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The solubility region of Ga in PbTe films prepared on Si-substrates by modified "hot wall" technique

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The chemical quantitative composition, phase constitution, and crystal structure of doped with Ga lead telluride films synthesized by "hot wall" technique on Si (100) or SiO_2/Si (100) substrates have been studied. The quantitative composition of $Pb_{1-y}Ga_yTe$ films (over 1 μm thick) was examined in dependence of partial pressures of metal components and chalkogene. By the EPMA and atomic absorption measurements it has been found that the concentration of Ga atoms y varied from 0.0011 to 0.045 in these deposited $Pb_{1-y}Ga_yTe$ films. The results of EPMA, SEM, and X-ray diffraction measurements show that formation of Ga solid solutions in lead telluride matrix revealed not only in PbTe–GaTe cross-section, but in PbTe–Ga_2Te_3 pseudobinary system also. The results of X-ray diffraction show that the lattice parameter a_{PbTe} of PbTe⟨Si⟩/Si and PbTe⟨Ga⟩/SiO_2/Si heterostructures is described by non-monotone function and does not obey the Vegard's law within concentration interval $0.0011 \le y \le 0.045$.

Исследованы границы области существования твердых растворов Ga в пленках PbTe, синтезированных методом "горячей стенки" на Si-подложках. Изучен количественный состав пленок $Pb_{1-y}Ga_yTe$ (толщиной более 1 мкм) в зависимости от парциальных давлений металлических компонентов и халькогена. Применены рентгенографические исследования, РЭМ и метод ЛРСА гомогенных пленок $Pb_{1-y}Ga_yTe$. Показано, что область гомогенности твердых растворов галлия в теллуриде свинца имеет асимметричную форму относительно квазибинарного разреза PbTe–GaTe. Установлено, что увеличение отклонения от стехиометрии пленок $Pb_{1-y}Ga_yTe$ в сторону избыточного содержания теллура способствует повышению растворимости галлия в матрице теллурида свинца.

1. Introduction

The small band gap and high carrier mobilities of $A^{IV}B^{VI}$ semiconductors identify them as the prospective materials for infrared (IR) optoelectronic devices in middle wave range [1]. The IR sensitivity of these materials is similar to that of $Cd_{1-x}Hg_xTe$ but processing procedures are much less demanding [2]. The electrical parameters of PbTe and its solid solutions can change significantly in the presence of III A group metals [3]. As it was demonstrated by numerous investigations the effect of Fermi level pinning has been established for lead telluride single crystals and thin films doped with Ga and In [3]. However, until now, many problems about the influence of III A group metals impurity atoms upon the crystal structure and energy spectrum of

PbTe are still unknown. Some fundamental aspects of the formation and saturation of quasi-local impurity levels in Ga-doped PbTe have not come to solution yet. As a practical matter, the growth of $A^{IV}B^{VI}$ thin films on Si substrates would allow to fabricate the monolithic structures for IR sensor arrays with the charge storage and signal multiplexing performed on the same chip [4,5].

Therefore, the main purposes of this study are to discuss the experimental results, obtained during the examination of the chemical quantitative composition and the real crystal structure of PbTe⟨Ga⟩ films deposited on Si (100) and SiO_2/Si (100) substrates, and to evaluate the solubility of Ga atoms in lead telluride thin films at different temperatures.

2. Experimental procedure

The modified "hot wall" epitaxy (HWE) technique has been employed to prepare the mirror-smooth surface PbTe thin films doped with Ga (thickness was about 0.5–5.0 μm), which were deposited directly on (100) Si high-ohmic substrates both with and without SiO_2 buffer layer [6]. Under optimal experimental conditions, the previously synthesized Ga_xPb_{1-x} ($0.60 \le x \le 0.97$) liquid alloys were used as the sources of gallium and lead vapours coincidentally. To form ternary $Pb_{1-y}Ga_yTe$ layers, an additional source of the tellurium vapours has been activated.

In this work, the HWE apparatuses were equipped by diffusion pumps and liquid nitrogen traps. As a result, the evacuation of $5\cdot10^{-5}$ Pa was realized in the external volume. It is known [7, 8] that during evaporation of initial substances in a graphite reaction chamber used in HWE technique the partial pressure of residual gases decreases practically by a factor of 1000 as compared with the value of these gases pressure in the external evacuated volume. The essential advantage of the graphite reaction chamber is the reductive nature of residual atmosphere. By mass-spectrometric researches was established that after desorption heating of the chamber the residual atmosphere contains predominantly N_2, CO, and C_2H_4 molecules [8]. Thus, the partial pressure of residual oxygen of about $5\cdot10^{-8}$ Pa can be realized in graphite reaction chamber during the evaporation process [8].

