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Electrical properties and mechanisms of the point defect formation in PbTe(In) films prepared by modified "hot wall" technique

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An attempt has been made to explain the complex character of electrophysical characteristics changes in $Pb_{1-y}In_yTe_{1\pm\delta}$ films grown on Si substrates basing on different mechanisms of point defect formation in view of the stoichiometry deviation extent in the contents of the main components under the control of scalar density value of extended defects (dislocations). For $Pb_{1-y}In_yTe_{1\pm\delta}$ films prepared by the single-stage synthesis method using the modified "hot wall " technique, it has been found that $Pb_{1-y}In_yTe_{1-\delta}$ samples with Te deficiency regarding the stoichiometric ratio show n-type conductivity. Within the scope of crystal-quasichemical approach, the amphoteric (donor and acceptor) behavior of In impurity atoms taking into account their different charge condition (In^+ and In^{3+}) and possible positions in the crystal lattice of the lead telluride (In_{Pb} and In_i) matrix are interpreted.

Сделана попытка объяснить сложный характер изменения электрофизических свойств пленок $Pb_{1-y}In_yTe_{1\pm\delta}$, выращенных на Si-подложках, различными механизмами образования точечных дефектов с учетом степени отклонения от стехиометрии в содержании основных компонентов при контроле величины скалярной плотности протяженных дефектов (дислокаций). Для пленок $Pb_{1-y}In_yTe_{1\pm\delta}$, полученных методом одностадийного синтеза при помощи модифицированного метода "горячей стенки", установлено, что образцы $Pb_{1-y}In_yTe_{1-\delta}$, характеризующиеся недостатком теллура относительно стехиометрического состава, обладают n-типом проводимости. В рамках кристалло-квазихимического подхода дана интерпретация амфотерного (донорного и акцепторного) поведения примесных атомов индия с учетом их различного зарядового состояния (In^+ и In^{3+}), а также возможного положения в кристаллической решетке исходной матрицы теллурида свинца (In_{Pb} и In_i).

1. Introduction

The chalcogenides of IV A group metals of the Periodic system can be used as the base materials for the active elements in different devices of IR optoelectronic engineering in middle and far spectral range [1] as well as in thermoelectric energy converters [2]. The energy spectrum of PbTe⟨In⟩ single crystals and films is known to be rather complex [3], and the presence of In impurity atoms is not reduced to the formation of only one impurity level resulting in the stabilization (pinning) of the Fermi level position. It has reliably demonstrated that in PbTe single crystals and thin films, the behavior of impurity atoms of III A group metals depends not only upon their concentration, but on doping technique, too. Nevertheless, the information presented in numerous publications is sometimes rather contradictory. For example, three versions are considered until now to be a reason of Fermi level pinning effect [4].

The main purpose of the present work is an attempt to explain the complex character of of the electrical characteristics evolution

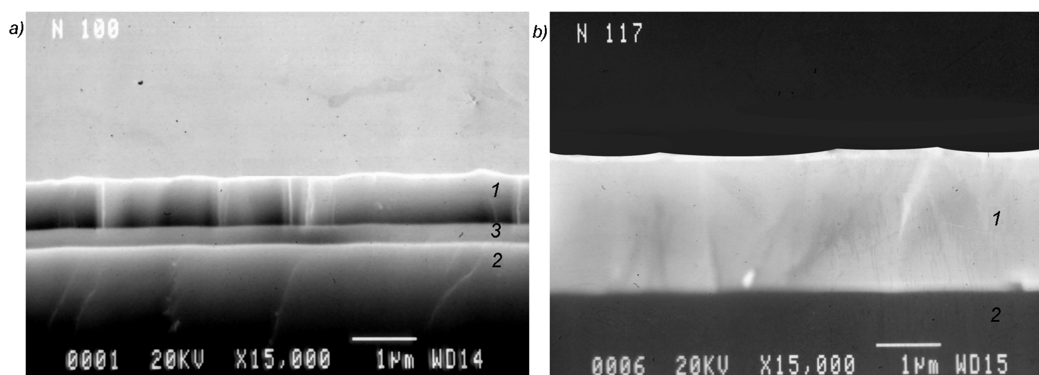


Fig. 1. The micrographs of the cross sections of the $Pb_{1-y}In_yTe_{1\pm\delta}/SiO_2/Si$ and $Pb_{1-y}In_yTe/Si$ heterostructures: *a*, $Pb_{1-y}In_yTe_{1\pm\delta}$ /SiO2/Si (100) film; *b*, $Pb_{1-y}In_yTe_{1\pm\delta}$ /Si (100) film; *1*, Si substrate; *2*, $Pb_{1-y}In_yTe$ film; *3*, SiO_2 buffer layer.

