Obtaining granular semiconductor intermetallic compound Zn-Sb and some of its electrical properties

Lutfiddin Olimov[1*] and *Utkirbek* Akhmadaliev[1]

[1]Andijan Machine Building institute, Andijan, Uzbekistan

Abstract. The article discusses the microstructure of the ZnSb intermetallic compound obtained by powder technology and the results of the study of charge transfer processes in it. Also, the article proposes a method of preparing a Zn-Sb intermetallic compound with a stem-shaped polycrystalline structure using powder technology. Semiconductor Zn-Sb polycrystalline structure preparation method is carried out by pressing Zn-Sb particles together, followed by thermal treatment in several stages. It was found that the stages and temperature of heat treatment have a significant effect on its electrophysical properties. Electrical conductivity (σ), charge carrier concentration (n) suddenly decreases with temperature increase at the initial stage of heat treatment. Such a process is not observed in the subsequent stages of heat treatment. At all stages of heat treatment, the mobility of charge carriers (μ) decreases. In this case, the residence time of charge carriers in the crystal lattice is τ~$1{,}52 \div 1{,}1 \cdot 10^{-12}$ sec. was determined to change between The results of the study were explained on the basis of the influence of intergranular boundary areas on charge transfer processes. Studies show that at T=300÷700 K, the potential barrier height (φ) in the intergranular boundary areas increases linearly with temperature. For example, φ~0,436 eV at the initial stages of thermal treatment at T=300 K, and φ~0,469 eV at later stages, and at T=700 K, it increases to φ~0,92 eV in all cases. It was shown that it depends on the amount of charges trapped in the localized traps in the intergranular boundary regions.

1 Introduction

It is known that the Zn-Sb intermetallic compound is one of the important semiconductor materials widely used in the field of energy, especially micro and nanoenergy, in transistors, infrared detectors, thermal imaging devices, and magnetic resistance devices (https://en.wikipedia.org/wiki/Zinc_antimonide). Despite the fact that some of its mechanical, thermal and chemical properties are close to metal alloys, its physical properties under certain conditions increase the interest in the preparation of various combination Zn-Sb intermetallic compounds and the study of electro physical and thermoelectric properties [1-12]. Currently, the Zn-Sb semiconductor intermetallic compound is considered to be

* Corresponding author: o.lut@mail.ru

sufficiently studied both theoretically and practically (see, for example, [1-12] and references therein). Studies show that the electro physical and thermoelectric properties of the compound depend on the physical processes that occur during the preparation of the Zn-Sb semiconductor intermetallic compound. In particular, it has been shown that the processes of preparation and pressing of ZnSb powders significantly affect the formation and growth of grains, as well as their electro physical and thermoelectric properties. In addition, charge transfer processes and thermoelectric characteristics depend on the method of obtaining ZnSb compounds, and it is justified that the increase in temperature has a significant effect on the increase of electrical conductivity and the Seebeck coefficient.

It should also, be noted that in recent years, the interest in preparing granulated semiconductors and obtaining thermoelectric materials based on them, studying their electro physical properties is increasing [13-20]. Production of thermoelectric material based on granulated semiconductors is based on powder technology, which is characterized by its relative simplicity and cost-effectiveness. The thermoelectric material consists of a heterogeneous medium, the atomic structure of which is fundamentally different from the atomic structure of a granular semiconductor core. It has been shown in the literature that an increase in temperature leads to an increase in electrical conductivity (σ) and the Seebeck coefficient (α), and on the contrary, a decrease in thermal conductivity (λ), depending on the characteristics of the heterogeneous environment.

However, today, charge transfer processes and thermoelectric phenomena during the preparation stages of granulated Zn-Sb semiconductor intermetallic compounds are one of the issues that have not been fully studied. Solving such issues may allow the preparation of new types of energy converters based on the Zn-Sb semiconductor intermetallic compound. Considering this, this work discusses the charge transfer processes during the preparation stages of granular Zn-Sb semiconductor intermetallic compounds and the results obtained in the study of some of its electro physical properties.

2 Materials and methods

It is known that today, there are several methods of preparing Zn-Sb semiconductor intermetallic compounds (see, for example, [1-9] and references therein). One of the most convenient methods is to prepare ZnSb powders from them, press them, and then obtain a Zn-Sb semiconductor intermetallic compound with thermal treatment. This method makes it possible to control the processes of preparation, pressing and thermal treatment of ZnSb powders of desired size.

