

ФИЗИКО-МАТЕМАТИЧЕСКИЕ НАУКИ

PIEZOPHOTORESISTIVE QUALITIES OF p -TlInSe₂ MONOCRYSTALS

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ABSTRACT. The effect of uniaxial unalloyed deformation, temperature and optical lighting on tenzoresistive properties of p -TlInSe₂ monocrystals is investigated. It is shown that with temperature increase sensitivity to TlInSe₂ of unalloyed crystals toward deformation increases considerably, coefficient of tenzosensitivity at the same time increases linearly with temperature.

Introduction. To date, the most widely used materials in semiconductor electronics are silicon and germanium. This is due to the wide spread of silicon on the earth, the proximity of the structure of germanium and silicon, the unique properties of these materials and, as a result, the greatest study of their physic-chemical characteristics.

However, the ever increasing demands of modern science and technology are not satisfied only with these materials and require materials that have various properties. Therefore, along with the improvement of the existing properties, the search for new semiconductor materials and the study of their various characteristics at present is one of the cardinal general problems of modern solid-state physics and leads to the discovery of very many semiconductor materials, including triple and more complex compounds. The discovery of new materials, the study of the interrelationships in the composition, structure, and properties of multi component semiconductor compounds, in addition to deepening the fundamental scientific understanding of semiconductors, opens up new prospects: new compounds tend to exhibit new qualities and thereby contribute to solving the necessary technical problems.

Knowledge of the laws of the interrelationships of properties, composition and structure makes it possible to develop the scientific foundations for the search for and creation of new, more efficient semiconductor materials with predetermined properties and, thereby, to satisfy the increasing demands of modern quantum and semiconductor microelectronics. The creation of new semiconductor materials is of particular value if it is possible to obtain them in the form of perfect large single crystals.

By the beginning of our study, the TlInSe₂ compounds belonged to the number of poorly studied semiconductors. There was only preliminary information on the electrical, thermoelectric, thermal, partial and photoelectric properties of unalloyed stoichiometric pure TlInSe₂ crystals, which testify to their prospects as new semiconductor materials, which stimulated the efforts undertaken in this research.

Interest in this compound TlInSe₂ from a scientific point of view is due to a specific feature of the structure of its crystal lattice. Its elementary cell contains two independent structural units, which ensure different coordination, valence state and character of chemical bonds for the constituents of dissimilar cations of the same group. These features cause a sharp anisotropy of the physical properties of semiconductors of this type. The chain structure and the feature of splitting their crystals

into filamentary ones with mirror faces is a consequence of the sharp asymmetry of the chemical bond.

We know that the temperature dependence of the initial resistance and the change in the coefficient of piezoelectricity with temperature are the most important indicators of semiconductor tenzometric materials, including TlInSe₂. In the case of using semiconductor strain gauges in constructions with variable temperature, it becomes necessary to take this change into account. The change in the initial resistance of the sensor with temperature is taken into account by applying the appropriate compensation methods, and the change in the sensitivity by introducing correction. But nevertheless, the loss in sensitivity at elevated temperatures was inevitable; since the tenzosensitivity of many materials known in semiconductor tensometry decreases significantly with increasing temperature [1]. Therefore, increasing the strain sensitivity at high temperatures is an urgent task.

Technique of the experiment. Crystals for research are synthesized by fusing the initial components according to stoichiometry. As initial components used: thallium brand (Tl - 000), indium (In - 000) and selenium (Se - PP - 17 - 4).

The strain sensitivity of semiconductor materials studied by us is measured in static modes [2 - 5]. The identical crystals required from the ingot are obtained from the ingot by the simplest pressing of the sharp knife, the thickness of the blade is $\leq 0,01$ mm, on the loose end of the thin but wide and long plate of the single crystal at an angle of 45°. Obtained in this way ("needle" in the case of TlInSe₂), crystals - blanks with mirror faces - without any additional treatments are ready to weld the contacts and install them on the substrate base. When soldering "antennae", i.e. the creation of mechanically reliable ohmic contacts on the indicated blanks, two methods were used:

a) Induction of indium in an inert gas flow followed by soldering copper (or nickel) wires ($\varnothing = 0,01$ mm).

b) Direct spot welding of the corresponding wires by a capacitor discharge to the ends of the preform heated in the inert gas stream.

