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Specific Features of Photoconductivity of Tl_{1-x}In_{1-x}Sn_xSe₂ Monocrystals at Low Temperatures

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The photoconductivity spectra in the temperature range $T \approx 36 - 200$ K and the spectra of thermostimulated currents in the temperature range $T \approx 70 - 300$ K of $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals obtained by directional crystallization of Bridgman-Stockbarger have been studied. The induced photoconductivity and long-term photoconductivity relaxation processes have been found. To interpret the found results, a model of two-center recombination has been suggested. It is illustrated that the role of the *r*-centers of slow recombination are formed by Tl vacancies. On the basis of the studies of the spectra of thermally stimulated currents, the thermal energy of electrons activation with *t*-levels of adhesion has been determined.

Keywords: single crystals, defects, photoconductivity, thermally stimulated conductivity.

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Introduction

The ternary thallium compound, $TIInSe_2$, is a structurally coordinated analog of the TISe binary com pound, in which TI^{3+} ions are substituted with In^{3+} ions, relates to the group of low dimensional semiconductors with a layered chain structure. The $TIInSe_2$ are characterized by anisotropic physical properties. The charge carriers in them can freely move inside the layers, while their motion between the layers is limited because of the van der Waals interaction and small overlap of wave functions of neighboring layers [1].

The peculiarity of such crystals is that it is possible to obtain semiconductor layers that do not contain dangling bonds, that is, they are stable with respect to adsorption, have a low surface recombination rate, and also have an increased radiation resistance, which corresponds to the requirements for modern semiconductor structures. Due to the combination of electrical and photoelectric properties, TlInSe₂ are promising materials for the creation 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]. solid solutions between various semiconductors in order to create heterojunctions that have become possible as a result of the identity of synthesis technologies. Application $TIInSe_2$ or creating heterostructures is due to the prospect of layered semiconductors which have a high sensitivity to visible, X-ray, gamma and IRradiation [7, 8].

It should also be taken into account, that Layered crystals of thallium indium sulfide $TIInS_2$, which belong to the family of ferroelectric semiconductors, have been actively investigated for several decades as model compounds [9]. Numerous experimental data show that the physical properties of the $TIInSe_2$ compound and $TIInSe_2$ -based alloys are controlled to a large extent by point defects of the crystal lattice. Data on the nature of these defects, as well as the interaction of these defects, are poorly studied to date [2, 9].

This study is aimed at comprehensive experimental investigations into the electrical and photoelectric properties of new $Tl_{1-x}In_{1-x}Sn_xSe_2$ 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 to determine certain parameters of these defects.

Recently, attention has been drawn to single-crystal

I. Experimental

The $Tl_{1-x}In_{1-x}Sn_xSe_2$ crystal growth technology, results of their X-ray structural analysis and some physical properties are presented in our previous We publications [10-12]. have investigated $Tl_{1-x}In_{1-x}Sn_xSe_2$ solid solutions containing x = 0.1, 0.2,0.25. According to [10-12], the peculiarity of the formation of the investigated solid solutions was the cationic substitution of In^{3+} on Sn^{4+} , which caused the partial filling of the crystallographic positions of 4a with Tl atoms. It was 0.9Tl, 0.8Tl, 0.25Tl for Tl_{1-x}In_{1-x}Sn_xSe₂ single crystals with x = 0.1, x = 0.2, x = 0.25, respectively.

Thus, taking into account the formation features of single crystals of the $Tl_{1-x}In_{1-x}Sn_xSe_2$ alloy, we can affirm that their physical properties will be affected by vacancies Tl (V_{Tl}), whose concentration increases with increasing x. It is also known that cation vacancies V_{TI} in chalcogenide semiconductors play the role of acceptors that compensate shallow donors [10]. That is, an increase in x will cause a redistribution of electrons at defect centers of single crystals. The importance of V_{TI} in heterostructures based on TlInSe₂ is shown in [7]. p-TlInSe₂/n-TlSe According to [7], in $\langle Ge \rangle$ heterostructures, defects involving VTl can affect the height of the structure barrier at various irradiation intensities by gamma rays.

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

To perform photoelectric studies, samples shaped as parallelepipeds ($4 \times 1 \times 0.2$ mm) were cut from the planeparallel cleavages. The electrical contacts were applied by indium fusing to opposite surfaces of the plates. Electrical measurements were performed with a Keithley 6430 Sub-Femtoamp SourceMeter.

II. Results and Discussion

The results of investigations of Tl_{1-x}In_{1-x}Sn_xSe₂ single crystals at room temperatures are presented in our papers [10-12]. A feature of photoproductivity spectra at T = 300 K was the presence of one clearly pronounced maximum, which was due to intrinsic optical transitions and whose position depended on the composition of the solid solution. The energy position of the photoconductivity maxima was used to estimate the bandgap (Eg) width of these single crystals. It is found that with increasing x and increased value E_g was 1.66 eV, 1.79 eV, 1.88 eV for the single crystals at x = 0.1, x = 0.2, x = 0.25 [10, 11]. It should be noted that the values of Eg determined in this way coincided with the values of $E_{\rm g}$ determined from the absorption spectra of light [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 Eg [10]. The most

photosensitive at T = 300 K were single crystals of the composition $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$.

