



REGULAR ARTICLE

Electrical and Photoelectrical Properties of ZnFe₂O₄/InSe Heterojunctions

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Photosensitive *n*-ZnFe₂O₄/*p*-InSe heterojunctions were fabricated by low-temperature spray pyrolysis. An aqueous solution of the appropriate composition was sprayed onto a heated InSe layered crystal substrate. As a result, a thin film of ZnFe₂O₄ was formed on its surface. The use of layered semiconductors as a substrate allows obtaining high-quality interfaces due to the absence of broken bonds on its surface. The photoelectric and optical properties of the obtained heterojunction were studied, and the corresponding graphical dependences were constructed: current-voltage characteristics at different temperatures, temperature dependence of the potential barrier height, spectral dependence of the relative quantum efficiency in the photon energy range of 1.2 ÷ 3.1 eV. Based on the analysis of the temperature dependences of forward and reverse current-voltage characteristics, the energy parameters of the heterojunction were calculated. The mechanisms of the formation of forward and reverse currents through the ZnFe₂O₄/InSe energy barrier were determined.

Keywords: Indium Selenide, Heterostructures, Spray pyrolysis, *I-V* Characteristics, Photosensitivity.

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1. INTRODUCTION

Today's problems, like nothing else, encourage us to develop own electronics, in particular, the search for new materials and the design of devices based on them. The creation of photosensitive elements has always been a priority for scientists and industry at the state level. In addition, such elements can be used in solar cells. Current problems have forced us to accelerate the process of transition to non-traditional sources of replenishment of lost electrical generation capacities. Until recently, the main material for high-power electronics was silicon, but the use of semiconductors with better parameters, such as larger breakdown voltage (higher operating voltage), larger value of charge carrier mobility (higher operating currents and frequencies), and better thermal conductivity (higher power density) allows to increase the stability threshold of semiconductor devices. One such semiconductor is InSe. It can be used to manufacture high-quality heterojunctions and various types of structures [1-3]. Layered semiconductor InSe is a promising material for the fabricate of photodetectors and light emitters in a wide range of the optical spectrum (from UV to near-IR) [4, 5]. The physical properties of InSe differ from those of classical non-layered semiconductors. By applying local deformation of 2D InSe

layers at the nanometer scale, it is possible to implement single-photon emitters, which are the main functional block of quantum computers, and to create nanotextured surfaces with high quantum yield of luminescence in a wide range of the optical spectrum [6]. In addition to deformation, the band parameters, electrical and optical properties of heterostructures based on layered materials can also be influenced by applying an electric field in a direction perpendicular to the plane of the layers [7, 8].

Ferrite thin films are fascinating materials that have been studied for decades due to their special electrical and magnetic properties, high chemical and mechanical hardness etc. [9], which enables their wide-spread use in various types of devices. Ferrite thin films have numerous applications such as magnetic recording media, magnetoelectric composites, sorbents for organic pollutants, microwave devices, gas sensors, transformers, magnetic core of coils, hydrogen production, batteries and many others [10, 11]. Among the large number of relevant solid iron oxides, ZnFe₂O₄ has attracted widespread attention due to its photochemical stability, cost-effectiveness, and significant visible light absorption capacity as a magnetically recoverable and iron-rich spinel ferrite.

ZnFe₂O₄ is a type of ferrite with a spinel structure, which has various functionalities, including soft

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magnetism, antibacterial properties and photocatalysis [12], and is inexpensive, non-toxic, environmentally friendly compared to other ferrites and is also a highly chemically stable material. The band gap of ZnFe_2O_4 depends on the technology of creation and is $1.9 \div 2.6$ eV [13], which ensures the efficiency of their use in the field of solar energy. Also, studies conducted with ZnFe_2O_4 confirmed their potential for use as a photothermal converter for photothermal therapy [14].

This work is a continuation of research on the creation of heterostructures based on layered InSe crystals and oxides of magnetic materials ($\text{NiFe}_2\text{O}_4/\text{InSe}$ [15], $\text{CuFeO}_2/\text{InSe}$ [16], $\text{Fe}_2\text{O}_3/\text{InSe}$ [17]), suitable for the design of photosensitive elements of electronics.

2. EXPERIMENTAL

To fabricate anisotype $n\text{-ZnFe}_2\text{O}_4/p\text{-InSe}$ heterojunctions, substrates with dimensions of $30 \times 40 \times 10$ mm³ were used, which were exfoliated from indium monoselenide $p\text{-InSe}$ crystals grown by the Bridgman method. Hole conductivity was ensured by doping with cadmium (0.1 % by weight). The charge carrier concentration determined on the basis of Hall studies was $p \approx 10^{14}$ cm⁻³ at room temperature. The hole mobility in the perpendicular direction relative to the symmetry axis c was equal to $\mu_{pH} \approx 55$ cm²/(V·s).

