INFLUENCE OF DOPING ON OPTICAL AND PHOTO-ELECTRIC PROPERTIES OF $In_4(Se_3)_{1-x}Te_{3x}$ SINGLE CRYSTALS

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The results of electron microscopy studies of the peculiarities in a distribution of structure defects caused by a crystal lattice anisotropy and the growth conditions for $In_4(Se_3)_{1-x}Te_{3x}$ single crystals ($0 \le x \le 0.2$ and $0.68 \le x \le 1.0$) are presented. The influence exerted by these peculiarities and by doping the crystals with Ge, Sn, Hg, and Se impurities on both the IR transmittance of the crystals and the spectral distribution of the transverse Dember photo-emf in them has been studied. An optical antireflection coating of $In_4(Se_3)_{1-x}Te_{3x}$ and In_4Se_3 single crystals has been carried out making use of SiO and three-layer SiO–Ge–Si films. The optimal conditions for the growing of crystals destined for the production of optical filters and photosensitive cells operating in the near and middle IR ranges have been determined.

1. Introduction

Indium selenide In_4Se_3 and solid solutions $In_4(Se_3)_{1-x}Te_{3x}$ are forward-looking materials from the viewpoint of their usage as cutting optical filters and photodetectors [1, 2]. These compounds are layered crystals, typical of which are a weak van der Waals coupling between layers and a strong covalent bond inside them. The In_4Se_3 and $In_4(Se_3)_{1-x}Te_{3x}$ crystals cleaved along the (100) plane manifest the chemical passivity of their surfaces [3] and can be applied as a base material for structures with a low density of surface states at the interface. While doping such layered crystals, dopants tend to move from covalent layers into interlayer spaces which, in their turn, are natural sinks [4, 5]. The doping of In_4Se_3 single crystals with a Ge impurity allows one to raise the optical transparency of In_4Se_3-based filters and to lower the concentration of current carriers down to values of $(1-2)\times10^{14}$ cm^{-1} [1]. $In_4(Se_3)_{1-x}Te_{3x}$ crystals possess a clear-cut cleavage plane (100). The width of the energy gap varies from 0.62 eV in In_4Se_3 to 0.48 eV in In_4Te_3 depending on the composition.

Optical filters that cut off radiation with wavelengths within the range of $2.0-2.5$ μm are of special interest for practical applications. It is this range that includes one of the maxima of a sunlight scattered by the atmosphere. By varying the composition of solid solutions, one can obtain a collection of cutting filters with a variable threshold wavelength extending from 1.7 (for In_4Se_3) to 2.5 μm (for In_4Te_3) [2]. Such filters possess a higher steepness of the short-wave front of the transmittance spectral curve in comparison with other filters that are used in this range to protect the detectors of IR facilities from an undesirable expose (Pb films, filters on the basis of GaAs crystals, etc.) [1, 2].

Indium selenide In_4Se_3 and solid solutions $In_4(Se_3)_{1-x}Te_{3x}$ with $0 \le x \le 0.16$ have high photosensitivity at room temperature and can be used as uncooled photoresistors which have a rather high stability of their parameters owing to the passivity of their surfaces.

This work aimed at studying the influence of various dopants on the IR-radiation transmission and photo-electric characteristics of those materials in order to improve the parameters of the cells fabricated on their basis.

2. Method of Research

$In_4(Se_3)_{1-x}Te_{3x}$ crystals were grown by the Czochralski method taking advantage of the Peltier effect. The synthesis of the material was carried out in quartz ampoules at a temperature of 1273 K. During the synthesis, the alloy was being vibrationally agitated and, simultaneously, the ampoule was being rotated. For growing $In_4(Se_3)_{1-x}Te_{3x}$ crystals, seeds oriented along [010] and [001] crystallographic directions were used. The growth rate of the crystals was $3-4$ mm/h, and the speed of the rotation of a crucible was $20-30$ r.p.m., provided that the density of the Peltier current that ran through the crystal–melt interface was 1 A/cm^{-2}. The diameter of the ingots obtained was $0.8-1$ cm, and their length $1.5-2$ cm. The Ge, Sn, Pb, and Sb dopants were introduced either during the crystal growing by the