In this work the synthesis of $Pb_{1-y}Ga_yTe_{1\pm\delta}$ films was carried out under following conditions:

1) The temperature of Ga_xPb_{1-x} melts varied within limits of 1023 K < T_{source} < 1153 K;

2) The temperature of Te vapours source T_{Te} = 560, 581 and 594 K;

3) The temperature of Si and SiO_2/Si substrates had two values: T_{sub} = 583 K and 620 K;

4) In dependence of the substrate temperature, "hot wall" was held at T_{wall} = 783 K or 820 K. All temperature regimes were controlled within about ±3 K.

The lead and tellurium partial pressures were kept at the same values as at fabrication of undoped PbTe/Si and PbTe/SiO_2/Si films (which were characterized by *p*-type of conductivity with charge carrier densities $5\cdot10^{16}$–$2\cdot10^{18}$ cm^{-3} at 298 K) described elsewhere [6]. For preparation of PbTe⟨Ga⟩ films high-purity Pb (99.999 %), Ga (99.999 %), and Te (99.995 %) were used.

The direct exposure of the Si substrate to Te_2 molecules during 20–30 min before the condensation of the binary semiconductor was used to remove a SiO_2 natural layer from substrate surface [9]. On the other hand, lead telluride layers were grown on Si substrates with the help of an intermediate buffer layers, which consist of 300±30 nm thick previously formed SiO_2. The presence of dielectric SiO_2 buffer layers is needed for further correct Hall coefficient and resistivity measurements in order to isolate PbTe⟨Ga⟩ films and Si wafers. As it can be seen from X-ray diffraction patterns, SiO_2 buffer layers were amorphous with trace amount of orthorombic phase (space group *Cmcm*) crystallines.

The precise estimation of the quantitative chemical composition in deposited PbTe⟨Ga⟩ films on Si and SiO_2/Si substrates has been carried out sequentially with the special carefulness. First, the presence of the Ga impurity has been established in all deposited films using energy dispersion (ED) spectrometry on JEOL JCM-6380 LV. Second, the quantitative chemical composition of PbTe⟨Ga⟩ layers was analysed in scanning and local mode with the help of wavelength dispersion (WD) spectrometry on JEOL-JCA-840 using $K_{\alpha1}$ and $L_{\alpha1}$ emissions of the elements. Third, some of PbTe⟨Ga⟩/Si and PbTe⟨Ga⟩/SiO_2/Si samples have been studied by atomic absorption method. During EPMA measurements

99.999 % pure Pb metal, 99.995 % Te, 99.999 % pure Ga metal, PbTe and GaAs single crystals have being used as reference standards. X-ray diffraction (XRD) patterns were obtained with filtered CoKα — and CuKα — radiation on a computer-interfaced DRON-4-07 and THERMOTECHNO AR-LX'pert diffractometers. In XRD experiments, single crystal Si (100) and Si (111) substrates were used as reference internal standards. The (400), (111), (444) X-ray reflection profiles of Si substrates of various orientation and (200), (400), (600) peaks of PbTe films, respectively, were obtained with special care with 0.01 degree step-by-step movement. The values of unit cell parameter of PbTe films have been precisely calculated by extrapolation to a diffraction angle $\theta = 90$ degrees. To eliminate systematic errors, we tried different approximation functions. The best results have been obtained with the Nelson-Riley function [6]:

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

where θ is the diffraction angle.

Structure identifications have been performed using JCPDS database [10]. The thickness and the crystal microstructure of the etched samples have been studied by a scanning electron microscopy (SEM) on JEOL JCM-6380 LV.

3. Results and discussion

The experimental data obtained previously at the examination of the evaporation process of Ga_xPb_{1-x} ($0.15 \le x \le 0.98$) liquid alloys were used to prepare PbTe layers doped with Ga by modified HWE technique. In previous works, the appropriate Si substrate temperature range has been determined where the PbTe/Si films with high crystallinity perfection could be deposited by modified HWE method [6]. As an example, the substrate temperature should be controlled at the range between 483±3 and 653±3 K in order to produce (100) PbTe films with mosaic single crystal structure more than 40 mm in diameter on Si wafers.

