Studies of the thermovoltaic effect in semiconductors in the medium temperature range

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Abstract. The possibilities of increasing the voltage generated due to the thermovoltaic effect in semiconductors by increasing the generation temperature are considered. It is shown on the example of SmS that an increase in voltage can be achieved by increasing the depth of impurity donor levels in semiconductors. The magnitude of the generated voltage is 0.15V in SmS/Sm₀.₇Eu₀.₃S as against 0.05 V in undoped SmS. The possibility of obtaining generation due to the thermovoltaic effect is also considered on a classical PbTe semiconductor operating in a higher-temperature region compared to SmS. Generation value of 0.11V was obtained.

1. Introduction

The thermovoltaic effect (TVE) is one of the new principles for the conversion of thermal energy into electrical energy. The effect was originally detected on SmS [1]. Subsequently, it was discovered in other semiconductor materials: ZnO [2], Ge, Si [3] and various semiconductors of complex composition. However, the magnitude of the generated voltage in them was lower than in SmS. The semiconductor samples in a uniform temperature field without any temperature gradient and with a gradient in volume of concentration of donor levels generated an electromotive force (emf) in the direction of this gradient. The nature of the effect in SmS is related to the change in valence of the defect Sm ions in the vacancies of the sulfur sublattice

\[ \text{Sm}^{2+} \rightarrow \text{Sm}^{3+} + e^- \]

In this case, the electrons transfer from 4f levels to the conduction band and create large local concentrations of charge carriers. Such electron transitions are collective. Electron transitions are accompanied by the appearance of electrical voltage pulses and synchronized thermal processes. The effect of emf generation in SmS was observed when samples were heated to 470 K. At higher temperatures, impurity levels are depleted with a \( N_i \) concentration and an activation energy of 0.04 eV, which concentration gradient over the sample volume causes a thermovoltaic effect [4]:

\[ E = K \text{ grad}N_i \]

(1)

E is the intensity of the generated electric field. The effect coefficient, K, depends in a complex way on the temperature and parameters of the semiconductor.
This paper solves the problem of increasing the magnitude of the voltage generated during the thermovoltaic effect. An emf of 0.05 V is achieved on bulk SmS samples in a continuous mode at T ~ 400K [1]. One of the ways to increase the generated voltage follows from the formula for the effect emf [5]:

$$U = \frac{kT}{e} \ln \frac{n_2}{n_1}$$

(2),

where T is the operating temperature of generation, $n_1$ and $n_2$ are the concentrations of conduction electrons in the contact regions of the generating semiconductor. An increase in the generated emf is possible with an increase in the sample temperature. It is necessary to solve the problem of converting the working temperature of SmS based materials to the medium temperature region, 700–1000 K. However, the maximum temperature for the generation process is determined by the position of the energy levels of the donor ion. The deeper the donors lie, the more they are depleted at a higher temperature and the generation of emf due to the thermovoltaic effect (in SmS it is up to 470 K) is possible to higher temperatures. Thus, in order to increase the working temperatures and the magnitude of the generated signal in SmS, it is necessary to deepen the donor levels. Evaluation of the effect of increasing the output signal, which can be obtained with such a depth, can be made on the basis of the formula that follows from (2) and is valid for nondegenerate semiconductors:

$$U = -\frac{k}{e} \left( T - T_0 \right) \ln \frac{N_{i2}}{N_{i1}} + \frac{E_{a2} - E_{a1}}{kT}$$

(3),

where $N_{i1}$, $N_{i2}$ are the concentrations of donor levels with activation energies $E_{a1}$ and $E_{a2}$ located in the contact areas, $T_0$ and $T$ are the initial temperature and the generation temperature.

To study the thermovoltaic effect in the medium-temperature region, we also measured the effect on heterostructures based on one of the semiconductors used in this temperature range, PbTe.

2. Samples

Samples of LnS, where Ln=Sm, Eu, Yb, were made by synthesis from elementary substances Ln and S [6]. To obtain samples of the solid solutions Sm$_{1-x}$Yb$_x$S and Sm$_{1-x}$Eu$_x$S, the LnS powders obtained as a result of the synthesis were taken in quantities corresponding to the required values of $x$, mixed, briquetted and annealed in vacuum at T=1600°C. Two-layer heterostructures with a gradient of europium ions concentration, SmS/Sm$_{1-x}$Eu$_x$S, were made by joint pressing layers of SmS and Sm$_{1-x}$Eu$_x$S powders and annealing briquettes in vacuum at T=1600° for 30 minutes.

