Electrical conductivity of uniaxial-deformed monocrystals Tl\(_{1-x}\)Ag\(_x\)InSe\(_2\)(0 ≤ X ≤ 0,03)

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Abstract. We have studied the effect of uniaxial compression (stretching) deformation on electrical conductivity along the crystallographic axis [00l] of monocrystals TlInSe\(_2\) and derivant solid solutions. It has been found that substitution of Tl atoms with Ag atoms in crystals of solid solutions based on TlInSe\(_2\) leads to a shift of the energy of indirect transitions to the long-wave zone. The obtained results have been compared to both theoretical calculations of the zone structure of TlInSe\(_2\) crystals and the multi-valley model.

1. Introduction

Compounds of \(A^{III}B^{III}C^{VI}\) class of semiconductor type are of scientific interest for modern optoelectronics and are currently being intensively studied [1–13].

TlInSe\(_2\) is a typical representative of the recently discovered non-full-valent semiconductor compounds, which, like its other crystal-chemical analogues from the above class, has a specific structure of the crystal lattice, composed of two independent structural units – an octahedron with monovalent thallium ions and a tetrahedron with trivalent indium ions, surrounded by four selenium atoms with covalent-tetrahedral bond [1].

The research purpose is to study the effect of uniaxial compression (stretching) deformation on electrical conductivity along the crystallographic axis [00l] of monocrystals TlInSe\(_2\) and derivant solid solutions. It has been found that substitution of Tl atoms with Ag atoms in crystals of solid solutions based on TlInSe\(_2\) leads to a shift of the energy of indirect transitions to the long-wave zone. The obtained results have been compared to both theoretical calculations of the zone structure of TlInSe\(_2\) crystals and the multi-valley model.

2. Methods and materials

The effect of uniaxial deformation on the electrical conductivity along the crystallographic axis [001] of the crystals TlInSe\(_2\), Tl\(_{0.99}\)Ag\(_{0.01}\)InSe\(_2\) and Tl\(_{0.97}\)Ag\(_{0.03}\)InSe\(_2\) has been studied in static mode, the
The essence of which is as follows: constant deformation is transmitted to the crystal under study by means of a special device designed for this purpose (Fig. 1). The test sample 1 in the form of a thin (1 ÷ 10 microns in thickness) rectangular "hair" with mirror planes of natural cleavage, is glued to a flat steel beam (2), \( t \) in thickness, bent by moving the middle part to (\( \Delta h \)) as relating to the plane of sharp ends of the side supports (3), located at a distance \( l \). Sputtered indium has been used as resistible contacts (up to 50 V).

\[ \epsilon = \frac{4t}{2R}, \]  
\[ R = \frac{(\Delta h)^2 + \left(\frac{l}{2}\right)^2}{2\Delta h}, \]

where \( l \) – length of the beam's section under pure deflection deformation; \( \Delta h \) – maximum deflection of the beam.

Substituting the value from formula (1) into formula (2) we finally get

\[ \epsilon = \frac{4t}{l^2} \Delta h \]  

\( \Delta h \) (both to positive and negative deformation) has been measured with an accuracy of \( \pm 0.001 \) mm by means of a time-sensitive indicator. Measurement of the sample resistance both in the absence and in the presence of deformation (\( R_{e,0} \)) has been carried out in the mode of low load resistance according to the diagram presented in Fig. 2. Vertical channel of the plotter "U" has been used to register the voltage drop on the load resistance both in the absence (\( V_0 \)) and in the presence (\( V_e \)) of deformation, and the horizontal "X" – for fixing the external temperature impact. Statistics of preliminary measurements has showed a significant change in resistance both in the presence and in the absence of deformation.
Figure 2. Basic diagram for measuring electrical conductivity in static mode

As a result of our numerous measurements on crystals carried out so far at "normal drying" and optimum thickness of suitable glue, approximately the same strain effect takes place, both at positive and at negative deformation of identical size.