As it can be seen from the results obtained by EPMA-WDS and atomic absorption, Ga concentration in these fabricated $Pb_{1-y}Ga_yTe/SiO_2/Si$ and $Pb_{1-y}Ga_yTe/Si$ layers varied from $0.0004 < y_{Ga} < 0.0450$, or the mole fraction of Ga atoms varied from 0.0002 to 0.0225. The experimental results show that for all deposited $Pb_{1-y}Ga_yTe$ layers, the Ga concentration rises with increase in vapour source temperature T_{source} at a fixed melt composition and T_{sub} or with increase in Ga concentration in initial Ga_xPb_{1-x} melts at the fixed temperatures T_{source} and T_{sub}. It is evident that Ga concentration in grown films may be strictly controlled by adjusting the initial composition and the T_{source} of Ga_xPb_{1-x} melts. The precise estimation of the quantitative chemical composition shows that the all deposited $Pb_{1-y}Ga_yTe/SiO_2/Si$ and $Pb_{1-y}Ga_yTe/Si$ films are characterized by both little excess and deficiency of Te atoms with regard to stoichiometric ratio (mole fraction of Te varied within the range from 0.4975±0.0002 to 0.5035±0.0002).

The XRD patterns of the deposited $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ films are presented in Fig. 1. The detailed analysis of these experimental results allows come to some conclusions. The all fabricated $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ films can be segregated into two main groups.

The first group of samples is formed of homogeneous $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ layers. It has been found that all $Pb_{1-y}Ga_yTe/Si$ films have mosaic single crystal structure with strong (100) orientation (Fig. 1, a) if Ga concentration does not exceed the value $y = 0.011 \pm 0.0002$ for layers prepared at $T_{sub} = 623$ K. In contrast, the $Pb_{1-y}Ga_yTe$ films deposited on Si substrates with SiO_2 intermediate buffer layers under the same experimental conditions, reveal clearly defined PbTe (211), (222), and (311) reflections in addition to (*h*00) peaks (Fig. 1b). It is to note that the intensity of these (*hkl*) lines is not significant. For example, the I_{200} to I_{211} ratio is always more than 400. Thus, it is clear that the presence of SiO_2 buffer layers on Si substrates brings the polycrystalline structure to the $Pb_{1-y}Ga_yTe$ films at $y < 0.011 \pm 0.0002$ ($T_{sub} = 623$ K). This fact is in agreement with the results reported before for undoped PbTe films on Si and SiO_2/Si substrates [11].

It is important to keep in mind that concentration of Te atoms is the key condition for the homogeneity of $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ films for $y < 0.011$ ($T_{sub} = 623$ K). The investigated PbTe⟨Ga⟩ samples with Te concentration over 0.5012 were heterogeneous. X-ray reflections of this group of $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ films exhibit the presence of slight excess of tellurium phase.

As can be seen in Fig. 1, the second group of prepared samples is formed of heterogene-