The second method proved to be more effective and reliable (especially for moderate temperatures). The calibration beams for glued sensors were plates of steel 45 with a thickness of 0,5 – 1,0 mm and a length of 20 mm to 80 mm. The surface of the substrate by class of treatment was not lower than grade 7.

These substrates were treated in toluene prior to application of the undercoat to degrease, and then

washed in ethyl alcohol. The epoxy-cresol lacquer (EP-96), which is a solution of E-40 epoxy resin modified with odinic acid, with the addition of a boozee-ionized Resole RB and K-421 - 02 resin, was applied to the substrates so cleaned (for the required surface area). The thickness of the sublayer corresponded to 10 - 15 μm . During the deposition of the underlayer, a uniform thickness coating was provided. After one hour at room temperature, the substrate is transferred to a drying cabinet for high temperature polymerization.

A slow rise in temperature to 453 K and holding the substrates at this temperature for 1 hour ensures complete polymerization and excludes air bubbles. On the substrate prepared in this way, a second layer of varnish is applied over the sublayer, slightly exceeding the dimensions of the strain gage. Single crystals of TlInSe_2 , with welded leads, are laid on a layer of varnish and slightly pressed. The surface of the crystal is

completely covered with varnish. At the same time, the crystal is given the required position in the plane of the substrate. To tightly contact the body of the sensor, as well as to maintain the specified orientation of the sensor relative to the substrate, the device was covered with a thin fluoroplastic tape with a width of 1,5 mm. The drying of the device is carried out in the mode 291 - 296 K for 1 hour, followed by annealing at 463 ± 3 K for about 1,5 hours. After drying, the fluoroplastic tape, if necessary, was easily separated from the finished sensor. The indicated drying regime proved to be the most optimal, and the instruments showed the maximum sensitivity.

Figure 1 shows the experimental design, where the strain gage 1 with the electrodes 2 on the insulated elastic substrate 3 under electromagnetic irradiation is in three positions.

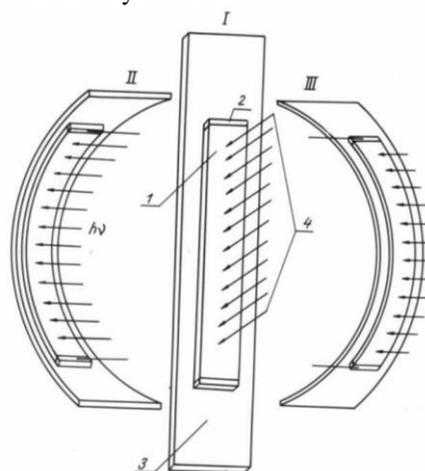


Fig. 1. Schematic representation of the TlInSe_2 load cell on an elastic substrate (1 – TlInSe_2 single crystal, 2 - electrodes, 3 - isolated elastic substrate, 4 - direction of electromagnetic irradiation without bending (I), compression (II) and stretching (III)).

Results of the study and their discussion. In this respect, our investigations showed that the sensitivity of unalloyed p- TlInSe_2 crystals to deformation increases significantly with increasing temperature (Fig. 2), while the coefficient of strain sensitivity grows linearly with temperature (Fig. 3). Relative change in the coefficient of strain sensitivity per unit degree in percent;

$$G_T = \frac{\Delta K / K}{\Delta T} 100\% = 0,13 - 0,15\% / \text{deg}.$$

Thus, strain gauges made of p- TlInSe_2 crystals make it possible to provide high accuracy of registration in thermostated operating conditions. And in conditions of variable temperature, it is necessary to take into account the corresponding temperature corrections. It is convenient to use p- TlInSe_2 crystals simultaneously and as thermoresistors; the temperature of the medium can be determined from the value of the initial resistance of the sensor and from the external two-coordinate instrument (H306). The p- TlInSe_2 crystals used for the sensors ($R_x \geq 100 \text{ m}\Omega$), above 813 K, were in the intrinsic conductivity region, where the potentiometer readings with temperature are also linear and

characterized by a factor of $0,8 \mu\text{A} / \text{deg}$ ($0,013 \text{ deg} / \text{div}$).

