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Electrical and Photoresponse Properties of $NiFe_2O_4$/InSe Heterojunction

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The conditions of application thin semiconducting ferrite $NiFe_2O_4$ films on n-InSe crystalline layered semiconductor substrates at a temperature of 623 K by the spray-pyrolysis method for the creation of photosensitive n-$NiFe_2O_4$/n-InSe heterojunctions were studied. The mechanisms of current flow through the heterojunction were established based on the temperature dependence of forward and reverse *I-V* characteristics. The spectral photosensitivity of the n-$NiFe_2O_4$/n-InSe heterojunction in the energy range of 1.26÷3.2 eV was analyzed.

Keywords: Indium Selenide, Heterostructures, Spray pyrolysis, *I-V* characteristics, Photoresponse.

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1. INTRODUCTION

Currently, the use of semiconductor technologies is reaching a new level due to the use of various materials for the creation of an electronic devices. The use of semiconductors is increasingly observed in various practical applications, such as precision technological instrumentation, sensors, medical diagnostic devices, and others. This requires new semiconductor structures to have a wide range of properties, such as mechanical strength, appropriate electrical and magnetic properties, radiation resistance, etc. A significant role is played by the low cost, ease of manufacture, and wide distribution of the elements on the basis of which these structures are created. One such example is nickel ferrite film, which contains chemical elements common in nature, and their application to substrates can be done by various methods.

Ferrites are interesting materials that have been studied for decades due to their special properties: electrical and magnetic, high chemical and mechanical hardness, radiation resistance [1, 2], which creates opportunities for their wide 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 coil core, hydrogen production, batteries, and many others [3-6].

Spinel ferrites of the MFe_2O_4 type ($M = Ni$, Co, Zn and others) have interesting physical properties that are widely used in practice and described in various studies. In particular, cubic inverse spinel $NiFe_2O_4$ is a promising candidate in many areas of electronics due to the peculiarities of the arrangement of atoms in the crystal lattice. It is important to prepare the film, the correctness and method of its application, which directly affects the characteristics of the film and the structures created on its basis. Currently, there are a variety of techniques proposed for ferrite thin film deposition, such as pulse laser deposition [7], chemical bath deposition [8], radio-frequency magnetron sputtering [9], pyrolysis spraying method [10] and other. Our choice fell on the spray pyrolysis method. The spray pyrolysis method is widely used due to the simplicity of the process, low cost and efficiency for fabricate large-area films. In addition, various advantages of the spray pyrolysis technique include convenience of coating, low energy consumption for sample preparation and film thickness control, etc. [11]. This technique involves the fabrication of multicomponent thin films from different aqueous mixtures, of which at least two mixtures are mixed to form a solution. This makes it possible to effectively dope the films by changing the quantitative composition of the raw materials. Film uniformity, controlled grain size, etc. can be achieved using this method.

Indium monoselenide was used as the substrate, which has a band gap $E_g \approx 1.2$ eV, which is in the range of optimal values for the photoelectric conversion of the spectrum of solar radiation. The layered structure of InSe crystals with weak van der Waals bonding between layers provides their advantage over other semiconductors in the manufacture of substrates for heterostructures due to the avoidance of ingot cutting operations (simple chipping along the layers is used), mechanical and chemical surface treatment, and the resistance of InSe to of radiation expands the scope of its use. The presence of a weak van der Waals bond between the layers and a strong ionic-covalent bond in the layers in InSe determines the peculiarities of the physical properties of the crystals. In particular, it significantly affects the electrical properties [12]. As a

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result of the layered structure in InSe, energy barriers E_δ are formed for the movement of charge carriers along the ***c*** axis, which causes large values of electrical conductivity anisotropy.

2. EXPERIMENTAL

Monocrystalline *n*-InSe grown by the Bridgman method was used to fabricate heterojunctions. From the InSe crystal ingot, a plane-parallel plates size of $3 \times 3 \times 1.2$ mm^3 with perfect mirror surfaces were chipped along the cleavage plane. Chipping was carried out in the air.