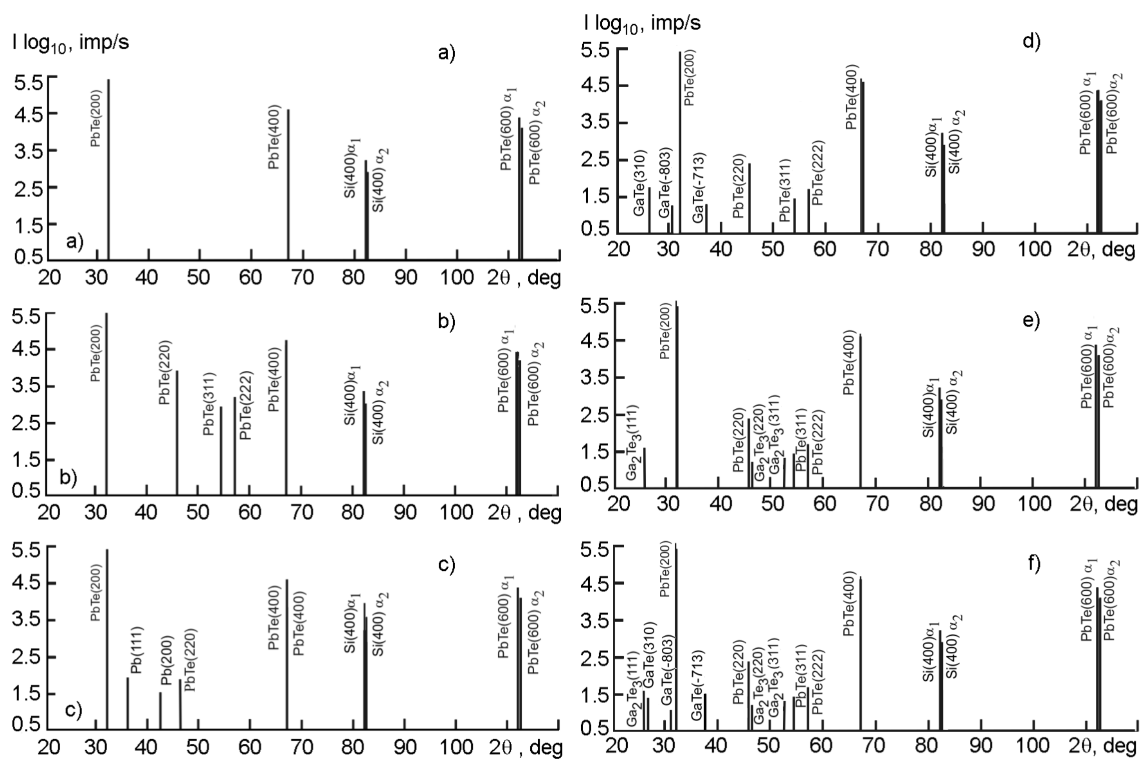


Fig. 1. a — $y_{Ga} < 0.011$, Si substrate; b — $y_{Ga} < 0.011$, SiO_2/Si substrate; c — $y_{Ga} < 0.011$, heterogeneous mixture PbTe + Pb; d — $y_{Ga} > 0.011$, Si substrate (mixture of PbTe⟨Ga⟩ + GaTe); e — $y_{Ga} > 0.011$; Si substrate (mixture of PbTe⟨Ga⟩ + Ga_2Te_3); f — $y_{Ga} > 0.011$; Si substrate (mixture of PbTe⟨Ga⟩ + GaTe + Ga_2Te_3).

ous $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si layers. At higher Ga contents $y > 0.013$–0.014 ($T_{sub} = 623$ K) or $y > 0.017$–0.018 ($T_{sub} = 653$ K), the crystal structures of $Pb_{1-y}Ga_yTe$ films are defined as polycrystalline and heterogeneous without regard to the substrate nature. These heterogeneous $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si samples, in their turn, can be divided into two subgroups (Fig. 1c–1e). The first subgroup of these two-phase samples is characterized by the presence of the little amount of monoclinic gallium monotelluride GaTe (space group $C2/m$ or $B2/m$) (Fig. 1d). To the same subgroup of samples should be gathered the two-phase $Pb_{1-y}Ga_yTe$ layers which are characterized by little excess of the main components of $Pb_{1-y}Ga_yTe$ films, lead (Fig. 1c) and tellurium. The XRD patterns of these films show the weak reflexes of tellurium, from one hand, or lead (Fig. 1c), from the other one. In addition, to this subgroup of two-phase films it is necessary to attribute the $Pb_{1-y}Ga_yTe$ samples consisting of two substances: the lead telluride and gallium telluride Ga_2Te_3 (Fig. 1e) with cubic crystal structure (space group $F\bar{4}3m$).

The second subgroup of the fabricated samples is formed by the three-phase heterogeneous $Pb_{1-y}Ga_yTe$ films. X-ray spectra of these samples consist of PbTe, monoclinic GaTe, and cubic Ga_2Te_3 reflections (Fig. 1f).

The comparison of experimental data on the phase nature of the synthesized $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si films with the results of real microstructure analysis by SEM are shown in Fig. 2.