Thin films of ZnFe_2O_4 were prepared by spray pyrolysis from aqueous solutions of $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salts with a concentration of 0.1 M, which were mixed using a magnetic stirrer in volumes corresponding to the ratio of elements $\text{Fe}/\text{Zn} = 2$. The surface of the indium selenide substrates was heated to 623 K before spraying the aerosol using a stage equipped with temperature-regulating devices. To obtain ZnFe_2O_4 films with a thickness of 0.3 μm , it was necessary to spray 25 ml of the solution at a rate of 3 ml/min to 5 ml/min. Spraying was carried out under atmospheric pressure to ensure a sufficient degree of oxidation of the metals. To control the thickness of ZnFe_2O_4 films on individual substrates made of opaque glass ceramics, a step was formed. This allowed determining the thickness of the films by the magnitude of the shift of the interference fringes using an MII-4 interferometer. According to optical studies using a spectrophotometer SF-2000, the transmittance was $T \approx 50 \div 70$ % in the wavelength range of $0.4 \div 1.1$ μm . According to studies of the optical transmittance, reflection and absorption of light, it was found that in thin ZnFe_2O_4 films produced by the spray pyrolysis method, direct optical transitions are realized, and the band gap is $E_g = 2.62$ eV.

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependences of the I - V characteristics in conventional linear coordinates. With decreasing temperature, the straight branches of the current-voltage (I - V) characteristic shift towards higher voltages. This indicates that with decreasing temperature,

the potential barrier of the $\text{ZnFe}_2\text{O}_4/\text{InSe}$ heterojunction increases. In turn, it is seen that the straight branches of the I - V characteristic move away from the current axis with decreasing temperature. This may indicate that decreasing the sample temperature leads to an increase in the series resistance of the heterojunction.

Extrapolation to the voltage axis of the I - V characteristics under forward bias (from straight sections) allows us to find the cutoff voltage and estimate the energy barrier height ϕ of $\text{ZnFe}_2\text{O}_4/\text{InSe}$ heterojunction. With increasing temperature from 244 K to 317 K, the value of ϕ linearly decreases from 0.5 V to 0.3 V (Fig. 2). The temperature coefficient $d(q\phi)/dT$ in the temperature range of the study is equal to $2.4 \cdot 10^{-3}$ eV/K. The order of magnitude of $d(q\phi)/dT$ is in good agreement with the temperature coefficient of change of the energy barrier height at indium selenide heterojunctions [16, 17].

To clarify the mechanism of current flow in the heterojunction under study, measurements of the temperature dependences of the I - V characteristic were carried out in the temperature range of $244 \div 317$ K. They are shown in semi-logarithmic coordinates in the Fig. 3. The I - V characteristic of an ideal heterojunction is described by the formula $I = I_s [\exp(eV/kT) - 1]$, and therefore Fig. 3 should consist of straight lines with different slopes. As can be seen at low voltages, this is not the case. We attribute this to the influence of shunt resistance. It can be associated with the formation of conductive channels that arise during the formation of the front oxide film. In this case, the I - V characteristic is described by the following expression [18].

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

where n is the ideality factor, I_s is saturation current, R_{sh} is the shunt resistance and R_s is the series resistance.

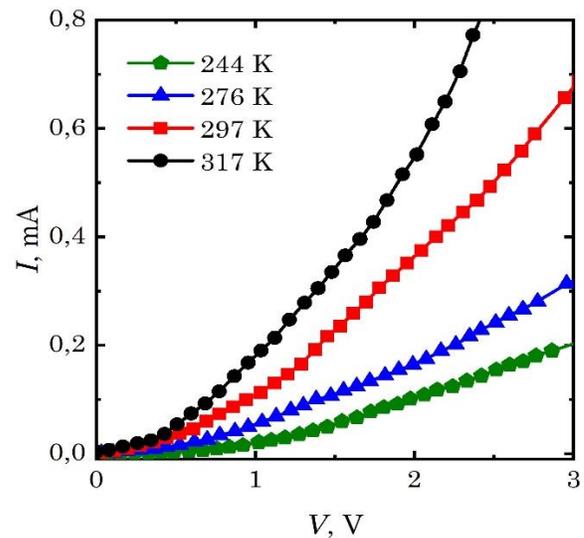


Fig. 1 – Forward I - V characteristics of $\text{ZnFe}_2\text{O}_4/\text{InSe}$ heterojunction