A three-layer sample was made from n-type PbTe for the experiments. The material of the layers had the following compositions. The first layer is PbTe + 0.065 mol.% PbI$_2$ + 1.5wt.% Pb. The middle layer is PbTe + 0.04 mol.% PbI$_2$ + 1.5wt.% Pb. The third layer is PbTe + 0.016 mol.% PbI$_2$ + 1.5wt.% Pb. The thermal emf coefficients of the layers at T=300 K were $\alpha_1$=150 μV/K, $\alpha_2$=120 μV/K, $\alpha_3$=70 μV/K, respectively. A gradual change in the thermoelectric power in thickness of a three-layer sample indicates the presence of a concentration gradient of impurity donor levels, which is necessary for the appearance of the thermovoltaic effect. This gradient is defined by different amounts of PbI$_2$ in the layers. Samples were prepared by vacuum pressing at a temperature of 750±10°C for 18–20 min. The composition of the samples was controlled by X-ray phase analysis.

3. Experiment

The thermovoltaic effect was measured using a setup that is shown schematically in figure 1. The heater 1 was linearly heated to the required temperature and kept in this state for a specified time. The heater was powered by the Volcraft PPS-11815 power supply unit (marked D1 in the figure). The temperature of the heater was controlled by a T2 thermocouple, its readings were taken with a UNI-T UT804 multimeter (D2). Then the power of the heater was turned off and the cooling took place naturally. The output signal from sample 2 was taken from the bottom (copper plate 3) and top (point 4) contacts with a RIGOL DM3061 multimeter (D3). The temperatures at the contacts were measured with thermocouples T1 and T3 and recorded with a Volcraft K204 digital thermometer (D4). The experiment was controlled and the data were recorded by a program created by LabVIEW software on a computer (PC).
Figure 1. The scheme of experiments on measuring the thermovoltaic effect.

The electrical conductivity was measured with direct current by a four-probe method.

4. Results and discussion
To deepen donor levels, it is necessary to dope SmS not with Sm ions, but with ions of other elements. We doped SmS with europium and ytterbium ions. Doping of Yb made it possible to increase the activation energy of donor levels to a value of 0.08 ÷ 0.29 eV, doping of Eu – to values of ~ 0.06 ÷ 0.4 eV, depending on the value of x in Sm$_{1-x}$Yb$_x$S and Sm$_{1-x}$Eu$_x$S solid solutions (figure 2). As can be seen, the use of europium is preferable.

Figure 2. The dependence of the activation energy of conductivity of solid solutions Sm$_{1-x}$Eu$_x$S (1) and Sm$_{1-x}$Yb$_x$S (2) on the values of x.
Figure 3 shows the temperature dependence of the signal obtained due to TVE. The signal in continuous mode on the $SmS/Sm_{0.7}Eu_{0.3}S$ sample was 0.15 V at $T=750K$ (figure 3). The same figure shows the calculated using formula (3) dependence. A satisfactory fit is observed. Inaccuracy is associated with the rough assumptions in the derivation of this formula. However, this measure of confidence allows us to assess the possibilities of increasing the output signal by doping.

![Figure 3](image3.png)

**Figure 3.** Temperature dependences of the generated signal as a result of thermovoltaic effect in the sample $SmS/Sm_{0.7}Eu_{0.3}S$ (points – experiment, curve – calculation by formula (3)).

Figure 4 shows temperature dependences of the values of generated voltage calculated by formula (3) for $SmS/Sm_{1-x}Eu_xS$ two-layer samples with different values of $x$. The values of activation energies for $Sm_{1-x}Eu_xS$ solid solutions are taken from figure 2. As follows from figure 4, the emf value in $SmS/Sm_{1-x}Eu_xS$ structures can be increased in the medium temperature range up to ~0.3 V.

![Figure 4](image4.png)

**Figure 4.** Calculated temperature dependences of the signal generated as a result of thermovoltaic effect by the double-layer $SmS/Sm_{1-x}Eu_xS$ heterostructures at different values of $x$. 


In addition to doped SmS, it is also possible to use semiconductors for the medium temperature range from classical thermoelectricity as a material for our study. We have conducted experiments on heterostructures based on PbTe. We have discovered a thermovoltaic effect in this typical for the medium temperature range thermoelectric material. Figure 5 presents the temperature dependence of the generated signal obtained on the PbTe-based heterostructure. The difference in the concentration of donor levels is created due to the difference in the amount of PbI₂ in layers. The magnitude of the generated voltage 0.11 V in the PbTe-based heterostructure was reached at T=732 K. This rather large value gives us cause to continue research in this direction.

5. Conclusions
1. Emf, arising at thermovoltaic effect, increases monotonically with increasing temperature.
2. The task of increasing the output signal generated by a thermovoltaic effect can be solved by increasing the generation temperature up to the medium temperature interval, 700-1000K.
3. Doping of SmS with europium allowed to increase the output signal of thermovoltaic effect from 0.05 to 0.15 V.
4. The use of existing thermoelectric materials developed for the medium temperature interval is promising for obtaining high values of the output TVE signal.

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