The novelty of our research is that the preparation of granulated ZnSb intermetallic compound obtained by the powder method was chosen as the object of this research, in which the method of Egor and Disselkhorsta [20, 21] was chosen to study charge transfer processes and thermoelectric phenomena. Initially, the ZnSb intermetallic compound is powdered in powder technology, in which the particle size is 10÷50 μm. The electrophysical and thermoelectric properties of the sample were conducted at the temperature of T=300-700 K based on the method of Egor and Disselhorsta [21]. Researches were carried out on the basis of Egor and Disselkhorsta method in the process of temperature change T=300-700 K [20]. This method makes it possible to study charge transfer processes and thermoelectric phenomena during the formation stages of granulated Zn-Sb semiconductor intermetallic compound (see, for example, [13-20] and references therein).

Figure 1 shows a simplified scheme of samples using the Egor and Disselhorsta method. ZnSb particles (1) are placed in a pipe-shaped dielectric (2). Two of the particles (A and B) are pressed by copper contacts (M_A and M_B), as shown in Figure 1. The pressure force is P~30÷50 kilograms [14, 18, 19]. In this case, the sample can be imagined in the form of a stem. Based on the method of Egor and Disselkhorsta, when Q heat is applied, the charges

generated in area A move to area B, and an electric current is generated due to the temperature difference in contacts M_A and M_B. The temperature difference is monitored using T_A and T_B thermocouples. It should be noted that all studies were conducted during the processes of increasing and decreasing the temperature of heat treatment and time intervals. Between each heat treatment, the sample was cooled for 1 h, then reexamined.

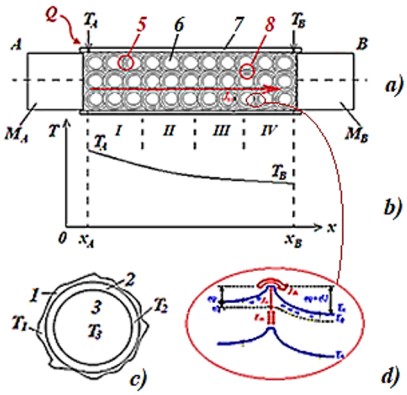

Fig. 1. A simplified scheme of measuring samples based on the Egor and Disselkhorsta method (a), temperature difference (b), ZnSb particle structure (a), zone diagram (d). Here, 6 – granulated ZnSb particles, 7 – heat-resistant dielectric case, 5 and 8 – interparticle boundary area, ohmic contacts and thermocouples in areas A and V, respectively, M_A and M_B, T_A and T_B.

3 Results and discussion

Figures 2÷4 show the dependence of electrical conductivity (σ), concentration of charge carriers (n) and mobility (μ) on temperature. It was observed that the thermal treatment steps and temperature have a significant effect on σ and n (Fig. 3). For example, at the initial stage of heat treatment, as the temperature increases, σ and n suddenly decrease. On the contrary, such a process is not observed in the later stages of thermal treatment. In the initial stage of heat treatment, 1 – σ_o~0,06 $(Om{\cdot}sm)^{-1}$, n_o~1,42·10^{18} sm^{-3}, and in later stages σ_o~0,017 $(Om{\cdot}sm)^{-1}$, n_o~4,03·10^{17} sm^{-3}; 3 – σ_o~0,019 $(Om{\cdot}sm)^{-1}$, n_o~4,47·10^{17} sm^{-3}; 4 – σ_o~0,0187 $(Om{\cdot}sm)^{-1}$, n_o~1,38·10^{17} sm^{-3} will have values. At the initial stage of heat treatment, when the temperature is T≥375 K, the electrical conductivity suddenly changes to σ_o~0,017 $(Om{\cdot}sm)^{-1}$, and the concentration of charge carriers changes to n_o~2,85·10^{17} sm^{-3}. However, such processes were not observed in the dependence of the mobility of charge carriers on temperature (Fig. 4). μ decreases with increasing temperature at all stages of heat treatment. This is due to a decrease in the residence time (τ) of charge carriers in the crystal lattice. In our case, in all cases τ~1,52÷1,1·10^{-12} sec. it was found to change between

A sudden change in electrical conductivity and charge carrier concentration can be attributed to the heterogeneous environment formed in the granular ZnSb intermetallic compound. It can be explained using the structure of the granulated ZnSb intermetallic compound obtained by the powder method and its simplified scheme shown in Fig. 1.

