JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 15 No 6, 06028(4pp) (2023)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 15 № 6, 06028(4cc) (2023)

p-SnS/*n*-InSe Heterostructures Fabricated by the Spray-Pyrolysis Method

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

[1] *Institute for Problems of Materials Science, Chernivtsi Branch, 5, I. Vilde st., 58001 Chernivtsi, Ukraine*
[2] *Yuriy Fedkovych Chernivtsi National University, 2, Kotsyubynsky st., 58012 Chernivtsi, Ukraine*

(Received 12 September 2023; revised manuscript received 20 December 2023; published online 27 December 2023)

This work is devoted to the fabrication and investigation of electrical and photoelectric characteristics of *p*-SnS/*n*-InSe anisotype heterojunctions. Low-temperature spray pyrolysis technology was used to deposit SnS thin films on InSe crystal substrates. Based on the analysis of temperature dependences of forward and reverse *I-V* characteristics, the dynamics of changes in the energy parameters of the heterojunction were investigated. Theoretical models describing the behavior of the forward and reverse *I-V* characteristics are proposed. The value of the series and shunt resistances, as well as their influence on the *I-V* characteristics of the heterojunction, was determined. The value of the contact potential difference was estimated. The charge transfer was analyzed. The spectral dependence of the quantum efficiency of the *p*-SnS/*n*-InSe heterostructure irradiated from the side of the SnS film in the photon energy range of 1.2÷3.2 eV was studied.

Keywords: Indium Selenide, Tin Sulfide, Heterostructures, Spray Pyrolysis, *I-V* Characteristics, Electrical Conductivity, Photosensitivity.

DOI: 10.21272/jnep.15(6).06028 PACS numbers: 73.40. – c, 78.66. – w

1. INTRODUCTION

There is an active phase of design and fabrication of new materials for use in thin-film solar cells and various types of electronic sensors in the modern world of semiconductor materials. An important condition of such research is the simplicity of technology, low cost and the availability of the materials used. Tin sulfide (SnS) is a promising semiconductor material for optoelectronic applications with a band gap of 1.2÷1.6 eV and a high absorption coefficient [1, 2, 3]. In addition, SnS is an environmentally safe and potentially affordable photovoltaic material.

Usually SnS films exhibit *p*-type conductivity and only in some cases they are *n*-type. The films can be deposited by various methods, such as: electrodeposition, thermal evaporation, chemical deposition, and others. The spray pyrolysis technique allows for mobile correction and control of the deposition process of tin sulfide on the surface of crystalline semiconductor [4, 5], which in this experiment are layered InSe crystals.

Indium selenide has a band gap of 1.26 eV, which is in the range of optimal values for photoelectric conversion of sunlight [6, 7]. There were created different types of photosensitive structures using indium selenide [8-10].

This paper presents the results of studies of the electrical and photovoltaic properties of *p*-SnS/*n*-InSe heterostructure produced by the spray pyrolysis method. Similar heterostructures produced by the physical vapor deposition method are described and analyzed in Ref. [11]. The differences of our research from heterojunctions with a planar contact configuration [11]: external contacts from the front and rear surfaces of the structure improve the electrical properties of the structures contributing to the reduction of internal resistance, the area of the heterojunction is increased, the thickness of SnS and InSe is increased to avoid shunting, and a low-cost non-vacuum manufacturing technology is used. In work [11], heterostructures were made from nanometer layers of SnS and InSe, the area of which was hundreds of microns. In our case, the thickness of InSe and SnS was 1 mm and 0.5 mm, respectively, and the area of the heterostructure was equal to 25 mm^2. Due to the low cost of fabrication of the SnS films, spray pyrolysis is a more attractive technology for the mass production of electronic devices compared to the physical vapor deposition method used by the authors of the work [11].

2. EXPERIMENTAL

The *p*-SnS/*n*-InSe heterostructures were produced by the method of low-temperature spray pyrolysis. The advantage of this technology is simplicity and cheapness. An aqueous solution of chemical reagents of a given composition was sprayed onto the InSe substrate, which was placed on the heater. The substrate was made from *n*-InSe single-crystal grown by the Bridgman method. From the InSe crystal ingot, plane-parallel plates were chipped along the cleavage plane, which were then cut to a size of $5 \times 5 \times 1$ mm^3. Chipping was carried out in the air. The substrates had perfect mirror surfaces. According to the study of the Hall effect, the concentration of charge carriers was $n \approx 10^{15}$ cm^{-3} and their mobility at room temperature in direction perpendicular to the symmetry axis ***c*** was equal to $\mu \approx 850$ cm^2/(V·s).