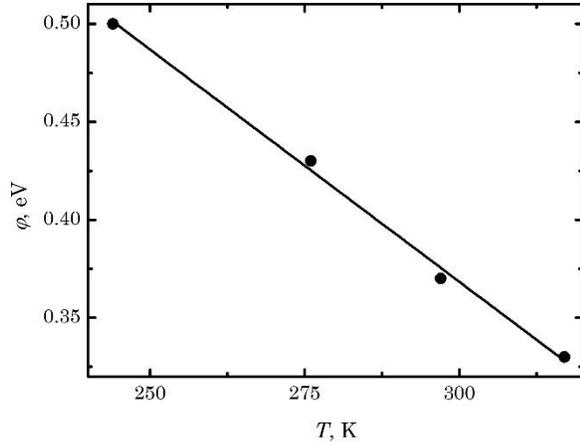


Fig. 2 – Temperature dependence of the height of the potential barrier of ZnFe₂O₄/InSe heterojunction

Fig. 3 shows the results of the approximation of experimental data using formula (1). The fitting parameters are given in Table 1. The determined values of the non-ideality coefficient at $V < 1$ B are $n = 4 \div 5$. The large value of the non-ideality index and the weak slope of the dependences $\ln(I) = f(V)$ at different temperatures is evidence of the tunneling nature of the current transfer mechanism in the low voltage range of $0 < V < 1$ V. At higher voltages, the current is determined by the value of the series resistance of the heterojunction.

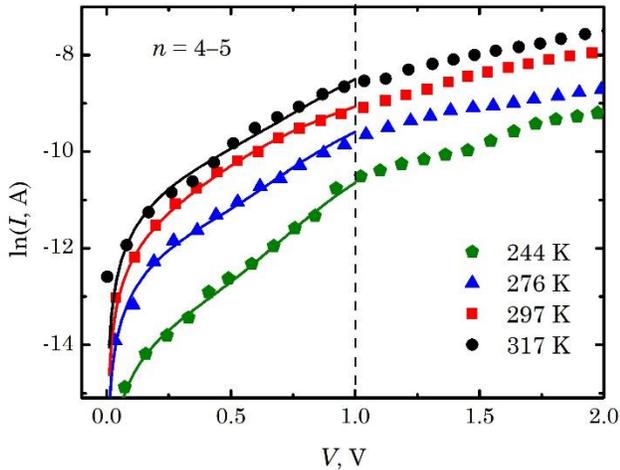


Fig. 3 – Forward I - V characteristics of ZnFe₂O₄/InSe heterojunction in a semi-logarithmic scale (points are experimental data, curves are approximation by formula (1))

Table 1 – Fitting parameters

T , K	n	R_s , kOhm	R_{sh} , kOhm
244	5	6.7	250
276	4	4.2	40
297	4	4	20
317	4	1	12

The reverse I - V characteristics of the ZnFe₂O₄/InSe heterojunction in the temperature range $T = 244 \div 317$ K correspond well to the expression for the tunnel current:

$$I = a_0 \exp[-b_0(\varphi - V)^{-1/2}] \quad (2)$$

According to formula (2), the I - V characteristic of the ZnFe₂O₄/InSe heterojunction in the coordinates $\ln(I) = f(\varphi - V)^{-1/2}$ is linear (Fig. 4). The reverse current in the ZnFe₂O₄/InSe heterojunction is formed by the tunneling of electrons from the InSe conduction band through the barrier into the ZnFe₂O₄ conduction band.