A feature of the spectral distribution of the photocurrent at a lower temperature (T = 200 - 36 K) was that in single crystals with the largest Sn concentration, along with the main maximum, a photocurrent maximum was observed in the impurity region, whose position corresponded to the energy of light quanta $hv \approx 1.25 - 1.45$ eV. The photocurrent spectra in the temperature range T = 200 - 36 K for one of the investigated single crystals $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ are shown in Fig. 1. The decrease in Eg with increasing temperature causes the shift of short-wave maxima to the long-wavelength region of the electromagnetic spectrum. The thermal coefficient of the change in the position of the photoconductivity peak is $4.3 \cdot 10^{-4}$ eB/K, close to the thermal coefficient of the change in the band gap E_g in



Fig. 1. Photocurrent spectra of $Tl_{0,75}In_{0,75}Sn_{0,25}Se_2$ solid solutions at different temperatures. The energy of photons of light 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 energy of light quanta decreased during scanning.

chalcogenide compounds [13-15].

In order to avoid excitation of the samples by highenergy photons, photoconductivity was initially measured with an increase in the photon energy of light quanta from 0.5 eV to 3.5 eV (Fig. 1 indicated by an arrow). Before each scan, the samples were heated to T =360 K, after which 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.

Under the same experimental conditions, single crystals were scanned with light quanta from high energies to smaller ones (Figure 2), as a result of which a difference in the photocurrent spectra from those shown in Fig. 1. 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 maximum photocurrent. 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 difference in the photoconductivity spectra in the forward and reverse directions was more clearly observed when scanning from high energies to smaller ones was carried out immediately after scanning in the forward direction (Fig. 3.). When measuring the photoconductivity spectra from from lower energies to large ones, the location of the photoconductivity maximum corresponds to 38 eV and 1.74 eV.

Since the shortwave maximum became less pronounced when scanning in the opposite direction, while the long-wave maximum remained more intense, it can be assumed that such a difference in the location of the photoconductivity maxima can indicate the presence of induced photoconductivity [16, 17]. 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 mode of double center recombination is suggested [16, 18], according to which, deep r centers of slow recombination and s centers of rapid recombination with various electron capture cross sections $S_{sn}/S_{rn} >> 10^3$, where S_{sn} , S_{rn} are the capture cross sections of electrons by s and r centers [16], as well as the attachment t levels arranged near the conduction band bottom are present in the crystal. Relative to r recombination centers, s centers are more distanced from the valence-band top. The role of t levels is in determining the filling of s and r centers with electrons and redistribution of the photoconductivity spectra, respectively. Induced photoconductivity is governed by s centers of rapid recombination with their filling and quenching of the photoconductivity with their emptying.

The presence of r recombination centers with low Srn leads to a longer electron lifetime, which was confirmed by studies of the photoconductivity relaxation of $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals, and an increase in photosensitivity. Moreover the long-lasting relaxations with characteristic times ~10²-10³ sec were observed. An abnormally long photoconductivity relaxation time



Fig. 3. Spectral distribution of the photoconductivity of the solid solution $Tl_{1-x}In_{1-x}Sn_xSe_2$: 1 - photon energy increased by scanning samples; 1' - photon energy decreased upon scanning the samples.

 $(\tau \approx 10^3 \text{ s})$ in TlInSe₂ crystals was observed by the authors of Ref. [19]. 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. [19].

The authors of [3] came to the conclusion that there are r, s t-levels in TlInSe₂ single crystals, in which the results of the passage of a current through TlInSe₂ single crystals in strong electric fields were analyzed. For Tl₁ $_{x}In_{1-x}Sn_{x}Se_{2}$ solid solutions, some parameters of these defect centers were determined in [10, 11], in which the recombination and adhesion center 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 CuInS₂-ZnIn₂S₄ based on CuInS₂ single crystals [15, 20, 21]. 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 localization centers (traps).

Acceptor levels, which are caused by V_{Tl} , play the role of r-centers of slow recombination. The concentration in CuInS₂-ZnIn₂S₄ of V_{Cu} defects increased with the increase of the ZnIn₂S₄ content [15, 20, 21], similar to the concentration of V_{Tl} in Tl_{1-x}In_{1-x}Sn_xSe₂.

