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Electrical Conductivity of Composite Materials Based on *n*-InSe and Thermally Expanded Graphite

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The composite material was obtained based on InSe semiconductor powder and thermally expanded graphite (TEG). The TEG content varied from 4 wt. % up to 20 wt. %, the starting materials were pressed into disks using a hydraulic press. The percolation nature of the electrical conductivity of such composite materials was studied. Since the electrical conductivity of InSe powder is almost 9 orders of magnitude lower than the electrical conductivity of TEG, TEG can be considered as a conducting phase in this composite. The dependences of the electrical conductivity on the TEG content and temperature were measured. The value of the percolation threshold was estimated from the graphical dependence of the electrical conductivity on the TEG content. When studying the electrical conductivity of composite materials, it should be taken into account that the current flows both inside individual crystallites and through the interface between them. The theoretical model was proposed that describes the obtained experimental results of the temperature dependences of electrical conductivity. The conclusions were made about the dominant current flow mechanism on the basis of the analysis of the temperature dependence of electrical conductivity.

Keywords: Indium selenide, Thermally expanded graphite, Composite material, Percolation threshold, Electrical conductivity.

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1. INTRODUCTION

When searching for new functional materials for electronics, electrically conductive composite mixtures with high electrical conductivity are important. The composites based on carbon materials (graphite, thermally expanded graphite (TEG), graphene, activated carbon) and semiconductor compounds make it possible to create materials with alternate areas of micro- and nanometer-sized semiconductor-dielectric-semiconductor type. It is of some interest to investigate the properties of composite compounds based on materials similar in structure but different in electrophysical properties, in particular graphite and layered semiconductors InSe or GaSe. Such compounds can be promising materials for electronics.

Thermally expanded graphite [1, 2] has a layered crystal structure in which the layers are arranged according to the dense packing of ABAB... along the *c* crystallographic axis. A strong covalent bond exists within a single carbon layer, while a weak van der Waals type bond exists between the layers.

The electrical conductivity of graphite in the plane of the layer is high and the material is a semi-metal. However, the electrical conductivity in the direction perpendicular to the plane of the layers is several orders of magnitude lower. A similar crystal structure is characteristic of layered III-VI semiconductors [3]. Therefore, these materials are characterized by anisotropy of physical and chemical properties along different crystallographic directions and their sensitivity to external pressure [4].

In the previous work [5], the technology for obtaining InSe-graphite composite materials was presented, and their photoelectric and partially electrical properties were studied. The purpose of this work is a more detailed study of the electrical conductivity of InSe–TEG composite materials.

2. EXPERIMENTAL

The samples of a two-component composite material based on a mixture of powders of InSe semiconductor and TEG were made. The samples were pressed into disk using a hydraulic press. The technology is described in [5]. Since the electrical conductivity of InSe powder is almost 9 orders of magnitude lower than the electrical conductivity of TEG, TEG can be considered as conducting phase in this composite.

The series of samples with different mass content of TEG (4, 8, 12 and 16 wt.%) was made for investigation. The measurements of the dependence of electrical conductivity on the mass content of TEG were carried out at room temperature using the Hall effect measurement setup in the DC mode. The rectangle samples were used and electrical contacts were made by silver paste.

The temperature dependences of electrical conductivity for the sample with 20 wt.% TEG in the range of 77÷300 K were measured.

3. RESULTS AND DISCUSSION

The starting materials of InSe and TEG had *n*-type electrical conductivity, which for their pressed samples was $1.2 \cdot 10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ and $1220\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at $T = 285$ K, respectively. The materials with different TEG content ($x = 4$, 8, 12 and 16 wt.%) were obtained with purpose to determine the percolation threshold. Fig. 1a shows the dependences of the electrical conductivity (σ)