for the $Pb_{1-y}In_yTe_{1\pm\delta}$ films grown on a Si (100) and SiO_2/Si (100) substrates using the single-stage variant of a modified "hot wall" technique. Within the scope of the crystal-quasichemical approach, the different mechanisms of point defects formation are reviewed taking into account the stoichiometry deviation extent in the contents of the basic components (lead and tellurium) under the scalar density control of extended defects (dislocations).

2. Experimental procedure

The modified "hot wall" technique (HWE) was employed to prepare the mirror-smooth surface PbTe thin films doped with In (about 0.5 – 5.0 mm thickness) deposited directly onto (100) Si high-ohmic substrates both with and without SiO_2 buffer layer [5]. Under optimal experimental conditions, the previously synthesized In_xPb_{1-x} ($0.10 \le x_{In} \le 0.70$) liquid alloys were employed simultaneously as the sources of indium and lead vapors. To form ternary $Pb_{1-y}In_yTe$ layers (Fig. 1), an additional source of the tellurium vapours was activated. The values of lead and tellurium partial pressures were kept the same as at preparation of undoped PbTe/Si and PbTe/SiO_2/Si films (characterized by *p*-type conductivity with charge carrier density of $5{\cdot}10^{16}$ – $2{\cdot}10^{18}$ cm^{-3} at 298 K) described elsewhere [5]. To prepare PbTe⟨In⟩ films, high-purity Pb (99.999 %), In (99.999 %), and Te (99.99 %) were used. The residual gas partial pressure of about $5{\cdot}10^{-7}$ Pa during the evaporation process can be realized in a graphite reaction chamber [6]. The direct exposure of the Si substrate to Te_2 molecules for 20-30 min prior the condensation of the binary semiconductor was used to remove the SiO_2 natural layer from the substrate surface. On the other hand, lead telluride layers were grown on Si substrates using an intermediate buffer layer consisting of 300±30 nm thick previously formed SiO_2. The presence of dielectric SiO_2 buffer layers is required for further correct Hall coefficient and resistivity measurements in order to isolate PbTe⟨In⟩ films and Si wafers. As it is seen from X-ray diffraction patterns, SiO_2 buffer layers were amorphous with trace amount of orthorombic phase (space group Cmcm) crystallites.

The surface and cleave morphology of the synthesized $Pb_{1-y}In_yTe_{1\pm\delta}$ films (Fig. 1) was studied by SEM using the JEOL-JCA-840 and JEOL JCM-6430 LV instruments. A quantitative elemental composition of all prepared layers was investigated by EPMA using the MAR-3 and JEOL-JCA-840 microanalyzers using spectrometers with a wave and energy dispersion. Selected parts of the $Pb_{1-y}In_yTe_{1\pm\delta}$ samples were studied by atomic absorption analyzer AAC QUANTUM - Z.ETA, too. The analysis of $Pb_{1-y}In_yTe_{1\pm\delta}$ layers by EPMA method was realized in local and raster modes, and has been duplicated for several spectral lines. Experimental results were compared with the different measurement standards. In all the prepared $Pb_{1-y}In_yTe_{1\pm\delta}$ films, K_α and M_α lines were used to determine lead concentration and L_α and L_β lines to determine indium and tellurium concentrations. As the measurement standards, Pb metal of 99.9999% purity, PbTe single crystals, In metal of 99.9999% purity, InAs single crystals, and Te of 99.999% purity were used. The calculation ZAF CORRECTION software was employed during the interpretation of the obtained data. This approach provided an improved interpretation of the statistical data, result-

ing in decreased determination error of lead Δx_{Pb} down to ±0.0001 mole fraction, and of indium and tellurium (Δx_{In} and Δx_{Te}) down to ±0.0002 mole fraction.