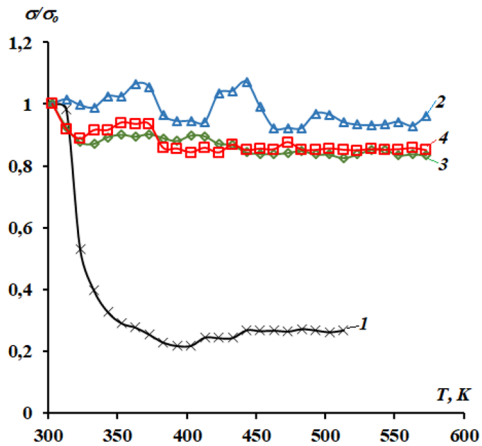

Fig. 2. Dependence of electrical conductivity on temperature: 1 – σ_o~0,06 $(Om{\cdot}sm)^{-1}$, 2 – σ_o~0,017 $(Om{\cdot}sm)^{-1}$, 3 – σ_o~0,019 $(Om{\cdot}sm)^{-1}$, 4 – σ_o~0,0187 $(Om{\cdot}sm)^{-1}$.

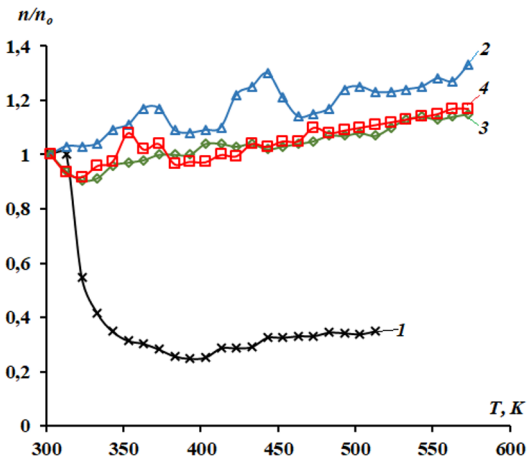

Fig. 3. Dependence of charge carrier concentration on temperature: 1 – n~1,42·10^{18} sm^{-3}, 2 – n~4,03·10^{17} sm^{-3}, 3 – n~4,47·10^{17} sm^{-3}, 4 – n~1,38·10^{17} sm^{-3}.

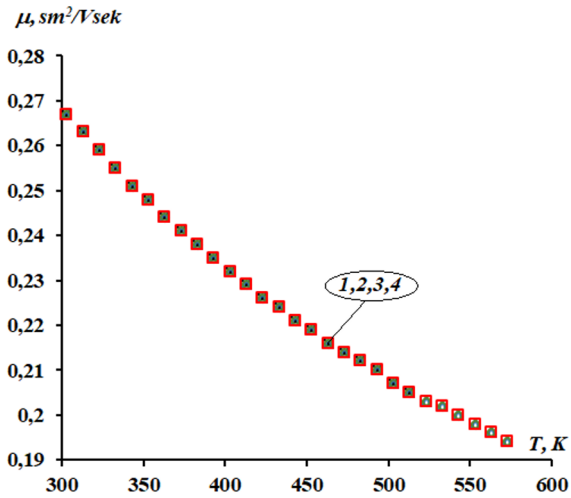

Fig. 4. Dependence of the mobility of charge carriers on temperature.