From the results presented in Fig. 3., it is possible to determine the energy distance between r and s centers in $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals at x = 0.25. It was E = 0.46 eV. The role of r-centers, according to the assumption made in [10], is performed by cation vacancies of the Tl. Shown in Fig. 1-3 the results support this assumption, since the single crystals of $Tl_{1-x}In_{1-x}Sn_xSe_2$ at x = 0.25 have the highest concentration of these defects in comparison with single crystals at x = 0.1, x = 0.2, which is reflected in the photoconductiveity spectra. It should be noted that in [7], acceptor centers in single crystals of TlInSe₂ with an ionization energy of $E_v+0.15$ eV were reported. Also, the role of acceptor centers in TlInSe₂ single crystals is



Fig. 4. Thermally stimulated currents of $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals at x = 0.25.



 $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals at x = 1.

performed by interstitial pin defects Se_i and In_i , while Tl_i exhibits donor properties [7]. The anti-structural defects Sn_{In} in $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals act as donors [10].

To determine the energy position of 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 attachment centers preliminarily filled via illumination into the conduction band.

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 $hv \approx 1.7 \text{ eV}$, which corresponds to the maximum of the induced PC. In the temperature range under study, the TSC spectrum has two maximum (Fig. 4, curve 3) at $T \approx 150$ K and $T \approx 220$ K as the photon energy increases or decreases relative to $hv \approx 1.7$, the TSC maximum becomes less

pronounced. It is seen from Fig. 3 (curve 3,) that two straight-linear segments, via the slope of which the thermal activation energy of electrons from t levels was determined, are observed in the TSC curve presented on the semilog scale. The values of the activation energy in various temperature ranges are mentioned in 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 results of similar studies of the TSC $Tl_{1-x}In_{1-x}Sn_xSe_2$ alloys with x = 0.1 are presented in Fig. 5. As in the previous case, in the temperature range under study, the TSC spectrum has two maximum at $T \approx 80$ K and T \approx 180 K. The shift of the TSC maximum to toward lower temperatures and, correspondingly, an increase in the thermal activation energy of electrons from the t-levels can be explained by an decrease in E_g upon with decreasing x in the Tl_{1-x}In_{1-x}Sn_xSe₂ alloy, which agrees with the assumption made in [10], about the attachment of t-levels to the valence band. At T > 250 K, a straight section with a slope of 0.49 eV was observed in Tl_{0.9}In_{0.9}Sn_{0.1}Se₂ single crystals on the spectra of thermally stimulated currents. The traps with in TIInSe₂ single crystals with an ionization energy of 0.5 eV, and 0.15 eV in TlInSe₂ crystals were reported by the authors of [3]. Since the single crystals of Tl_{0,9}In_{0,9}Sn_{0,1}Se₂ contain the lowest concentration of Sn atoms, we can assume that the nature of the attachment centers is identical with a of 0.49 eV and 0.2 eV depth with those observed by the authors of Ref. [3].

Conclusions

The feature of the low-temperature (T \approx 36 - 200 K) photoconductivity of Tl_{1-x}In_{1-x}Sn_xSe₂ single crystals is impurity- and induced photoconductivity. To interpret the found results, a model of two-center recombination is suggested, according to which, acceptor levels, which are caused by V_{Tl} , play the role of r-centers of slow recombination Energy distance between r centers of slow recombination and s centers of rapid recombination in $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals with the highest content of Sn atoms was 0,46 eV. The thermal activation energy of electrons from the attachment t-levels was 0,13 eV and 0,28 eV for $Tl_{0,75}In_{0,75}Sn_{0,25}Se_2$ single crystals. An decrease in the Sn content in the $Tl_{1-x}In_{1-x}Sn_xSe_2$ single crystals leads to a decrease in the decrease the energy of these levels. In the $Tl_{0.9}In_{0.9}Sn_{0.1}Se_2$ single crystals there are three defect centers that act as t-levels at different temperature range.

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Особливості фотопровідність монокристалів Tl_{1-x}In_{1-x}Sn_xSe₂ при низьких температурах

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Основні результати досліджень полягають у тому, що особливістю низькотемпературної фотопровідності монокристалів $Tl_{1-x}In_{1-x}Sn_xSe_2 \in$ домішкова та індукавана фотопровідність, а також довготривалі процеси релаксації фотопровідності. Оцінене значення часу релаксації фотопровідності становило ~10²-10³ с. Термічна енергія активації електронів з *t*-рівнів у монокристалах $Tl_{0.75}In_{0.75}Sn_{0.25}Se_2$ становила 0,13 еВ та 0,28 еВ. Зменшення вмісту Sn в $Tl_{1-x}In_{1-x}Sn_xSe_2$ призводить до зменшення глибини залягання цих рівнів. У монокристалах $Tl_{0.9}In_{0.9}Sn_{0.1}Se_2$ існує три дефектні центри, які виконують роль *t*-рівнів прилипання у різних температурних інтервалах.

Ключові слова: монокристали, дефекти, фотопровідність, термостимульована провідність.