ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 10, pp. 2242–2251. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.M. Samoilov, S.V. Belenko, M.K. Sharov, S.I. Lopatin, Yu.V. Synorov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 10, pp. 1609–1619.

Synthesis of Films in the System Ga–Pb with Precision Control over Quantitative Composition

A. M. Samoilov[a], S. V. Belenko[a], M. K. Sharov[a], S. I. Lopatin[b], and Yu. V. Synorov[c]

[a] *Voronezh State University, Voronezh, Russia*

[b] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg , 198504 Russia*
e-mail: sergeylopatin2009@yandex.ru

[c] *Voronezh State University of Engineering Technologies, Voronezh, Russia*

Received March 17, 2015

Abstract—According to high-temperature differential mass spectrometry, analytical form of the dependence of structure of the saturated vapor composition over melts of the system Ga–Pb on partial pressures of components and total pressure in the system was determined. On the basis of this dependence, taking into account corrections for the deviations from thermodynamic equilibrium conditions in the reaction cell, the scientifically-proved method of the synthesis of Ga_yPb_{1-y} (y = 0.002–0.050) films with precision control over their quantitative composition structure was developed.

Keywords: system gallium-lead, lead telluride, epitaxy from a gas phase, infra-red optoelectronics, thermodynamic equilibrium

DOI: 10.1134/S1070363215100059

It is expedient to use Ga_yPb_{1-y} (y = 0.002–0.050) films as precursors for the synthesis of nano- and heterostructures based on lead telluride alloyed by gallium, which is traditionally considered as a material for making optoelectronic devices working in the IR spectral region [1–3]. The interest to studying lead telluride and solid solutions on its basis has accelerated in the last few years, as photoconductivity in the THz-band of electromagnetic radiation was detected [4].

The presence of admixed atoms of metals with variable valence, including gallium, in the lead telluride crystal lattice leads to reorganization of the energy spectrum of the initial material, which ensures its functional properties. The production of opto-electronic devices based on PbTe alloyed by gallium, which operate in THz and IR spectral regions would be ready for commercial production, if it will be possible to solve some problems. In particular, it is necessary to establish conclusively the reason of amphoteric behavior of gallium atoms in lead telluride, which can form both donor and acceptor admixture levels [5, 6]. In [6, 7] the facts are presented, which show that the manifestation of donor or acceptor properties by dopant Ga atoms depends not only on the alloying method, but also on the degree of deviation from the stoichiometric ratio of the components forming cation and anion sublattices. According to the *P–T–x* diagram of the lead-tellurium system [8], it is possible to control in various ways the degree of deviation of the chalcogen fraction δ from stoichiometric ratio for the $Pb_{1-y}Ga_yTe_{1\pm\delta}$ single crystals and films alloyed by gallium. For example, by annealing in tellurium vapor at various pressure of this component it is possible to obtain $Pb_{1-y}Ga_yTe_{1\pm\delta}$ samples characterized by both a chalcogen deficit and its excess in relation to the stoichiometric ratio. If Ga_yPb_{1-y} films (y = 0.002–0.050) are alloyed in isothermal conditions at various pressures of tellurium vapor, it is possible to synthesize $Pb_{1-y}Ga_yTe_{1\pm\delta}$ samples alloyed by gallium, which will be characterized by various deviations from the stoichiometric ratio δ of anion sublattice at the fixed concentration of dopant gallium atoms. Results of studying the phase nature, electric properties, and photoconductivity of $Pb_{1-y}Ga_yTe_{1\pm\delta}$ films will make it possible to solve several fundamental problems: to establish as precisely as possible the borders of homogeneity area of solid $Pb_{1-y}Ga_yTe_{1\pm\delta}$ solutions at

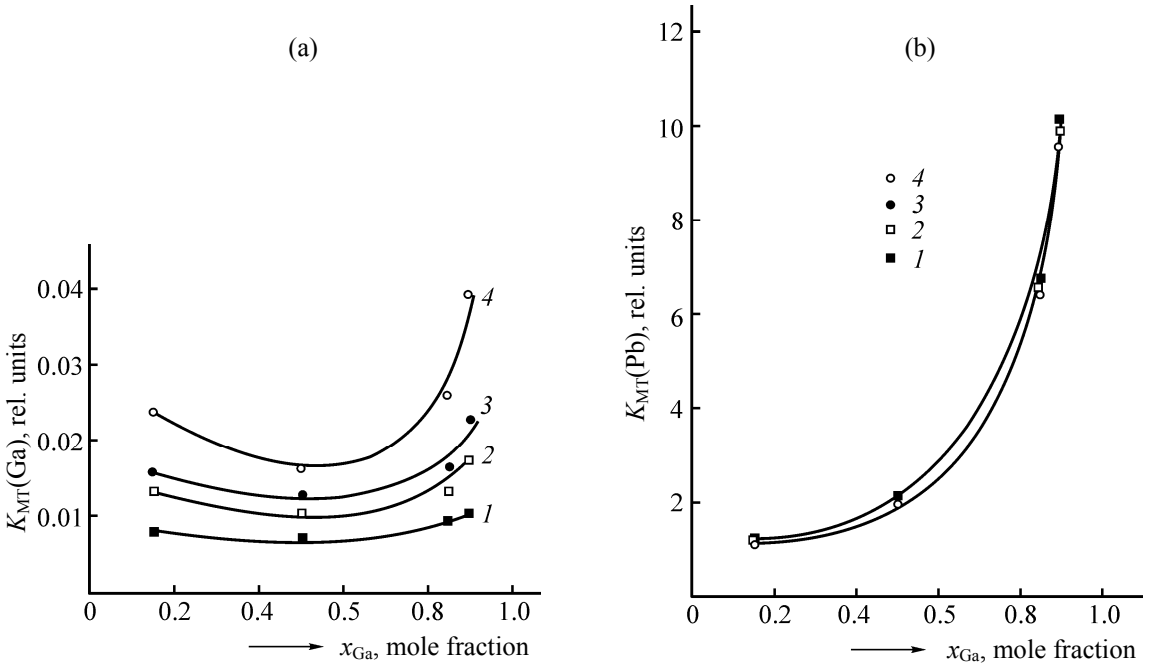

Fig. 1. Dependence of mass-transfer coefficients of (a) gallium K_{MT}(Ga) and (b) lead K_{MT}(Pb) on the composition of initial Ga_xPb_{1-x} melts at the synthesis of films Ga_yPb_{1-y} by the "hot wall" method: (*1*) 1023, (*2*) 1103, (*3*) 1153, and (*4*) 1300 K.

various temperatures; to determine the character of the dependence of donor or acceptor activity of gallium dopant atoms in the $Pb_{1-y}Ga_yTe_{1\pm\delta}$ films on the degree of deviation from stoichiometry in the anion sublattice; to establish the character of changing conductivity type in the $Pb_{1-y}Ga_yTe_{1\pm\delta}$ films depending on the concentration of dopant Ga atoms and the degree of the deviation from stoichiometry in the anion sublattice.