X-ray diffraction (XRD) patterns were obtained with filtered CoK_α and CuK_α radiation on a computer-interfaced DRON-4-07 and THERMOTECHNO ARLX'pert diffractometers. During XRD experiments, single crystal Si (100) and Si (111) plates were used as internal standards. The (400), (444) and (200), (400), (600) X-ray reflection profiles of Si substrates of various orientation and PbTe films, respectively, were obtained with special care by DRON-4-07 diffractometer at 0.01 deg step-by-step movement. The lattice parameter values of PbTe films were calculated precisely by extrapolation to a diffraction angle θ = 90 deg. To eliminate systematic errors, different approximation functions were tried. The best results were obtained using the Nelson-Riley function [5]:

$$f(\theta) = 0.5\ (\cos^2\theta/\theta\ + \cos^2\theta/\sin\theta), \quad (1)$$

where θ is the diffraction angle.

The researches of electrical parameters for $Pb_{1-y}In_yTe_{1\pm\delta}$ thin films are associated with a number of experimental difficulties. The of electrical conductivity σ and Hall factor R_H of PbTe⟨In⟩ films were measured by Van der Pauw dc four-probe technique under account for correction factors dependent on the particular sample geometry as well as by investigation of the C - V curves ("Hg probe" method). Prior to the electrical measurements, the contact pads of 0.5 mm diameter were formed by thermal deposition of silver in vacuum onto the surface of $Pb_{1-y}In_yTe_{1\pm\delta}$ films through a special mask immediately after etching the surface in argon plasma atmosphere within the framework of the same technological cycle. As a material for the contact pads, silver was selected owing to close values of a photoelectric work function of electrons.

To study the $\sigma = f(T)$ and $R_H = f(T)$ temperature dependences, the $Pb_{1-y}In_yTe_{1\pm\delta}$ samples together with the holder were placed in a special cryostat excluding the direct contact of the film under study with liquid nitrogen. The deep cooling of $Pb_{1-y}In_yTe_{1\pm\delta}$ samples (down to 77 K) was reached by continuous feeding gaseous N_2 from the cryostat volume to the film surface. Thus, during all cycle of measurements, the sample was in protective atmosphere, that protected its surface from freezing of water vapors. The last circumstance

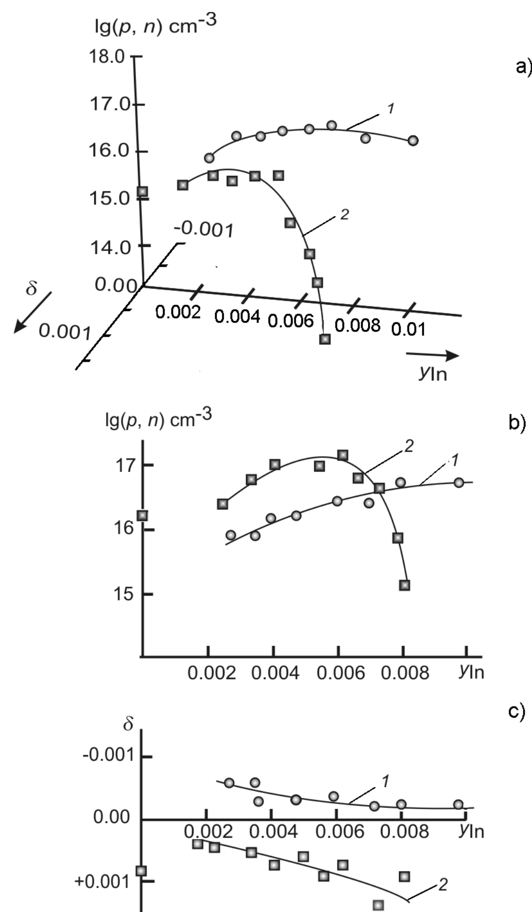


Fig. 2. The dependences of the conductivity type and charge carrier density on In impurity concentration y_{In} and the deviation from stoichiometric ratio δ in $Pb_{1-y}In_yTe_{1\pm\delta}$ /SiO_2/Si and $Pb_{1-y}In_yTe_{1\pm\delta}$ /Si films at 77 K: (a) 3D dependence; (b) ln(p, n) - y_{In} - projection; (c) the deviation from stoichiometric ratio δ – y_{In} – projection. *1*, samples with n-type conductivity; *2*, samples with p-type conductivity.

is of a special imporce when it is necessary to realize repeated measurements on the same object. During the determination of general inaccuracy of the electrical measurements, only the systematic component was taken into account. The errors associated with usage of measuring instruments, were evaluated using the errors of the measuring means. In view of the circumstance, the general error at determination of the Hall factor R_H and electrical conductivity σ did not exceed 10 %.

