

Comparative Characteristics of GaAs and InAs Langmuir Evaporation - Monte Carlo Simulation

Anna A. Spirina^{1,2,a*}, Igor G. Neizvestny^{1,2,b} and Nataliya L. Shwartz^{1,2,c}

¹Novosibirsk State Technical University, Novosibirsk, Russia

²A.V. Rzhanov Institute of Semiconductor Physics SB RAS, Novosibirsk, Russia

^aspirina.anna.alex@gmail.com, ^bneizv@isp.nsc.ru, ^cnataly.shwartz@gmail.com

Keywords: Langmuir evaporation, GaAs, InAs, simulation, Monte Carlo.

Abstract. The process of GaAs and InAs substrates high-temperature annealing under the Langmuir evaporation conditions is studied by Monte Carlo simulation. The temperature range of gallium arsenide and indium arsenide congruent and incongruent evaporation are determined. It was demonstrated that the congruent evaporation temperature T_c is sensitive to the vicinal surface terrace width. The decrease of the terrace width results in a decrease in the congruent evaporation temperature. The Ga and In diffusion lengths along the (111)A and (111)B surfaces at congruent temperatures are estimated. The surface morphology transformation kinetic during high-temperature annealing is analyzed.

Introduction

In the process of the $A^{III}B^V$ semiconductor substrates high-temperature annealing in vacuum (Langmuir evaporation), the surface relief develops and metal droplets are formed due to different volatilities of material components. An important parameter of the process is the congruent evaporation temperature T_c , the temperature above which the V group elements evaporate more intensively than the III group elements. A significant number of theoretical and experimental contributions on the Langmuir evaporation of $A^{III}B^V$ semiconductors, such as GaAs [1–3] and InAs [4, 5] has been published to date. The GaAs Langmuir evaporation has been studied for a long time. A large number of experimental studies are devoted to the Langmuir evaporation of this semiconductor. It was experimentally shown that the GaAs congruent evaporation temperature depends on the surface orientation [2]. The studies of InAs Langmuir and equilibrium evaporation are rather fragmentary and do not give a complete picture of the processes occurring during a high-temperature annealing of the material. The theoretical temperature dependences of equilibrium As_2 partial pressure in congruent and incongruent temperature ranges for InAs substrates can be found in [6]. The equilibrium pressure of group III metal vapor is equally over the $A^{III}B^V$ melt solution surface and over the pure group III element melt [7–9]. The temperature dependence of In vapor pressure is given in [8]. The results in [8] are consistent with the temperature dependence of the equilibrium indium vapor pressure over the indium-arsenic melt solution [9]. The indium droplets movement kinetics along the InAs(111)B surface during the annealing at incongruent evaporation conditions was investigated in [5]. The indium droplets formation on the InAs(111)B was observed starting from $T_c = 633$ K. The estimation of InAs components Langmuir evaporation rate in the incongruent high temperature range at $T = 983 \div 1033$ K was carried out in [4]. It was found that, during InAs substrate evaporation, liquid indium layer, uniformly saturated with arsenic, was formed. As defined in [4], the Langmuir evaporation rate of the components in the incongruent region depends on the As_2 dimers formation and desorption at the liquid indium-vacuum interface. Literary data indicate a spread in the T_c values, even on GaAs surfaces with a certain surface orientation.

In this work the factors affecting the GaAs and InAs substrates congruent evaporation temperature are analyzed using Monte Carlo (MC) simulation. The model T_c and the evaporation activation energy values for different GaAs surface orientations are compared with the available experimental data. Similar dependences for InAs are predictions of the model.

Monte Carlo Model

The simulations were carried out using a program package SilSim3D [10] on the base of the kinetic lattice Monte Carlo model. The elementary events included in the model are schematically shown in Fig. 1. They are: Me(*s*), Me(*l*) and As₂ desorption from the surface, diffusion of all components over the surface, As₂ dissociation and formation, phase transformations (crystallization, melting, dissolution), As diffusion in a liquid metal. Here Me(*s*) and Me(*l*) mean metal in solid and liquid states, the metal is gallium or indium.

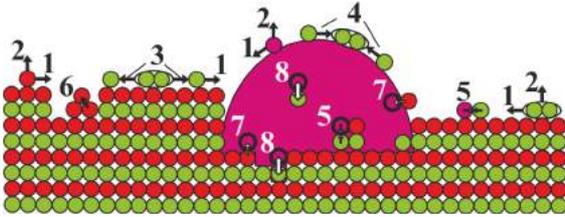


Fig. 1. Schematic representation of elementary events in the model: 1 – particle diffusion along the surface; 2 – Me and As₂ desorption; 3 – As₂ dissociation; 4 – As₂ formation; 5 – Me crystallization; 6 – Me melting; 7 – Me dissolution; 8 – As dissolution in liquid metal and diffusion through a liquid drop. As is marked in white, Me(*s*) – in gray, Me(*l*) – in black; As₂ – circled in an ellipse. (On-line Me(*l*) is marked in pink, Me(*s*) in red, As – in green.) The same coloration corresponds to the figures below.