It is known that the structure and morphology of granulated semiconductor particles depends on the technology of their production [13-20]. For example, the structure of particles obtained on the basis of powder technology can be conditionally divided into 3 parts (Fig. 1c). In [20], we used the same method to explain the physical processes in Mg_3Sb_2. Based on it, the powdering process is performed mechanically. In the mechanical method, the phenomenon of friction depends on the heating of the powders, as well as the atomic structure of the powder core and the surface of the powder. The amount of atomic crystallographic distortion increases from the powder core to the surface, which leads to phase changes in each domain. Also, the reactivity of the surface area increases from the powder core to the surface [17]. In our case, the granulated ZnSb intermetallic compound has a particle size of 10÷50 μm. Their arrangement on the heat-resistant ceramic substrate can be described as ZnSb particles arranged in series and parallel to each other, as shown in Fig. 1a. Through the metal contacts M_A and M_B, ZnSb particles are pressed together with a specified force from both sides. The compressive strength was selected by measuring the sample resistance. It was observed that when pressed together with a force of 30-50 kG, the resistance was ~1 kOhm. It should be noted that ZnSb particles have a resistivity of ρ~0,221 (*Om·sm*) when measured on a PIUS-3 device.

Interparticle boundary regions rich in defects and crystallographic distortions are formed between series and parallel ZnSb particles (areas 3 and 4 in Fig. 1a). They form Ein-level localized traps for charge carriers (Fig. 1d). Because the interparticle boundary regions create a barrier effect for charge carriers, the ZnSb particle structure pressed together causes the resistance to change from Ohm to kOhm. The process of charge transfer in series and parallel ZnSb particles can be divided into two parts. If the particles are located in series with each other, the process of charge transfer from the first particle to the second particle takes place through the interparticle boundary areas formed between them (area 3, Fig. 1a). If the particles are located parallel to each other, the charge transfer process takes place mainly along the 4th region, which is parallel to each other.

Now let's try to explain the results of the research based on the given considerations.

If the charge transfer process is carried out from the first particle to the second particle through area 3, the charge carriers are trapped in localized traps with the energy level Ein appearing in sequence (Fig. 1d). This process leads to an increase in the height of the potential

barrier (φ) in the interparticle boundary region. Based on the Setto model, the dependence of φ on ρ can be expressed as follows:

$$\rho = \frac{k}{q\langle a\rangle A^{*}T}\exp\left(\frac{q\varphi}{kT}\right) \tag{1}$$

where, q – electron charge, k – Boltzmann's constant, $\langle a\rangle$ – particle size, A^{*} – Richardson's efficiency constant, T – temperature.

Figure 5 shows the dependence of the height of the potential barrier (φ) on temperature. Studies show that at T=300÷700 K, φ increases linearly with temperature. At T=300 K, φ~0,436 eV at the initial stages of thermal treatment, and φ~0,469 eV, at later stages, and at T=700 K, it increases to φ~0,92 eV in all cases.

It is known that φ depends on the amount of charges trapped in localized traps (Q_i):

$$\varphi = Q_i^2 \big/ (8\varepsilon\varepsilon_o q N_G) \tag{2}$$

where, N_G is the concentration of electrically active alloying elements, ε and ε_o are the relative and absolute dielectric constants of the medium and vacuum, respectively.

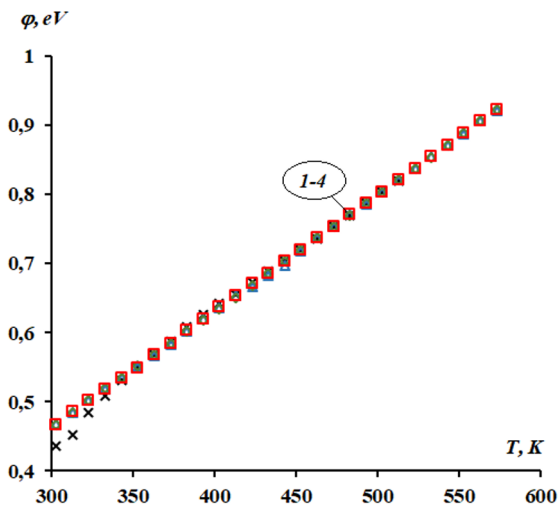

Fig. 5. Dependence of potential barrier height on temperature.

So, it can be seen from expression (2) that the increase of charges (Q_i) trapped in localized traps leads to an increase of φ, which in turn leads to an increase of ρ. Based on the above considerations, the processes of charge transfer in ZnSb particles can be explained as follows.