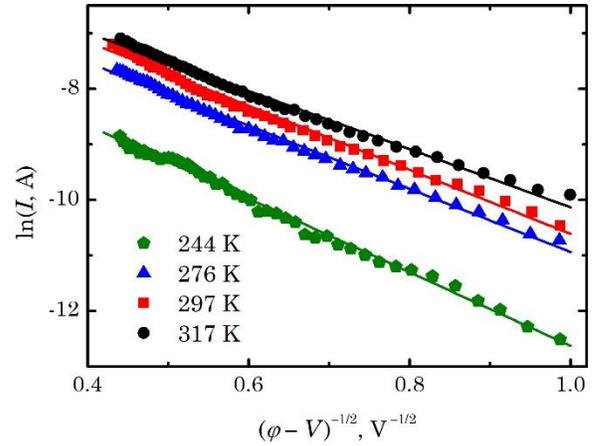


Fig. 4 – Reverse I - V characteristics of ZnFe₂O₄/InSe heterojunction

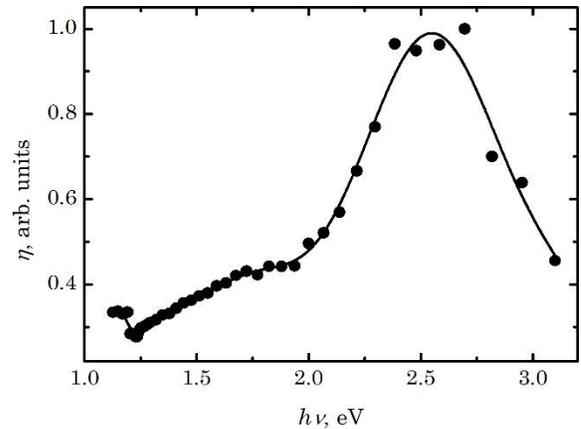


Fig. 5 – Relative quantum efficiency of ZnFe₂O₄/InSe heterojunction

The spectral dependence of the relative quantum efficiency of ZnFe₂O₄/InSe heterostructure irradiated from the side of the ZnFe₂O₄ film were investigated in the photon energy range of $1.2 \div 3.2$ eV (Fig. 5). The maximum is at approximately 2.6 eV. According to measurements of the transmission coefficient in the ZnFe₂O₄ film, at this energy most of the light does not reach InSe. Considering that the determined band gap of ZnFe₂O₄ is 2.62 eV, it can be assumed that the peak in the curve of photoresponse is determined by the absorption in ZnFe₂O₄. The long-wavelength photosensitivity edge at $h\nu \approx 1.24$ eV is due to the fundamental absorption edge in InSe. When irradiated

with quantum energies $h\nu > 2.6$ eV, the region of the most intense generation of electron-hole pairs approaches the frontal surface of ZnFe_2O_4 , which is characterized by a high recombination rate, and the photosensitivity of $\text{ZnFe}_2\text{O}_4/\text{InSe}$ structures decreases. The full width of the relative quantum efficiency spectrum is not less than 1.75.

4. CONCLUSION

The parameters of photosensitive $n\text{-ZnFe}_2\text{O}_4/p\text{-InSe}$ heterojunctions fabricated by low-temperature spray pyrolysis of thin ZnFe_2O_4 films on InSe crystalline substrates were investigated. Analysis of the temperature dependences of the forward and reverse I-V characteristics allowed us to determine the energy parameters of the heterojunction, such as the value of the height of the potential barrier ($\varphi = 0.3 \div 0.5$ V), the values of the series ($R_s = 1 \div 6.7$ kOhm) and shunt resistances

($R_{sh} = 12 \div 250$ kOhm). The value of the non-ideality coefficient $n = 4 \div 5$ is determined. It was established that the main mechanism for the formation of forward and reverse currents through the $\text{ZnFe}_2\text{O}_4/\text{InSe}$ energy barrier is tunneling. It is shown that at $V < 1$ V the direct current is affected by the shunt resistance associated with the conduction channels that arise during the formation of the frontal layer of the heterojunction.

The spectral dependence of the relative quantum efficiency of $\text{ZnFe}_2\text{O}_4/\text{InSe}$ heterojunction irradiated from the side of the ZnFe_2O_4 film was investigated. It was found that the heterojunction is photosensitive in the photon energy range of $1.2 \div 3.2$ eV. The long-wavelength photosensitivity edge at $h\nu = 1.2$ eV is due to the fundamental absorption edge in InSe. The maximum on the photoresponse curve at 2.6 eV is determined by absorption in the frontal layer of ZnFe_2O_4 .

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Електричні та фотоелектричні властивості гетероз'єднань $\text{ZnFe}_2\text{O}_4/\text{InSe}$

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Фоточутливі $n\text{-ZnFe}_2\text{O}_4/p\text{-InSe}$ гетероз'єднання були виготовлені методом низькотемпературного піролізу розпиленням. Для цього водний розчин відповідного складу наносили розпиленням на підігріту підкладку з шаруватого кристалу InSe, в результаті чого на її поверхні формувалася тонка плівка ZnFe_2O_4 . Використання шаруватих напівпровідників як підкладки дозволяє отримувати високоякісні інтерфейси завдяки відсутності порушених зв'язків на їхній поверхні. Було досліджено фотоелектричні та оптичні властивості отриманого гетероз'єднання та побудовано відповідні графічні залежності: 1) вольт-амперні характеристики за різних температур, 2) температурну залежність висоти потенційного бар'єру, 3) спектральну залежність відносної квантової ефективності в діапазоні енергій фотонів $1,2 - 3,1$ eV. На основі аналізу температурних залежностей прямих і зворотних ВАХ були розраховані енергетичні параметри гетероз'єднання. Визначено механізми формування прямих і зворотних струмів через енергетичний бар'єр $\text{ZnFe}_2\text{O}_4/\text{InSe}$.

Ключові слова: Селенід індію, Гетероструктури, Піроліз розпиленням, Вольт-амперні характеристики, Фоточутливість.