Thin films of tin sulfide with a thickness of 0.5 μm were made from a 0.1 M aqueous solution of tin dichloride $SnCl_2 \cdot 2H_2O$ and thiourea $(NH_2)_2CS$ (99 %). The solution was prepared in bidistilled water. The ratio of [Sn]:[S] components was 1:3 to provide the required amount of sulfur when forming a SnS film with a composition that is close to stoichiometric. During the pyrolysis of salts on the surface of the InSe substrate, due to its

*ivan.tkachuk.1993@gmail.com

high volatility, a large part of the sulfur leaves the surface. The pyrolysis temperature for obtaining the film was $T = 623$ K, the specific resistance of the film was $\rho = 50$ kOhm·cm. The film thickness was measured using a Linnyk MII-4 interferometer. Contacts to the InSe base material and to the SnS film were formed using silver-based conductive paste. The *I-V* characteristics were studied on a Solartron 1255 measuring complex in the temperature range from 247 K to 333 K. The photosensitivity spectra of the 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

For a correct analysis of the current mechanisms in the heterojunctions, which are made using high-resistance semiconductors, it is necessary to take into account that part of the external applied voltage falls on the series resistance $I \cdot R_s$. Let's start by comparing the experimental data with the theoretical dependence, which describes a *I-V* characteristics, taking into account the influence of series and shunt resistances. It has the following form [12]:

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

where n is the diode coefficient, R_s is the series resistance, and R_{sh} is the shunt resistance.

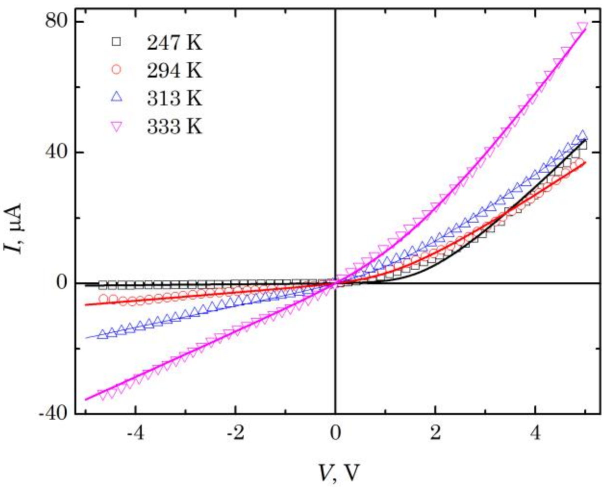

Fig. 1 – *I-V* characteristics of *p*-SnS/*n*-InSe heterostructure at different temperatures (points are experimental data, curves are approximation by formula (1))

The results of approximation of experimental data using formula (1) are shown in Fig. 1a (solid curves). The value of the differential resistance at zero and high ($V > 4$ V) voltages was taken as the initial values of R_{sh} and R_s, respectively. It can be seen that this formula does not accurately describe the forward *I-V* characteristics at forward bias of V < 1.5 B, and the calculated values of $n = 14 \div 16$ are quite large. The temperature-independent slope angle of the dependences $\ln I = f(V)$ indicates the tunneling mechanism of current flow through the barrier. In this case, a forward *I-V* characteristics are described by the following expression [13]:

$$I = B \cdot \exp(a(V - I \cdot R_s)). \quad (2)$$

Fig. 2 shows the results of approximation using formula (2). We see that when $V > 1$ V, formula (1) describes the experimental data quite accurately. The found values of R_s are given in Table. 1. At small forward bias $V = 0 \div 1$ V, the graphical dependence can no longer be described by formula (1), but a power-law dependence $I = a \cdot V^m$ is observed, where $m \approx 1.5$ for $T < 294$ K and $m \approx 1$ for $T > 294$ K. We assume that the value $m \approx 1.5$ indicates the dominance of the current limited by the space charge (Child-Langmuir law), and $m \approx 1$ is due to the current flowing through the shunt resistance. Thus, with increasing temperature at small forward bias, the shunt resistance begins to play a decisive role in charge transfer.

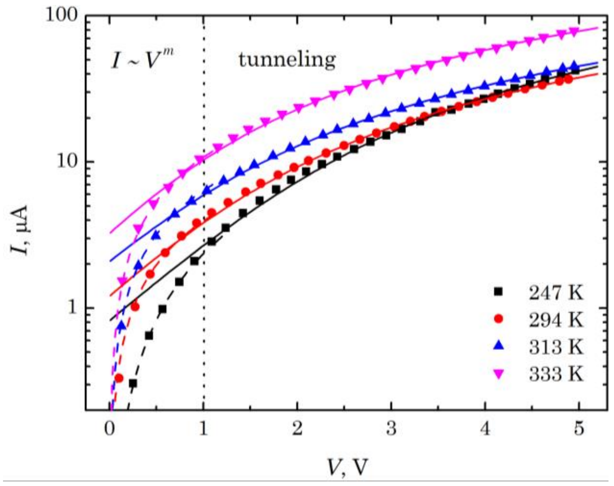

Fig. 2 – Forward *I-V* characteristics of *p*-SnS/*n*-InSe heterostructure at different temperatures (points are experimental data, curves are approximation by formula (1) and $I = a \cdot V^m$)

