PHYSICS AND CHEMISTRY OF SOLID STATE
V. 26, No. 2 (2025) pp. 231-234
Section: Physics
DOI: 10.15330/pcss.26.2.231-234

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 26, № 2 (2025) С. 231-234
Фізико-математичні науки

PACS: 78.66.–w

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

I.G. Tkachuk[1,3], I.G. Orletskii[2], Z.D. Kovalyuk[1], V.I. Ivanov[1], A.V. Zaslonkin[1], B.V. Kusnir[1]

Photoelectric properties of heterojunctions based on semiconducting metal oxides and indium selenide

[1]*Institute for Problems of Materials Science, Chernivtsi Branch, Chernivtsi, Ukraine,* chd.ipm@gmail.com
[2]*Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine,* office@chnu.edu.ua
[3]*Bukovinian State Medical University, Chernivtsi, Ukraine,* office@bsmu.edu.ua

The results of a comparison of the photosensitivity of heterojunctions based on InSe layered semiconductor and various wide band gap oxides (Mn_2O_3, $CuFeO_2$, Fe_2O_3) produced by the spray pyrolysis method are given. The photoresponse of the heterojunction irradiated from the side of metal oxides was studied in the photon energy range of 1.2÷3 eV. The possibility of the formation of In_2Se_3 phase between of InSe and oxides and its effect on the photosensitivity of the heterostructures have been considered.

Keywords: indium selenide, heterostructure, photoresponse.

Received 03 June 2024; Accepted 07 April 2025.

Introduction

In the field of modern instrumentation, the photovoltaic properties of semiconductor materials and heterojunctions based on them are no less important than electrical properties. The ability of heterojunctions to convert optical radiation into electrical energy allows the manufacture of various optoelectronic devices, such as photodetectors, photoresistors, solar panels, etc. Such devices have a wide field of use - from the peaceful industry for the production of ecologically clean energy to tracking of missile launches. Therefore, our goal is to create heterojunctions not only with diode parameters but also with photovoltaic ones. The layered structure of the InSe semiconductor, where the atoms within the layers are bound by a strong covalent bond, and the interaction between the layers is weak van der Waals, determines the anisotropy of its physical properties. Because of this crystal structure, InSe is easily chipped in a direction parallel to the layers. As a result, a mirror surface is obtained, which contains almost no broken bonds. Accordingly, on such a surface there is no adsorption of atoms of a foreign substance, which makes InSe an ideal candidate as a base material in the manufacture of various heterojunctions. The band gap width of InSe $E_g \approx 1.2$ eV is in the range of optimal values for the photoelectric conversion of solar radiation [1,2]. In addition, InSe is a material with increased radiation resistance [3]. This determines the prospects of InSe for the manufacture of various optoelectronic devices [4-6].

The choice of the material of the front layer and the fabricating technology are important technological tasks. It is necessary to ensure the formation of a defect-free interface, as well as the maximum absorption of radiation in the base material, that is, the transparency of the front layer. It is the optimal choice of raw materials and manufacturing technology that allow us to create high-quality, competitive heterostructures with the necessary electrical and photovoltaic parameters. Transparent conductive oxides are promising materials for the front layer of heterojunctions. They have high electrical conductivity and low optical absorption of visible light. Their thin films are widely used in various devices such as flat panel displays, touch panels and solar cells.

This paper compares the spectra of heterojunctions based on the contact of InSe and semiconductor oxides Mn_2O_3, $CuFeO_2$, and Fe_2O_3, produced by the spray pyrolysis method [7-10].

I. Methodology of the experiment

Single-crystal n-InSe and p-InSe grown by the Bridgman method were used as the base material of the heterojunctions. From the InSe crystal ingot, plane-parallel plates, which had perfect mirror surfaces, were chipped along the cleavage plane. Chipping was carried out in the air.

Then rectangular substrates with side lengths ≤ 5 mm were cut from the plates using a blade. The original InSe has n-type conductivity. To ensure the p-type, doping with cadmium (0.1 wt.%) was carried out. The concentration (n) and mobility (μ) of charge carriers in the perpendicular direction relative to the symmetry axis c was calculated on the basis of Hall studies at room temperature: $p \approx 10^{14}$ cm^{-3}, $\mu_p \approx 50$ cm^2/(V·s) for p-type samples; $n \approx 10^{15}$ cm^{-3}, $\mu_n \approx 850$ cm^2/(V·s) for n-type samples.

