1 eV, and are an *n*-type semiconductor. Fe_2O_3 is successfully used to create gas sensors [9] and as a photocatalytic material [10]. In addition, it has magnetic properties, which expands the scope of their application: magnetic storage devices, magneto-optical sensors.

This work presents the fabrication of a heterojunction based on a *p*-type InSe crystal substrate and an *n*-type Fe_2O_3 film. Its electrical and optical properties were studied.

2. EXPERIMENTAL

The layered structure of InSe crystals with a weak van der Waals bond provides convenience in the fabricate of substrates for heterostructures and eliminates the operations of cutting ingots into plates and their mechanical and chemical processing. As a result, we will get a simple technology for producing semiconductor substrates for various purposes. Plane-parallel plates measuring $3 \times 2 \times 0.5$ mm, which had perfect mirror surfaces, were chipped from the InSe crystal ingot along the cleavage plane. Chipping was carried

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out in air, before applying films, the surface of the crystal substrate was degreased with ethanol.

Structures based on the n-Fe_2O_3/p-InSe contact were produced by growing Fe_2O_3 oxide films on prepared p-InSe surfaces, which were heated to a temperature of $T = 703$ K, using the spray pyrolysis method. Atmospheric air was used as a carrier gas. First, the iron chloride hexahydrate salt $FeCl_3 \cdot 6H_2O$ was dissolved in 200 ml of bidistilled water. Under the influence of temperature, the $FeCl_3$ salt decomposes on the surface of p-InSe substrates with the formation of elemental iron, which combines with atmospheric oxygen to form a binary chemical compound α-Fe_2O_3 (hematite). The obtained films had n-type conductivity (according to the sign of thermal electromotive force). Their specific resistance at room temperature was equal to $\rho \approx 2.5 \cdot 10^6$ Ω·cm (controlled by the four-probe method). The band gap (optical) of the films is $E_g \approx 2.1$ eV. If we take into account the low mobility of electrons in the α-Fe_2O_3 polycrystalline films $\mu \approx 0.01$ cm^2·V^{-1}·s^{-1}, then it is possible to calculate the concentration of free charge carriers, which is $n \approx 2.5 \cdot 10^{14}$ cm^{-3}. The thickness of the n-Fe_2O_3 hematite films grown by spray pyrolysis was measured by a MII-4 microinterferometer and was ≈ 0.3 μm.

Contacts to the p-InSe base material and to the n-Fe_2O_3 film were created using silver-based conductive paste. The I-V characteristics of n-Fe_2O_3/p-InSe heterostructures were studied on the SOLARTRON 1255 measurement complex in the temperature range of 243÷325 K. The photosensitivity spectra of the heterojunctions were measured at room temperature on the MDR-3 monochromator. The spectra were normalized with respect to the photon flux.

3. RESULTS AND DISCUSSION

Fig. 1 shows the I-V characteristics of the n-Fe_2O_3/p-InSe heterojunction at temperatures from 243 K to 325 K. Extrapolation of the straight sections of the straight branches to the voltage axis made it possible to follow the dynamics of the change in the height of the potential barrier with temperature. When the temperature increases from 243 K to 325 K, the barrier height decreases from 0.82 eV to 0.7 eV (see Fig. 2). The temperature coefficient of change of the barrier height is equal to $-1.51 \cdot 10^{-3}$ eV/K. The rectification factor RR is about 10^2 at voltages of 1 V and – 1 V.

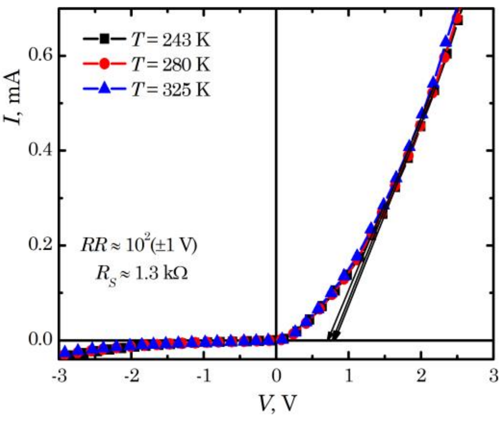

Fig. 1 – I-V characteristics of n-Fe_2O_3/p-InSe heterojunction at different temperatures

The series resistance of the heterostructure R_s was determined by the cotangent of the angle of inclination of the straight sections of the forward I-V characteristics of n-Fe_2O_3/p-InSe heterojunction. It almost does not depend on the temperature and is equal to about 1.3 kOhm (see Fig. 3). The reason for the temperature-independent series resistance is the complete ionization of impurities in Fe_2O_3 and p-InSe.