The results of the precise determination of unit cell parameter $a_{PbTe\langle Ga\rangle}$ values of $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si are plotted in Fig. 3. It is to note that during XRD investigations, we have studied over one hundred $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si films prepared at substrate temperatures $T_{sub} = 583$ K and 623 ± 3 K by modified HWE technique. These experimental results provide observation of the variation in the unit cell parameter $a_{PbTe\langle Ga\rangle}$ in $Pb_{1-y}Ga_yTe$ films on Si and SiO_2/Si substrates. The values of unit cell parameter of $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si layers have been found to be the same within the accuracy of XRD experiments, when these layers have been prepared under the identical growth con-

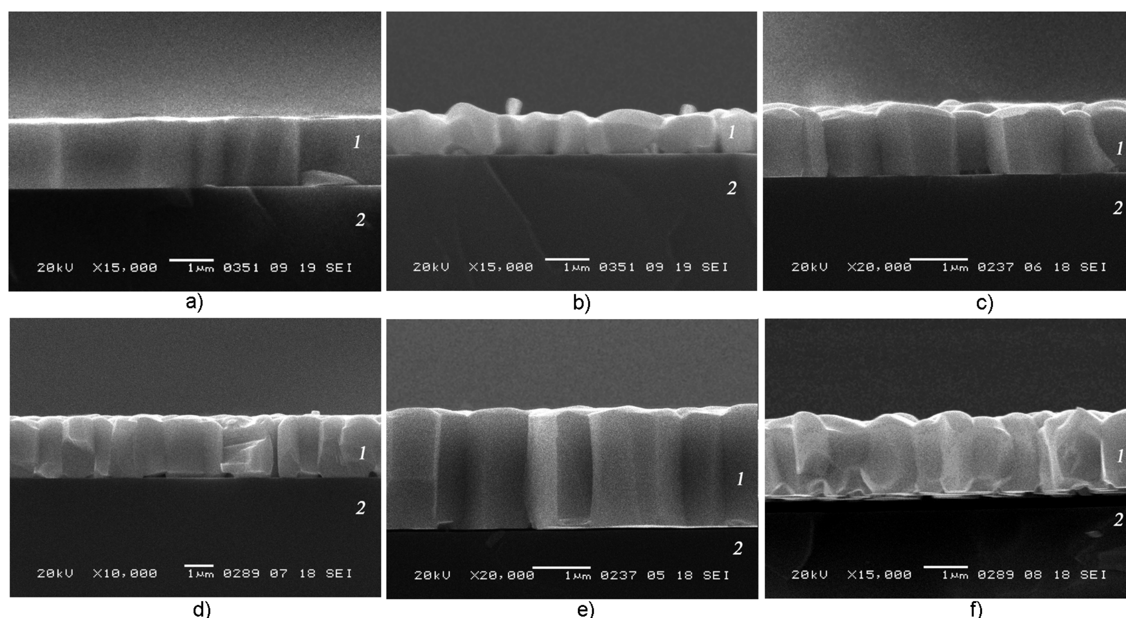


Fig. 2. The micrographs of the cross sections of the $Pb_{1-y}Ga_yTe$/Si heterostructures: *a* — $y_{Ga} < 0.011$, homogeneous mosaic single crystal film, *b* — $y_{Ga} < 0.011$, heterogeneous polycrystalline film (mixture of PbTe⟨Ga⟩ + Pb); *c* — $y_{Ga} < 0.011$, heterogeneous polycrystalline film (mixture of PbTe⟨Ga⟩ + GaTe + Te); *d* — $y_{Ga} > 0.011$, heterogeneous polycrystalline film (mixture of PbTe⟨Ga⟩ + GaTe); *e* — $y_{Ga} > 0.011$; heterogeneous polycrystalline film (mixture of PbTe⟨Ga⟩ + Ga_2Te_3); *f* — $y_{Ga} > 0.011$; heterogeneous polycrystalline film (mixture of PbTe⟨Ga⟩ + GaTe + Ga_2Te_3). *1* — Si substrate; *2* — $Pb_{1-y}Ga_yTe$ film.

ditions. It is evident that the presence of SiO_2 intermediate layers on Si substrates does no effect the lattice parameter values of the $Pb_{1-y}Ga_yTe$ films at the thickness over 1 μm.

These experimental data allow us to observe the evolution of the unit cell parameter $a_{PbTe\langle Ga\rangle}$ values with the concentration of Ga impurity atoms y in $Pb_{1-y}Ga_yTe$/Si and $Pb_{1-y}Ga_yTe/SiO_2$/Si films.