All these facts show the urgency of creating methods for obtaining Ga_yPb_{1-y} films with preset quantitative composition, which will be used in further researches as precursors for the synthesis of $Pb_{1-y}Ga_yTe_{1\pm\delta}$.

The basic principles of the formation of Ga_yPb_{1-y} films with a specified composition by the "hot wall" method with due accounting for the results of previous experiments have been developed in the present work in several steps. The data of [9] demonstrated that quantitative compositions of the initial Ga–Pb melt and the sample obtained upon condensation of vapor over this melt differed from each other. It was assumed in [9] that the formation of Ga_yPb_{1-y} layers by means of evaporation of the gallium–lead system melts in a vacuum occurred in thermodynamically nonequilibrium conditions. The graphic interpretation of the experimental data [9] on the growth of Ga_yPb_{1-y} films by the "hot wall" method is presented in Figs. 1a and 1b, curves *1,* in the form of the dependences of mass-transfer coefficients K_{MT}(Ga) and K_{MT}(Pb) on the initial melt composition on the silicon substrate and on the its temperature at the constant substrate temperature of 420 K.

$$K_{MT}(Ga) = y^F_{Ga}/x_{Ga};\ K_{MT}(Pb) = (1 - y^F_{Ga})/(1 - x_{Ga}). \quad (1)$$

Here y^F_{Ga} is the gallium mole fraction in the growing film; x_{Ga} is the gallium mole fraction in the initial Ga_xPb_{1-x} melt.

Changes in gallium and lead mass-transfer coefficients while growing Ga_yPb_{1-y} films by the "hot wall" method are characterized by a number of contradiction. For example, for the whole studied range of temperatures and compositions of Ga–Pb melts $K_{MT}(Ga) < 1$, whereas $K_{MT}(Pb) > 1$.

The mass-transfer coefficient of lead K_{MT}(Pb) monotonically increases as the gallium fraction in Ga–Pb melts increases, whereas K_{MT}(Ga) values change nonmonotonically and have a minimum point at x_{Ga} = 0.5. At a constant composition of the Ga–Pb melt K_{MT}(Ga) increases as temperature increases, whereas K_{MT}(Pb) slightly decreases.

In the next stage we made the attempt to find out why the gallium fraction y^F_{Ga} in Ga_yPb_{1-y} condensates exceeded the fraction of this component in the vapor phase (x^0_{Ga}) calculated on the assumption that the

Raoult's law is obeyed for the gallium–lead system. In [10] the dependences of quantitative composition of saturated vapor over melts of the gallium–lead system on the condensed phase composition and temperature in the region above coordinates of a critical point on the phase diagram [11] has been studied by the high-temperature mass spectrometry method.

The derivation of the equations of temperature dependence of partial pressures of components in the vapor over melt of the gallium–lead system should be regarded as the most important result of [10]. Aside from that, the character of the dependence of the gallium fraction in vapor over melts of the gallium–lead system on its quantitative composition in the temperature range of 980–1153 K has been established. It was found in [10, 11] that the gallium–lead system is characterized by essential positive deviations from ideal behavior in the temperature range of 980–1153 K, and the fraction of less volatile gallium in saturated vapor over Ga_xPb_{1-x} (x^V_{Ga}) melts considerably exceeds the value calculated on the basis of the ideal solution model.

In the present work we have studied the reasons influencing the degree of the deviation from equilibrium conditions during growing Ga_yPb_{1-y} films by the modified "hot wall" method, and have analyzed possible factors capable of affecting the degree of deviation of actual conditions of the Ga_yPb_{1-y} films synthesis from the thermodynamic equilibrium conditions. In the course of the synthesis of Ga_yPb_{1-y} films by the "hot wall" method partial pressures of the components, and hence the total pressure in the reaction cell, change largely depending on the composition of the Ga–Pb system initial melt and its temperature. Temperature dependences of the total pressure of saturated vapor (curves *1–5*) and of the atomic gallium partial pressure (curves *6–10*) over melts of the Ga–Pb system are presented in Fig. 2. In the temperature range of 950–1300 K the total equilibrium vapor pressure over the Ga–Pb system melts containing 0.70–0.97 mole fraction of gallium sharply decreases, whereas the gallium partial pressure slightly increases. It gives the chance to vary gallium quantity in Ga_yPb_{1-y} films in rather wide limits by variation of the ratio of gallium and lead partial pressures p_{Ga}/p_{Pb} in the saturated vapor over initial melts of the Ga–Pb system. Gallium concentration in the Ga_yPb_{1-y} films can be set and regulated by not only variation of the composition of Ga–Pb system melts, but also by temperature variation. Thus, there are two possibilities of changing gallium and lead partial pressures, which ensures more exact and reliable control over the composition of forming Ga_yPb_{1-y} films.

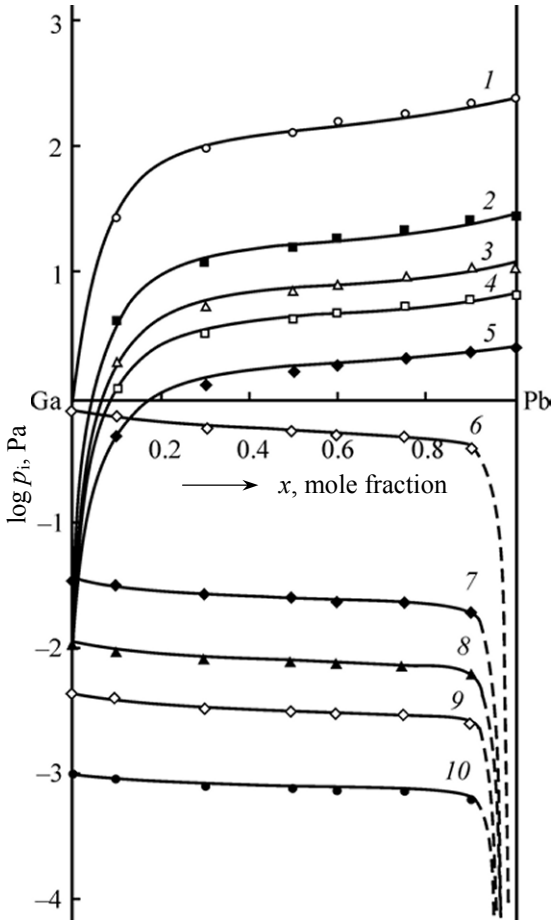

Fig. 2. Temperature dependences of saturated vapor (*1–5*) total pressure and (*6–10*) Ga partial pressure over the Ga–Pb system: (*1*), (*6*) 1300; (*2*), (*7*) 1153; (*3*), (*8*) 1103; (*4*), (*9*) 1073; (*5*), (*10*) 950 K.

In the present work we have studied with great care the influence of partial pressure of vapor molecular forms on the degree of deviation from thermodynamic equilibrium conditions and also on the changes in the character of the mass transfer in the reaction cell in the course of the synthesis of Ga_yPb_{1-y} films.

