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**Measurement of Thermoelectric Parameters of Thin-Film Semiconductor Materials Using the Harman Method**

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For the analysis of the measurement of thermoelectric parameters of semiconductors, the Harman pulsed method was used. The authors propose a new approach to determine the thermoelectric quality factor of thin semiconductor films in the temperature interval (300 ÷ 500) K by directly measuring a series of electric circuit parameters. The theory of the method and its application in the measurement methodology are described in detail. The dependences of electrical quantities on the time, namely voltage – V(t), are investigated at different values of current pulses for thin films PbTe<Tl> grown by the pulsed laser deposition.

**Keywords:** thin films, lead telluride, thermoelectric quality factor, the Harman method, pulsed-laser deposition.

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**Introduction**

Thin-film semiconductor materials are of great interest for use in thermoelectric devices since they are able to increase the Seebeck coefficient (S) and reduce the thermal conductivity (k) of the films by nanostructuring the material. In particular, superlattice structures are studied to achieve an increase in S and a decrease in k without significant reduction of the electrical conductivity (σ) of the material. These factors influence the thermoelectric quality factor (ZT) \cite{1}.

The thermoelectric efficiency $Z = S^2\sigma/k$, where S – is the Seebeck coefficient, $\sigma$ – is the specific electrical conductivity, k – is the coefficient of thermal conductivity, is the most important characteristic of the thermoelectric material, which requires the most accurate definition. A standard average measurement error of individual parameters is about 5%; then the average measurement error of Z is 20%. Therefore, for the measurement of Z, a special method \cite{2} was developed, which allows measuring all these parameters on one sample in one measurement cycle, with the identical temperature differences being included in the calculation of S and k subject to same sample geometry. The total error of this technique is about 10%.

It is the Harman method which is the most universal for measuring Z \cite{3,4}. At the heart of the method lies the idea that, with a small current I through sample of Joule heat, which is quadratic to I, can be neglected.

In this case, from the conditions of the thermal balance at the ends of the sample in adiabatic conditions, we can obtain the relation:

$$ZT = \frac{U_s}{IR_s} - 1,$$

where $U_s$ – is the voltage drop on the sample when current I passes through it and $R_s$ – is the sample resistance. This method allows you to determine ZT by measuring the voltage drop on a sample subject to constant and alternating current – $U\approx U_s$ and $U\approx IR_r$, respectively \cite{5}.

In fact, the requirement for adiabaticity is inappropriate because, when passing arbitrarily small current, this leads to the endless heating of the sample. Therefore, real conditions are never adiabatic, and this should be taken into account. In this case, $Z_{df}T = \frac{U}{U\approx} - 1$ is measured instead of Z. The $Z_{df}$ value at room temperature is 5-12% less than Z. Taking into account heat losses can significantly reduce this discrepancy, and the overall error of determination does not exceed 5% \cite{6, 7}.

This method makes it possible to determine the quality of the material directly. The measurements are reduced to the determination of the potential difference $U_r$ on the contacts when passed through a sample the alternating current and the difference of the potentials $U_r$. 

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when passed through a sample the direct current. For identical quantities of alternating and direct currents $I$:

$$Z = \frac{1}{T} \frac{U_\sim - U_\sim}{U_\sim},$$

(2)

where $T$ – is the average temperature of the sample. In addition, the Harman method makes it possible to find the values of $\alpha$, $\sigma$ and $k$ on the same sample [8].

The coefficient of thermal EMF is determined from the formula:

$$\alpha = \frac{U_\sim - U_\sim}{\Delta T},$$

(3)

where $\Delta T$ is the temperature difference $T_1 - T_2$ at the ends of the sample when passed of direct current. The conductivity of the sample material is determined from the expression

$$\sigma = \frac{I_\sim}{U_\sim} \cdot \frac{l}{S},$$

(4)

where $I_\sim$ – is the value of the alternating current, $l$ – is the length of the sample, $S$ – is its cross-section. The thermal conductivity of the material is determined from Fourier's law [9, 10].

$$\kappa = \frac{\alpha I_\sim}{\Delta T} \cdot \frac{l}{S}$$

(5)

I. Experiment

Samples of PbTe ta PbTe<Tl> were obtained by pulsed laser deposition (PLD) using stoichiometric targets. The targets were made of Pb, Te and Tl elements having a purity of 5N and placed in vacuum quartz ampoules for synthesis reaction. For deposition, YAG: Nd<sup>3+</sup> laser was used with parameters: laser wavelength 1064 nm, power peak in pulse 0.4 J, power density $4 \times 10^8$ W/cm<sup>2</sup>, pulse duration 10 ns, pulse frequency 0.5 Hz. The pressure inside the PLD chamber was $1 \cdot 10^{-5}$ mm Hg, and the substrate temperature was 200°C.

We used the Harman method as one of the techniques for measuring the thermoelectric parameters of semiconductor materials, which makes it possible to determine the thermoelectric quality factor. The analysis of the Harman method was carried out to determine other parameters of thin films in one experiment. The results are given of investigations of the voltage dependence on...
time with a certain value of the current pulse passing through the sample.