As it can be seen in Fig. 3, the curve $a_{PbTe\langle Ga\rangle} = f(y_{Ga})$ is a nonmonotonic function and does not obey the Vegard's law. It can be divided into three sections. The first section exhibits a decrease in $a_{PbTe\langle Ga\rangle}$ values within the concentration range $0 < y < 0.0037$. At $y = 0.0037 \pm 0.0002$, the minimum value of $a_{PbTe\langle Ga\rangle}$ is observed. The second section of this dependence shows the increase in the unit cell parameter $a_{PbTe\langle Ga\rangle}$ values within the concentration range of about $0.0037 < y < 0.010$. It is to note that increase in the $a_{PbTe\langle Ga\rangle}$ values did not reported before at the analysis of Ga-doped lead telluride bulk crystals. On the third fragment of $a_{PbTe\langle Ga\rangle} = f(y_{Ga})$ curve, at the concentration of Ga impurity atoms $y > 0.011$, the values of lattice parameter do not vary essentially within accuracy limits of the XRD experiment. Because the unit cell parameter values are fixed essentially at $y > 0.01$, this concentration may be interpreted as the solubility limit of Ga atoms in PbTe at $T = 623 \pm 3$ K. It is necessary to emphasise that experimental data obtained in this work show that the extension of the region of Ga solid solutions in PbTe matrix is narrower than it had been reported before for bulk PbTe⟨Ga⟩ alloys [12].

As the atomic and cationic radii of Ga are smaller than those of Pb, it is possible to make following conclusions from the given view of $a_{PbTe\langle Ga\rangle} = f(y_{Ga})$ relations if synthesizing and doping of films take place simultaneously:

1. The initial fragment of the curve introduced in Fig. 3 corresponding to decreasing of the lattice constant, it is possible to esteem as an indication of the preferential formation of substitutional solid solutions. Thus, according to the theory of self-compensation, the decreasing of identity period can be promoted by formation of Te vacancies;

2. The intermediate section of $a_{PbTe\langle Ga\rangle} = f(y_{Ga})$ relation it is possible to explain by changing in the dominating mechanism of solid solution formation: the one part of Ga atoms, as before, is placed in regular sites of the cationic sublattice, while other part is placed in tetrahedral interstices. As the sizes of interstitial tetrahedral voids in

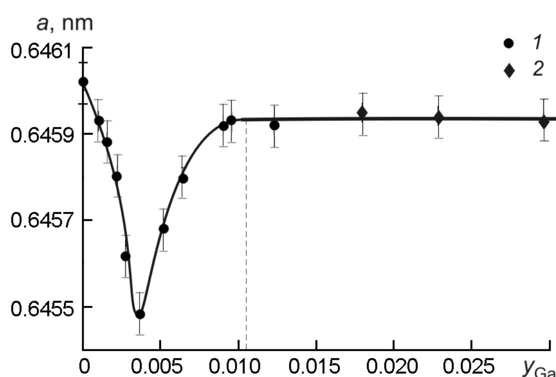


Fig. 3. Dependences of the lattice parameter a_{PbTe} on the Ga atoms impurity concentration y_{Ga} in ternary $Pb_{1-y}Ga_yTe$ films prepared at T_{sub} = 623±3 K: *1* — homogeneous samples; *2* — heterogeneous polycrystalline samples.

PbTe crystal structure are a little bit smaller than ionic radii of metals of III A group, their occupation them with Ga results in increase in unit cell parameter. Therefore, at this range of Ga impurity atoms concentration, the mixed type of solid solutions "substitution — interstitial" is realized. The existence of such solid solutions is established before, in particular, in the silicon-gold and silicon-carbon systems [13];

3. The analysis of the third part of $a_{PbTe\langle Ga\rangle} = f(y_{Ga})$ curve shows that the increase in the concentration of Ga impurity atoms $y_{Ga} > 0.011$ in $Pb_{1-y}Ga_yTe_{1+\delta}$ films does not result in the enlargement of the unit cell parameter values. This fact is to estimate as an approach to the solubility limit of Ga in the initial matrix of PbTe.

The correlation between XRD results and the quantitative chemical composition of deposited $Pb_{1-y}Ga_yTe/Si$ and $Pb_{1-y}Ga_yTe/SiO_2/Si$ films is presented in Fig. 4. The boundary of limited gallium solubility region in lead telluride matrix has been drawn based on the microstructural observations, XRD and EPMA results. The Pb–Ga–Te phase diagram (Fig. 4a) provides an useful framework for understanding of solid-state interaction in this system. From the representation on a Gibbs composition triangle, it is clear that the analysis of the PbTe–GaTe quasibinary cross section only does not exhaust the process of galliums solubility in PbTe matrix as a whole. As it can be seen in Fig. 4, the Ga solubility region in PbTe matrix is asymmetric regarding to the PbTe–GaTe quasibinary cross section. The formation of Ga solid solutions is to be revealed in $PbTe–Ga_2Te_3$ pseudobinary system also.