When studying the strain-specific features of p- TlInSe_2 crystals, a new effect was also discovered, consisting in changing the sensitivity from the presence of optical illumination. This effect - the sensation of crystals to deformation under the action of light - we called the piezophotoresistive effect.

It is interesting to emphasize that the magnitude of the photoresistive effect sharply depends on the intensity and spectral composition of the optical illumination. (Fig. 4 and 5).

The change in the coefficient of sensitivity (K) of the crystal p- TlInSe_2 ($R_0 = 108 \Omega$) per unit of strain for different values of the intensity of the optical illumination and deformation (in the static regime) is shown in Fig. 4 and 5 in Table 1.

The relative change in the coefficient of sensitivity $\Delta K / K$ per unit light intensity (I lux) in percentage, regardless of the degree of deformation of the same order: for a deformation $\varepsilon = 2,2 \cdot 10^{-4}$, the constant

$$g_1 = \frac{\Delta K / K}{\Delta I} 100\% = 2 \cdot 10^{-3} \% / \text{lux in } \varepsilon = 1 \times 10^{-5}$$

this coefficient is $g_1 = \frac{\Delta K / K}{\Delta I} 100\% = 1,17 \cdot 10^{-3} \%$

/ lux.

Optical illumination, apparently, fills interband local levels, and the latter contribute to the redistribution of carriers between the corresponding valleys. It should

be emphasized that the piezophotorestrictive effect observed by us in essence has nothing in common with the familiar effects known by name: piezooptic [3] (photoelasticity) - change in the refractive index by mechanical stresses, photomechanical [4] - decrease in hardness when exposed to light, etc. It is

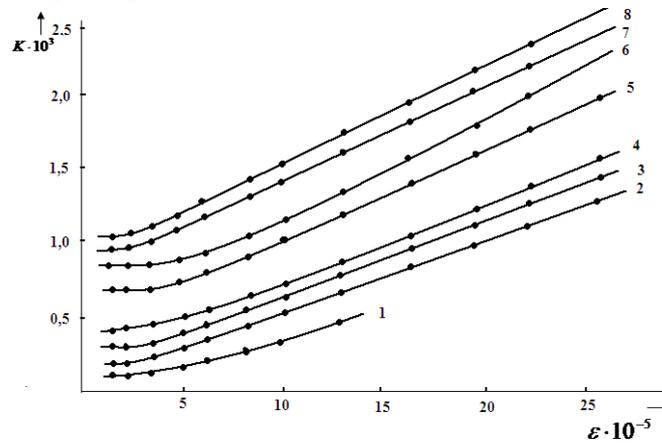


Fig.2. Dependence of the strain-strain coefficient on the degree of deformation at temperature: 1 - 315 K; 2 - 393 K; 3 - 398 K; 4 - 438 K; 5 - 473 K; 6 - 500 K; 7 - 533 K; 8 - 556 K in the $p-TlInSe_2$

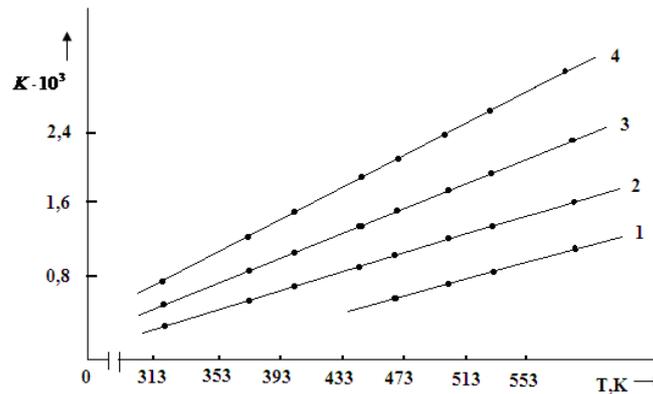


Fig.3. Dependence of the coefficient of strain sensitivity on temperature under deformation: 1 - $4 \cdot 10^{-5}$; 2 - $10 \cdot 10^{-5}$; 3 - $16 \cdot 10^{-5}$; 4 - $22 \cdot 10^{-5}$ in the $p-TlInSe_2$

