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

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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 ZnSb intermetallic compound with a stem-shaped polycrystalline structure using powder technology. Semiconductor ZnSb polycrystalline structure preparation method is carried out by pressing ZnSb 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 (\(\sigma\)), 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 (\(\mu\)) decreases. In this case, the residence time of charge carriers in the crystal lattice is \(\tau\sim1,52\div1,1\times10^{-12}\) sec. was determined. 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 (\(\phi\)) in the intergranular boundary areas increases linearly with temperature. For example, \(\phi\sim0,436\) eV at the initial stages of thermal treatment at T=300 K, and \(\phi\sim0,469\) eV at later stages, and at T=700 K, it increases to \(\phi\sim0,92\) 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 electrophysical and thermoelectric properties [1-12]. Currently, the Zn-Sb semiconductor intermetallic compound is considered to be...
Sufficiently studied both theoretically and practically (see, for example, [1-2] and references therein). Studies show that the electrophysical 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 electrophysical 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 electrophysical 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 ($\sigma$) and the Seebeck coefficient ($\alpha$), and on the contrary, a decrease in thermal conductivity ($\lambda$), 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 electrophysical 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 Disselkhorst [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. Researches were carried out on the basis of Egor and Disselkhorst 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 Disselkhorst 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 $P \sim 30 ÷ 50$ kilograms [14, 18, 19]. In this case, the sample can be imagined in the form of a stem.
generated in area A move to area B, and an electric current is generated due to the temperature difference in contacts МА and МВ. The temperature difference is monitored using ТА and ТВ 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.

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, σ₀~0.06 (Om·sm)~1, n₀~1.42·10¹⁸ sm⁻³; in later stages σ₀~0.017 (Om·sm)~1, n₀~4.03·10¹⁷ sm⁻³. At the initial stage of heat treatment, when the temperature is T≥375 K, the electrical conductivity suddenly changes to σ₀~0.017 (Om·sm)~1, and the concentration of charge carriers changes to n₀~2.85·10¹⁷ 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...
Fig. 2. Dependence of electrical conductivity on temperature: 1 – $\sigma / \sigma_0 \sim O m sm^{-1}$, 2 – $\sigma_0 \sim O m sm^{-1}$, 3 – $\sigma_0 \sim O m sm^{-1}$, 4 – $\sigma_0 \sim O m sm^{-1}$.

Fig. 3. Dependence of charge carrier concentration on temperature: 1 – $n / n_s \sim 1.42 \times 10^{18} sm^{-3}$, 2 – $n \sim 4.03 \times 10^{17} sm^{-3}$, 3 – $n \sim 4.47 \times 10^{17} sm^{-3}$, 4 – $n \sim 1.38 \times 10^{17} sm^{-3}$. 

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It is known that the structure and morphology of granulated semiconductor particles depends on the technology of their production [1-20]. 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$_3$Sb$_2$.

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 $\approx 1$ kOhm. It should be noted that ZnSb particles have a resistivity of $\rho \approx 0.221$ (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 $E_{in}$ appearing in sequence (Fig. 1d). This process leads to an increase in the height of the potential $E_{3S}$.

![Fig. 4](image-url)

**Fig. 4.** Dependence of the mobility of charge carriers on temperature.
barrier \( \phi \) in the interparticle boundary region. Based on the Setto model, the dependence of \( \phi \) on \( \rho \) can be expressed as follows:

\[
\rho = \frac{k}{q\langle a \rangle A^* T} \exp\left(\frac{q\phi}{kT}\right)
\]

where, \( q \) – electron charge, \( k \) – Boltzmann's constant, \( a \) – particle size, \( A^* \) – Richardson's efficiency constant, \( T \) – temperature.

Figure 5 shows the dependence of the height of the potential barrier \( \phi \) on temperature. Studies show that at \( T=300\div700 \text{ K} \), \( \phi \) increases linearly with temperature. At \( T=300 \text{ K} \), \( \phi \approx 0.436 \text{ eV} \) at the initial stages of thermal treatment, and \( \phi \approx 0.469 \text{ eV} \), at later stages, and at \( T=700 \text{ K} \), it increases to \( \phi \approx 0.92 \text{ eV} \) in all cases.

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

\[
\phi \approx \frac{Q_i}{\varepsilon \varepsilon_0 qN_G}
\]

where, \( N_G \) is the concentration of electrically active alloying elements, \( \varepsilon \) and \( \varepsilon_0 \) are the relative and absolute dielectric constants of the medium and vacuum, respectively.

So, it can be seen from expression (2) that the increase of charges \( Q_i \) trapped in localized traps leads to an increase of \( \phi \), which in turn leads to an increase of \( \rho \). 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 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 \( \sigma \) 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 \( T \approx 450\div600 \text{ K} \) \([1-12]\). In our case, \( T=300\div700 \text{ K} \) 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 $\sigma$ 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 $T \approx 450-600$ 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