3. Results and discussion

The $Pb_{1-y}In_yTe_{1\pm\delta}$ samples synthesized by the single-stage method using In_xPb_{1-x} melts as the sources of metallic component

vapors and intended to realize the electrical measurements were controlled carefully by X-ray investigation. To measure the R_H and σ, homogeneous $Pb_{1-y}In_yTe_{1\pm\delta}$ films were selected with the scalar dislocation density about $6\cdot10^4$ - $8\cdot10^5$ cm^{-2}. The scalar dislocation density was determined by the technique described in [5].

When considering the electrical characteristics of $Pb_{1-y}In_yTe_{1\pm\delta}$ films, a rather complex pattern is observed (Fig. 2). It has been found that $Pb_{1-y}In_yTe_{1-\delta}$ samples ($0.002 < y_{In} < 0.0098$), characterized with a little excess of lead over the stoichiometric ratio always show the n-type conductivity, the increase in the contents of impurity indium atoms being accompanied by increase of the electron density, regardless of the fact that the common excess contents of Pb and In decreased in these samples, i.e. their composition would come nearer to stoichiometric ratio (Fig. 2b and 2c). On the other hand, in $Pb_{1-y}In_yTe_{1+\delta}$ films, which with a little excess of tellurium, the relation between the type of conductivity and charge carrier density is not so unequivocal. As it is seen in Fig. 2, all the studied $Pb_{1-y}In_yTe_{1+\delta}$ samples with tellurium excess at In concentration $y_{In} < 0.009$ show the p-type conductivity irrespective of the impurity indium atoms contents therein. Nevertheless, the character of the hole density dependence upon the concentration of In impurity is unmonotonous (Fig. 2b). In an interval of In concentration $0.002 < y_{In} < 0.0065$, the increase in the indium impurity atom content is accompanied by increase in hole density. When the concentration of impurity atoms $y_{In} = 0.0065$ is attained, a further increase in the impurity content results in decreasing hole density.

It is reasonable to compare the results of the electrical measurements of $Pb_{1-y}In_yTe_{1\pm\delta}$ films with earlier data on the lattice constant evolution in these layers depending on the contents of In impurity atoms therein [7, 8].

As is seen in Fig. 3, the curve $a_{PbTe\langle In\rangle} = f(y_{In})$ is a nonmonotonic function and does not obey the Vegard law. It can be divided into three sections. The first section of this curve corresponds to the decrease in $a_{PbTe\langle In\rangle}$ values within the concentration interval $0 < y_{In} < 0.0063$. At $y_{Ga} = 0.0063\pm0.0002$, the minimum $a_{PbTe\langle In\rangle}$ value is observed. The second section of this dependence shows the increase in the lattice parameter $a_{PbTe\langle In\rangle}$ within the concentration interval of about $0.0068 < y_{In} < 0.014$. On the other hand, the further rising of In impurity

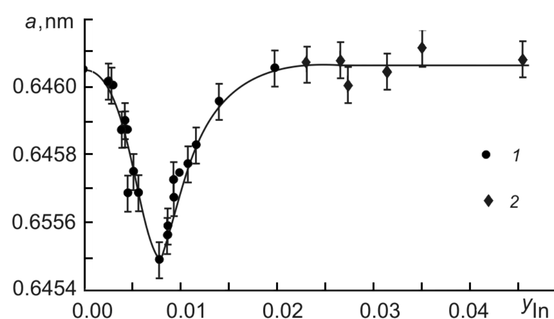


Fig. 3. The dependences of the lattice parameter a_{PbTe} on the In impurity concentration y_{In} in ternary $Pb_{1-y}In_yTe$ films obtained at $T_{sub} = 623\pm3$ K: *1*, homogeneous samples; *2*, heterogeneous polycrystalline samples.

atoms content at $y_{Ga} > 0.014$ is accompanied by essentially constant unit cell parameter values of PbTe⟨In⟩ films. Because the lattice parameters values are fixed at essentially $y_{In} > 0.014$, this concentration may be interpreted as the solubility limit of In in PbTe at $T = 583\pm3$ K. It is necessary to emphasise that experimental data obtained in this work show that the range of the In solid solutions region in PbTe matrix is narrower than that reported before for bulk PbTe⟨In⟩ alloys [4].

The similar nature of the lattice constant change was observed before when considering the In-doped bulk samples of PbTe.