For the experiment, the studied PbTe <Tl> sample deposited on glass substrates was placed in a thermostat on two conductors. Electric and thermal contacts were made on the ends of the sample to create its homogeneous thermal and electric field of the sample. In order for the Harman transition method to be exact, the following experimental conditions must be achieved: the adiabaticity of the device and the maximum constant temperature gradient for this current value. The scheme of the Harman method is presented in Fig. 1.

To calculate the parameters of the sample, the following geometrical dimensions were used: \( t = 5 \times 10^{-5} \text{ cm} \) (thickness), \( a = 2 \times 10^{-1} \text{ cm} \) (width), \( l = 4 \times 10^{-1} \text{ cm} \) (length of sample).

In fig. 2 shows the scheme of the measuring device based on the Harman method, modernized taking into account the achievements of modern measuring technology (stabilized DC and AC sources, the use of a computer for measuring operations and obtaining information about samples, etc.).

II. Results and discussion

In the research process, the following experimental conditions were achieved for the Harman method to be exact: the adiabaticity of the device and the maximum steady temperature gradient for the given magnitude of current \( I \). The effect of the current magnitude on the thermoelectric properties is an important factor since the average temperature of the heat-release thermoelectric device can radically change according with the direction of \( I \). In this case, the use of the smallest possible \( I \) to achieve the desired values of the signal in the measurement of transient voltage will lead to the results that will reduce the impact of temperature dependence of \( \Delta T \) and affect measurement accuracy.

The researched/tested samples of the corresponding geometric sizes were mounted in an isolated model of the measuring device by means of current contacts. The thin

![Fig. 2](image)

**Fig. 2.** Dependent scheme of the measuring device based on the Harman method, modernized taking into account the achievements of modern measuring technology (stabilized DC and AC sources, the use of a computer for measuring operations and obtaining information about samples, etc.).

![Fig. 3](image)

**Fig. 3.** Dependences of \( V \) (t) on time at different values of input pulses of current for a thin film PbTe <Tl> and different sample temperatures: a) PbTe<Tl> – \( U = 2 \text{ V} \); \( T = 20^\circ \text{C} \); b) PbTe<Tl> – \( U = 20 \text{ V} \); \( T = 20^\circ \text{C} \); c) PbTe<Tl> – \( U = 0.2 \text{ V} \); \( T = 120^\circ \text{C} \); d) PbTe<Tl> – \( U = 20 \text{ V} \); \( T = 120^\circ \text{C} \).
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films PbTe<Te> with an area of $10^{-3}$ cm$^2$ were also checked for the dependence of the $ZT$ parameter on their size, which can be the result of non-adiabatic conditions of the device due to thermal leakage through to an electrical contact. To connect with the measuring devices two-wire electrical lines were used to supply current and measure the resulting voltages on the entire device proper.

Fig. 3 shows the time dependences of the voltage $V(t)$ at different values of the current pulse through an electric circle containing a measuring sample in the form of a thin film PbTe<Te> 5·$10^{-5}$ cm thick with the area of $10^{-3}$ cm$^2$. The magnitude of the pulse of the voltage from the generator of 10 ms duration was changed in the range of 0.2÷20 V, which corresponds to the current value 0.2÷20 μA.

Measurement of $V_R$ at the pulse front was used to determine the electrical resistance of the thin films PbTe<Te>. This high-speed measurement of electrical resistance ensures that the generated thermoelectric voltages do not cause errors when measuring the resistance of a sample of thin films PbTe<Te>.

The timing values of the $V_R$ measurement of the device indicate that the relaxation of the electric field is achieved at about 10 μs after the droop on the edge of the current pulse. Fig. 4 shows the time dependence of the $V_S$ parameter at high resolution – pulse growth and decrease in semi-logarithmic coordinates for the sample PbTe<Te>. An extrapolation of the curve was used to determine the value of $V_S$ at the edge of the curve ($t = 0$).

By formula: $Z_{T} = \frac{U}{U_T}$ parameter $ZT$ was estimated which was ≈7 giving the value of parameter Z ≈0.02 1/K for the operating temperature of 120°C.

Conclusions

The carried out analysis of the Harman method as one of the most effective methods for measuring the thermoelectric parameters of thin-film semiconductors allowed to investigate the time dependencies of the passage of a current pulse in thin films PbTe<Te> under different values of the pulse current and different temperatures. From the time dependences of the electric field value, the $ZT$ and $Z$ parameters were determined, which were 7 and 0.02 1/K respectively for the working temperature of the film material – 120°C.

Fig. 4. Time dependence of the $V_S$ parameter at high resolution - pulse droop (on the tab - pulse increase) for the sample PbTe<Te> ($U = 0.2$ V; $T = 120^\circ$C).

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Вимірювання термоелектричних параметрів тонкоплівкових напівпровідникових матеріалів методом Хармана

Для аналізу вимірювання термоелектричних параметрів напівпровідників, використано імпульсний метод Хармана. Запропоновано новий підхід для визначення термоелектричної добротності тонких плівок PbTe<Tl> вирощених імпульсним лазерним осадженням. Детально описано теорію методу, застосування його у методі вимірювань. Досліджено залежність електричних величин, зокрема напруги - \( V(t) \), від часу при різних значеннях імпульсів струму для тонких плівок PbTe<Tl>, вирощених імпульсним лазерним осадженням.

Ключові слова: тонкі плівки, теллурид свинцю, термоелектрична добротність, метод Хармана, імпульсно-лазерне осадження.