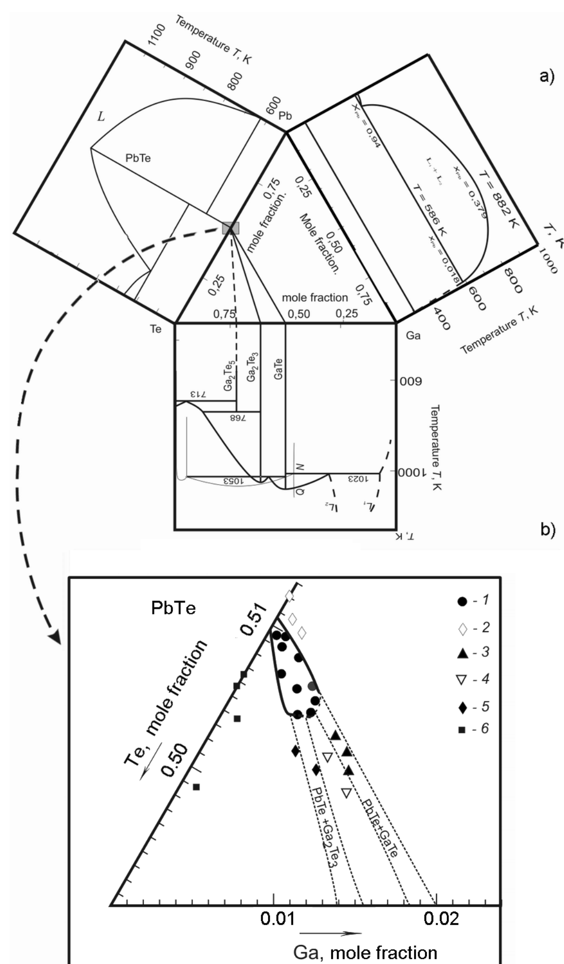
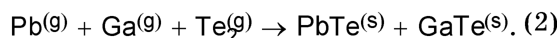


Fig. 4a. The binary phase diagrams and Gibbs composition triangle of Pb–Ga–Te ternary system. Fig. 4b. The isothermal cross section through the phase microdiagram of Pb–Ga–Te ternary system at T = 623±3 K: *1* — homogeneous $Pb_{1-y}Ga_{yTe}$ films; *2* — heterogeneous $Pb_{1-y}Ga_yTe$ films (PbTe⟨Ga⟩ + Pb); *3* — heterogeneous $Pb_{1-y}Ga_yTe$ films (PbTe⟨Ga⟩ + GaTe); *4* — heterogeneous $Pb_{1-y}Ga_yTe$ films (PbTe⟨Ga⟩ + GaTe + Ga_2Te_3); *5* — heterogeneous $Pb_{1-y}Ga_yTe$ films (PbTe⟨Ga⟩ + Ga_2Te_3); *6* — heterogeneous $Pb_{1-y}Ga_yTe$ films (PbTe⟨Ga⟩ + Te).

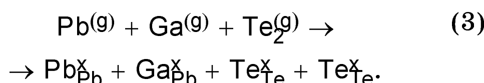
In view of the fact that all $Pb_{1-y}Ga_yTe$ films were deposited at approximately constant values of Te_2 partial pressure, it is possible to say that Fig. 4b represents the isothermal and isobaric p_{Te_2}-sections of Pb–Ga–Te phase microdiagram. A closer look to Fig. 4 allows us to assume that at fixed temperature, boundaries of homogeneity region and phase constitution of PbTe⟨Ga⟩ films depend upon the two main factors: the ratio between Ga and Pb concentrations from the one hand, and content

of Te atoms, from the other one. During the formation of the PbTe⟨Ga⟩ layers from the vapour phase, the heterogeneous chemical reactions can be expressed through the following schemes:



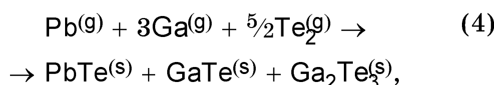
$$Pb^{(g)} + Ga^{(g)} + Te_2^{(g)} \rightarrow PbTe^{(s)} + GaTe^{(s)}. \quad (2)$$