3. Results

Crystals of solid solutions, as well as crystals TlInSe\textsubscript{2} show a sufficiently high sensitivity to changes in electrical conductivity under deformation ($\varepsilon = 1.52 \cdot 10^{-3}$) of both stretching and compression along the crystallographic axis [001]. Analysis of temperature dependencies of electrical conductivity of crystals TlInSe\textsubscript{2}, Tl\textsubscript{0.99}Ag\textsubscript{0.01}InSe\textsubscript{2} and Tl\textsubscript{0.97}Ag\textsubscript{0.03}InSe\textsubscript{2} presented in Fig. 3 a, b, c, both in the absence of uniaxial deformation and in its presence (stretching and compression along the crystallographic axis [001]) has allowed determining the energies of impurity levels ionization. The ionization energy in crystals p-TlInSe\textsubscript{2} in the absence of deformation is $\Delta E_\alpha = 1.21$ eV, which is quite well consistent with the value of the energy of indirect transitions $E_{\text{ind}} = 1.22$ eV at 300 K for these crystals [1].

Substitution of monovalent thallium (Tl) atoms with silver (Ag) atoms causes shift of indirect transitions to the long-wave zone. Stretching deformation along the crystallographic axis [001] shifts the energy of indirect transitions to the short-wave zone, while compression deformation, on the contrary, shifts the energy to the long-wave zone. The obtained results are presented in Table 1. As can be seen from Table 1, the values of baric coefficients of change in the indirect energy gap both in TlInSe\textsubscript{2} crystals and in the crystals of derived solid solutions at a room temperature fluctuate within:

$$G^{[001]} = (3.19 \div 3.65) \cdot 10^{-10} \text{ eV/Pa}$$

It is known that the strain-resistive properties of semiconductor materials are mainly determined by elastic constants of the material in the corresponding crystal-like directions. The higher the value of the Young's modulus ($E_i$), the higher the sensitivity of electric conductivity to deformation.

Table 1. Displacement of the long-wave edge of indirect energy gap in crystals Tl\textsubscript{1-x}Ag\textsubscript{x}InSe\textsubscript{2}, both in the presence and in the absence of uniaxial deformation

| Crystal Type | $P = 0$, Pa | $E_i$, eV | $G^{[010]}$, V/Pa | $P = 2.189 \cdot 10^9$, Pa |
|--------------|-------------|-----------|-------------------|---------------------------|
| TlInSe\textsubscript{2} | $P = -2.189 \cdot 10^9$, Pa | 1.14 | 3.38$\cdot10^{-10}$ | 1.2 |
| Tl\textsubscript{0.99}Ag\textsubscript{0.01}InSe\textsubscript{2} | $P = -2.189 \cdot 10^9$, Pa | 1.13 | 3.70$\cdot10^{-10}$ | 1.2 |
| Tl\textsubscript{0.97}Ag\textsubscript{0.03}InSe\textsubscript{2} | $P = 2.189 \cdot 10^9$, Pa | 1.05 | 3.65$\cdot10^{-10}$ | 1.25 |

The value of the Young's modulus in the crystallographic direction [001] for TlInSe\textsubscript{2} crystals makes $E_i = 14.4 \cdot 10^{11}$ DIN/cm\textsuperscript{2} [1] at 300 K, which significantly exceeds the corresponding values of materials known in semiconductor tensometry.
Figure 3. Temperature dependence of specific electrical conductivity of the crystals Tl\(_{1-x}\)Ag\(_x\)InSe\(_2\): 1 – TlInSe\(_2\); 2 – Tl\(_{0.99}\)Ag\(_{0.01}\)Se\(_2\); 3 – Tl\(_{0.97}\)Ag\(_{0.03}\)Se\(_2\); 4 – Tl\(_{0.97}\)Ag\(_{0.03}\)Se\(_2\)

Apparently, some of the main reasons for the observed relatively large piezoresistive effect in monocrystals of TlInSe\(_2\) and derivative solid solutions are their complex energy structure, multilinearity, sharp anisotropy of effective masses, mobility, etc.

As it follows from the theory of groups, in TlInSe\(_2\) and TlSe crystals [1], surfaces of constant energy are three-axis ellipsoids of a general form. The observed tensor-resistive properties in crystals based on \(p\)-TlInSe\(_2\) can be qualitatively explained on the basis of a 4-ellipsoid model (Fig. 4) [1] at the location of extremes at points \(G(N_g = I\) ellipsoid), \(T(N_T = 4 \cdot 1/4 = I\) ellipsoid) and \(N(N_N = 4 \cdot 1/2 = 2\) ellipsoid) with elongated ellipsoid axes along the corresponding axes of symmetry (Fig. 3). The law of dispersion on planes for carriers in valleys has the form:

\[
N - \varepsilon = \frac{\hbar^2}{2} \left(\frac{K_x^2}{m_{//}} + \frac{K_z^2}{m_{\perp}}\right),
\]

\[
T - \varepsilon = \frac{\hbar^2}{2} \left(\frac{K_x^2}{m_{//}} + \frac{K_z^2}{m_{\perp}}\right)
\]

and

\[
G - \varepsilon = \frac{\hbar^2}{2} \left(\frac{K_x^2}{m_{//}} + \frac{K_z^2}{m_{\perp}}\right)
\]

