PHOTOCONDUCTIVITY OF Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) SINGLE CRYSTALS AT LOW TEMPERATURES

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Abstract. The photoconductivity spectral dependencies and the spectra of thermostimulated currents of Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) single crystals obtained by Bridgman-Stockbarger directional crystallization method have been studied in the temperature range \(T \approx 30-300\) K. The induced photoconductivity and long-term photoconductivity relaxation processes have been identified. To interpret the found results, a model of two-centre recombination has been suggested. It is shown that the \(r\)-centres of slow recombination are formed by Tl vacancies. From the thermally stimulated current spectra, the thermal activation energies of electron trapping \(t\)-levels have been determined.

Key words: single quaternary crystals, defects, photoconductivity, thermally stimulated conductivity.

1. INTRODUCTION

The ternary compound of thallium, indium and selenium, TlInSe\(_2\), is a structural and configurational analogue of the binary TlSe compound, in which Tl\(^{3+}\) ions are substituted by In\(^{3+}\) ions. Because of its layered chain structure, TlInSe\(_2\) could be attributed to the group of low-dimensional semiconductors and thus is characterized by anisotropic physical properties. The charge carriers in them can freely move within the layers, while their motion between the layers is limited because of the Van der Waals interaction and small overlap of wave functions of neighbouring layers [1].

The peculiarity of such crystals is a possibility of obtaining semiconductor layers that do not contain dangling bonds. Therefore they are stable with respect to adsorption, have a low surface recombination rate and an increased radiation resistance, thus being attractive for modern semiconductor engineering. Due to the suitable combination of electrical and photoelectric properties, TlInSe\(_2\) is a promising material for the engineering of radiation detectors and receivers, devices controlled by an electric field in conditions of increased radiation [2,3]. The importance of using layered semiconductors as materials for sensors was reported in [4–6].

Recently, the single-crystalline solid solutions of various semiconductors became the focus of investigations aiming at the creation of heterojunction structures on their basis. This became possible because of the identical synthesis technologies. Attractiveness of TlInSe\(_2\) for creating heterostructures is due to the prospect of layered semiconductors which have a high sensitivity to visible, X-ray, gamma and IR-radiation [7,8].

It should also be noted, that layered crystals of thallium indium sulphide TlInS\(_2\), which belongs to the family of ferroelectric semiconductors, have been actively investigated as model compounds for several decades [9]. Numerous experimental data show that the physical properties of the TlInSe\(_2\) compound and TlInSe\(_2\)-based alloys are controlled to a large extent by point defects of the crystal lattice. Nevertheless, data on the nature of these defects, as well as the interaction of these defects, are poorly studied to date and therefore are intensively investigated [2,9].

This study is aimed at comprehensive experimental investigations into the electrical and photoelectric properties of new Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) crystals at low temperatures with the purpose of revealing the influence of
structural defects on the electrical conductivity and photoconductivity of these crystals and also determining specific parameters of these defects.

2. EXPERIMENTAL

The growth technology of Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) crystals, results of their X-ray structural analysis and some physical properties are presented in our previous publications [10–12]. We have investigated Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) solid solutions with \(x = 0.1, 0.2, \) and \(0.25\). According to [10–12], the peculiarity of the formation of the investigated solid solutions was the cationic substitution of In\(^{3+}\) with Sn\(^{4+}\), which caused the partial filling of the 4\(a\) crystallographic positions with Tl atoms. It was 0.9Tl, 0.8Tl, 0.75Tl for Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) single crystals with \(x = 0.1, 0.2, \) and 0.25, respectively. Therefore, disappearance of Tl atoms in their crystallographic positions with growing number of Sn atoms lead to the monotonic decrease of the volume of the unit cells.

Thus, taking into account the formation features of the single crystals of Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) alloy, one can affirm that their physical properties should be affected by Tl vacancies (V\(_{\text{Tl}}\)), the density of which increases with increasing \(x\). It is also known that cation vacancies V\(_{\text{Tl}}\) in chalcogenide semiconductors play the role of acceptors that compensate shallow donors [10]. That is, an increase in \(x\) should cause a redistribution of electrons at defect centers of single crystals. The importance of V\(_{\text{Tl}}\) in heterostructures based on TlInSe\(_2\) is shown in [7]. According to [7], in p-TlInSe\(_2\)/n-TlSe:Ge heterostructures, defects involving V\(_{\text{Tl}}\) can affect the height of the structure potential barrier at various irradiation intensities by gamma rays.

The samples to be studied were obtained by the cleaving of the grown crystals from the central region of the single crystal ingot along the (001) cleavage plane. The crystal surfaces were mirror flat, which allowed their use for studies without any additional treatment.