Using the data of [10], we have calculated the quantitative composition of the equilibrium vapor phase over Ga–Pb melts depending on partial pressures of molecular forms of vapor components and on the total pressure in the system. The calculations allowed us to deduce the equation of the surface describing the dependence of the gallium fraction (x^V_{Ga}) in the equilibrium vapor phase over melts of the Ga–Pb system on the gallium partial pressure (p_{Ga}) and the

Table 1. Coefficients a_1, b_1, and c_1 in Eq. (3) in the temperature range of 900–1300 K

T, K	$a_1 \pm \Delta a_1$	$b_1 \pm \Delta b_1$	$c_1 \pm \Delta c_1$	R	R_{sqr}
1023 ± 3	$-3.317 \times 10^{-3} \pm 6.479 \times 10^{-4}$	$5.183 \pm 8.280 \times 10^{-1}$	$-8.842 \times 10^{2} \pm 1.273 \times 10^{1}$	0.9987	0.9974
1103 ± 3	$-1.512 \times 10^{-3} \pm 1.554 \times 10^{-4}$	$3.836 \times 10^{-1} \pm 2.099 \times 10^{-2}$	$-9.598 \times 10^{1} \pm 2.153$	0.9923	0.9846
1153 ± 3	$-2.158 \times 10^{-4} \pm 1.750 \times 10^{-5}$	$7.004 \times 10^{-2} \pm 6.602 \times 10^{-3}$	$-2.831 \times 10^{1} \pm 4.481 \times 10^{-1}$	0.9917	0.9835
1300 ± 3	$-2.791 \times 10^{-5} \pm 2.159 \times 10^{-6}$	$4.385 \times 10^{-3} \pm 3.501 \times 10^{-4}$	$-1.248 \pm 1.215 \times 10^{-2}$	0.9948	0.9897

Table 2. Coefficients a_2, b_2, and c_2 in Eq. (4) in the temperature range of 900–1300 K

T, K	$a_2 \pm \Delta a_2$	$b_2 \pm \Delta b_2$	$c_2 \pm \Delta c_2$	R	R_{sqr}
1023 ± 3	$1.927 \times 10^{-2} \pm 3.784 \times 10^{-4}$	$-6.864 \times 10^{-3} \pm 2.021 \times 10^{-4}$	$9.124 \times 10^{-1} \pm 8.591 \times 10^{-2}$	0.9995	0.9989
1103 ± 3	$3.938 \times 10^{-2} \pm 3.339 \times 10^{-3}$	$-1.941 \times 10^{-3} \pm 3.746 \times 10^{-4}$	$5.851 \times 10^{-1} \pm 1.349 \times 10^{-2}$	0.9969	0.9937
1153 ± 3	$6.900 \times 10^{-2} \pm 6.489 \times 10^{-3}$	$-1.073 \times 10^{-3} \pm 2.795 \times 10^{-4}$	$4.732 \times 10^{-1} \pm 9.239 \times 10^{-2}$	0.9983	0.9966
1300 ± 3	$6.336 \times 10^{6} \pm 3.563 \times 10^{-19}$	$-8.192 \times 10^{3} \pm 5.245 \times 10^{-16}$	$5.369 \times 10^{6} \pm 4.626 \times 10^{-19}$	0.9976	0.9953

total pressure (p_{int}) in the temperature range of 1000–1153 K in the form of Taylor expansion (2).

$$x^{V}_{Ga}(p_{Ga}, p_{int}) = 0.0031202 + 2.21793p_{Ga} - 202.574p^2_{Ga} + 11606.8p^3_{Ga} - 199742p^4_{Ga} - 0.00343765p_{int} - 0.232843p_{Ga}p_{int} + 0.241037p^2_{Ga}p_{int} + 0.00070126p^2_{int} + 0.0108855p_{Ga}p^2_{int} - 0.0000470359p^3_{int} + 8.43574 \times 10^{-7}p^4_{int}. \quad (2)$$

The separation of variables in Eq. (2) allowed us to determine the analytical form of the dependence of gallium fraction in the equilibrium vapor phase on the partial gallium pressure $x^{V}_{Ga} = f(p_{Ga})$ and on the total pressure in the system $x^{V}_{Ga} = f(p_{int})$. These dependences represent monotonous smooth curves and can be described by Eqs. (3) and (4), respectively.

$$x^{V}_{Ga}(p_{Ga}) = a_1 + b_1\exp(c_1p_{Ga}), \quad (3)$$

$$x^{V}_{Ga}(p_{int}) = a_2 + b_2\exp(-c_2p_{int}), \quad (4)$$

Coefficients a_1, b_1, and c_1 in Eq. (3) and also coefficients a_2, b_2, and c_2 in Eq. (4) are given in Tables 1 and 2, respectively.

Calculated compositions of saturated vapor x^{V}_{Ga} are presented in Fig. 3 in the form of the dependence $x^{V}_{Ga} = f(\log p_{Ga}, \log p_{int})$ for the temperature range of 1000–1300 K. Application of logarithmic coordinates is dictated by the necessity to present the obtained results in the compact form on a graph, as the total pressure of saturated vapor in the temperature range of 1000–1300 K over the melts varies within a wide range (from 0.2 up to 240.2 Pa).

As it is seen from Fig. 3a, the increase in temperature up to 1300 K is accompanied by the increase in gallium concentration in saturated vapor up to 0.047 mole fraction.

Thus, in the present work the dependence of quantitative composition of the equilibrium vapor phase over binary melts of the Ga–Pb system was determined in the analytical and graphic forms for the first time. These data are necessary for the subsequent studying and simulating processes occurring in the reaction cell of the modified "hot wall" method during the synthesis of Ga_yPb_{1-y} films.

We have analyzed possible reasons of the deviation from equilibrium thermodynamic conditions in the reaction cell in the course of the synthesis of the binary Ga_yPb_{1-y} layers by the modified "hot wall" method. For this purpose we have synthesized 48 Ga_yPb_{1-y} films of various compositions on single crystal silicon substrates by means of the above method. The optimal choice of synthesis conditions is based on the analysis of the $x^{V}_{Ga} = f(\log p_{Ga})$ and $x^{V}_{Ga} = f(\log p_{int})$ isotherms presented in Fig. 3. Compositions of the initial melts of the Ga–Pb systems, partial pressures of vapor components, and also p_{Ga}/p_{Pb} and p_{Ga}/p_{int} ratios were determined by simultaneous solution of Eqs. (2)–(4). Further study was carried out on the samples $Ga_{0.15}Pb_{0.85}$, $Ga_{0.25}Pb_{0.75}$, $Ga_{0.35}Pb_{0.65}$, $Ga_{0.50}Pb_{0.50}$, $Ga_{0.70}Pb_{0.30}$, $Ga_{0.85}Pb_{0.15}$, $Ga_{0.90}Pb_{0.10}$, and $Ga_{0.95}Pb_{0.05}$. According to preliminary estimates, evaporation of the Ga–Pb system samples in the temperature range of 1023–1300 K ensures such ratio of gallium and lead in the vapor phase that its condensation on silicon substrates makes possible the formation of Ga_yPb_{1-y} films, in which the value of y can vary within the range of 0.001–0.04 mole fractions.