(4)

\(m_{//}\) and \(m_{\perp}\) are the longitudinal and transverse effective masses according to the axes of the ellipsoids. Corresponding mobilities at this:
\[ \mu_{||} = \frac{q\tau}{m_{||}}, \quad \mu_{\perp} = \frac{q\tau}{m_{\perp}} \]  
(5)

If the total number of carriers in the valleys is \( n_0 \), then the number of carriers in the valleys \( G, T \) and \( N \) will be \( n_0/4, n_0/4, 2 \cdot n_0/4 \), respectively.

The contribution to conductivity from the respective valleys in a direction parallel to the tetragonal axis will be:

\[ \sigma_{g||} = e \frac{n_0}{4} \mu_{||}; \quad \sigma_{T||} = e \frac{n_0}{4} \mu_{||}; \]

and \( \sigma_{N||} = e \cdot 2 \cdot \frac{n_0}{4} \mu_{\perp} \).

(6)

Thus, the total electrical conductivity along the crystallographic axis [001]:

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Figure 4. Four-ellipsoid model TlInSe₂

However, one-sided deformation of crystals along the axis [001] will change the ratio of the number of "heavy" (with mobility \( \mu_{||} \)) and "light" (with mobility \( \mu_{\perp} \)) holes, taking part in the electrical conductivity in this direction. This change, caused by the flow of carriers from valley to valley, apparently, causes tenzo- or piezoresistive effect. When stretching TlInSe₂ crystals and derived solid solutions along the axis [001], the relative number of heavy holes,

\[ \sigma_0 = \sigma_z = en_0 \left( \frac{3\mu_{\perp} + \mu_{||}}{4} \right) \]

(7)
moving in this direction will increase. Therefore, the conductivity will decrease. At compression, however, the conductivity will increase. The reason for redistribution of carriers in the valleys is obviously the fact that the extremes with respect to the unilateral deformation are in different conditions. Stretching crystals of the type TlInSe$_2$ along [001] inevitably causes compression in the direction of [001] and [010]. As a result, the extremum $T$ on the axis [001] is raised, and the corresponding extremes $N$ on the axes [001] and [010] are lowered (dotted lines in Fig. 4). Thus the contribution of the respective valleys to electrical conductivity in the direction [001] changes due to the flow of carriers from $T(\frac{\Delta n}{3}/4)$ and $N(\frac{2\Delta n}{3}/4)$ into the valleys $G(\frac{\Delta n}{3})$. Thus, the conductivity of crystals of both $p$-TlInSe$_2$ and crystals of derived solid solutions along the direction [001] when they are stretched in the same direction:

$$\sigma^u_p = \frac{en_0}{4}(3\mu_\parallel + \mu_\parallel) + \frac{en_0}{4}(\mu_\parallel - \mu_\perp)$$

(8)

Therefore, electrical conductivity changed due to stretching will be negative in this case:

$$\Delta \sigma^u_p = \frac{e\Delta n_0}{4}(\mu_\parallel - \mu_\perp) < 0$$

(9)

since $\mu_\perp > \mu_\parallel$. In case of compression:

$$\Delta \sigma^u_p = \frac{e\Delta n_0}{4}(\mu_\parallel - \mu_\perp) > 0$$

(10)

i.e. the conductivity along [001] decreases under stretching and increases under compression, which is qualitatively consistent with the experiment results.

4. Conclusion

1. It has been found that substitution of Tl atoms with Ag atoms in crystals of solid solutions based on TlInSe$_2$ leads to a shift of the energy of indirect transitions to the long-wave zone.
2. We have determined the values of baric coefficients of changes in the width of forbidden values for uniaxial deformations of stretching and compression.
3. Stretching along the crystallographic axis [001] for the studied crystals shifts the energy of indirect transitions to the short-wave zone, while compression, on the contrary, to the long-wave zone. This is also confirmed by the data on temperature dependence of electrical conductivity and finds a qualitative explanation on the basis of the 4-ellipsoid model.

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