To perform photoelectric studies, samples shaped as parallelepipeds (4×1×0.2 mm) were cut from the plane-parallel cleavages. The ohmic electrical contacts were formed by indium fusion on the ends of the samples. Electrical measurements were performed with a Keithley 6430 Sub-Femtoamp SourceMeter.

3. RESULTS AND DISCUSSION

The results of investigations of Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) single crystals at room temperature are presented in our papers [10–12]. A feature of photoconductivity spectra at \(T = 300\) K was the presence of one clearly pronounced maximum, which was due to intrinsic optical transitions. Its position depended on the composition of the solid solutions. The energy position of the photoconductivity maxima was used to estimate the bandgap \((E_g)\) of these single crystals. It was found that with increasing \(x = 0.1, 0.2, 0.25,\) the value of \(E_g\) increased, too: 1.66 eV, 1.79 eV, 1.88 eV [10,11]. It should be noted that the values of \(E_g\) determined in this way coincided with the values of \(E_g\) determined from the light absorption spectra [10]. When the temperature was lowered to 200 K, a smooth shift of the photoconductivity maxima to the short-wavelength region was observed, which was explained by the increase in \(E_g\) [10]. The most photosensitive at \(T = 300\) K were single crystals of the composition Tl\(_{0.75}\)In\(_{0.75}\)Sn\(_{0.25}\)Se\(_2\).

The photocurrent spectra in the temperature range \(T = 36–200\) K for one of the investigated Tl\(_{0.75}\)In\(_{0.75}\)Sn\(_{0.25}\)Se\(_2\) single crystals are shown in Fig. 1. Spectral dependencies of Tl\(_{1-x}\)In\(_{1-x}\)Sn\(_x\)Se\(_2\) single crystals with \(x = 0.1\) and \(x = 0.2\) were presented earlier in [10,11] in the temperature region 170–300 K. They were similar also at lower temperatures. A characteristic feature of the spectra in Fig.1 is that in single crystals with the largest Sn concentration, along with the main maximum, an additional photocurrent maximum was observed in the impurity region, corresponding to the energy of light quanta \(h\nu \approx 1.25–1.45\) eV. The decrease in \(E_g\) with increasing temperature causes the shift of short-wave maxima to the lower energies. The thermal coefficient of this shift of the photoconductivity peak is \(4.8 \times 10^{-4}\) eV/K, being close to the thermal coefficient of the change in the band gap \(E_g\) in chalcogenide compounds [13–15].

In order to avoid excitation of the samples by high-energy photons, photoconductivity spectra were initially measured by increasing the photon energy of light quanta from 0.5 eV to 3.5 eV (Fig. 1, indicated by arrows). Before each scan, the samples were heated up to \(T = 360\) K, after that they were cooled to the temperature indicated in Fig. 1. The samples were cooled at a voltage of 0 V. After cooling, a voltage of 25 V was applied to the samples.
Photoconductivity of $Tl_{1-x}In_{1-x}Sn_se_2$ single crystals at low temperatures

Fig. 1 – Photocurrent spectra of $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ solid solutions at different temperatures. The energies of light photons were increased during scanning.

Fig. 2 – Spectra of the photocurrent of $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ solid solutions at different temperatures. The energies of light quanta were decreased during scanning.

Fig. 3 – Spectral distribution of the relative photoconductivity of the solid solution $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$:
1 – photon energy increased by scanning the samples; 2 – photon energy decreased upon scanning the samples.

Under the same experimental conditions, single crystals were scanned with light quanta from high energies to smaller ones (Fig. 2), as a result of which a difference in the photocurrent spectra from those shown in Fig. 1 was observed. The difference consisted in the decrease in the height of the short-wave maximum, which could indicate the participation of impurity levels in the formation of this photocurrent maximum. It should be noted that this difference was most clearly observed for $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ single crystals (Fig. 2).

A more detailed analysis and investigation of the photoconductivity of $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ single crystals showed that the differences in the photoconductivity spectra scanned in both directions were more clearly observed, when scanning from higher energies to lower ones was carried out immediately after scanning in the forward direction (Fig. 3).