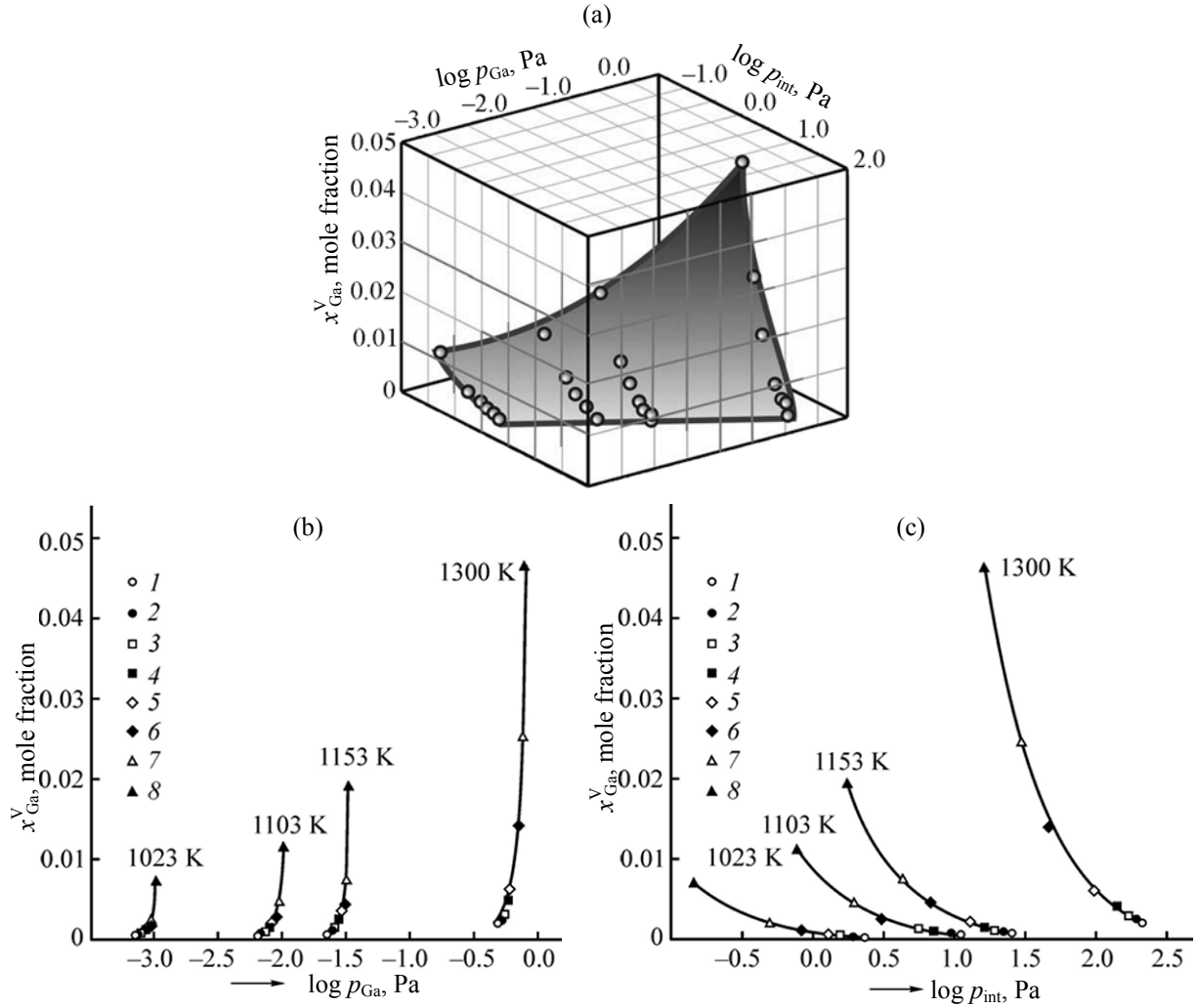

Fig. 3. The dependence of gallium fraction in saturated vapor over Ga_xPb_{1-x} melts on (a) the values of logarithms of gallium partial pressure log p_{Ga} and of total pressure log p_{int} of all components in the temperature range of 1023–1300 K; the dependences (b) x^V_{Ga}– log p_{Ga} and (c) x^V_{Ga}–log p_{int}. (*1*) $Ga_{0.15}Pb_{0.85}$, (*2*) $Ga_{0.25}Pb_{0.75}$, (*3*) $Ga_{0.35}Pb_{0.65}$, (*4*) $Ga_{0.5}Pb_{0.5}$, (*5*) $Ga_{0.7}Pb_{0.3}$, (*6*) $Ga_{0.85}Pb_{0.15}$, (*7*) $Ga_{0.9}Pb_{0.1}$, and (*8*) $Ga_{0.95}Pb_{0.05}$.

Quantitative elemental composition of grown Ga_yPb_{1-y} films was determined by the local X-ray spectral microanalysis. The results are presented in Fig. 4.

The examination of dependences of synthesized films compositions on the logarithms of gallium partial pressure and total pressure in the reaction cell presented in Figs. 3 and 4 shows that the layers obtained by the "hot wall" method have a much higher gallium concentration than its equilibrium concentra-tion in the vapor phase over initial melts of the Ga–Pb system.

Mathematical processing of the obtained experimental data has allowed us to deduce analytical forms [Eqs. (5), (6)] of the dependences of gallium fraction in Ga_yPb_{1-y} condensates on the gallium partial pressure and total pressure over melts of the Ga–Pb system.

$$y(p_{Ga}) = (a_1 + b_1p_{Ga})/(1 + c_1p_{Ga}), \quad (5)$$

$$y(p_{int}) = (a_2 + b_2p_{int})/(1 + c_2p_{int}). \quad (6)$$

Coefficients a_1, b_1, and c_1 in Eq. (5), and also coefficients a_2, b_2, and c_2 in Eq. (6) are given in Tables 3 and 4, respectively.