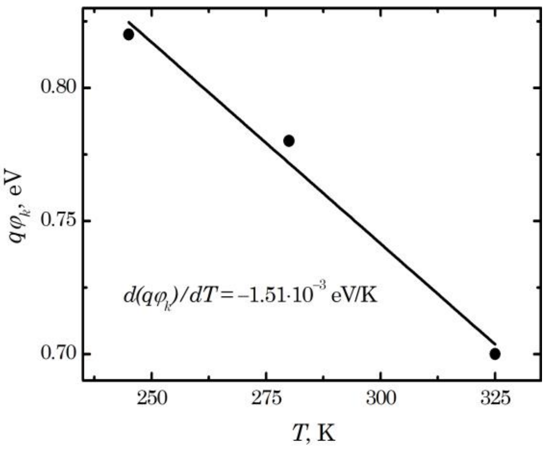

Fig. 2 – Temperature dependence of the energy barrier height of n-Fe_2O_3/p-InSe heterojunction

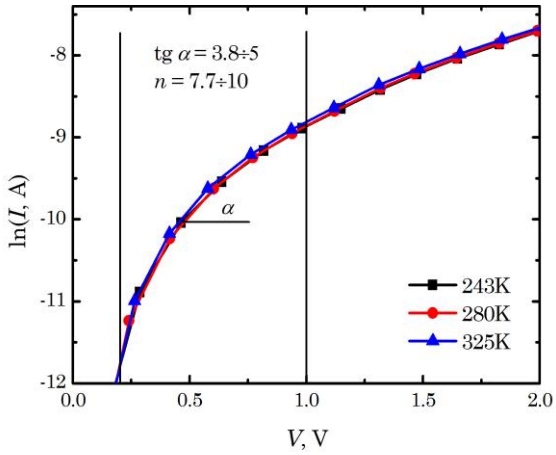

Fig. 3 – Forward I-V characteristics of n-Fe_2O_3/p-InSe heterojunction

Fig. 3 shows the dependences of the forward I-V characteristics of the n-Fe_2O_3/p-InSe heterojunction at temperatures from 243 K to 325 K in the coordinates of $\ln I = f(V)$. This graph was used to determine the mechanisms of current through the heterojunction in forward bias. The nonideality factor $n = (e/kT)(dV/d\ln I)$ in the range of direct bias from 0.2 V to 1 V was from 7.7 to 10. A value of n greater than 2 rejects the recombination and over-barrier mechanisms of current formation. At voltages from 0.2 V to 1 V, the independence of the angle of inclination of the I-V curves to the voltage axis from the temperature is observed. This is characteristic of the tunneling mechanism of current flow.

The reverse I-V characteristics of n-Fe_2O_3/p-InSe heterojunction, which were measured at temperatures from 243 K to 325 K in the voltage range from – 3 V to 0 V, are shown in Fig. 4. The dependences of ln I from $(\varphi_k - V)^{-1/2}$ were constructed in order to confirm the tunneling mechanism of current flow in n-Fe_2O_3/p-InSe heterojunction. In this case, the expression for the I-V characteristics has the form [11]:

$$I = a_0 \exp(-b_0(\varphi_k - V)^{-1/2}). \quad (1)$$

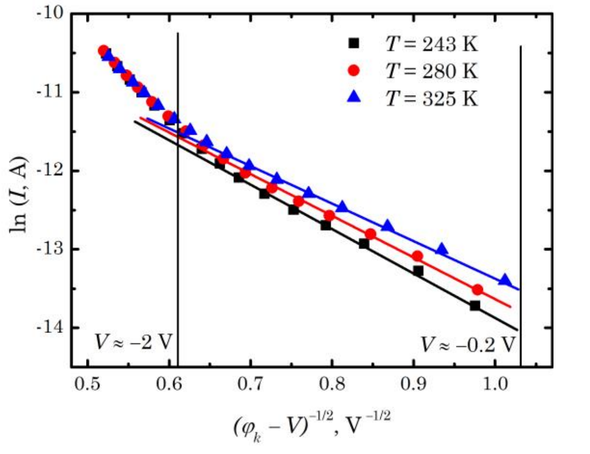

Fig. 4 – The dependence of ln $I = f(\varphi_k - V)^{-1/2}$ for detecting the tunneling current mechanism in n-Fe_2O_3/p-InSe heterojunction under reverse bias

As can be seen from fig. 4, rectilinear sections of I-V curves are observed on the dependence of ln I from $(\varphi_k - V)^{-1/2}$ at reverse bias from – 0.2 V to – 2 V. This indicates the tunneling of charge carriers. At voltages exceeding –2 V, deviation of the I-V curves towards higher currents is observed, which is associated with an avalanche multiplication of the number of charge carriers in the heterojunction.