In the second section of $a_{PbTe\langle In\rangle} = f(y_{In})$ curve at $0.0063 < y_{In} < 0.014$, a smooth increase in the identity parameter is revealed. In the third fragment of $a_{PbTe\langle In\rangle} = f(y_{In})$ curve at the concentration of In impurity $y_{In} > 0.014$, the values of lattice parameter do not vary appreciably within the error limits of XRD experiment. The constancy of $a_{PbTe\langle In\rangle}$ values is revealed within the In impurity concentration $y_{In} > 0.015 - 0.045$. As the atomic and cationic radii of In are smaller than those of Pb, the following conclusions are possible to be drawn from the found $a_{PbTe\langle In\rangle} = f(y_{In})$ relatioships in conditions when synthesizing and doping of films take place simultaneously:

(i) The initial fragment of the curve in Fig. 3 corresponding to decreasing lattice constant it is possible to consider as an indication of the primary formation of substitutional solid solutions. Thus, according to the self-compensation theory, the decreasing in the identity period can be promoted by formation of Te vacancies; (ii) The intermediate section of $a_{PbTe\langle In\rangle} = f(y_{In})$ relationship is possible to be explained by changing

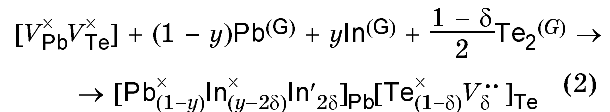
of the dominating mechanism of solid solutions formation: one fraction of In atoms, as before, is positioned in regular sites of the cationic sublattice, while another fraction is in interstices. As the sizes of interstitial tetrahedral voids in PbTe crystal structure are a somewhat smaller than ionic radii of metals from III A group, the filling them by In results in increasing lattice parameter. Therefore, at this interval of In impurity concentration, the mixed type of solid solutions "substitution - interstitial" is realized. The existence of such solid solutions was found before, in particular, in the silicon-gold and silicon-carbon systems [9]; (iii) The third part of $a_{PbTe\langle In\rangle} = f(y_{In})$ curve shows that the increase in the of In impurity concentration $y_{In} > 0.014$ in $Pb_{1-y}In_yTe_{1+\delta}$ films does not result in any enlargement of the unit cell parameter. This fact can indicate to approach to the solubility limit of III A group metals in the initial PbTe matrix.

Comparing the experimental data presented in Fig. 2 and Fig. 3, it is possible to find out a certain correlation between the evolution of the lattice parameter $a_{PbTe\langle In\rangle}$ and the changing of charge carrier density depending on the concentration of In impurity in $Pb_{1-y}In_yTe_{1+\delta}$ films with excess of tellurium. The decreasing of the hole density in $Pb_{1-y}In_yTe_{1+\delta}$ samples at $y_{In} > 0.0065$ can be associated with the changing of the preferential mechanism of In impurity implantation in the PbTe crystalline matrix.

The amphoteric behavior of In atoms in PbTe is quite logical to be explained by their different valence conditions [4]. The comparison of the In impurity concentration with the maximum possible charge carrier density in PbTe within limits of homogeneity region demonstrates that in this case, the neutral state is the ground one for In atoms. For example, under condition that each In atom is singly ionized, their concentration of about 0.0025 mole fraction should correspond to the charge carrier density ~ $3.6\cdot10^{19}$ cm^{-3}. It is seen from experimental data (Fig. 2) that it is impossible to obtain the PbTe⟨In⟩ films possessing so high charge carrier density by direct doping during the growth process. Taking into account the fact that for In atoms, the $5s^15p^2$ neutral condition is paramagnetic and consequently less stable [4], it is possible to suspect that low efficiency of doping ($N_d + n_d >> [n]$ or $N_a + n_a >> [p]$) is connected to preferential segregation of In impurity atoms along the intercrystalline boundaries.

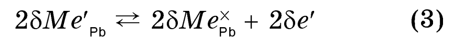
Basing on comparison of the experimental electrical measurement results (Fig. 2) with non-linear and nonmonotonous evolution of the $a_{PbTe\langle In\rangle}$ lattice parameter (Fig. 3) within the scope of crystal-quasichemical approach [10], a model was proposed able to explain complex amphoteric (donor and acceptor) behavior of In impurity in PbTe⟨In⟩ films taking into account the dimensional factor of In atoms and ions (Table), their different charge condition (In^+ and In^{3+}), and possible positions in the crystal lattice of the initial lead telluride matrix (In_{Pb} and In_i). Four possible cases are reviewed:

1) Statistical distribution of In impurity atoms in regular sites of the Te-deficient cationic PbTe sublattice during single-stage synthesis from the vapor phase (deviations from the stoichiometry $\delta < 0$):