The comparison between Eqs. (3), (4) describing the dependence of the gallium fraction x^V_{Ga} in saturated vapor over the Ga–Pb system melts and Eqs. (5), (6) describing the dependence of a gallium concentration

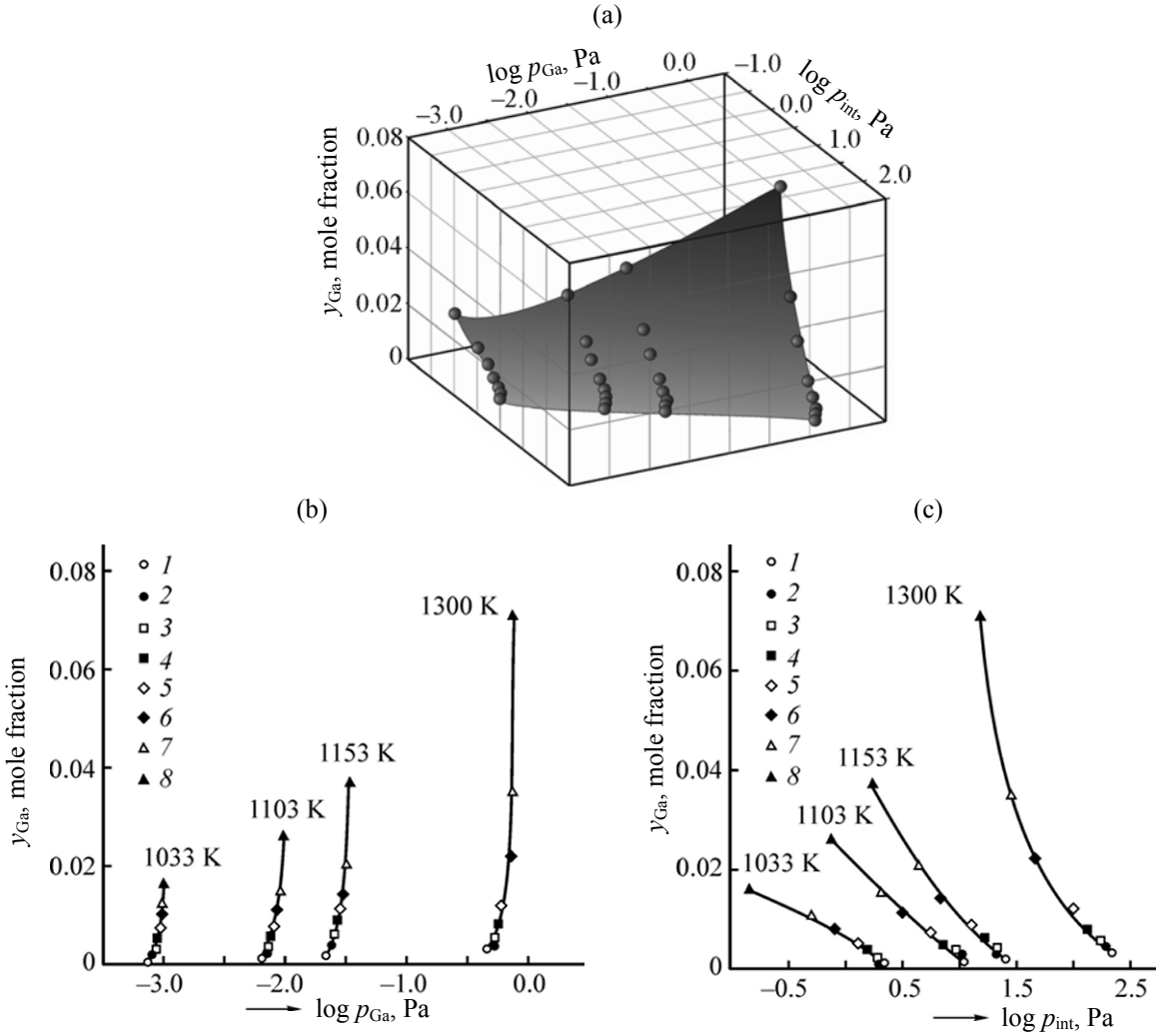

Fig. 4. Dependence of gallium fraction y_{Ga} in the synthesized Ga_yPb_{1-y} films on (a) the values of logarithms of gallium partial pressure log p_{Ga} and of total pressure log p_{int} over initial Ga_xPb_{1-x} melts; the dependences (b) log p_{Ga}–y_{Ga} and (c) log p_{int}–y_{Ga}. (*1*) $Ga_{0.15}Pb_{0.85}$, (*2*) $Ga_{0.25}Pb_{0.75}$, (*3*) $Ga_{0.35}Pb_{0.65}$, (*4*) $Ga_{0.5}Pb_{0.5}$, (*5*) $Ga_{0.7}Pb_{0.3}$, (*6*) $Ga_{0.85}Pb_{0.15}$, (*7*) $Ga_{0.9}Pb_{0.1}$, (*8*) $Ga_{0.95}Pb_{0.05}$.

in the synthesized Ga_yPb_{1-y} films on p_{Ga} and p_{int} values shows that these functions have different characters. It can be considered as the evidence that the synthesis of Ga_yPb_{1-y} films by the modified "hot wall" method occurs through the mass transfer in the conditions, which are distinct from the thermodynamic equilibrium conditions. To estimate the degree of such deviation from the thermodynamic equilibrium conditions, we have introduced a coefficient K [Eq. (7)].

$$K = y/x^{V}_{Ga}. \quad (7)$$

Here y is the mole fraction of gallium atoms in a Ga_yPb_{1-y} film.

The variation of K values for all grown up Ga_yPb_{1-y} films is shown in Fig. 5 against logarithms of Ga partial pressure and the total pressure over melts of Ga–Pb samples, which were used in the synthesis as precursors for the formation of Ga_yPb_{1-y} films. The examination of the obtained data shows that, depending on p_{Ga} and p_{int} values, coefficient K changes in rather wide limits (from 1.38 to 7.45). It is obvious that the deviation from the equilibrium state depends mainly on the ratio between p_{Ga} and p_{int}.

It is seen from Fig. 5a that the surface $K = f(\log p_{Ga})$, is not monotonous and has a bend in the form of a set of maximal points. The additional information is given by the analysis of projections of $K = f(\log p_{Ga})$ and $K = f(\log p_{int})$ presented in Figs. 5b and 5c.

Consideration of the data presented in these figures shows that:

Table 3. Coefficients a_1, b_1, and c_1 in Eq. (5) in the temperature range of 900–1300 K

T, K	$a_1 \pm \Delta a_1$	$b_1 \pm \Delta b_1$	$c_1 \pm \Delta c_1$	R	R_{sqr}
1023 ± 3	$-3.317 \times 10^{-3} \pm 6.479 \times 10^{-4}$	$5.183 \pm 8.280 \times 10^{-1}$	$-8.842 \times 10^{2} \pm 1.273 \times 10^{1}$	0.9987	0.9974
1103 ± 3	$-1.512 \times 10^{-3} \pm 1.554 \times 10^{-4}$	$3.836 \times 10^{-1} \pm 2.099 \times 10^{-2}$	$-9.598 \times 10^{1} \pm 2.153$	0.9923	0.9846
1153 ± 3	$-2.158 \times 10^{-4} \pm 1.750 \times 10^{-5}$	$7.004 \times 10^{-2} \pm 6.602 \times 10^{-3}$	$-2.831 \times 10^{1} \pm 4.481 \times 10^{-1}$	0.9917	0.9835
1300 ± 3	$-2.791 \times 10^{-5} \pm 2.159 \times 10^{-6}$	$4.385 \times 10^{-3} \pm 3.501 \times 10^{-4}$	$-1.248 \pm 1.215 \times 10^{-2}$	0.9948	0.9897