For the fabrication of heterostructures, a thin layer of various semiconducting wide band gap oxides was deposited to the surface of the InSe substrate by spray pyrolysis. This technology is simple, cheap and does not require complex technological equipment. Spray pyrolysis took place under atmospheric pressure conditions, and ordinary air was used as the carrier gas. Before spraying, the surface of the substrate was degreased by a chemical method. Next, an aqueous solution of the appropriate composition was sprayed onto the heated InSe substrate. The temperature of the substrate was 620÷700 K, depending on the grown oxide. As a result of pyrolysis, a thin oxide film is formed on the surface and a heterojunction is obtained. The contacts were made using a conductive paste that containing finely dispersed silver particles. The spectral photosensitivity of the heterojunctions was studied at room temperature using the MDR-3 monochromator. The thickness of the films grown by spray pyrolysis was measured by a MII-4 microinterferometer.

We fabricated the following heterostructures based on the contact of InSe and semiconductor oxide: n-Mn_2O_3/p-InSe, n-Mn_2O_3/n-InSe, p-$CuFeO_2$/n-InSe and n-Fe_2O_3/p-InSe. All of them were made according to the same technological algorithm, only the chemical composition of the aqueous solution used to generate an aerosol over the surface of the substrates changed: $MnCl_2 \cdot 4H_2O$ for n-Mn_2O_3/p-InSe and n-Mn_2O_3/p-InSe [7,8]; $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ for p-$CuFeO_2$/n-InSe [9]; $FeCl_3 \cdot 6H_2O$ for n-Fe_2O_3/p-InSe [10]. In the table 1 shows the thickness of the obtained films, the contact potential difference of the heterojunction, and the width of the band gap (E_g) of the oxide. The main mechanism of charge transfer in these heterojunctions is tunneling.

II. Results and discussion

Fig. 1 shows the photoresponse spectra of the heterojunctions. Illumination was carried out from the side of the oxides. The front layer is transparent in the region of maximum photosensitivity of InSe, which makes it possible to effectively exploit the optical properties of the latter. We see that the heterojunctions are photosensitive in the photon energy range of 1.2÷3 eV. The long-wavelength edge of photosensitivity at $h\nu \approx 1.2$ eV is caused by the fundamental absorption edge in InSe. Due to the polycrystalline nature of the oxide films, the fundamental absorption edge in some samples may be blurred compared to single crystal materials (see curves for n-Mn_2O_3/n-InSe and n-Fe_2O_3/p-InSe). At energies lower than band gap of the oxide, part of the radiation is absorbed at the grain boundaries. Accordingly, the number of photons entering InSe decreases.

As can be seen from the presented spectra, peaks of different intensity are observed at their long-wavelength

Table 1.

Parameters of the heterojunctions

	oxide thickness, μm	InSe thickness, mm	φ, eV	oxide band gap, eV
n-Mn_2O_3/n-InSe	0.5	1	1.4	2.12
n-Mn_2O_3/p-InSe	0.5	1	1.1	2.12
p-$CuFeO_2$/n-InSe	0.3	1.2	1.02	2.6
n-Fe_2O_3/p-InSe	0.3	0.5	0.74	2.1

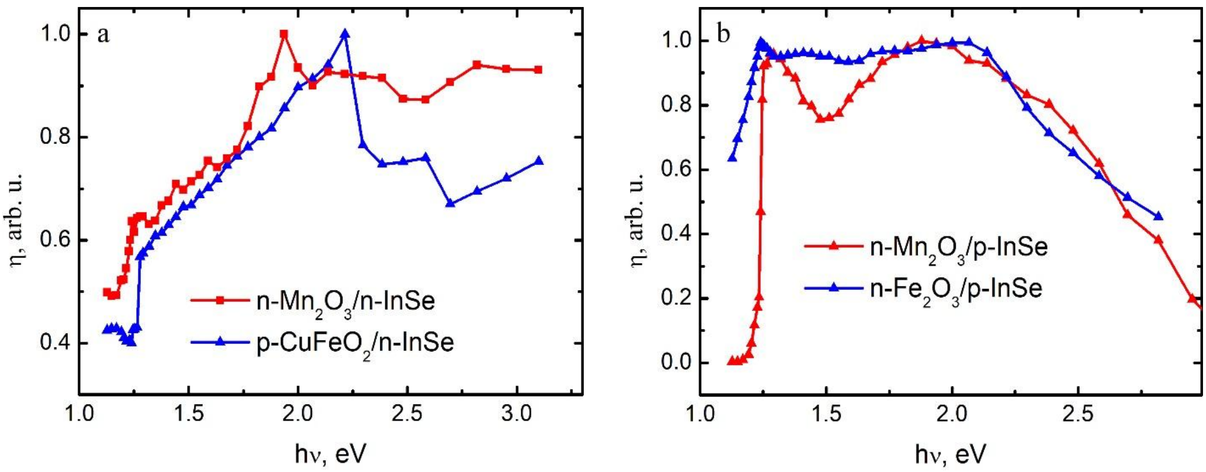

Fig. 1. Photoresponse spectra: a) – n-InSe; b) – p-InSe.

edge depending on the type of heterojunction. It is related to the formation of excitons. The observation of excitons at room temperature indicates the high perfection of InSe crystals.