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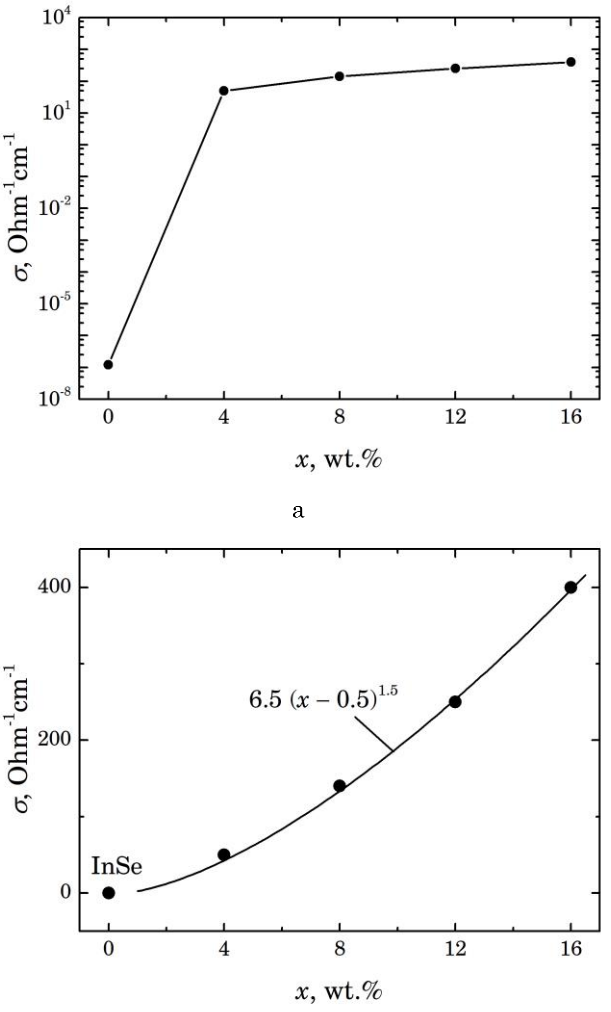
on TEG content. The value of σ increases by more than 9 orders of magnitude in the region $0 < x \leq 4$. This confirms the percolation nature of electrical conductivity, due to the flow of current through the conductive channels of contacting graphite grains, which form a percolation cluster. It can be seen that the electrical conductivity of the investigated composite materials is in the region beyond the percolation threshold.



a

b

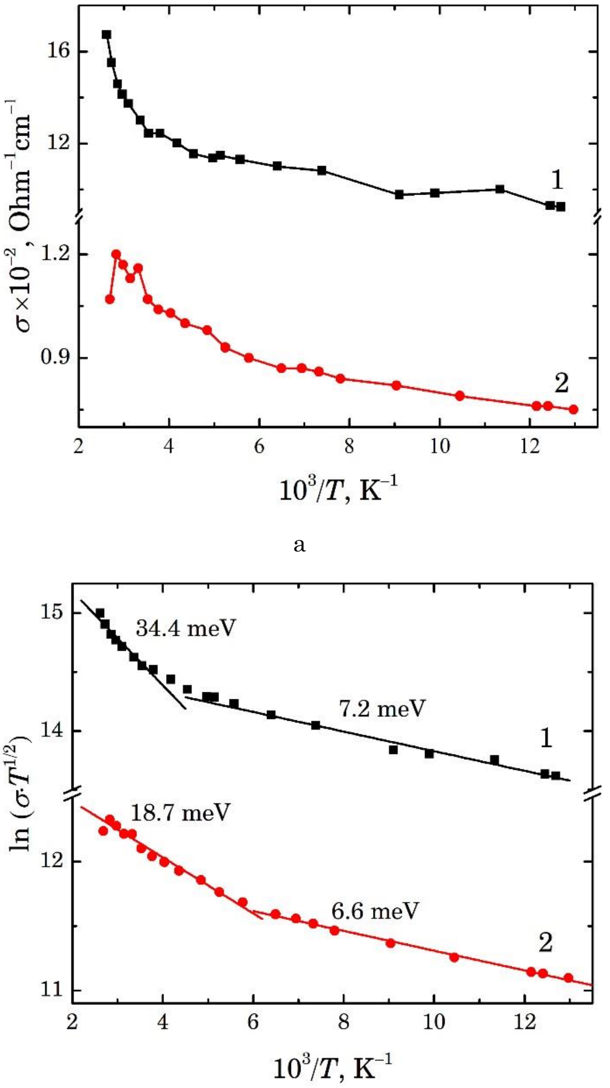
Fig 1 – Dependence of electrical conductivity on TEG content and the results of approximation (b, solid curve)

The electrical conductivity of two-phase materials increases with increasing content of the conductive phase according to the formula [6]:

$$\sigma = \sigma_0(x - x_c)^t, \qquad (1)$$

where σ_0 is a constant, x is the concentration of the conductive phase (TEG), x_c is the percolation threshold. This formula is valid for $x \geq x_c$, and $x < x_c$ $\sigma = 0$. $t \approx 2$ for many two-phase materials.