Table 4. Coefficients a_2, b_2, and c_2 in Eq. (6) in the temperature range of 900–1300 K

T, K	$a_2 \pm \Delta a_2$	$b_2 \pm \Delta b_2$	$c_2 \pm \Delta c_2$	R	R_{sqr}
1023 ± 3	$1.927 \times 10^{-2} \pm 3.784 \times 10^{-4}$	$-6.864 \times 10^{-3} \pm 2.021 \times 10^{-4}$	$9.124 \times 10^{-1} \pm 8.591 \times 10^{-2}$	0.9995	0.9989
1103 ± 3	$3.938 \times 10^{-2} \pm 3.339 \times 10^{-3}$	$-1.941 \times 10^{-3} \pm 3.746 \times 10^{-4}$	$5.851 \times 10^{-1} \pm 1.349 \times 10^{-2}$	0.9969	0.9937
1153 ± 3	$6.900 \times 10^{-2} \pm 6.489 \times 10^{-3}$	$-1.073 \times 10^{-3} \pm 2.795 \times 10^{-4}$	$4.732 \times 10^{-1} \pm 9.239 \times 10^{-2}$	0.9983	0.9966
1300 ± 3	$6.336 \times 10^{6} \pm 3.563 \times 10^{-19}$	$-8.192 \times 10^{3} \pm 5.245 \times 10^{-16}$	$5.369 \times 10^{6} \pm 4.626 \times 10^{-19}$	0.9976	0.9953

– The curves describing the dependences $K = f(\log p_{int})$ are more flat as compared to the dependences $K = f(\log p_{Ga})$;

– As temperature increases and consequently p_{Ga} and p_{int} increase, the absolute values of the maximal points in all curves decrease;

– Irrespective of temperature and pressure all $K = f(\log p_{int})$ and $K = f(\log p_{Ga})$ curves have maxima corresponding to the composition of the initial $Ga_{0.70}Pb_{0.30}$ melt.

In this work we made an attempt to study the change in the mass transfer mechanism depending on the integral pressure p_{int} and partial pressures of components p_{Ga} and p_{Pb} in the reaction cell of the "hot wall" modified method. The change of the mean free path $\bar{l}_i$ of Ga and Pb atoms depending on real conditions of the synthesis in the reaction cell was studied as one of the basic criteria. The calculations of $\bar{l}_i$ were based on the fact that the saturated vapor over gallium and lead melts consists mainly of monatomic molecules [10, 12, 13]. The mean free paths of components in the equilibrium vapor phase over melts of the systems were calculated by formula (8) [13].

$$\bar{l}_i = (kT)/(\pi\sqrt{2}d_i^2 p). \quad (8)$$

Here k is the Boltzmann constant equal to 1.380662×10^{-23} J/K; T is the absolute temperature; d_i is the diameter of a molecule (atom) in the vapor (diameter of the lead atom $d_{Pb} = 3.5 \times 10^{-10}$ m, diameter of the gallium atom $d_{Ga} = 2.82 \times 10^{-10}$ m [14]); p is the partial pressure ($p = p_{int}$), Pa. The distance from the hole in the container with the melt to the silicon substrate was 9×10^{-2} m.

The dependences of the mean free paths $\bar{l}_i$ of gallium and lead atoms on the logarithm of the total pressure log p_{int} observed in the course of growing Ga_yPb_{1-y} films is presented in Fig. 6. It is seen from this figure that the $\bar{l}_i$ values of gallium and lead atoms vary in very wide limits with the total pressure in the reaction cell during growing up Ga_yPb_{1-y} layers. For example, the value of $\bar{l}_{Ga}$ decreases practically by a factor of 1170 from 27.49 to 0.0235 cm, as the integrated pressure p_{int} increases from 0.0146 to 216.21 Pa. In the same pressure interval the $\bar{l}_{Pb}$ value decreases from 17.845 to 0.0153 cm. It is obvious that $\bar{l}_{Ga}$ and $\bar{l}_{Pb}$ values define the mechanism of the transfer of gallium and lead atoms from a vapor source to the surface of the forming condensate. When the $\bar{l}_i$ value of Ga and Pb atoms is comparable with the distance from the hole in the container with a melt to a substrate the mass transfer in the evacuated reaction cell occurs in the molecular beams mode, i.e. the formation of the Ga_yPb_{1-y} condensate is carried out by the molecular beam epitaxy method. Such technology of films formation is nonequilibrium, and the resulting layers, as a rule, are subjected to additional annealing.

It follows from Fig. 6 that at the total pressure from 0.0153 to 2.2 Pa and the $\bar{l}_{Pb}$ values from 0.0153 to 1.2 Pa the $\bar{l}_{Ga}$ values are comparable with the distance between a vapor source and a substrate. This is the