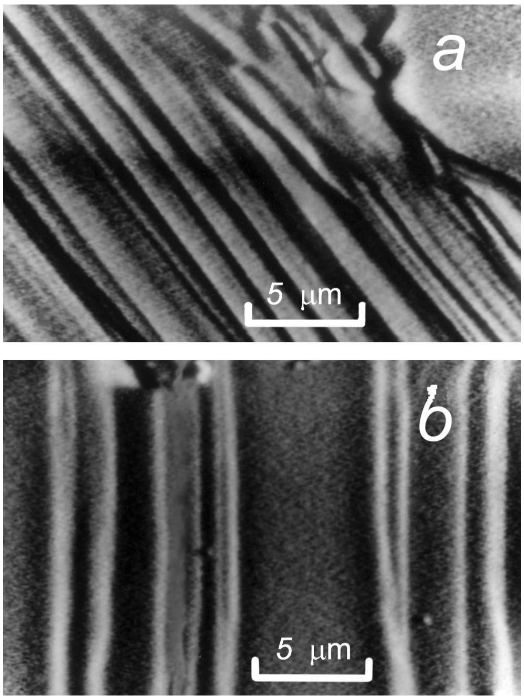

Fig. 1. Structural defects in $In_4(Se_3)_{1-x}Te_{3x}$ single crystals ($x = 0.2$) grown in [001] (*a*) and [010] (*b*) directions

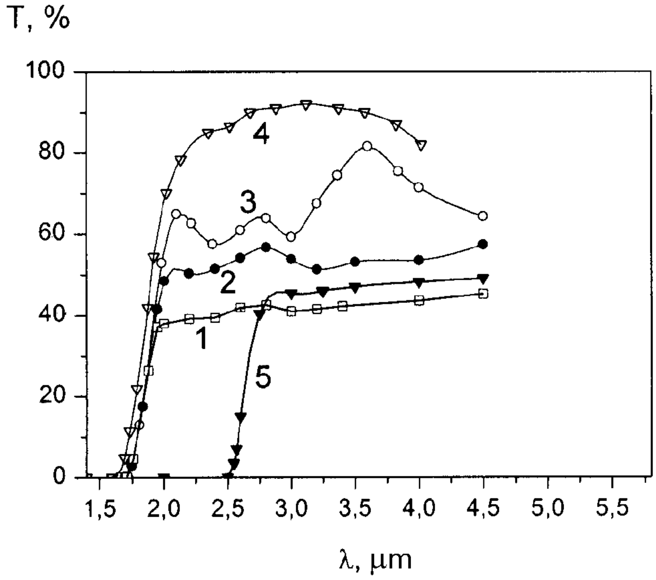

Fig. 2. Transmittance spectra of $In_4(Se_3)_{0.88}Te_{0.12}$ single crystals: an undoped specimen (*1*), a Ge-doped specimen before (*2*) and after (*3*) the application of an antireflecting coating; of In_4Se_3 single crystals with an antireflecting coating (SiO–Ge–SiO film) (*4*); and of Sn-doped $In_4(Se_3)_{0.06}Te_{0.94}$ single crystals without antireflecting coating (*5*)

Czochralski method or during the crystal annealing in vapors of the corresponding elements (Se, S, Hg).

The topography of the crystal surface was studied making use of a REM-100U scanning electron microscope (SEM) operating in the modes of "secondary electrons" and "crystalline contrast" at the accelerating voltage $U = 30$ kV and the probe current of $2 \times 10^{-11} - 3 \times 10^{-10}$ A.

The SEM studies of the alloy compositions, carried out by the method of electron probe x-ray spectrum microanalysis, showed that the resulting $In_4(Se_3)_{1-x}Te_{3x}$ crystals were sufficiently homogeneous in the ranges of $0 \leq x \leq 0.2$ and $0.68 \leq x \leq 1.0$. In $In_4(Se_3)_{1-x}Te_{3x}$ single crystals, typical were lengthy structural defects with the prevailing alignment along the [001] crystallographic axis. They were observed in both electron microscopy patterns and X-ray topograms.

The density of lengthy defects on the (100) cleavage surface, when growing the $In_4(Se_3)_{1-x}Te_{3x}$ crystals in [001] and [010] crystallographic directions, was higher in the former case (Fig. 1). It can be explained by the variation of the anisotropy of structural defects (dislocations, inclusions, block interfaces, and twins), which depends on their orientation upon growing [2]. Provided that a Ge impurity in a quantity of up to 0.2 wt.% was introduced during the crystal growing, a decrease of the density of those structural defects by an order of magnitude was observed, so that $In_4(Se_3)_{1-x}Te_{3x}$ crystals with $0 \leq x \leq 0.2$ and a more perfect cleavage plane were obtained. To enhance the transparency of optical filters fabricated on the basis of $In_4(Se_3)_{1-x}Te_{3x}$ solid solutions and to improve their homogeneity, we doped the compounds with Ge, Sb, Pb, and Sn impurities in the course of their synthesis, followed by drawing the crystal from the melt.

