JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 18 No 3, 03001(4pp) (2026)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 18 № 3, 03001(4cc) (2026)

REGULAR ARTICLE

$CoFe_2O_4$/InSe Heterostructures Based on Layered Crystals: Electrical and Photoelectric Properties

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(Received 23 February 2026; revised manuscript received 19 June 2026; published online 26 June 2026)

The electrical and photoelectric properties of an *n*-$CoFe_2O_4$/*p*-InSe anisotype heterojunction formed on the basis of thin films of cobalt ferrite and a layered indium selenide have been investigated. $CoFe_2O_4$ films were obtained by the spray pyrolysis method. The *p*-InSe substrates were fabricated from single crystals grown by the Bridgman method. The *I-V* characteristics of the heterostructures were measured in the temperature range of 244 ÷ 317 K. The potential barrier height was evaluated. The influence of series resistance on the shape of the forward *I-V* characteristics was analyzed, and the main factors determining it were identified. Based on the analysis of experimental dependences, the charge transport mechanisms through the heterojunction under forward and reverse bias were studied. The experimental data were approximated within the framework of appropriate theoretical models. The main regularities governing the formation of the spectral response in the photon energy range of 1.2 ÷ 3.2 eV were established. The obtained results can be used in the development of electronic devices based on heterostructures of this type.

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

DOI: 10.21272/jnep.18(3).03001 PACS numbers: 73.40. – c, 78.66. – w

1. INTRODUCTION

The fabrication of semiconductor structures based on materials with different types of conductivity opens up broad prospects for the creation of advanced electronic and spintronic devices. Of particular interest are heterojunctions formed using materials with different electronic and magnetic properties, in particular layered semiconductors [1, 2] and ferromagnetic oxides [3] with a high degree of spin polarization. Such systems enable the realization of new functionalities associated with the control of both charge and spin degrees of freedom of charge carriers.

One of the promising classes of materials for the fabrication of such heterostructures is layered chalcogenides, in particular InSe, which is characterized by high carrier mobility, anisotropy of electrophysical properties, and the possibility of effective control of the conductivity type [4]. Due to weak van der Waals bonding between the layers, these materials are convenient for forming high-quality interfaces with a low density of structural defects. Another important advantage of indium selenide is the ease of substrate fabrication for film deposition. Owing to the weak van der Waals bonding, no additional cutting processes are required, as the ingots cleave easily and do not require chemical treatment.

On the other hand, spinel ferrites, in particular $CoFe_2O_4$, attract considerable attention due to their unique magnetic, electronic, and optical properties, such as high coercivity, chemical stability, and stable magnetic characteristics at room temperature [5, 6]. These materials are widely studied in the context of applications in sensors, spintronics, data storage devices, and energy systems [7]. In recent years, significant attention has been paid to the investigation of $CoFe_2O_4$ thin films. It has been established that their physical properties strongly depend on the growth conditions [8-10]. Film parameters such as grain size, defect structure, and morphology significantly affect the charge transport mechanisms and magnetic properties of the material.

The combination of layered semiconductors with ferromagnetic oxides in the form of heterojunctions opens up the possibility of studying new physical effects at the interface, in particular the features of energy band alignment, charge transport mechanisms, and the influence of spin polarization on electrical characteristics. In this regard, the investigation of the electrophysical and photoelectric properties of *n*-$CoFe_2O_4$/*p*-InSe heterojunctions, as well as the determination of the main charge transport mechanisms and the formation of photosensitivity in such structures, is of considerable interest and relevance.

2. EXPERIMENTAL

Anisotype *n*-$CoFe_2O_4$/*p*-InSe heterojunctions were fabricated using substrates with dimensions of 30 × 30 × 5 mm, cleaved from *p*-type indium monose-

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Cite this article as: I.G. Tkachuk et al., *J. Nano- Electron. Phys.* 18 No 3, 03001 (2026) https://doi.org/10.21272/jnep.18(3).03001

lenide (p-InSe) single crystals grown by the Bridgman method. Hole conductivity was achieved by cadmium doping (0.1 wt. %). The carrier concentration, determined from Hall measurements, was $p \approx 10^{14}$ cm^{-3} at room temperature. The hole mobility perpendicular to the crystallographic $\boldsymbol{c}$-axis was $\mu_{pH} \approx 55$ cm^2/(V·s).