Usually, the photosensitivity of heterostructures is limited on the one hand by the band gap of the base material, where the main absorption of radiation occurs, and on the other hand by the band gap of the front layer. This behavior is demonstrated by n-Mn_2O_3/p-InSe and n-Fe_2O_3/p-InSe heterostructures (see Fig. 1b). The p-$CuFeO_2$/n-InSe and n-Mn_2O_3/n-InSe heterostructures have slightly different behavior (Fig. 1a). In the case of p-$CuFeO_2$/n-InSe heterostructures, this is explained by the formation of the In_2Se_3 film, which we will discuss below, and isotype n-Mn_2O_3/n-InSe heterostructures are less sensitive to losses caused by light absorption in the front layer.

A feature of our heterostructures manufacturing is the possibility of formation of extraneous phases on the InSe surface during the sample manufacturing process. It is known that when InSe is heated in air to temperatures of 573÷773 K, In_2Se_3 and $In_2(SeO_4)_3$ phases are formed, and at higher temperatures – In_2O_3 [11,12]. The band gap width of α-In_2Se_3 films depends on its thickness: E_g increases with decreasing thickness and can reach 2.8 eV for 3.1 nm [13]. The formation of such phases is an uncontrolled process. We established the formation of a thin In_2Se_3 film between InSe and oxide in the process of fabrication of p-$CuFeO_2$/n-InSe [9] and n-Fe_2O_3/p-InSe [10] heterostructures. These phases can cause changes in the spectra of photosensitivity. Exactly which part of the InSe surface changes is not known, this requires additional research. But it is obvious that when such changes affect some critical percentage of the InSe surface area, this is reflected in the photosensitivity spectra in the form of the appearance of additional maxima (2.3 eV for p-$CuFeO_2$/n-InSe) or a change in the shape of the photoresponse curves due to the redistribution of absorbed photons between InSe and In_2Se_3. Thus, the analysis of the spectra can be a confirmation of the phase transformations of InSe.

Conclusions

The photosensitivity of heterostructures based on the layered semiconductor InSe and wide band gap oxides of various types (Mn_2O_3, $CuFeO_2$, Fe_2O_3) was analyzed. Heterostructures were produced by the spray pyrolysis method. These heterostructures effectively convert light into electric current in the photon energy range of 1.2÷3 eV. It is shown that the main absorption of light occurs in InSe, since the oxides are transparent in the range of its maximum photosensitivity. Peaks corresponding to exciton absorption are visible on the photoresponse curves. The fact that they are observed at room temperature confirms the perfection of InSe crystals.

Due to the heating of InSe in the technological process, a thin film of In_2Se_3 can form on its surface, which affects the photoresponse spectra.

Tkachuk I.G. – Candidate of physical and mathematical sciences, Researcher;
Orletskii I.H. – Associate Professor;
Kovalyuk Z.D. – Professor, Doctor of physics and mathematics;
Ivanov V.I. – Candidate of physical and mathematical sciences, Researcher;
Zaslonkin A.V. – Junior research fellow;
Kusnir B.V. – Junior research fellow.