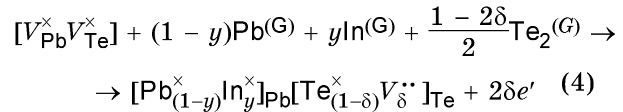
$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1-\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y)}^{\times}In_{(y-2\delta)}^{\times}In'_{2\delta}]_{Pb}[Te_{(1-\delta)}^{\times}V_{\delta}^{\bullet\bullet}]_{Te} \quad (2)$$

Taking into account ionization of In atoms:



$$2\delta Me'_{Pb} \rightleftarrows 2\delta Me_{Pb}^{\times} + 2\delta e' \quad (3)$$

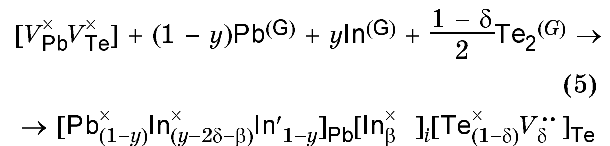
And finally:



$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1-2\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y)}^{\times}In_{y}^{\times}]_{Pb}[Te_{(1-\delta)}^{\times}V_{\delta}^{\bullet\bullet}]_{Te} + 2\delta e' \quad (4)$$

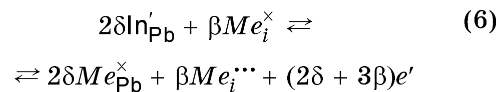
There is an increase in the electron density by $2\delta e'$.

2) Implantation of In impurity atoms in interstitial sites (tetrahedral voids) of Te-deficient PbTe crystal structure during single-stage synthesis from the vapor phase (deviations from the stoichiometry $\delta < 0$; β – fraction of In atoms occupying interstices, $0 < \beta < 2\delta$):



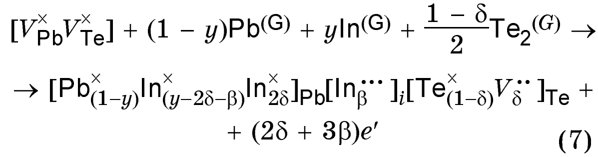
$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1-\delta}{2}Te_2^{(G)} \rightarrow \quad (5)$$
$$\rightarrow [Pb_{(1-y)}^{\times}In_{(y-2\delta-\beta)}^{\times}In'_{1-y}]_{Pb}[In_{\beta}^{\times}\ ]_i[Te_{(1-\delta)}^{\times}V_{\delta}^{\bullet\bullet}]_{Te}$$

Taking into account ionization of In atoms:



$$2\delta In'_{Pb} + \beta Me_i^{\times} \rightleftarrows \quad (6)$$
$$\rightleftarrows 2\delta Me_{Pb}^{\times} + \beta Me_i^{\bullet\bullet\bullet} + (2\delta + 3\beta)e'$$

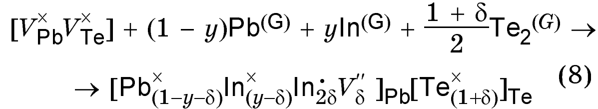
And finally:



$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1-\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y)}^{\times}In_{(y-2\delta-\beta)}^{\times}In_{2\delta}^{\times}]_{Pb}[In_{\beta}^{\bullet\bullet\bullet}]_i[Te_{(1-\delta)}^{\times}V_{\delta}^{\bullet\bullet}]_{Te} + (2\delta+3\beta)e' \quad (7)$$

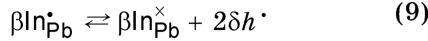
There is an increase in the electron density by $(2\delta+3\beta)e'$.

3) Statistical distribution of In impurity atoms in regular sites of the cationic sublattice of PbTe with excess of Te during single-stage synthesis from the vapor phase (deviations from the stoichiometry $\delta > 0$):



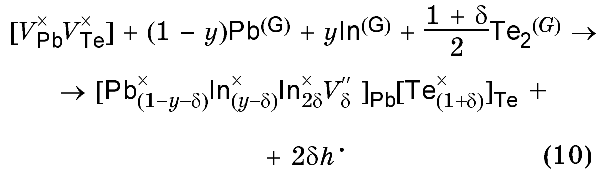
$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1+\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y-\delta)}^{\times}In_{(y-\delta)}^{\times}In_{2\delta}^{\bullet}V_{\delta}'']_{Pb}[Te_{(1+\delta)}^{\times}]_{Te} \quad (8)$$