Fig. 1b shows the approximation of experimental data using formula (1) with parameters $\sigma_0 = 6.5$, $x_c = 0.5$ and $t = 1.5$ (solid curve). The theoretical values of σ agree well with the experimental values, that confirms the reliability of the calculation. The deviation of the value of t from 2 may indicate the presence of tunnel contacts between individual graphite crystallites in the material, rather than ohmic ones. The low value of the percolation threshold x_c is related to the high porosity of TEG, as a result of which the volume content of TEG is much higher than that of InSe.



a

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Fig. 2 – Temperature dependences of electrical conductivity of TEG (1) and InSe- TEG (20 wt.% TEG) (2)

Fig. 2 shows the temperature dependences of the electrical conductivity of pressed powders of TEG and InSe- TEG composite material (20 wt.% TEG) in the temperature range from 80 K to 300 K. It seems likely that the increase in the electrical conductivity is due to the predominant increase in the concentration of charge carriers over the decrease in mobility due to the scattering of charge carriers. The given temperature dependences of electrical conductivity are consistent with the data of works [7, 8].

The investigations of pressed powders of pure InSe were also carried out. An increase in electrical conductivity from $5 \cdot 10^{-9}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 170 K to $1.3 \cdot 10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 370 K was established, which is due to the increase in σ with temperature in InSe due to the activation of donor levels [9]. The obtained values of σ InSe have no significant effect on the electrical conductivity of the composite materials.

The current flow in TEG powders and composite materials is determined by the conductivity of individual crystallites σ_{cr} and the grain boundary conductivity σ_{gr} [7, 8]. The value of σ_{cr} significantly exceeds the value of σ_{gr}, which is determined by the mechanisms of transfer of charge carriers across grain boundaries. If the energy of the charge carriers is greater than the barrier height, over-barrier passage of carriers takes place, which leads to an increase in σ with temperature. In addition, tunneling of charge carriers through the barrier may occur.

Taking into account the presence of energy barriers that form at the grain boundaries, the temperature dependence of electrical conductivity is described by the formula [10]:

$$\sigma(T) \sim T^{-1/2}\cdot\exp(-E_b/kT), \qquad (2)$$

where E_b is the barrier height.

There are two linear sections can be distinguished on the graphic dependences of electrical conductivity plotted in the coordinates of $\ln(\sigma\cdot T^{1/2})$ versus $(1/T)$ (see Fig. 2b) in the low- and high-temperature regions. The height of the energy barrier E_b was found by the slope of these sections: 7 meV and 34 meV for TEG and 6.6 meV and 19 meV for InSe-TEG.

The characteristics of the energy barriers at the grain boundary are the thickness of the charged depletion region δ and the density of energy states in this region N_t [11, 12]:

$$\delta = (2\varepsilon_r\varepsilon_0 E_b/q^2 n)^{1/2}, \qquad (3)$$

$$N_t = (8\varepsilon_r\varepsilon_0 n E_b/q^2)^{1/2}, \qquad (4)$$

where n is the concentration of charge carriers, $\varepsilon_r \approx 2$ is the dielectric constant of graphite, $m^* = 0.054m_0$ is the effective mass of electrons.

The concentration of charge carriers in graphite at room temperature is about 10^{20} cm^{-3} [13]. Assuming that this is also true for our material, the mobility of charge carriers μ of composite materials was estimated from the measured values of σ: 76 cm^2/V·s, 16 cm^2/V·s, and 7 cm^2/V·s for TEG, InSe TEG (20 wt. % TEG), and InSe- TEG (10 wt. % TEG), respectively.

We will use the following parameters for calculations: $n = 10^{20}$ cm^{-3}, $m^* = 0.054m_0$, $\varepsilon_r = 2$, $E_b = 34$ meV for TEG and $E_b = 19$ meV for InSe-TEG. Then we found: $\delta = 0.25$ nm, $N_t = 5.2\cdot10^{12}$ cm^{-2} for TEG; $\delta = 0.21$ nm, $N_t = 4.1\cdot10^{12}$ cm^{-2} for InSe-TEG (20 wt. % TEG).

The temperature coefficient of resistance is proportional to the height of the energy barriers between the crystallites:

$$TCR = R^{-1}\cdot dR/dT \approx -E_b/(kT^2). \qquad (5)$$

In our case, the estimated values of TCR at room temperature are 0.0044 K^{-1} for TEG and 0.0025 K^{-1} for InSe-TEG (20 wt. % TEG).

The calculations of the band structure of single-crystal graphite performed in [14] showed that graphite is a semi-metal with a small overlap of the valence and conduction band (0.04 eV), the extremes of which are located at different points of the Brillouin zone. In this case, its conductivity is determined by the total contribution of carriers of two types – conduction band electrons and valence band holes. As the temperature increases, electrons flow into the conduction zone and their relative number increases. Since the mobility of electrons is greater than the mobility of holes in the valence band, this is manifested in the increase of the total electrical conductivity. The increase in the concentration of electrons with increasing temperature in graphite was established in works [15, 16].