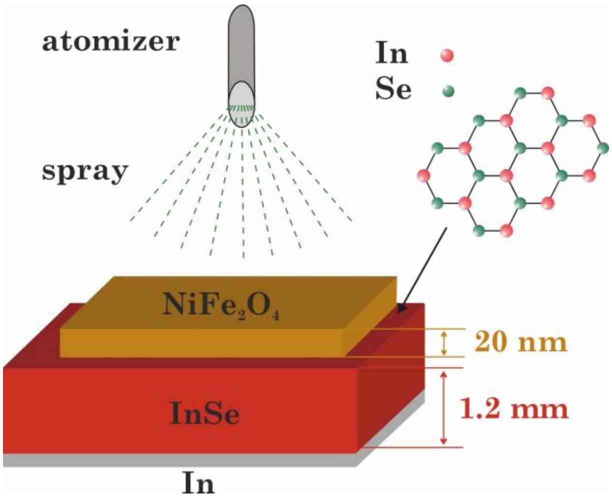

Fig. 1 – Schematic representation of the method of applying NiFe$_2$O$_4$ films

NiFe$_2$O$_4$ thin films were produced by spray pyrolysis of a 0.1 M aqueous solution of nickel dichloride NiCl$_2$·2H$_2$O and iron trichloride FeCl$_3$·6H$_2$O. A schematic representation of the method is shown in Fig. 1. Distilled water was used to dissolve metal salts. Separately prepared solutions of nickel and iron salts were mixed in the proportion of Fe:Ni = 2:1 by volume using a magnetic stirrer for 60 minutes at room temperature before application. The pyrolysis temperature when obtaining samples of NiFe$_2$O$_4$ thin films on substrates was T_S = 623 K. Compressed air was used as the carrier gas. The spray pyrolysis process allowed simultaneous application of films on several substrates. To obtain the steps of the film, which were used in determining the thickness, specially made masks were used. The thickness of the *n*-NiFe$_2$O$_4$ films was about 0.2 μm. It was determined by the displacement of interference lines at the film-substrate boundary on an MII-4 microinterferometer.

Contacts to the InSe base material were applied by sputtering pure indium, and to the *n*-NiFe$_2$O$_4$ film they were formed using silver-based conductive paste. The *I-V* characteristics of *n*-NiFe$_2$O$_4$/*n*-InSe heterostructures were studied on a Solartron 1255 measuring complex in the temperature range from 244 K to 317 K. The photosensitivity spectra of heterojunctions 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. 2 shows the forward *I-V* characteristics of the *n*-NiFe$_2$O$_4$/*n*-InSe heterojunction at temperatures from 244 K to 317 K. The height of the potential barrier ($e\varphi$) was determined by extrapolation of the straight sections of the forward *I-V* characteristics to the voltage axis. It depends weakly on temperature and is equal to about 0.65 eV.

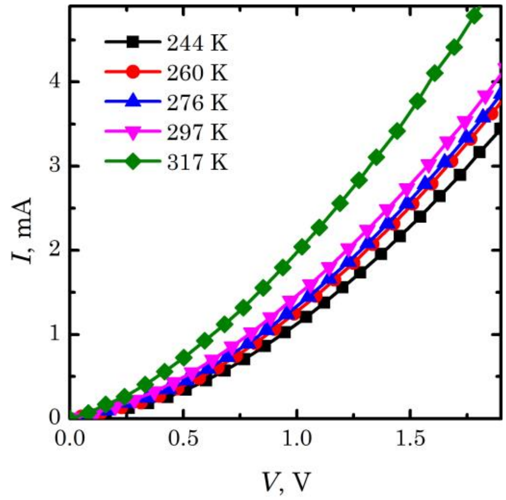

Fig. 2 – Forward *I-V* characteristics of *n*-NiFe$_2$O$_4$/*n*-InSe heterojunction