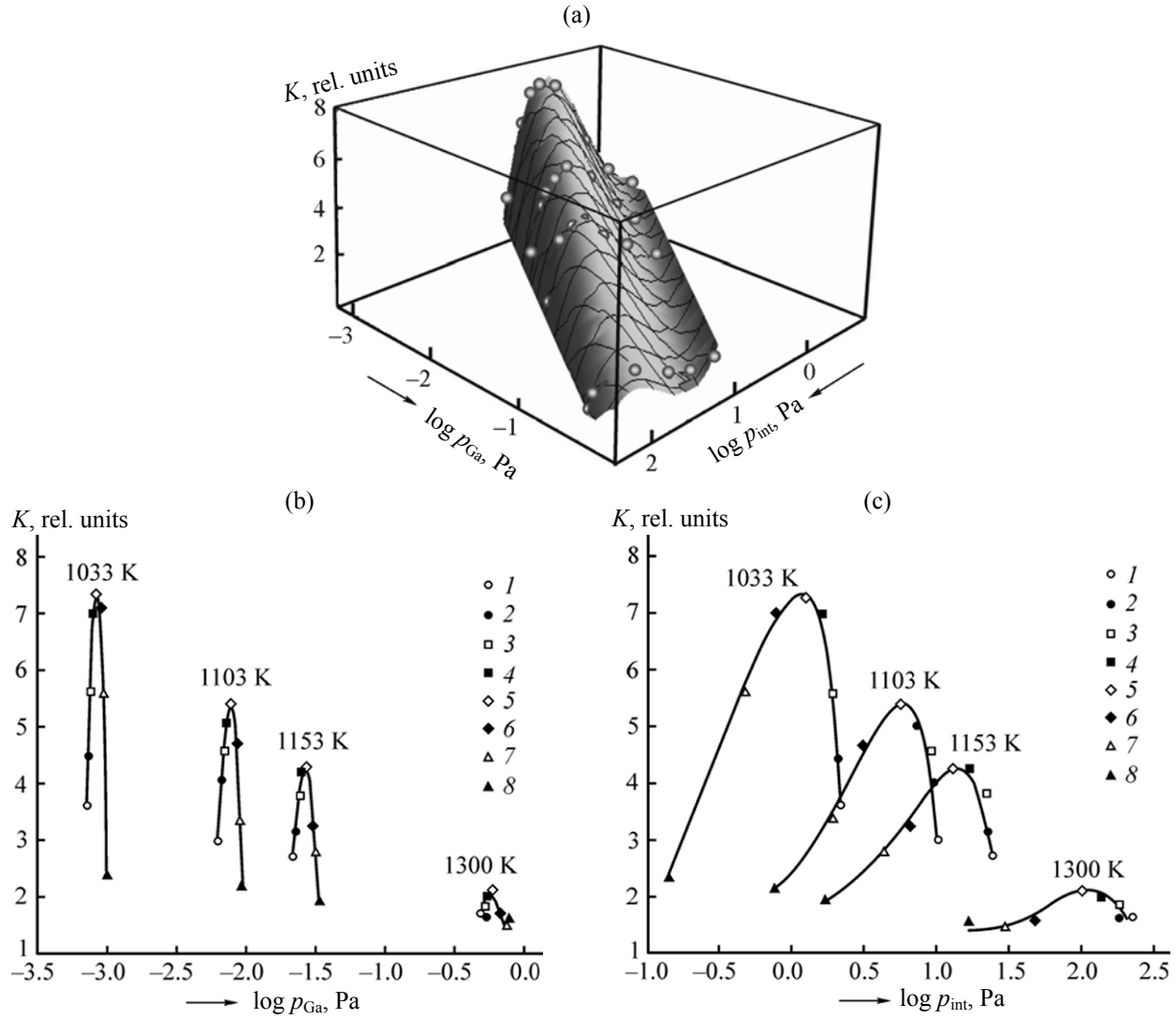

Fig. 5. Dependence of coefficient K on (a) the values of logarithms of gallium partial pressure log p_{Ga} and of total pressure log p_{int} over initial Ga_xPb_{1-x} melts; the dependences (b) log p_{Ga}–y_{Ga} and (c) log p_{int}–y_{Ga}. (*1*) $Ga_{0.15}Pb_{0.85}$, (*2*) $Ga_{0.25}Pb_{0.75}$, (*3*) $Ga_{0.35}Pb_{0.65}$, (*4*) $Ga_{0.5}Pb_{0.5}$, (*5*) $Ga_{0.7}Pb_{0.3}$, (*6*) $Ga_{0.85}Pb_{0.15}$, (*7*) $Ga_{0.9}Pb_{0.1}$, and (*8*) $Ga_{0.95}Pb_{0.05}$. Temperature of silicon substrate T_{sub} = 420 K.

range of the total pressure in the reaction cell where the highest values of the coefficient K are observed.

A noticeable decrease was found at total pressures greater than 7 Pa in the K values, which practically tend to 1 at the further increase in the total pressure. In this case the films are formed with a minimal deviation from the thermodynamic equilibrium. At the total pressure greater than 7 Pa the mass transfer mechanism in the reaction cell occurs according to the mode of dynamic vapor flows. In the range of pressure from 2.2 to 7.0 Pa the mass transfer mechanism changes from molecular beams to the dynamic mode.

The calculations of the mean free paths of gallium and lead atoms explain the general tendency to the decrease in the K value, and hence the degree of the deviation from thermodynamic equilibrium, with the increase in the total pressure in the reaction cell at growing Ga_yPb_{1-y} films. However the results of these calculations do not allow us to interpret maxima in the curves $K = f(\log p_{Ga})$ and $K = f(\log p_{int})$, which correspond to the melt composition $Ga_{0.7}Pb_{0.3}$ for the temperature range of 1023–1300 K under study (Fig. 5).

In the final stage of the work we have optimized conditions for the synthesis of Ga_yPb_{1-y} films taking

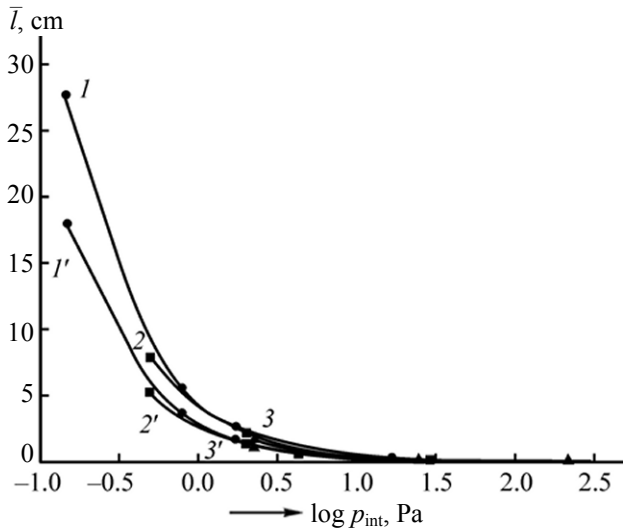

Fig. 6. Dependence of the mean free paths $\bar{l}_i$ of gallium and lead atoms on the logarithm of the total pressure log p_{int} observed in the course of growing up Ga_yPb_{1-y} films: (*1–3*) $\bar{l}_{Ga}$; (*1'–3'*) $\bar{l}_{Pb}$; (*1*), (*1'*) $Ga_{0.95}Pb_{0.05}$ melt; (*2*), (*2'*) $Ga_{0.9}Pb_{0.1}$ melt; (*3*), (*3'*) $Ga_{0.15}Pb_{0.85}$ melt.

into account the results of mathematical processing of the experimental data. It is evident from Figs. 4a and 4b that the synthesis of the Ga_yPb_{1-y} condensate with the specified ratio of the components can be carried out for infinite set of the p_{Ga}/p_{int} ratios of pressures, which are defined by the quantitative composition of the initial melt of the Ga–Pb system and by its temperature. The essential feature of each mode of the synthesis is only the coefficient *K,* which characterizes the degree of deviation from the thermodynamic equilibrium conditions.

The mode of the synthesis of Ga_yPb_{1-y} films with a predetermined quantitative composition was optimized by the solution of Eqs. (5), (6) and by the introduction of corrections taking into account the dependence $K = f(\log p_{Ga}, \log p_{int})$. The corrected modes were used for the preparation of a new series of Ga_yPb_{1-y} samples with compositions presented in Table 5.

It is seen from Table 5 that the results of the determination of the gallium fraction in the Ga_yPb_{1-y} films correspond to the predetermined values of gallium concentration y^*_{Ga}, which were theoretically calculated by Eqs. (5), (6), within an error of the local X-ray spectral microanalysis method with the probability of 90%. Therefore we can conclude that the complex of research carried out in the present work has resulted in the creation of scientifically well-founded method of synthesizing Ga_yPb_{1-y} films with predetermined compositions.