To construct the energy diagram of n-Fe_2O_3/p-InSe heterojunction (see Fig. 5), the values of the energy parameters of the starting materials, known from the literature, were used [12-14]. For the Fe_2O_3 film: $E_{g1} = 2.1$ eV (determined according to the analysis of the absorption coefficient); electron affinity $\chi_1 = 4.88$ eV; the depth of the Fermi level $\delta_1 = 0.31$ eV. For the InSe substrate: $E_{g2} = 1.2$ eV; $\chi_2 = 4.6$ eV; $\delta_2 = 0.25$ eV.

The parameters of the energy diagram (see Fig. 5a) were calculated according to the following formulas:

$$A_1 = \chi_1 + \delta_1 = 4.88 \text{ eV} + 0.31 \text{ eV} = 5.19 \text{ eV},$$

$$A_2 = \chi_2 + (E_{g2} - \delta_2) = 4.6 \text{ eV} + (1.2 - 0.25) \text{ eV} = 5.55 \text{ eV},$$

$$q\Phi = q\varphi_{k1} + q\varphi_{k2} = A_2 - A_1 = 5.55 \text{ eV} - 5.19 \text{ eV} = 0.36 \text{ eV},$$

$$\Delta E_C = \chi_1 - \chi_2 = 4.88 - 4.6 = 0.28 \text{ eV},$$

$$q\Phi_b = q\Phi + \Delta E_C = 0.64 \text{ eV},$$

$$\Delta E_V = (\chi_1 + E_{g1}) - (\chi_2 + E_{g2}) = (4.88 + 2.1) - (4.6 + 1.2) = 1.18 \text{ eV},$$

where A_1 and A_2 are the work function for Fe_2O_3 and p-InSe respectively; $q\Phi$ is the height of the barrier is determined by the contact potential difference; $q\Phi_b$ is the total height of the potential barrier; ΔE_C is the conduction zone discontinuity; ΔE_V is the valence band discontinuity.

As can be seen from the calculations, the total barrier height of n-Fe_2O_3/p-InSe heterojunction $q\Phi_b = 0.64$ eV differs from the experimentally determined $q\Phi_k = 0.74$ eV by 0.1 eV. A good agreement between the experimental and calculated values is obtained when taking into account the presence of a tunnel-thin layer of In_2Se_3 [15] at the boundary of the heterojunction (see Fig. 5b). This layer can be formed in an uncontrolled manner due to high temperatures of the technological process. The voltage drops on this layer by 0.1 V. The presence of the In_2Se_3 layer explains the observed tunnel current mechanism.

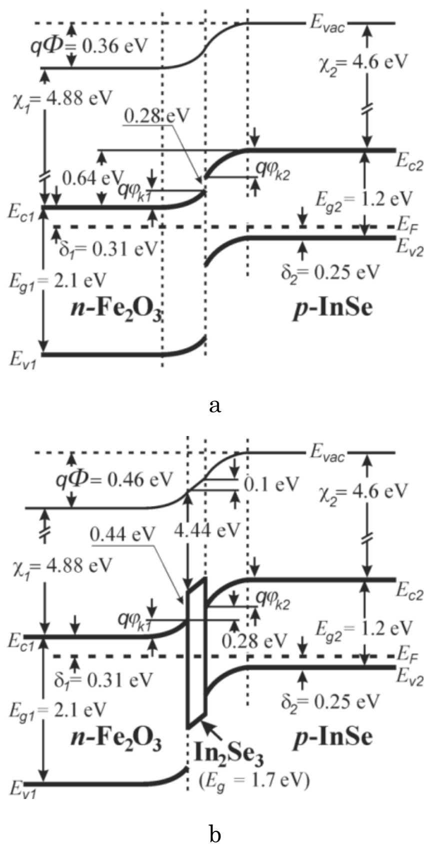

Fig. 5 – Energy diagram of n-Fe_2O_3/p-InSe heterojunction without (a) and with (b) consideration tunnel thin layer In_2Se_3