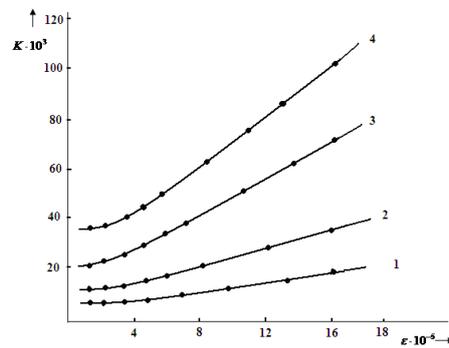


Fig.4. Dependence of the strain-strain coefficient on deformation at various illuminations: 1 - $L = 0$ lux; 2 - $L = 1000$ lux; 3 - $L = 10000$ lux; 4 - $L = 48000$ lux, in $p-TlInSe_2$

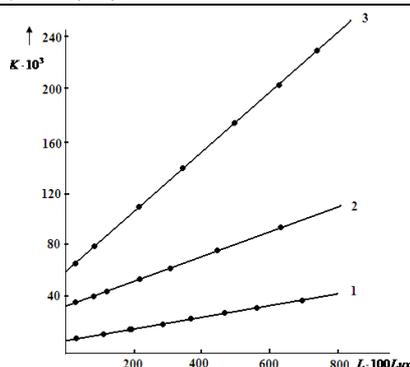


Fig.5. Dependence of the coefficient of sensitivity on the intensity of illumination for various deformations: 1- $\epsilon = 1 \cdot 10^{-5}$; 2- $\epsilon = 10 \cdot 10^{-5}$, 3 - $\epsilon = 22 \cdot 10^{-5}$, in p-TlInSe₂

Table 1. Dependence of the tensorsensitivity of a TlInSe₂ single crystal on the deformation and intensity of optical illumination

№	Illumination intensity (Lux)	Tenzosensitivity coefficient: K · 10 ³		
		$\epsilon = 1 \cdot 10^{-5}$	$\epsilon = 10 \cdot 10^{-5}$	$\epsilon = 22 \cdot 10^{-5}$
1	0	8	19,5	56
2	1000	10	26	59
3	2800	12	34	65
4	10000	16	41	85
5	19000	18	49	110
6	60000	40	87,5	220

interesting to check the presence of the so-called piezoelectro-resistive effect in strong electric fields and the effect of this field on the piezoresistive effect.

It should be emphasized that an increase in the sensitivity of the conductivity to deformation by optical, thermal (and possibly electric) methods can greatly enhance the capabilities of semiconductor tensometry.

Table 2 shows the results of measuring the tensometric parameters of the crystals studied. In the same place, the characteristics of other semiconductor strain gauges are given for comparison. Comparison shows

that in crystals of TlInSe₂ there is a strong piezoresistive effect in the [001] direction. Because of their sensitivity to deformation, TlInSe₂ crystals considerably exceed all materials known to us in semiconductor tensometry (Table 2). In Table 2 for comparison, the characteristics of semiconductor strain gauges based on Si <Ni> single crystals [5,6], which are one of the best for today, are given. The coefficient of tensorsensitivity of TlInSe₂ single crystals of various series at 300 K, depending on the degree of relative deformation ($\epsilon = \Delta l / l = (1 - 57) \cdot 10^{-5}$) varied from 2000 to 30300.

Table 2. Some characteristics and coefficients of tensorsensitivity of semiconductor tenzo sensors

№	Material of conductor	Tenzosensitivity coefficient K (300K)	boundary of deformation (%)	Specific resistance (Ω · cm)	Size of sensor (mm ³)
1	p – TlInSe ₂	2000 – 30000	0,50	(1-5) · 10 ⁸	10x1,0x0,25
2	Si<Ni>	100 – 8000	0,3	-	4x2x2

Another important feature of TlInSe₂ crystals in terms of semiconductor tensometry is their considerable flexibility (elasticity) and mechanical tensile strength; for example, p-TlInSe₂ crystals with dimensions of 0,25x1x10 mm³ withstand bending deformation up to a curvature radius of 6 - 8 mm (see Fig. 6).