3. Experimental Results

The optical filters fabricated from Ge-doped single crystals had a higher transparency T in comparison with those from undoped crystals (Fig. 2, curves *1* and *2*).

The single-crystal plates of $In_4(Se_3)_{1-x}Te_{3x}$ were made antireflecting by coating them with the films of silicium monoxide SiO in order to obtain cutting filters. SiO coatings have a significant mechanical and thermal stability, being widely used in the $1 - 25$-μm wavelength range. The index of refraction of SiO equals 1.85, which provided the condition of optical matching with a substrate according to the relation $n_{\text{antirefl.coat.}} = \sqrt{n_{\text{substr}}}$, where $n_{In_4Se_3} = 3.2$. In solid solutions with a higher content of telluride, $0.68 \leq x \leq 1$, the index of

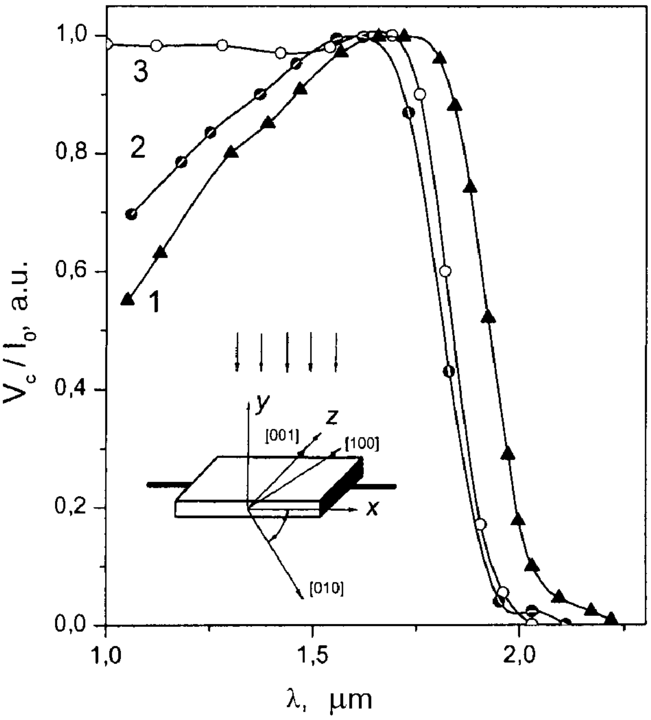

Fig. 3. Spectral dependences of the photoconductivity (*1*) and the transverse Dember photo-emf for In_4Se_3 crystals with a Hg impurity: an as-annealed specimen (*2*) and after a long storage (*3*). A specimen of the anisotropic semiconductor for studying the TDE is shown in the inset

refraction grows up to $n \approx 4$, and it was expedient to make the antireflecting coating with ZnS films possessing $n_{\mathrm{ZnS}} = 2.15$ [2]. The SiO films were sputtered at a VUP-5 installation making use of the laser monitoring of the film thickness (an LG-126 laser with $\lambda_1 = 0.63$ μm, $\lambda_2 = 1.15$ μm, and $\lambda_3 = 3.30$ μm). After sputtering the antireflecting SiO film, the maximal value of the transmission factor T amounted to 82% in the antireflecting wavelength range (Fig. 2, curve *3*). The transmission minima resulted from the interference inside the films and can be eliminated with the help of a three-layer antireflecting coating. By sputtering a three-layer film system SiO–Ge–SiO onto an In_4Se_3 single crystal, we managed to achieve the transmittance $T \geq 80\%$ in a wide spectral range (Fig. 2, curve *4*).

Doping with a Sb impurity resulted in some increase of the transmittance of $In_4(Se_3)_{1-x}Te_{3x}$ crystals with $0.68 \leq x \leq 0.75$, but the slope of the spectral characteristics decreased owing to the presence of an additional absorption at the edge of the intrinsic absorption range. Such a result was not achieved for Pb-doped crystals with an arbitraty composition x. Moreover, the crystal transmittance diminished in this case. An increase of the transmittance, with a large steepness of the absorption edge being preserved, was obtained when doping the crystals with Sn (up to 0.2 wt.%), which resulted in the p-type of crystal conductivity and the current carrier concentration of up to 7×10^{14} cm^{-3}. An enhancement of the transparency of the Sn-doped $In_4(Se_3)_{1-x}Te_{3x}$ crystals was especially important for compositions $0.68 \leq x \leq 1$, where the initial transmittance was less than even that of crystals with composition $x \leq 0.2$ (Fig. 2, curve *5*).