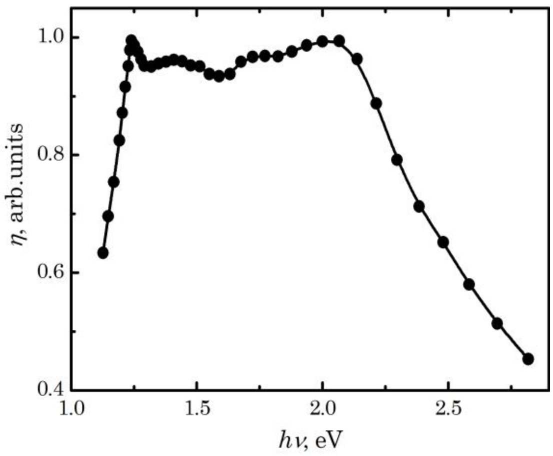

Fig. 6 – Spectral characteristics of the quantum efficiency of n-Fe_2O_3/p-InSe heterojunction

The spectral dependence for the quantum efficiency of n-Fe_2O_3/p-InSe heterojunction is shown in Fig. 6.

Illumination was carried out from the side of the wide-band Fe_2O_3 film. The heterostructure is photosensitive in the photon energy range of 1.2÷2.8 eV. The long-wavelength edge for photosensitivity at energy $h\nu = 1.2$ eV is determined by the band gap width of *p*-InSe. At $h\nu > 2.1$ eV, the photosensitivity begins to decrease, which is due to the interband absorption of light in Fe_2O_3, as a result of which the number of photons falling into InSe decreases.

Photosensitivity in the energy range of 1.2÷2.8 eV facilitates the use of *n*-Fe_2O_3/*p*-InSe heterojunctions as radiation photodetectors.

4. CONCLUSION

A photosensitive *n*-Fe_2O_3/*p*-InSe heterojunction was fabricated by the spray pyrolysis method at 703 K of an aqueous solution of $FeCl_3 \cdot 6H_2O$ salt on *p*-InSe substrates. Rectification of the current in the heterojunction is caused by an energy barrier with a height of 0.74 eV (300 K). The forward and reverse currents of *n*-Fe_2O_3/*p*-InSe heterojunction flow as a result of electron tunneling through the thin In_2Se_3 layer that appears on the surface of the *p*-InSe substrates upon heating before the spray pyrolysis process. Due to the tunnel mechanism of current flow, the *I-V* characteristics of heterostructures almost do not change under the influence of temperature in the studied temperature range.

The *n*-Fe_2O_3/*p*-InSe heterojunctions are photosensitive in the energy range of 1.2÷2.8 eV. Photosensitivity is determined by light absorption in the InSe base material.

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Гетероструктури Fe_2O_3/*p*-InSe, виготовлені методом спрей-піролізу

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Досліджено спосіб виготовлення методом спрей-піролізу при 703 К плівок Fe_2O_3 на підкладках *p*-InSe для утворення і вивчення анізотипних гетеропереходів *n*-Fe_2O_3/*p*-InSe. Перевагою даного методу є простота та дешевизна. Він не потребує складного технологічного обладнання чи приміщення високого класу чистоти. Проведено дослідження електричних та фотоелектричних параметрів гетеропереходу. Вивчено вплив температури, наведена закономірність зміни енергетичного бар'єра гетеропереходу при підвищенні температури. На основі аналізу вольт амперних характеристик, встановлено природу струмів, які протікають у гетеропереході. Для пояснення отриманих експериментальних результатів, побудована енергетична діаграма гетеропереходу, яка базується на відомих числових значеннях енергетичних параметрів матеріалів, з яких гетероструктура виготовлена. Експериментальні дані і запропонована енергетична діаграма добре узгоджується між собою. Виміряна та проаналізована спектральна квантова фоточутливість гетеропереходу. Встановлено, що гетеропереходи *n*-Fe_2O_3/*p*-InSe є фоточутливими в діапазоні енергій 1.2÷2.8 еВ.

Ключові слова: Селенід індію, Гематит, Гетероструктури, Спрей-піроліз, Вольт-амперні характеристики, Фоточутливість.