Taking into account the influence of series and shunt resistances, the *I-V* characteristics can be described by the next formula [13]:

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

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

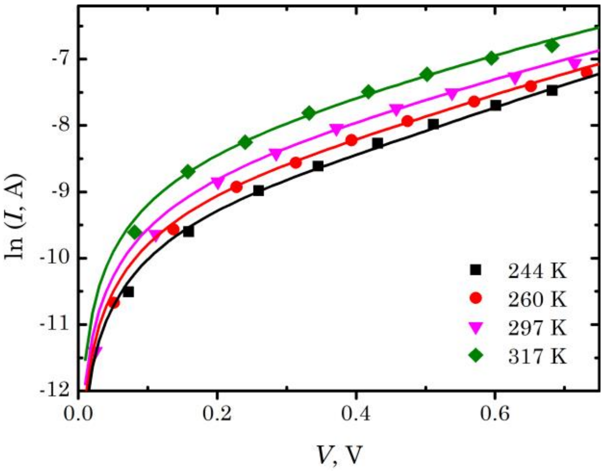

Fig. 3 – Forward *I-V* characteristics of *n*-NiFe$_2$O$_4$/*n*-InSe heterojunction (points are experimental data, curves are approximation by formula (1))

The forward *I-V* characteristics of the *n*-NiFe$_2$O$_4$/*n*-InSe heterojunction in semi-logarithmic coordinates at different temperatures are shown in Fig. 3. Points correspond to experimental values, and solid curves are results of approximation using formula (1). The values of n, R_s, and R_{sh} are given in Table 1. A large value of n and a weak dependence of the slope of the forward *I-V* characteristics on temperature may be evidence of the tunnel nature of the current transfer mechanism.

With reverse bias in the case of a sharp transition, the expression for the tunnel current has the form [14]:

$$I = a_0 \exp[-b_0(\varphi_k - V)^{-1/2}], \qquad (2)$$

where a_0 and b_0 are voltage-independent parameters.

The fact that the reverse *I-V* characteristics (see Fig. 4) are straight lines in the coordinates $\ln(I^t_{rev}) = f(\varphi_0 - eV)^{-1/2}$, according to equation (2), indicates the dominance of the tunnel mechanism of current transfer in the region of reverse bias $|V| > 3kT/e$.

Table 1 – Fitting parameters

T, K	n	R_s, Ohm	R_{sh}, Ohm
244	6	200	2200
260	6	180	1800
276	5.4	170	1500
297	6	150	1500
313	5.4	120	1020