Table 1 – Fitting parameters

T, K	R_s, kOhm	R_{sh}, 10^6 Ohm
247	48	7.6
257	48	4.7
273	54	2.5
294	70	0.7
313	64	0.23
333	40	0.1

As can be seen from Fig. 1, the shunt resistance has a significant effect on the *I-V* characteristics. This is especially true for reverse bias, when the dependence of current on the voltage is linear ($I \approx U/R_{sh}$). The value of R_{sh} can be found from the slope of the reverse *I-V* characteristics (see Table 1). The nature of R_{sh} is determined by crystal defects at the interface, which lead to the formation of alternative current flow paths. On the basis of the linear dependence of the reverse *I-V* characteristics at different temperatures, it can be assumed that the reverse current in the heterostructure is determined not by tunneling, but by the flow of current through the shunt resistance. It should be noted that in other heterojunctions based on InSe and semiconductor oxides, produced by us using the spray pyrolysis method, such a significant effect of R_{sh} was not observed [14, 15]. This is explained by the higher pyrolysis temperature of fabrication of the *p*-SnS/*n*-InSe heterostructure (623 K vs. 523 K) – the higher the temperature, the more defects are formed at the interface, which causes the appearance of shunt currents.

In the investigated temperature range, the value of the contact potential difference found from the extrapolation to the axis of the voltages of the straight sections of the forward *I-V* characteristics was approximately $\varphi \approx 0.1 \div 0.3$ V. These data correlate with the work [11], where the maximum value of φ was 0.33 V. Note, that the significant influence of the shunt resistance makes it difficult to accurately determine the contact potential difference.

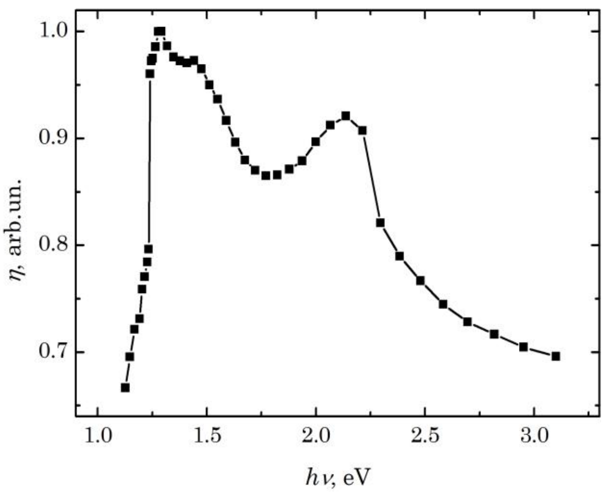

Fig. 3 – Spectral characteristics of *p*-SnS/*n*-InSe heterostructure

Fig. 3 shows the spectral dependence of the quantum efficiency of *p*-SnS/*n*-InSe heterostructure irradiated from the side of the SnS film in the photon energy range of 1.2÷3.2 eV. The maximum at 1.45 eV corresponds to the SnS band gap. The long-wavelength edge of photosensitivity at $h\nu = 1.2$ eV is caused by the fundamental absorption edge in *n*-InSe. *p*-SnS thin films are polycrystalline, as a result of which the eigenabsorption edge is blurred due to partial absorption at the grain boundaries compared to single-crystalline materials. At energies $h\nu < E_g = 1.45$ eV, part of the radiation is absorbed at the grain boundaries. At the same time, the light that can be absorbed in *n*-InSe does not penetrate into the base region due to absorption in SnS. The full width of the spectrum of the relative quantum efficiency at half height $\delta_{1/2} \approx 1.56$.

4. CONCLUSION

A photosensitive *p*-SnS/*n*-InSe heterojunction was produced by the method of low-temperature spray pyrolysis. *I-V* characteristics were measured in the temperature range from 247 K to 333 K at forward and reverse biases of the *p-n*–heterojunction ($V = -5 \div 5$ V). It was established that the current flow is mainly determined by two factors – tunneling of charge carriers and shunt resistance. The first is decisive at forward biases greater than 1 V. The second is responsible for the linear dependence of the reverse *I-V* characteristics, and also, starting from some temperatures ($T > 294$ K), plays a decisive role for forward bias of $V < 1$ B. In addition, there is a region where the forward *I-V* characteristics are described by the Child-Langmuir law (space charge limited current): $T < 294$ K, $V < 1$ B. Based on the approximation of experimental data by theoretical models, the values of series and shunt resistance at different temperatures were calculated: $R_s = 40 \div 70$ kOhm, $R_{sh} = 0.1 \div 7.6$ mOhm.