In our opinion, at the initial stages of thermal treatment, with an increase in temperature, the amount of charges trapped in E_{in} energy level localized traps (Q_i), which appear successively in the interparticle boundary between ZnSb particles (areas 3 and 4, Fig. 2a), leads to a decrease in σ and n will come In this case, ZnSb particles combine to form an intermetallic compound. It is known that the crystallization of ZnSb intermetallic compound corresponds to T~450÷600 K [1-12]. In our case, T=300÷700 K is sufficient for the crystallization of the ZnSb intermetallic compound. In the 2nd, 3rd, 4th and 5th heat treatment steps, the ZnSb intermetallic compound is further strengthened. Research has

shown that when the sample is taken from the substrate, it is found that the ZnSb intermetallic compound has formed a polycrystalline structure. Therefore, the decrease of σ and n with increasing temperature at the initial stage of thermal treatment belongs to ZnSb particles. The results of the next (2nd, 3rd, 4th, 5th and 5th) stages of heat treatment refer to the ZnSb intermetallic compound with a polycrystalline structure. Its electrophysical properties correspond to charge transfer processes in polycrystalline semiconductors.

4 Conclusions

Thus, the results obtained for ZnSb particles differ significantly from the results obtained for ZnSb material presented in the literature, for example, in works [1-12]. By powder technology, it can be achieved by pressing Zn-Sb particles together, followed by heat treatment in several steps, to prepare a granular Zn-Sb intermetallic compound with a polycrystalline structure. For this, it is required that the temperature of the thermal treatment corresponds to the crystallization of the ZnSb intermetallic compound T~450÷600 K. The resulting ZnSb intermetallic compound has a polycrystalline structure, and its electrophysical properties depend on the characteristics of the heterogeneous medium consisting of intergranular boundary areas. The method of preparation of granulated Zn-Sb intermetallic compound with polycrystalline structure by powder technology can enable the preparation of new types of energy converters based on semiconducting Zn-Sb intermetallic compound.

The results of the research and the considerations given to explain it can be of great importance in obtaining granular materials and explaining the kinetic phenomena in them.

References

1. M.I. Fedorov, L.V. Prokof'eva, D.A. Pshenay-Severin, A.A. Shabaldin & P.P. Konstantinov. New Interest in Intermetallic Compound ZnSb. Journal of Electronic Materials. Volume 43, pages 2314–2319 (2014) https://link.springer.com/article/10.1007/s11664-014-3053-1
2. X. Song, K. Valset, J.S. Graff, A. Thøgersen, A.E. Gunnæs, S. Luxsacumar, O.M. Løvvik, G.J. Snyder & T.G. Finstad. Nanostructuring of Undoped ZnSb by Cryo-Milling. Journal of Electronic Materials. Volume 44, pages 2578–2584 (2015). https://link.springer.com/article/10.1007/s11664-015-3708-6
3. Takao Morimura, Masayuki Hasaka & Hiromichi Nakashima. Microstructures and Thermoelectric Properties of Melt-Spun $Zn_x Sb_3$ Ribbons. Journal of Electronic Materials. Volume 42, pages 951–1955 (2013) https://link.springer.com/article/10.1007/s11664-013-2481-7
4. Xiao Li, Xiying Zhou, Lingling Du, Wenhua Zhou & Zhijun Fan. Preparation and modification of ZnSb-based phase change storage films. Journal of Materials Science: Materials in Electronics. Volume 32, pages 8503–8513 (2021) https://link.springer.com/article/10.1007/s10854-021-05472-x
5. Zhuang-hao Zheng, Ping Fan, Jing-ting Luo & Guang-xing Liang. Enhanced Thermoelectric Properties of In-Doped ZnSb Thin Film with Surface Nanocrystallization. Journal of Electronic Materials. Volume 46, pages 1319–1323 (2017). https://link.springer.com/article/10.1007/s11664-016-5123-z
6. Sedat Sürdem. Determination of some properties of ZnSB thin films deposited by a thermionic vacuum arc technique. Journal of Materials Science: Materials in Electronics. volume 30, pages19060–19068 (2019). https://link.springer.com/article/10.1007/s10854-019-02263-3