EXPERIMENTAL

To grow up Ga_yPb_{1-y} films on silicon substrates, we applied the "hot wall" modified method using a graphite reaction cell [15], which was arranged on a VUP-6 universal vacuum installation of a serial production. To synthesize the films, working volume was evacuated to the residual pressure of 5×10^{-4} Pa.

Table 5. Comparison between calculated y^*_{Ga} values and experimental data y_{Ga} on the composition of Ga_yPb_{1-y} films obtained under optimized synthesis conditions with account of deviations from equilibrium conditions

T, K	Melt composition	p_{Ga}, Pa	Total pressure p_{int}, Pa	Coefficient of deviation from equilibrium conditions *K*, rel. units	y^*_{Ga} (calc.)	y_{Ga} (exp.)
1023 ± 3	$Ga_{0.25}Pb_{0.75}$	0.000752	2.0845	4.44	0.00173	0.0016 ± 0.0005
	$Ga_{0.5}Pb_{0.5}$	0.000823	1.62265	6.96	0.00348	0.0036 ± 0.0005
	$Ga_{0.9}Pb_{0.1}$	0.000958	0.50238	5.55	0.01078	0.0106 ± 0.0005
1103 ± 3	$Ga_{0.25}Pb_{0.75}$	0.006934	9.63857	4.02	0.00274	0.0028 ± 0.0005
	$Ga_{0.5}Pb_{0.5}$	0.00757	7.30633	5.02	0.00547	0.0058 ± 0.0005
	$Ga_{0.9}Pb_{0.1}$	0.00919	2.00449	3.34	0.00156	0.0162 ± 0.0005
1300 ± 3	$Ga_{0.25}Pb_{0.75}$	0.51337	187.6682	1.64	0.00453	0.0048 ± 0.0005
	$Ga_{0.5}Pb_{0.5}$	0.55738	134.8963	1.97	0.00794	0.0078 ± 0,0005
	$Ga_{0.9}Pb_{0.1}$	0.7348	28.9941	1.42	0.03851	0.0372 ± 0.0005

Almost 1000-fold reduction of the partial pressure of residual gases was observed during the substance vaporization in the reaction cell used in the "hot wall" method, as compared to the pressure of these gases in the external evacuated volume [16, 17]. Graphite ensures reducing character of the residual atmosphere in the reaction cell, which is an advantage over vaporization systems made of other materials. Owing to such character of residual atmosphere and to gettering gases by graphite vessel walls, the partial pressure of oxygen in the reaction volume decreases to the level of 5×10^{-7} Pa in the course of substance evaporation [16, 17].

The phase nature of the Ga_yPb_{1-y} films was determined with the help of a ThermoTechno ARLX'pert diffractometer using filtered CuK_α and CoK_α radiations. Surface morphology was studied by the method of raster electronic microscopy with the use of a JEOL JCM-6380 LV instrument at the 25000-fold magnification. The local X-ray spectral analysis was carried out on a JEOL-JCM-840 microanalyzer.

The quantitative elemental analysis of the grown condensates was carried out with the utmost care using spectrometers with wave dispersion. The analysis of Ga_yPb_{1-y} samples was carried out in local and raster modes, and was also duplicated on several spectral lines by comparison with various standards. To determine concentrations of elements in the obtained films, we used lines of the following series [18]: lead, K_α and M_α lines and gallium, L_α and L_β lines. Pure metal lead (99.999% purity) and also gallium arsenide single crystals of the SAGOCh-9-5 grade were used as the standards.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Scientific Fund (grant no. 14-13-01470).

REFERENCES

1. *Lead Chalcogenides: Physics and Applications*, Khokhlov, D., Ed., New York: Gordon&Breach, 2002.
2. Rahim, M., Khiar, A., Fill, M., Felder, F., and Zogg, H., *Electron. Lett*., 2011, vol. 47, no. 18, p. 1037. DOI: 10.1049/el.2011.2201.
3. Zogg, H., Rahim, M., Khiar, A., Fill, M., Felder, F., and Quack, N., *Opto-Electronics Rev*., 2010, vol. 18, no. 3, p. 231. DOI: 10.2478/s11772-010¯1028-5.
4. Ryabova, L.I. and Khokhlov, D.R., *Uspekhi Fiz. Nauk*, 2014, vol. 184, no. 10, p. 959. DOI: 10.3367/UFNe.0184.201410b.1033.
5. Volkov, B.A., Ryabova, L.I., and Khokhlov, D.R., *Uspekhi Fiz. Nauk*, 2002, vol. 172, no. 8, p. 905.
6. *Lead Salt Thin Film Semiconductors for Microelectronic Applications*, Mukherjee, S., Ed., Kerala: Transworld Research Network, 2010.
7. Samoylov, A.M., Belenko, S.V., Sharov, M.K., Dolgopolova, E.A., and Zlomanov, V.P., *J. Cryst. Growth*, 2012, vol. 351, no. 1, p. 149. DOI: 10.1016/j.jcrysgro.2012.01.042.
8. Zlomanov, V.P. and Novoselova, A.B., *R–T–x Diagrammy sostoyaniya sistem metall-khal'kogen* (R–T–x State Diagrams of Metal-Chalcogen Systems), Moscow: Nauka, 1987.
9. Samoilov A.M., *Doctorate (Chem.) Dissertation*, Voronezh, 2006.
10. Samoilov, A.M., Naumov, A.V., Lopatin, S.I., and Zagorodnii A.A., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 1, p. 27. DOI: 10.1134/S1070363211010051.
11. Naumov, A.V., Samoilov, A.M., and Lopatin, S.I., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 1, p. 26. DOI: 10.1134/S1070363213010040.
12. *Janusz Groszkowski, Technika Wysokiej Prozni* (High Vacuum Technique), Warszawa: Wydaw. Nauk.-Techn., 1972.
13. Kuchling, H., *Taschenbuch der Physik* (Handbook on Physics), Leipzig: VEB Fachbuchverlag, 1979.
14. Emsley, J., The Elements, Oxford: Clarendon Press, 1991.
15. Samoylov, A.M., Buchnev, S.A., Khoviv, A.M., Dolgopolova, E.A., and Zlomanov, V.P., *Mater. Sci. Semicond. Proc.*, 2003, vol. 6, nos. 5–6, p. 481.
16. Laska, V.L., Kondrat'ev, A.V., and Potapenko, A.A., *Inzh.- Fiz. Zh*., 1984, vol. 46, no. 6, p. 949.
17. *Vacuumnoe nanesenie plenok v kvazizamknutom ob"eme* (Vacuum Deposition of Films in a Quasiclosed Volume), Bubnov, J.Z., Lur'e, M.S., Staros, F.G., and Filaretov, G.A., Eds., Moscow: Sovetskoe Radio, 1975.
18. *Microanalyse et Microscopie Electronique a Balayage* (Microanalysis and Raster Electronic Microscopy), Maurice, F., Meny, L., and Tixier, R., Eds., 1979.