The magnitude of the contact potential difference found from *I-V* characteristics was about $\varphi \approx 0.1 \div 0.3$ V in the studied temperature range.

It is shown that the *p*-SnS/*n*-InSe heterojunction is photosensitive in the energy range $h\nu = 1.2 \div 3.2$ eV, which makes it promising for use in the near-infrared region of the spectrum.

REFERENCES

1. N.K. Reddy, K.T.R. Reddy, *Thin Solid Films* **325**, 4 (1998).
2. A.M.S. Arulanantham, S. Valanarasu, K. Jeyadheepan, V. Ganesh, M. Shkir, *J. Mol. Struct.* **1152**, 137 (2018).
3. M. Patel, I. Mukhopadhyay, A. Ray, *J. Alloy. Compd.* **619**, 458 (2015).
4. K. Jeganath, N.J. Choudhari, G.S. Pai, A. Rao, Y. Raviprakash, *Mater. Sci. Semicond. Process.* **113**, 105050 (2020).
5. R. Shashidhar, N. Choudhary, *J. Sol-Gel Sci. Technol.* **96**, 188 (2020).
6. J. Martínez-Pastor, A. Segura, J.L. Valdés, A. Chevy, *J. Appl. Phys.* **62**, 1477 (1987).
7. M. Teena, A.G. Kunjomana, K. Ramesh, R. Venkatesh, N. Naresh, *Sol. Energy Mater. Sol.* **166**, 190 (2017).
8. C. Dua, H. Gao, W. Du, J. Li, J. Lenga, K. Lia, W. Wanga, *J. Alloy. Compd.* **919**, 165586 (2022).
9. R. Cao, H.-D. Wang, Z.-N Guo, D.K. Sang, L.-Y. Zhang, Q.-L. Xiao, Y.-P. Zhang, D.-Y. Fan, J.-Q. Li, H. Zhang, *Adv. Opt. Mater.* **7**, 1900020 (2019).
10. S.E.Al Garnia, A.A.A. Darwish, *Sol. Energ. Mater. Sol.* **160**, 335 (2017).
11. P. Gao, M. Yang, C. Wang, H. Li, B. Yang, Z. Zheng, N. Huo, W. Gao, D. Luo, J. Li, *Nanoscale* **14**, 14603 (2022).
12. A. Fahrenbruch, R. Bube, *Fundamentals of Solar Cells. Photovoltaic Solar Energy Conversion* (New York: 1883).
13. S.M. Sze, K.K. Ng, *Physics of Semiconductor Devices* (Wiley: New Jersey: 2007).
14. I.G. Tkachuk, I.G. Orletskii, V.I. Ivanov, A.V. Zaslonkin, Z.D. Kovalyuk, *J. Nano- Electron. Phys.* **14**, 04016 (2022).
15. I.G. Orletskii, I.G. Tkachuk, Z.D. Kovalyuk, P.D. Maryanchuk, V.I. Ivanov, *Funct. Mater.* **28**, 245 (2021).

Гетероструктури *p*-SnS/*n*-InSe створені методом спрей-піролізу

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

[1] *Інститут проблем матеріалознавства ім. І.М. Францевича НАН України, Чернівецьке відділення, вул. І. Вільде, 5, 58001, Чернівці, Україна*

[2] *Чернівецький національний університет ім. Юрія Федьковича, вул. Коцюбинського, 2, 58012, Чернівці, Україна*

Дана робота присвячена виготовленню та дослідженню електричних та фотоелектричних характеристик анізотипних гетеропереходів *p*-SnS/*n*-InSe. Для нанесення тонких плівок SnS на кристалічні підкладки InSe використовувалась технологія низькотемпературного спрей-піролізу. На основі аналізу температурних залежностей прямих і зворотних гілок вольт-амперних характеристик досліджено динаміку зміни енергетичних параметрів гетеропереходу. Запропоновано теоретичні моделі, що описують поведінку прямих та зворотних гілок вольт-амперних характеристик. Визначено величину послідовного та шунтуючого опорів, а також їх вплив на вольт-амперні характеристики гетеропереходу. Оцінено величину контактної різниці потенціалу. Встановлено основні механізми протікання струму. Досліджена спектральна залежність квантової ефективності опроміненої зі сторони плівки SnS гетероструктури *p*-SnS/*n*-InSe в інтервалі енергій фотонів 1.2÷3.2 eV.

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