Within the frameworks of the quasi-chemical method [14] this reaction may be written:

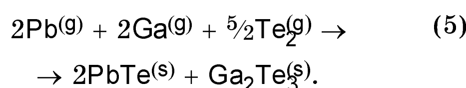


$$Pb^{(g)} + Ga^{(g)} + Te_2^{(g)} \rightarrow \rightarrow Pb_{Pb}^{x} + Ga_{Pb}^{x} + Te_{Te}^{x} + Te_{Te}^{x}. \quad (3)$$

It is to note that Eq.(2) and Eq.(3) satisfy the preparation process of PbTe⟨Ga⟩ films with stoichiometric ratio of metal components and Te atoms only and correspond the formation of Ga solid solutions along PbTe–GaTe pseudobinary section. If tellurium partial pressure goes beyond the stoichiometric ratio, the following reactions occurs:

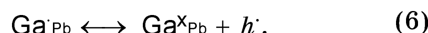


$$Pb^{(g)} + 3Ga^{(g)} + 5/2Te_2^{(g)} \rightarrow \rightarrow PbTe^{(s)} + GaTe^{(s)} + Ga_2Te_3^{(s)}, \quad (4)$$



$$2Pb^{(g)} + 2Ga^{(g)} + 5/2Te_2^{(g)} \rightarrow \rightarrow 2PbTe^{(s)} + Ga_2Te_3^{(s)}. \quad (5)$$

Thus, Ga^{3+} ions may exist together with lead vacancies V_{Pb}^{x} within the region of nonstoichiometry outside PbTe–GaTe pseudobinary section (Fig. 4b). These Ga^{3+} ions have surplus positive charge relative to Pb_{Pb}^{x} atoms in regular positions and may affect the charge carrier density in PbTe:



$$Ga_{Pb}^{\cdot} \longleftrightarrow Ga_{Pb}^{x} + h^{\cdot}. \quad (6)$$

As it was established before [3], the influence of Ga impurity atoms on the energy spectrum of PbTe shows the dependence upon its concentration and, in general, can be classified as ambiguous. The summary of the experimental data obtained in this work allows us to assume that amphoteric (donor and acceptor) character of Ga impurity atoms is connected with its different values of oxidation number (+1) or (+3) as well as its different position ($Ga_{Pb}^{\cdot}$ and $Ga_i^{\cdot\cdot\cdot}$) in PbTe crystal matrix also.

4. Conclusions

The boundary of Ga limited solubility region in PbTe matrix has been drawn based on the microstructural observations, XRD and EPMA results. From the representation on a Gibbs composition triangle, it is clear that the analysis of the PbTe–GaTe pseudobinary cross section only does not exhaust the process of Ga solubility in PbTe matrix as a whole. The formation of Ga solid solutions is to be considered in $PbTe–Ga_2Te_3$ pseudobinary system also. It is necessary to assume that at fixed temperatures, boundaries of homogeneity region and phase constitution of PbTe⟨Ga⟩ films depend upon the two main factors: the ratio between Ga and Pb concentration and content of Te atoms. In the case when Te_2 partial pressure goes beyond the stoichiometric ratio, the formation of Ga^{3+} ions with oxidation number (+3) is possible. Summarizing of the experimental data obtained in this work allows us to assume that amphoteric (donor and acceptor) character of Ga impurity atoms is connected with its different values of oxidation number (+1) or (+3) as well as its different position in PbTe crystal matrix also.

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Розчинність Ga у плівках PbTe, вирощених на кремнієвих підкладках за допомогою модифікованого методу "гарячої стінки"

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Досліджено межі області існування твердих розчинів Ga у плівках PbTe, синтезованих методом "гарячої стінки" на Si підкладках. Вивчено кількісний склад плівок $Pb_{1-y}Ga_yTe$ (товщиною понад 1 мкм) в залежності від парціальних тисків металічних компонентів і халькогену. Застосовано рентгенографічні дослідження, РЕМ та метод ЛРСА гомогенних плівок $Pb_{1-y}Ga_yTe$. Показано, що область гомогенності твердих розчинів галію у телуриді свинцю має асиметричну форму відносно квазібінарного розрізу PbTe–GaTe. Встановлено, що збільшення відхилення від стехіометрії плівок $Pb_{1-y}Ga_yTe$ у бік надлишкового вмісту телуру сприяє підвищенню розчинності галію у матриці телуриду свинцю.