Thin films of cobalt ferrite $CoFe_2O_4$ were deposited by spray pyrolysis from an aqueous solution containing cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) with a total concentration of 0.1 M and a component ratio $FeCl_3 \cdot 6H_2O/CoCl_2 \cdot 6H_2O = 2$. The InSe substrates were heated to 623 K during deposition. Compressed air was used as the carrier gas, and the solution spray rate was 3÷5 ml/min. Bidistilled water was used for solution preparation. Separately prepared 0.1 M salt solutions were mixed using a magnetic stirrer for 1 hour at room temperature. Dielectric glass-ceramic substrates (1 × 2 cm) and transparent soda-lime glass substrates (2 × 2 cm) were used to study the electrical and optical properties of the films. Prior to deposition, both types of substrates were cleaned of possible organic contaminants in an ammonia-peroxide solution H_2O_2:$(NH_2)OH$:H_2O = 2:1:4. After degreasing, the substrates were treated with a 5 % $K_2Cr_2O_7$ solution in sulfuric acid (H_2SO_4, 85 %). Finally, the substrates were rinsed in bidistilled water and dried in a flow of nitrogen gas. The deposition time for $CoFe_2O_4$ films with a thickness of 0.3 μm was about 10 minutes.

Film thickness was measured using a Linnik microinterferometer MII-4. For this purpose, areas without film were formed on ceramic substrates using shadow masks to create a step between the film and substrate. The measured film thickness was approximately 0.4 μm. After deposition on ceramic substrates, the electrical resistivity of the $CoFe_2O_4$ films was measured at room temperature using the four-probe method and was found to be $\rho \approx 10^7$ Ohm·cm. The conductivity type was determined from the thermoelectric power (Seebeck effect) polarity, indicating n-type conductivity in the $CoFe_2O_4$ films. Optical studies of $CoFe_2O_4$ thin films deposited by spray pyrolysis were carried out using an SF-2000 spectrophotometer in the wavelength range of 0.4÷1.1 μm. The transmittance of the $CoFe_2O_4$ layer was found to be 50÷70 %. It was also established that direct optical transitions occur in the films, with a bandgap energy of $E_g = 1.95$ eV.

Electrical contacts to the InSe substrates and $CoFe_2O_4$ films were fabricated using a conductive paste containing finely dispersed silver particles. The *I-V* characteristics of the n-$CoFe_2O_4$/p-InSe heterojunctions were measured using a SOLARTRON 1255 system in the temperature range of 244÷317 K. The spectral photosensitivity of the heterojunctions was investigated at room temperature using an MDR-3 monochromator with a spectral resolution of 2.6 nm/mm.

3. RESULTS AND DISCUSSION

Fig. 1 shows the *I-V* characteristics of the n-$CoFe_2O_4$/p-InSe heterojunctions measured at different temperatures. The potential barrier height (φ_0) was estimated by extrapolating the linear regions of the forward *I-V* characteristics to the voltage axis. It was found that within the investigated temperature range, the barrier height remains nearly constant and is approximately 0.3 eV.

The analysis of the forward *I-V* characteristics of the n-$CoFe_2O_4$/p-InSe heterostructure reveals the influence of series resistance, which leads to a decrease in the slope of the forward *I-V* curves at voltages exceeding φ_0. In this case, the *I-V* characteristics under forward bias are described by the following equation [11]:

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

where I_s is the saturation current, n is the ideality factor, and R_s is the series resistance.

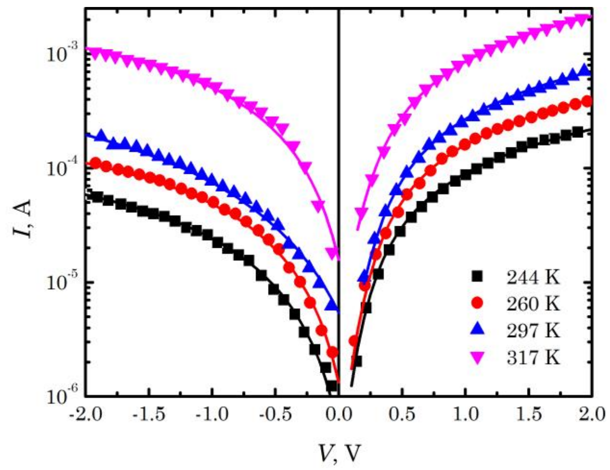

Fig. 1 – *I-V* characteristics of $CoFe_2O_4$/InSe heterojunction (points are experimental data, curves are approximation by Eqs. 1-2)

We performed an approximation of the experimental data using equation (1). The results are shown by solid curves in Fig. 1. The obtained parameters I_s, n, and R_s are presented in Table 1. It can be seen that the value of n does not depend on temperature, while R_s decreases with increasing temperature. The main contribution to R_s arises from the resistance of relatively thick InSe.

Based on the large values of the ideality factor n and literature data on similar heterojunctions fabricated by spray pyrolysis on InSe substrates [12, 13], it can be assumed that in n-$CoFe_2O_4$/p-InSe heterojunctions the dominant current transport mechanism under forward bias is tunneling.