The crystals of TlInSe₂ differ from all the materials known in semiconductor tensometry in that, as indicated above, the features of their crystal structure provide cleavage in the desired direction for filamentary

samples with mirror faces and the required geometric configuration (Fig. 7). This feature also provides the simplest technology for manufacturing strain gauges based on them.

Thus, from the foregoing piezo-photoresistive characteristics of TlInSe₂ single crystals and due to high strain sensitivity, considerable flexibility and the ability to split into desired filamentary plates with mirror faces in the direction of the maximum piezoresistive effect [001], it is possible to create tenzosensors functioning by

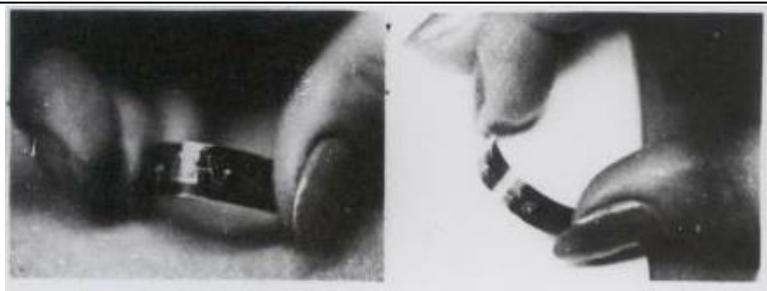


Fig. 6. Bending of TIInSe₂ crystals and a photo of strain gauges

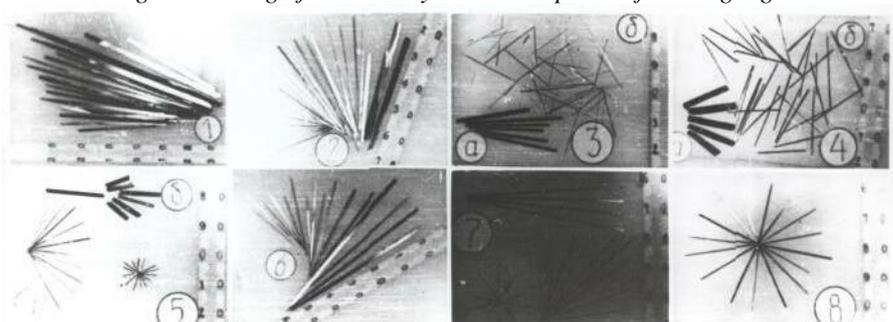


Fig. 7. Photographs of grown TIInSe₂ single crystals

method of multipoint tenzometry that applied in medical practice to determine the temperature simultaneously at different points of the body and vital parameters of the lungs:

a) in therapeutic direction for simultaneous detection Temperature of different points of the body to within 0.01 degrees;

b) in pulmonological studies, one can determine the parameters of the lungs of a person when breathing, using the effect of elastic deformation of the chest by the piezoelectric effect method. For example, the Breath volume (BV), the minute volume of the Doha (VD), the reserve volume of inspiration (RVI) and the reserve volume of exhalation (RVE), the vital capacity of the lungs (VCL), the retention of respiration on inspiration and exhalation,

Conclusions. It was found that with increasing temperature and under the influence of light, the coefficient of tensosensitivity of TIInSe₂ crystals increases sharply. It is assumed that the temperature and the optical illumination change the character of the filling of local levels in the forbidden band, and thus contribute to the redistribution of carriers between the corresponding valleys.

For TIInSe₂ crystals, a record coefficient of strain sensitivity was obtained ($K = 2000-30330$ for deformations of the order of $\varepsilon = 0,1-3,0 \cdot 10^{-3}$). The thermo resistive properties of these crystals remain stable at thousand fold repetitions of the deformation and temperature cycles.

Thus, due to the high sensitivity, considerable flexibility and the ability to crack on the desired filamentary plates with mirror faces in the direction of the maximum piezoresistive effect [001], TIInSe₂ crystals are promising materials for semiconductor tensometry used in various fields of national economy and medical practice.

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