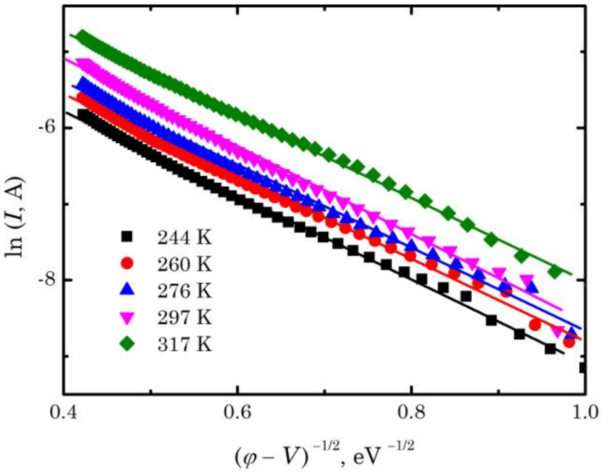

Fig. 4 – Reverse *I-V* characteristics of n-NiFe$_2$O$_4$/n-InSe heterojunction

Fig. 5 shows the spectral dependence of the photoresponse of the n-NiFe$_2$O$_4$/n-InSe heterostructure irradiated from the side of the n-NiFe$_2$O$_4$ film in the photon energy range of 1.26÷3.2 eV. The curve has a maximum at 2.48 eV. The long-wavelength edge at $h\nu \approx 1.26$ eV is caused by the fundamental absorption in n-InSe. The sharp edge of the intrinsic absorption indicates that the light is not scattered in the NiFe$_2$O$_4$ layer and completely enters into InSe at $h\nu \approx E_g$(InSe). This can be a confirmation of the homogeneity of the NiFe$_2$O$_4$ film. With a further increase in the energy of photons, the photoresponse of the heterostructure increases due to an increase in the absorption coefficient. NiFe$_2$O$_4$ have two direct band gaps at 2.35 and 2.8 eV [15]. When $h\nu$ reaches the values of the band gap of NiFe$_2$O$_4$, the latter begins to absorb light and the photoresponse decreases, as the number of photons entering into InSe decreases. The full width of the spectrum $\delta_{1/2}$ is about 1.96 eV.

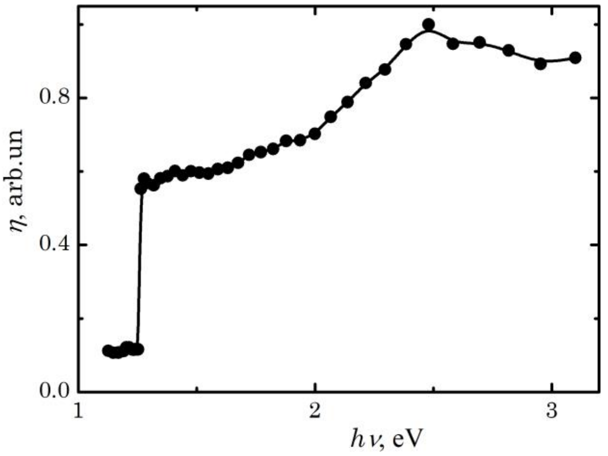

Fig. 5 – Photoresponse spectra of n-NiFe$_2$O$_4$/n-InSe heterojunction

4. CONCLUSION

The n-NiFe$_2$O$_4$/n-InSe heterojunctions were fabricated by the spray pyrolysis method. The aqueous solution of nickel dichloride NiCl$_2$·2H$_2$O and iron trichloride FeCl$_3$·6H$_2$O was used to deposit the NiFe$_2$O$_4$ film on InSe substrate heated to 623 K. The study of *I-V* characteristics at different temperatures (244÷317 K) confirms the formation of an energy barrier with height $e\varphi \approx 0.65$ eV. The height depends weakly on temperature. It is found that tunneling is the dominant mechanisms of current transport in the n-NiFe$_2$O$_4$/n-InSe heterojunctions at forward and reverse bias.

Photoelectric parameters of n-NiFe$_2$O$_4$/n-InSe heterojunctions were investigated. It is shown that n-NiFe$_2$O$_4$/n-InSe heterojunction effectively converts light in the energy range of 1.26÷3.2 eV. The fundamental absorption edge of InSe determines the sharp long-wavelength edge of the heterostructure photosensitivity which is observed at $h\nu \approx 1.26$ eV. The photoresponse spectra has maximum at 2.48 eV and the full width is about 1.96 eV.

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Електричні властивості та фотовідгук гетеропереходу $NiFe_2O_4$/InSe

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Досліджені умови нанесення методом спрей-піролізу при температурі 623 К тонких напівпровідникових феритових плівок n-$NiFe_2O_4$ на підкладки з кристалічного шаруватого напівпровідника n-InSe для створення фоточутливих гетеропереходів n-$NiFe_2O_4$/n-InSe. За температурною залежністю прямих і зворотних вольт-амперних характеристик встановлено механізми протікання струмів крізь гетероперехід. Проаналізована спектральна фоточутливість гетеропереходу n-$NiFe_2O_4$/n-InSe в діапазоні енергії 1.26÷3.2 еВ.

Ключові слова: Селенід Індію, Гетероструктури, Спрей-піроліз, Вольт-амперні характеристики, Фотовідгук.