[1] M. Teena, A.G. Kunjomana, K. Ramesh, R. Venkatesh, N. Naresh, *Architecture of monophase InSe thin film structures for solar cell applications*, Sol. Energy Mater. Sol., 166, 190 (2017); https://doi.org/10.1016/j.solmat.2017.03.027.
[2] J. Martínez-Pastor, A. Segura, J.L. Valdés, A. Chevy, *Electrical and photovoltaic properties of indium-tin-oxide/p-InSe/Au solar cells*, J. Appl. Phys., 62, 1477 (1987); https://doi.org/10.1063/1.339627.
[3] I.V. Mintyanskii, P.I. Savitskii, Z.D. Kovalyuk, *Two-band conduction in electron-irradiated n-InSe single crystals*, Phys. St. Sol. (b), 252 (2), 346 (2015); https://doi.org/10.1002/pssb.201451146.
[4] W. Luo, Y. Cao, P. Hu, K. Cai, Q. Feng, F. Yan, T. Yan, X. Zhang, K. Wang, *Gate tuning of high-performance InSe-based photodetectors using graphene electrodes*, Adv. Opt. Mater., 3(10), 1418 (2015); https://doi.org/10.1002/adom.201500190.
[5] X. Sun, J. He, B. Shi, B. Zhang, R. Wang, *Alpha-phase indium selenide saturable absorber for a femtosecond all-solid-state laser*, Opt. Lett., 44, 699 (2019); https://doi.org/10.1364/OL.44.000699.
[6] Y. Pan, Q. Zhao, F. Gao, M. Dai, W. Gao, T. Zheng, S. Su, J. Li, H. Chen, *Strong in-plane optical and electrical anisotropies of multilayered γ-InSe for high-responsivity polarization-sensitive photodetectors*, ACS Appl. Mater. Interfaces, 14(18), 21383 (2022); https://doi.org/10.1021/acsami.2c04204.
[7] I.G. Tkachuk, I.G. Orletskii, V.I. Ivanov, Z.D. Kovalyuk, A.V. Zaslonkin, V.V. Netyaga, *Photoelectric properties of the Mn_2O_3/n-InSe heterojunction*, J. Nano- Electron. Phys., 15(2), 02022 (2023); https://doi.org/10.21272/jnep.15(2).02022.
[8] I.G. Orletskii, I.G. Tkachuk, V.I. Ivanov, Z.D. Kovalyuk, A.V. Zaslonkin, *Electrical properties and photosensitivity of n-Mn_2O_3/p-InSe heterojunctions produced by the spray pyrolysis method*, J. Nano- Electron. Phys., 15(5), 05025 (2023); https://doi.org/10.21272/jnep.15(5).05004.
[9] I.G. Tkachuk, I.G. Orletskii, V.I. Ivanov, A.V. Zaslonkin, Z.D. Kovalyuk, *Photosensitive $CuFeO_2$/n-InSe heterojunctions*, J. Nano- Electron. Phys., 14 (4), 04016 (2022); https://doi.org/10.21272/jnep.14(4).04016.
[10] I.G. Orletskii, I.G. Tkachuk, Z.D. Kovalyuk, V.I. Ivanov, A.V. Zaslonkin, *Fe_2O_3/p-InSe heterostructures produced by spray pyrolysis method*, J. Nano- Electron. Phys., 16(2), 02007 (2024); https://doi.org/10.21272/jnep.16(2).02007.

[11] O.A. Balitskii, K.V. Lutsiv, V.P. Savchyn, J.M. Stakhira, *Thermal oxidation of cleft surface of InSe single crystal*, Mater. Sci. Eng., 56(1), 5 (1998); https://doi.org/10.1016/S0921-5107(98)00213-X.
[12] V.P. Savchyn, V.B. Kytsai, *Photoelectric properties of heterostructures based on thermo-oxidated GaSe and InSe crystals*, Thin Solid Films, 361–362, 123 (2000). https://doi.org/10.1016/S0040-6090(99)00796-8.
[13] J. Quereda, R. Biele, G. Rubio-Bollinger, N. Agraït, R. D'Agosta, A. Castellanos-Gomez, *Strong Quantum Confinement Effect in the Optical Properties of Ultrathin α-In_2Se_3*, Adv. Opt. Mat. 4(12), 1939 (2016); https://doi.org/10.1002/adom.201600365.

І.Г. Ткачук[1,3], І.Г. Орлецький[2], З.Д. Ковалюк[1], В.І. Іванов[1], А.В. Заслонкін[1], Б.В. Кушнір[1]

Гетеропереходи на основі напівпровідникових оксидів металів та селеніду індію

[1]*Чернівецьке відділення Інституту проблем матеріалознавства імені І.М. Францевича НАН України, Чернівці, Україна,* *chd.ipm@gmail.com*
[2]*Чернівецький національний університет ім. Юрія Федьковича, Чернівці, Україна,* *office@chnu.edu.ua*
[3]*Буковинський державний медичний університет, Чернівці, Україна,* *office@bsmu.edu.ua*

Приведено результати порівняння фоточутливості гетеропереходів на основі шаруватого напівпровідника InSe та різних широкозонних оксидів (Mn_2O_3, $CuFeO_2$, Fe_2O_3), виготовлених методом спрей піролізу. Досліджено спектри фотовідгуку, опроміненого зі сторони плівок оксидів металів гетеропереходу в інтервалі енергій фотонів 1.2÷3 еВ. Встановлено виникнення фази In_2Se_3 між поверхнею кристалу InSe та плівками оксидів та її вплив на фоточутливость гетероструктур.

Ключові слова: селенід індію, гетероструктури, фотовідгук.