When measuring the photoconductivity spectra from lower energies to higher ones, the location of the photoconductivity maximum corresponds to 1.38 eV and 1.77 eV. It can be seen in Figs. 1 and 2, that the shortwave maximum became less pronounced when scanning in the opposite direction, while the long-wave maximum remained more intense. Such different behaviour can be caused by the induced photoconductivity...
phenomenon [16, 17], related to presence of different defects and potential inhomogeneities present in the crystals. The complex effects related to the charge redistribution between different defects were reported also in a simpler materials, as, e.g., GaAs [18–22]. Results thus found cannot be interpreted within the context of a simple theory, which associates the induced photoconductivity with filling of the donor levels due to the emptying of acceptor levels without the recombination mechanism. Correspondingly, to interpret the results, a model of the double centre recombination should be applied [16, 23], according to which, deep \( r \)-centres of slow recombination and \( s \)-centres of fast recombination with different electron capture cross sections \( S_m/S_{2m} > 10^3 \), where \( S_m \) are the capture cross sections of electrons by \( s \)- and \( r \)-centres [16], respectively, as well as the trapping \( t \)-levels located near the conduction band bottom are present in the crystal. As compared to \( r \)-recombination centres, \( s \)-centres are more distanced from the valence-band top. The role of \( t \)-levels is in determining the filling of both \( s \)- and \( r \)-centres with electrons, thus causing redistribution of the photoconductivity spectra, respectively. Induced photoconductivity is governed by \( s \)-centres of fast recombination due to their filling; and quenching of the photoconductivity takes place upon their emptying.

The presence of \( r \)-recombination centres with low \( S_m \) leads to a longer electron lifetime, an increase in photosensitivity and slower decay of photoconductivity. The latter was confirmed by studies of the photoconductivity relaxation of \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \) single crystals. Moreover the long-lasting relaxations with characteristic times \( \sim 10^{-2}-10^{-3} \) s were observed. Similar very long photoconductivity relaxation times \( \tau \approx 10^3 \) s were observed in \( \text{TlInSe}_2 \) crystals by the authors of Ref. [24]. To explain the long-term photoconductivity relaxation processes, the barrier theory of a disordered semiconductor with high-resistance inclusions in a low-resistance matrix was used in Ref. [24].

The authors of Ref. [3], in which the results of the current flow through \( \text{TlInSe}_2 \) single crystals in strong electric fields were analysed, also came to the conclusion that there are \( r \)-, \( s \)- and \( t \)-levels in \( \text{TlInSe}_2 \) single crystals. For \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \) solid solutions, some parameters of these defect centres were determined in [10, 11], in which the recombination and trapping centre distribution model described above was used. The phenomenon of induced photoconductivity and long-term relaxation of photoconductivity was observed by us in solid solutions of \( \text{CuInS}_2\text{ZnIn}_2\text{Se}_4 \) based on \( \text{CuInS}_2 \) single crystals [15, 25, 26]. In [15], an analysis of the long-term relaxation of photoconductivity was carried out on the basis of the concept of capture of free charge carriers by point trapping centres.

Acceptor levels, which are caused by \( \text{V}_{\text{Cu}} \), play the role of \( r \)-centres of slow recombination in \( \text{CuInS}_2\text{ZnIn}_2\text{Se}_4 \). The concentration of \( \text{V}_{\text{Cu}} \) defects increased with the increase of the \( \text{ZnIn}_2\text{Se}_4 \) content in \( \text{CuInS}_2\text{ZnIn}_2\text{Se}_4 [15, 25, 26] \), similar to the concentration of \( \text{V}_{\text{Tl}} \) in \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \).

From Fig. 3 it can be seen that the energy distance between two well expressed relative photoconductivity maxima is 0.39 eV. This value gives the energy distance between \( r \) and \( s \) centres in \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \) single crystals at \( x = 0.25 \). The \( r \)-centres, according to the assumption made in [10], are formed by cation vacancies \( \text{V}_{\text{Tl}} \). The results shown in Figs. 1–3 support this assumption, since the single crystals of \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \) at \( x = 0.25 \) have the highest concentration of these defects in comparison with the crystals containing \( x = 0.1 \), \( x = 0.2 \), which is reflected in the photoconductivity spectra. It should be noted that in [7], acceptor centres with an ionization energy of \( E_i + 0.15 \) eV were reported in single crystals of \( \text{TiInSe}_2 \). These acceptor centres are formed by interstitial point defects \( \text{Se}_i \) and \( \text{In}_i \), while \( \text{Tl} \) exhibits donor properties [7]. The anti-structural defects \( \text{Sn}_{\text{In}} \) in \( \text{Tl}_1\text{In}_{1-x}\text{Sn}_x\text{Se}_2 \) single crystals also act as donors [10]. The role of \( s \)-centres is usually played by different structural defects [10, 11]. E.g., upon investigation of single crystals of \( \text{CuInS}_2\text{ZnIn}_2\text{Se}_4 \) it was demonstrated that \( s \)-centres are formed by In vacancies \( \text{V}_{\text{In}} [25, 26] \).