4. CONCLUSIONS

The electrical conductivity of composite materials fabricated from a mixture of InSe semiconductor powders and TEG has a percolation character, which is associated with the flow of current through the conductive channels of contacting graphite crystallites. Based on the measurements, it can be concluded that the percolation threshold in InSe-TEG composite materials is less than 1 wt.% TEG.

The electrical conductivity of InSe-TEG composite materials increases with temperature and is described within the framework of a model that takes into account the presence of energy barriers at grain boundaries. Grain boundaries play a crucial role in current transfer processes.

The parameters of the energy barriers were calculated such as the thickness of the charged depletion region and the density of energy states in this region at room temperature.

REFERENCES

1. I.G. Chernysh, I.I. Karpov, G.P. Prikhod'ko, V.M. Shay, *Fiziko-khimicheskiye svoystva grafita i yego soyedineniy* (Kiyev: Naukova dumka: 1990) [In Russian].
2. L.R. Radovic, *Chemistry and Physics of Carbon* (New York: Marcel Dekker: 2004).
3. K.D. Tovstyuk, *Poluprovodnikovoye materialovedeniye* (Kiyev: Naukova dumka: 1984) [In Russian].
4. Z.D. Kovalyuk, M.M. Pyrlya, V.B. Boledzyuk, V.V. Shevchyk, *Ukr. J. Phys.* **56**, 368 (2011).
5. V.M. Kaminskii, V.B. Boledzyuk, V.M. Vodopyanov, P.I. Savitskii, A.V. Zaslonkin, M.V. Zapolovskyi, *J. Nano-Electron. Phys.* **13** No 4, 04020 (2021).
6. B.I. Shklovskiy, A.A. Efros, *Elektronnyye svoystva legirovannykh poluprovodnikov* (Moskva: Nauka: 1976) [In Russian].
7. A. Celzard, E. McRae, J.F. Marêché, G. Furdin, B. Sundqvist, *J. Appl. Phys.* **83**, 1410 (1998).
8. I.V. Ovsiyenko, L.YU. Matsuy, O.I. Prokopov, O.V. Zhuravkov, *J. Nano- Electron. Phys.* **8** No 2, 02017 (2016).
9. V.M. Kaminskii, Z.D. Kovalyuk, M.V. Tovarnitskii, V.I. Ivanov, M.V. Zapolovskyi, *J. Phys. Stud.* **24** No 3, 3704 (2020).
10. J.Y.W. Seto, *J. Appl. Phys.* **46**, 5247 (1975).
11. C.H. Seager, *J. Appl. Phys.* **52**, 3960 (1981).
12. S.M. Sze, K.N. Kwok, *Physics of Semiconductor Devices* (New Jersey: Wiley: 2007).

13. H.O. Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes* (Park Ridge: New Jersey: 1997).
14. R.S. Tatar, S. Rabii, *Phys. Rev. B* **25**, 4126 (1982).
15. N. Garcıa, P. Esquinazi, J. Barzola-Quiquia, S. Dusari, *New J. Phys.* **14**, 053015 (2012).
16. C.A. Klein, W.D. Stratub, *Phys. Rev.* **123**, 1581 (1961).

Електропровідність композитних матеріалів на основі *n*-InSe і терморозширеного графіту

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Одержано композитні матеріали на основі напівпровідникового порошку InSe та терморозширеного графіту (ТРГ). Концентрація ТРГ змінювалась від 4 мас. % до 20 мас. %, вихідні матеріали пресувались у шайби за допомогою гідравлічного пресу. Досліджено перколяційний характер електропровідності таких композитних матеріалів. Оскільки електропровідність порошку InSe майже на 9 порядків менша від електропровідності ТРГ, то ТРГ можна вважати провідною фазою в даному композиті. Проведено виміри залежності електропровідності від вмісту ТРГ та температури. З графічної залежності електропровідності від вмісту ТРГ оцінено значення порогу перколяції. При дослідження електропровідності композитних матеріалів потрібно враховувати, що струм протікає як всередині окремих кристалітів так і через інтерфейс між ними. Запропоновано теоретичну модель, яка описує отримані експериментальні результати температурних залежностей електропровідності. На основі аналізу температурних залежностей електропровідності зроблено висновки про домінуючий механізм протікання струму.

Ключові слова: Селенід індію, Терморозширений графіт, Композитний матеріал, Поріг перколяції, Електропровідність.