Photosensitive cells (PCs) functioning on the basis of the lateral diffusion photoeffect, or the transverse Dember effect (TDE), are of practical interest and possess a number of advantages. This effect is typical of bipolar anisotropic semiconductors. It has been discovered for the first time experimentally in In_4Se_3 [6].

The photo-emf that arose across the specimen at illuminating it by light, which is strongly absorbed, was measured along the X axis (see the inset in Fig. 3). Its amplitude depends on the anisotropy parameter a, which is determined by both the difference of the relative anisotropies of electron and hole mobilities and the geometry of the specimen [6]. Nevertheless, the photosensitivity of such In_4Se_3- and $In_4(Se_3)_{1-x}Te_{3x}$-based PCs at room temperature is less by an order of magnitude than that of photoresistors fabricated from the same materials. In order to find an opportunity to increase it, we carried out the researches concerning the influence of doping and thermal treatment in various environments on the sensitivity of the TDE-based PCs. Annealing in vacuum did not give rise to the photosensitivity increase, but led to its reduction in some cases.

The positive result was obtained after annealing the In_4Se_3 crystals cut off in (001) plane in saturated mercury vapors at a temperature of 620 – 640 K for 10 – 30 h. Afterwards, the specimens were cut off at a certain angle to the main crystallographic axes (Fig. 3). The specific resolution of such samples $D^*_{\lambda_m}$, being, as a rule, of the order of 10^{10} cm Hz$^{1/2}$ W^{-1} for $\lambda_m = 1.67$ μm, became 5 – 10 times as much after the annealing at room temperature and more than an order of magnitude as much at the cooling down to 240 K. Similar results were also obtained for $In_4(Se_3)_{1-x}Te_{3x}$ crystals with $x \leq 0.16$, when introducing a Ge dopant in a quantity of 0.2 wt.% during the crystal growing.

The spectral distributions of the TDE for doped and undoped In_4Se_3 did not differ from each other, with the photosensitivity maxima corresponding to the wavelength $\lambda = 1.65$ μm. The long-wave edges of the TED spectral curves were expectedly shifted towards shorter wavelengths in comparison with the photoconductivity case (Fig. 3, curves *1* and *2*).

The sensitivity of photoresistors based on $In_4(Se_3)_{1-x}Te_{3x}$ crystals, the latter being closer by composition to In_4Te_3 ones, decreased appreciably. The TDE in them was small, and the TDE spectral dependence had abnormal character. An additional long-wave peak of photosensitivity (Fig. 4, curve *1*), which testified to the presence of the photo-emf stimulated by the nonhomogeneity of the sample specific resistance [7], was observed only in some crystals with $x \leq 0.16$. At the same time, the spectral curves of the photo-emf for $In_4(Se_3)_{1-x}Te_{3x}$ crystals with $x \geq 0.60$ behaved differently. The photo-emf induced by nonhomogeneity exceeded the value of the TDE (Fig. 4, curve *2*). After those crystals having been annealed in vacuum, the shape of the photo-emf spectral dependence did not change practically (Fig. 4, curve *3*).

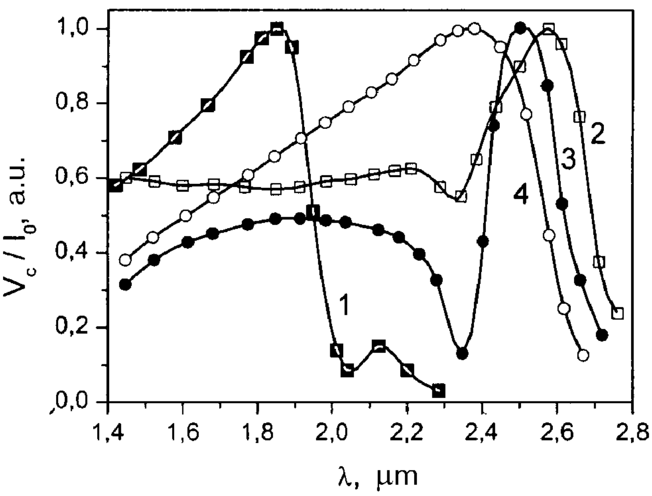

Fig. 4. Spectral dependences of the transverse photo-emf for $In_4(Se_3)_{1-x}Te_{3x}$ crystals with various compositions: (*1*) $x = 0.16$; (*2*) $x = 0.70$; (*3*) $x = 0.75$, annealing in vacuum; (*4*) $x = 0.75$, annealing in selenium vapors