To determine the energy position of the shallow \( t \) traps in the samples, to which the induced photoconductivity is inherent, thermally stimulated currents (Fig. 4) were investigated. It is known [16] that they are determined by the thermal escape of electrons from the trapping centres preliminarily filled by light illumination into the conduction band. The thermally stimulated current method was shown to be very sensitive and universal, as it can successfully be applied also to the disordered organic structures [27].

The TSC spectrum (curve 3) is obtained by subtraction of the dark current (curve 1) from the current measured after preliminary illumination of the crystal (curve 2). The crystals were illuminated for 30 min by photons with an energy of \( h\nu \approx 1.7 \) eV, which corresponds to the maximum of the induced PC. The TSC spectrum has two maxima at \( T = 150 \) K and \( T = 220 \) K. As the photon energy increases or decreases relative to \( h\nu \approx 1.7 \), the TSC maximum becomes less pronounced. In the TSC curve, presented in \( \log(I) - 1/T \) scale (Fig. 4, curve 3), the two linear segments can be singled out. From their slopes the thermal activation
energies of electrons from $t$ levels were determined, being 0.13 eV and 0.28 eV as indicated on Fig. 4. At temperatures $T > 200$ K, the dark current (Fig. 4, curve 1) increased exponentially with increasing temperature. The conduction activation energy determined from the slope was 0.39 eV.

The TSC spectrum in Tl$_{1-x}$In$_{1-x}$Sn$_x$Se$_2$ alloys with $x = 0.1$ is presented in Fig. 5. As in the previous case, the TSC spectrum has two maxima at $T \approx 80$ K and $T \approx 180$ K. The shift of the TSC maxima towards lower temperatures and, correspondingly, a decrease in the thermal activation energy of electrons from the $t$-levels can be explained by a decrease in $E_g$ upon with decreasing $x$ in the Tl$_{1-x}$In$_{1-x}$Sn$_x$Se$_2$ alloy, which agrees with the assumption made in [10], about the pinning of the $t$-levels to the valence band. At $T > 250$ K, a linear part with a slope of 0.49 eV was observed in Tl$_{0.9}$In$_{0.9}$Sn$_{0.1}$Se$_2$ single crystals on the TSC spectra. The traps with an ionization energy of 0.5 eV, and 0.15 eV were reported in TlInSe$_2$ single crystals by the authors of [3]. Since the single crystals of Tl$_{0.9}$In$_{0.9}$Sn$_{0.1}$Se$_2$ contain the lowest concentration of Sn atoms, one can assume that the nature of these trapping centres and those observed in Fig. 5 is identical. Notably, the peak at 80 K is characterized by the activation energy value of 0.28 eV, which coincides with the value obtained in Fig. 4 for the maximum at 220 K, but is shifted towards lower temperatures due to the interaction with fast recombination $s$-centres, because of their higher concentration.

4. CONCLUSIONS

In Tl$_{1-x}$In$_{1-x}$Sn$_x$Se$_2$ single crystals the defect-related induced photoconductivity phenomenon was evidenced in the low-temperature region between 36 K and 200 K. A characteristic feature of the photoconductivity spectra in single crystals with the largest Sn of concentration $x = 0.25$ is that, along with the main maximum, an additional photocurrent maximum was observed in the impurity region, corresponding to the energy of light quanta $h\nu \approx 1.25–1.45$ eV. The decrease in $E_g$ with increasing temperature causes the shift of short-wave maxima to the lower energies. To interpret the results, a model of the two-center recombination was applied, according to which, acceptor levels related to V$_{\text{Tl}}$, play the role of the $r$-centers of slow recombination, meanwhile $s$-centres of fast recombination are formed by In vacancies V$_{\text{In}}$. Energy distance between the $r$-centers of slow recombination and $s$-centers of fast recombination in Tl$_{0.75}$In$_{0.75}$Sn$_{0.25}$Se$_2$ single crystals was 0.39 eV. The thermal activation energy of electrons from the trapping $r$-levels was 0.13 eV and 0.28 eV for Tl$_{0.75}$In$_{0.75}$Sn$_{0.25}$Se$_2$ single crystals. A decrease in the Sn content in the Tl$_{1-x}$In$_{1-x}$Sn$_x$Se$_2$ single crystals leads to the decrease of the activation energies of these levels close to the values observed in TlInSe$_2$. 

![Fig. 4 – Thermally stimulated currents of Tl$_{0.75}$In$_{0.75}$Sn$_{0.25}$Se$_2$ single crystals.](image)

![Fig. 5 – Thermally stimulated currents of Tl$_{0.9}$In$_{0.9}$Sn$_{0.1}$Se$_2$ single crystals.](image)
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