Taking into account ionization of In atoms:



$$\beta In_{Pb}^{\bullet} \rightleftarrows \beta In_{Pb}^{\times} + 2\delta h^{\bullet} \quad (9)$$

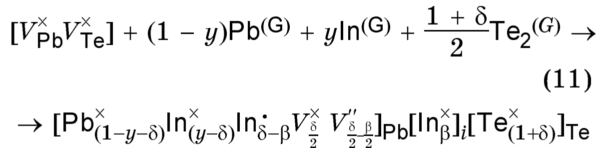
And finally:



$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1+\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y-\delta)}^{\times}In_{(y-\delta)}^{\times}In_{2\delta}^{\times}V_{\delta}'']_{Pb}[Te_{(1+\delta)}^{\times}]_{Te} + 2\delta h^{\bullet} \quad (10)$$

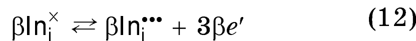
There is an increase in the hole density by $2\delta h^{\bullet}$.

4) Implantation of In impurity atoms in interstitials (tetrahedral voids) of PbTe crystal structure with excess of Te during single-stage synthesis from the vapor phase (deviations from the stoichiometry $\delta > 0$; β – fraction of In atoms occupying interstices, $0 < \beta < 2\delta$):



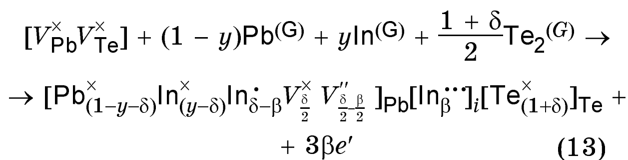
$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1+\delta}{2}Te_2^{(G)} \rightarrow \quad (11)$$
$$\rightarrow [Pb_{(1-y-\delta)}^{\times}In_{(y-\delta)}^{\times}In_{\delta-\beta}^{\bullet}V_{\frac{\delta}{2}}^{\times}V_{\frac{\delta}{2}-\frac{\beta}{2}}'']_{Pb}[In_{\beta}^{\times}]_i[Te_{(1+\delta)}^{\times}]_{Te}$$

Taking into account ionization of In atoms:



$$\beta In_i^{\times} \rightleftarrows \beta In_i^{\bullet\bullet\bullet} + 3\beta e' \quad (12)$$

And finally:



$$[V_{Pb}^{\times}V_{Te}^{\times}] + (1-y)Pb^{(G)} + yIn^{(G)} + \frac{1+\delta}{2}Te_2^{(G)} \rightarrow$$
$$\rightarrow [Pb_{(1-y-\delta)}^{\times}In_{(y-\delta)}^{\times}In_{\delta-\beta}^{\bullet}V_{\frac{\delta}{2}}^{\times}V_{\frac{\delta}{2}-\frac{\beta}{2}}'']_{Pb}[In_{\beta}^{\bullet\bullet}]_i[Te_{(1+\delta)}^{\times}]_{Te} + 3\beta e' \quad (13)$$

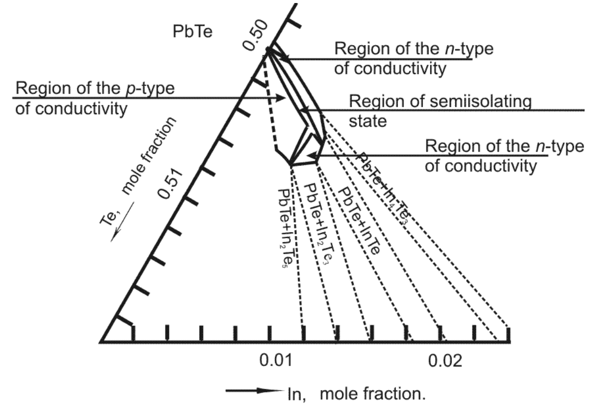


Fig. 4. The area of In solid solution existence in PbTe with regions of the different conductivity types.

There is an increase in electron density by $3\beta e'$.

As it can be seen from equations (2-7), in a Te-deficient PbTe matrix, the In impurity atoms exhibit the donor properties and facilitated the generation of electrons. In PbTe with excess of Te, the behavior of In atoms is more complex. At statistical distribution in the cationic sublattice, In impurity atoms exhibited acceptor properties (equations (8-10)). In case that In is built into interstices, the generation of electrons takes place (donor properties) and hole compensation in initial PbTe with p-type conductivity. In this case, the evolution of the electrical properties should depend upon the ratio β and δ.