Table 1 – Fitting Parameters

T, K	*n*	*Is*, mkA	*Rs*, kOm
244	3	0.38	7.3
260		0.58	3.9
297		1.0	2.1
317		7.5	0.72

Under reverse bias, the current flow in the heterojunctions has a tunneling nature. The reverse *I-V* characteristics, in the case of a tunneling transport mechanism of charge carriers through the barrier, are described by the following equation [11]:

$$I = a_0 \exp\left(-b(\varphi_0 - V)^{-1/2} \right) \qquad (2)$$

where φ_0 is the potential barrier height, a_0 and b are constants.

The results of the approximation of the reverse *I-V* characteristics using equation (2) are shown in Fig. 1 (solid curves). In the calculations, the value $\varphi_0 = 0.3$ eV, obtained from the forward *I-V* characteristics, was used. It can be seen that the theoretical curves agree well with the experimental data, confirming the tunneling mechanism of reverse current transport.

The performed analysis shows that equations (1-2) describe the experimental *I-V* data under both forward and reverse bias with sufficient accuracy and can be used for the analysis of experimental results.

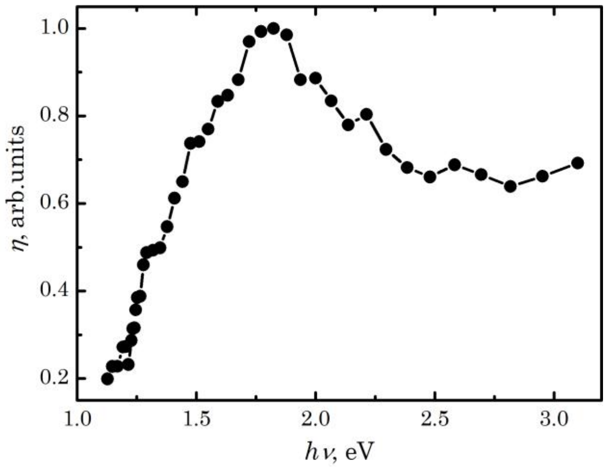

Fig. 2 – Relative quantum efficiency of $CoFe_2O_4$/InSe heterojunction

The spectral dependence of the quantum efficiency of the heterostructure n-$CoFe_2O_4$/p-InSe, irradiated from the $CoFe_2O_4$ film side, was studied in the photon energy range of 1.2÷3.2 eV. The maximum occurs at approximately 1.8 eV, and the full width of the relative quantum efficiency spectrum is at least 1.8 eV. The long-wavelength edge of the photosensitivity at $h\nu \approx 1.2$ eV is determined by the fundamental absorption edge of InSe. The $CoFe_2O_4$ film, at photon energies exceeding its bandgap (1.95 eV), begins to absorb light, which reduces the number of photons reaching the InSe layer. A decrease in the signal is observed in Fig. 2. This indicates that the photon absorption efficiency in InSe is higher, and these photons contribute more to the photocurrent than if they were absorbed in $CoFe_2O_4$.

4. CONCLUSION

A The studies have shown that n-$CoFe_2O_4$/p-InSe heterostructures exhibit stable rectifying properties in the temperature range of 244÷317 K, indicating the formation of a high-quality potential barrier at the material interface.

It was established that charge carrier transport in the investigated structures is governed by tunneling processes under both forward and reverse bias, which is associated with the features of the energy structure and the presence of defect states in the near-surface layers.

It was shown that the series resistance, mainly determined by the properties of the underlying InSe semiconductor, has a significant influence on the electrical characteristics of the heterojunction. This factor should be taken into account when optimizing the parameters of devices based on such heterostructures.

The heterostructures were found to be photosensitive in the photon energy range of 1.2÷3.2 eV, with a maximum at 1.8 eV.

The obtained results reveal the potential of these heterostructures for application in functional electronic devices.

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Гетероструктури $CoFe_2O_4$/InSe на основі шаруватих кристалів: електричні та фотоелектричні властивості

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Досліджено електричні та фотоелектричні властивості анізотипного гетеропереходу *n*-$CoFe_2O_4$/*p*-InSe, сформованого на основі тонких плівок фериту кобальту та шаруватого напівпровідника селеніду індію. Плівки $CoFe_2O_4$ отримано методом спрей-піролізу. Підкладки *p*-InSe виготовлено з монокристалів, вирощених методом Бріджмена. Приведено результати вимірювань вольт-амперних характеристик гетероструктур в інтервалі температур 244÷317 К. Проведено оцінку висоти потенціального бар’єра. Розглянуто вплив послідовного опору на форму прямих гілок вольт-амперних характеристик та визначено основні чинники, що його обумовлюють. На основі аналізу експериментальних залежностей досліджено механізми переносу заряду через гетероперехід при прямому та зворотньому зміщеннях. Проведено апроксимацію експериментальних даних у рамках відповідних теоретичних моделей. Встановлено основні закономірності формування спектрального відгуку в діапазоні енергій фотонів 1.2÷3.2 еВ. Отримані результати можуть бути використані при розробці електронних пристроїв на основі гетероструктур даного типу.

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