7. A. A. Ivanov, D. I. Bogomolov, V. T. Bublik, M. V. Voronov, M. G. Lavrentev, V. P. Panchenko, Yu. N. Parkhomenko & N. Yu. Tabachkova. Effect of Synthesis Conditions on the Structure and Thermoelectric Properties of β-Zn_4Sb_3-Based Materials. Journal of Electronic Materials. Volume 49, pages 2704–2709 (2020). https://link.springer.com/article/10.1007/s11664-020-08056-3
8. Zhuang-hao Zheng, Dong Yang, Xiao-lan Huang, Fu Li, Yue-Xing Chen, Guang-xing Liang, Jing-ting Luo & Ping Fan. High-performance zinc antimonide thermoelectric thin films achieved by a layer-by-layer combination reaction approach. Journal of Materials Science: Materials in Electronics. Volume 31, pages 16968–16974 (2020). https://link.springer.com/article/10.1007/s10854-020-04253-2
9. Jianping Lin, Lingzhi Ma, Zhonghua Zheng, Yilong Chen, Zhichao Cui, Jiping Wang & Guanjun Qiao. Thermoelectric Properties of Zn_4Sb_3 Composites with Incomplete Reaction. Journal of Electronic Materials. Volume 48, pages 159–1163 (2019). https://link.springer.com/article/10.1007/s11664-018-06851-7
10. N Karthikeyan, B Kavin Kumar, G Sathish Kumar & R Akilan. Intriguing metal–semiconductor transport properties on Se-substituted β-Zn_4Sb_3 compounds. Bulletin of Materials Science. Volume 46, Article number: 37 (2023). https://link.springer.com/article/10.1007/s12034-022-02866-3
11. Hong-xia Liu, Shu-ping Deng, Lan-xian Shen, Jin-song Wang, Feng Cheng & Shu-kang Deng. Electrical Transport Properties of Single Crystalline β-Zn_4Sb_3 Prepared by α-Sn Flux Method. Journal of Electronic Materials. Volume 46, pages 2867–2872 (2017). https://link.springer.com/article/10.1007/s11664-016-5014-3
12. Kinga Niedziółka & Philippe Jund. Influence of the Exchange–Correlation Functional on the Electronic Properties of ZnSb as a Promising Thermoelectric Material. Journal of Electronic Materials. Volume 44, pages 1540–1546 (2015). https://link.springer.com/article/10.1007/s11664-014-3459-9
13. Patent UZ № FAP 01593 "Method of preparation of thermoelectric material". L.O. Olimov, I.I. Anarboev, A.Mamirov, F.L. Omonboev, M.L. Omonboeva (eds) (2021)
14. Patent Uz IAP 0561 Thermoelectric material and its preparation method. 29.06.2018. Bull., No. 6. B.M. Abdurakhmanov, M.M. Adilov, M.Kh. Ashurov, and others.
15. L.O. Olimov, Anarboyev I.I. Some Electrophysical Properties of Polycrystalline Silicon Obtained in a Solar Oven. Silicon 14(8), PP3817 – 3822. 2022. https://doi.org/10.1007/s12633-021-01596-1
16. I.I. Anarboyev, L.O. Olimov. Microcructure of Polycrystal Silicon Heated by Sunlight. Ra Journal Of Applied Research. 7(11), PP2669 – 2671. 2021.
17. L.O. Olimov, I.I. Anarboyev. Energy converter based on nano-structured si. International Bulletin of Applied Science and Technology. 3(6), PP248 – 252. 2023.
18. F.L. Omonboev L.O. Olimov, B.M. Abdurakhmanov. The Influence of Alkali Metal Atoms on the Electrical Conductivity of Granular Silicon. International Journal of Advanced Research in Physical Science (IJARPS). 7(12), PP7-10. 2020. https://www.arcjournals.org/international-journal-of-advanced-research-in-physical-science/volume-7-issue-12/
19. L.O. Olimov, B.M. Abdurakhmanov, Z.Sohibova. Influence of alkali metals on the transfer of charge carriers in granulated silicon. Euroasian Journal of Semiconductors Science and Engineering. 2(1), PP8. 2020.
20. F.L. Omonboev, A.T. Mamadalimov, L.O. Olimov. Charge Transfer Processes In Granulated Mg_3Sb_2 Particles. Journal E3S Web of Conferences. June 2023. PP?.

21. Thermal conductivity of materials: textbook / A.G. Korotkih; Tomsk Polytechnic University. - Tomsk: Publishing House of Tomsk Polytechnic University, 2011. - 97 p.