The data obtained before have shown [8] that the region of In solubility in PbTe is asymmetrical and enlarged with the temperature. In this connection, taking into account the model presented above, the regions with the different types of conductivity can be pointed inside the area of In dissolubility in the PbTe matrix (Fig. 4).

Thus, it follows from the data obtained that in $Pb_{1-y}In_yTe_{1\pm\delta}$ films the behavior of In impurity is connected in certain manner with deviation from the stoichiometry in the content of the main components (lead and tellurium). The presented model confirms the fact of low doping efficiency ($N_d + n_d >> [n]$ or $N_a + n_a >> [p]$). In Te-deficient $Pb_{1-y}In_yTe_{1-\delta}$ films regarding to the stoichiometric ratio, the In impurity atoms exhibit donor properties only. In $Pb_{1-y}In_yTe_{1+\delta}$ samples with excess of tellurium, In demonstrates amphoteric behavior: at low-level concentrations it acts as an acceptor, while at $y_{In} > 0.0065$, it exhibits the donor properties.

Table. Nuclear, covalent, ionic radii, ionization and electron affinity energies for lead, tellurium and indium [11].

Element	"Metallic" atomic radius, nm	Orbital atomic radius, nm	Crystallographic ionic radii, nm				Ionization energy I, kJ/mole				Electron of affinity energy E, kJ/mole
			2 −	1 +	2 +	3 +	I_1	I_2	I_3	I_4	
Pb	0.175	0.1215 0.154	---	---	0.126 0.125 0.132	---	715.5	1450.4	3081.5	4083	35.1
Inδ	0.162	0.150	---	0.132	---	0.92	558.3	1820.6	2704	5200	~30
Te	0.17 0.143	0.1111 0.137	0.211	---	---	---	869.2	1795	2698	3610	190.2

5. Conclusions

The results of electrical measurements have shown that $Pb_{1-y}In_yTe_{1-\delta}$ samples ($0.002 < y_{In} < 0.0098$), characterized by deficiency in Te regarding to the stoichiometric ratio, always show the n-type conductivity. On the other hand, $Pb_{1-y}In_yTe_{1+\delta}$ films characterized by excess of Te regarding to the stoichiometric ratio show p-type conductivity at $y_{In} < 0.009$ irrespective of In impurity content therein, however, evolution of the hole density depending on the impurity atoms content is nonmonotonous. Within the concentration interval $0.002 < y_{In} < 0.0065$, the increase in the In content is accompanied by increase in hole density. At achievement of concentration $y_{In} = 0.0065$, the further rising of the impurity atom content result in reduction of the hole density.

The model proposed in the scope of crystal-quasichemical approach confirms that the behavior of In impurity atoms in $Pb_{1-y}In_yTe_{1\pm\delta}$ is connected in certain manner with deviation from the stoichiometry in the content of the main components (lead and tellurium) and demonstrates low efficiency of PbTe doping by In impurity atoms.

Taking into account the obtained experimental results and conclusions from the proposed model, the regions with the different conductivity types inside the existence area of In solid solutions in PbTe are indicated.

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Електрофізичні властивості та механізми дефектоутворення у плівках PbTe(In), вирощених модифікованим методом "гарячої стінки"

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Зроблено спробу пояснити складний характер зміни електрофізичних властивостей плівок $Pb_{1-y}In_yTe_{1\pm\delta}$, вирощених на Si-підкладках, різними механізмами утворення точкових дефектів з урахуванням міри відхилення від стехіометрії у вмісті основних компонентів при контролі значення скалярної густини протяжних дефектів (дислокацій). Для плівок $Pb_{1-y}In_yTe_{1\pm\delta}$, одержаних методом одностадійного синтезу за допомогою модифікованого методу "гарячої стінки", встановлено, що зразки $Pb_{1-y}In_yTe_{1-\delta}$, які характеризуються дефіцитом телуру відносно стехіометричного складу, мають *n*-тип провідності. У рамках кристало-квазіхімічного підходу дано інтерпретацію амфотерної (донорної та акцепторної) поведінки домішкових атомів індію з урахуванням їхнього різного зарядового стану (In^+ та In^{3+}), а також можливого положення у кристалічній гратці вихідної матриці телуриду свинцю (In_{Pb} та In_i).