4. Discussion of Results

An increase of the TDE value after the long-term annealing in mercury vapors can be explained by the penetration of an impurity into interlayer spaces and by the accompanying variation of the anisotropy of electron and hole mobilities, which results in an increase of the anisotropy parameter a. A long-term storage (for several years) of doped In_4Se_3 and $In_4(Se_3)_{1-x}Te_{3x}$ ($x \leq 0.16$) specimens did not cause a reduction of their photosensitivity. As time went by, a broadening of the spectral range of the PC sensitivity occurred owing to a reduction of the short-wave recession (Fig. 3, a curve 3). The origin of the photo-emf growth in the range of high absorption can be the variation in time of the majority current carrier concentration near the surface and the emergence of an electric field which induces the appearance of a drift TDE component in addition to a diffuse one.

In this case, the photosensitivity maximum was shifted farther towards the long-wave range than the photoconductivity one. This testifies to that the photo-emf, which was observed in the range of weak absorption of radiation, was not a diffusion-induced transverse photo-emf. Really, the TDE is characterized by a displacement of the photosensitivity maximum to the short-wave side, because the strong absorption of radiation accompanied by the emergence of the nonequilibrium carrier concentration gradient is necessary for the diffusion-induced transverse photo-emf to appear. It is also corroborated by the character of the variation of the photo-emf spectral dependences in the case where the specimens were illuminated from their back side. Namely, the photosensitivity signal changed its sign only for the shorter-wave component of the photo-emf, which is of the diffuse nature.

For $In_4(Se_3)_{1-x}Te_{3x}$ crystals with $x > 0.60$, the SEM researches revealed a high concentration of lengthy defects and disoriented blocks. Lengthy nonhomogeneities, being mainly aligned along (001) axis, stimulate the variation of the conductivity anisotropy and the emergence of an additional photo-emf.

To enhance the sensitivity of the TDE-based PCs and to eliminate the photo-emf, which is connected with nonhomogeneities in both the X and Y directions (see Fig. 3), we studied the influence of annealing and doping on the value and the spectral distribution of photosensitivity. The greatest growth of photosensitivity for $In_4(Se_3)_{1-x}Te_{3x}$ with $x > 0.60$ was obtained when the crystals had been annealed in the Se or S vapor: the corresponding TDE value became an order of magnitude as large; the spectral dependence of the photo-emf changed its shape (Fig. 4, curve *4*). The maximum of the photo-emf for a crystal with $x = 0.75$ ($\lambda_{\max\,PC} = 2.4$ μm) was located at the short-wave side of the photoconductivity maximum, which evidences for a substantial reduction of the specimen nonhomogeneity.

Annealing did not result in the desired effect in the case where the crystal stresses caused by substantial distortions of the crystal lattice and the appearance of another phase at block interfaces developed. Annealing in the Se or S vapor promoted a reduction of the number of local decay regions in the crystals, an enhancement of their resistance to the action of the environment, and the stabilization of electric, optical, and photo-electric parameters.

The results of our researches testify to that a proper selection of dopants and doping procedure, taking into account the distribution peculiarities of structural defects in anisotropic $In_4(Se_3)_{1-x}Te_{3x}$ crystals, may optimize indeed the optical and photo-electric properties of the latter, changing these properties in a direction which is required for a practical use.

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ВПЛИВ ЛЕГУВАННЯ НА ОПТИЧНІ ТА ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ $In_4(Se_3)_{1-x}Te_{3x}$

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Р е з ю м е

Наведено результати електронно-мікроскопічного дослідження особливостей розподілу структурних дефектів, пов'язаних з анізотропією кристалічної гратки і умовами росту монокристалів $In_4(Se_3)_{1-x}Te_{3x}$ ($0\leq x \leq 0{,}2$ і $0{,}68\leq x \leq 1{,}0$). Вивчено вплив цих особливостей і легування домішками Ge, Sn, Hg, Se на пропускання ІЧ-випромінювання і на характер спектрального розподілу поперечної фото-ерс Дембера в кристалах. Здійснено оптичне просвітлення плівками SiO і тришаровим просвітлюючим покриттям SiO—Ge—SiO монокристалів $In_4(Se_3)_{1-x}Te_{3x}$ і In_4Se_3. Визначено оптимальні умови вирощування кристалів для отримання оптичних фільтрів і фоточутливих елементів, що функціонують в близькій і середній областях ІЧ-спектра.