The MC model realization details can be found elsewhere [11]. The choice of the model energy parameters for GaAs was carried out according to the same procedure, as described in [11, 12]. The activation energies of Me(*s*) dissolution in a liquid drop and Me(*l*) crystallization at the liquid-crystal interface were chosen by fitting the simulated and experimental solubility [13] of the A^{III}B^V semiconductor in the liquid A^{III} metal for the thermodynamic equilibrium conditions similar to [11]. The energy parameters estimation of the model responsible for gallium (indium) and arsenic evaporation was done by fitting the simulated and experimental [9] data of GaAs or InAs components partial pressures temperature dependence during equilibrium annealing. The experiment [9] was carried out in the temperature range $T = 1038 \dots 1253$ K for GaAs and $T = 906 \dots 1056$ K for InAs. To calculate the equilibrium Ga (In) and As₂ pressures over the gallium (indium) solution, the following system was considered: the A^{III}B^V substrate with a liquid metal thick layer over it was covered with reflective lid located at some distance from liquid-vapor interface. The equilibrium pressure was determined by the Ga (In) and As₂ impingements number against the lid. An appropriate choice of the energy model parameter allows matching the simulated and experimental data (Fig. 2).

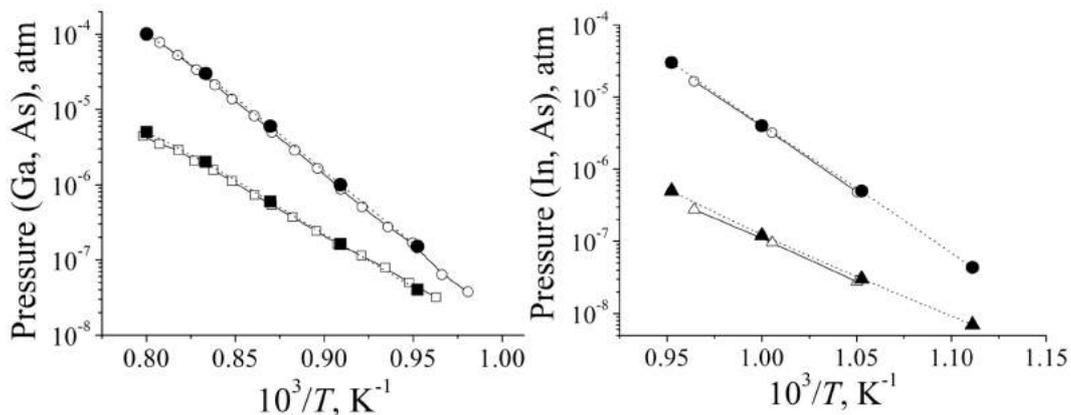


Fig. 2. Temperature dependence of equilibrium Ga (In) and As₂ pressure over the metal-arsenic melt: Ga – squares, In – triangles, As₂ – circles, simulation – solid symbols, experimental data [9] – open symbols.

The GaAs and InAs substrates high-temperature annealing simulation was fulfilled with the molecular arsenic formation and decay activation energies – $E_{\text{form}} = 3.0$ eV; $E_{\text{dec}} = 1.2$ eV and other energy parameter values are presented in Table 1.

Table 1. The energy parameter values of the binding energy between atoms ($E_{\text{Me-As}}$), dissolution and crystallization activation energies (E_{dis} , E_{cr}) for GaAs and InAs.

	$E_{\text{Me-As}}$, eV	$E_{\text{Me-Me}}$, eV	$E_{\text{As-As}}$, eV	E_{dis} , eV	E_{cr} , eV	E_{form} , eV	E_{dec} , eV
GaAs	0.9	0.6	0.7	1.2	1.25	3	1.2
InAs	0.8	0.5	0.7	1.25	1.3	2.8	1.2

Results and Discussions

The simulations are carried out on vicinal GaAs and InAs substrates in the temperature range of 800–1100 K for gallium arsenide and 600–900 K for indium arsenide. The vicinal surface terrace width L varied from 20 nm to 360 nm. The As_2 and In evaporation rates on temperature $V_{\text{des}}(T)$ dependences during the InAs substrates high-temperature annealing are shown in Fig. 3a. At $T > T_c$, the arsenic evaporation rate becomes higher than that of the In evaporation rate. At these temperatures, metal droplets appear on the surface. From the plots $V_{\text{des}}(T)$ in Fig. 3a the InAs T_c values are estimated for two substrate surface orientations: $T_c(\text{InAs}(111)\text{A}) = 650$ K, $T_c(\text{InAs}(111)\text{B}) = 620$ K for $L = 20$ nm. The congruent evaporation temperature on the (111)B surface is lower than that on the (111)A surface. This fact is confirmed by the experiments on gallium arsenide [2, 3]. For the InAs, the T_c value was experimentally determined only for the (111)B surface [5]. This value is in agreement with the model one. The experimental values of GaAs congruent evaporation temperature T_c are higher than that of InAs: $T_c(\text{GaAs}(111)\text{A}) = 930$ K, $T_c(\text{GaAs}(111)\text{B}) = 890$ K [3]. These T_c values for GaAs are also consistent with the model values. The $V_{\text{des}}(T)$ dependence slope in Arrhenius coordinates (Fig. 3a) determines the effective desorption activation energy of the evaporating component. The effective desorption activation energies of Ga from GaAs and In from InAs for the (111)A surface orientation in the model are: $E_{\text{des}}(\text{Ga}) = 2.5$ eV, $E_{\text{des}}(\text{In}) = 2.3$ eV. As is evident from Fig. 3a, there are different arsenic desorption activation energy values in low and high temperature ranges. Previously, a similar dependence was observed during the GaAs(111)A Langmuir evaporation [14]. The desorption activation energy increase in the high temperature range was explained by the substrate surface coverage with a liquid Ga film. Liquid metal acts as a pump increasing the arsenic evaporation from the (111)A surface. This “pump” acts more effectively for InAs. The temperature dependences of total evaporating arsenic flux to gallium (indium) flux ratio during the GaAs(111)A and InAs(111)A substrates annealing are presented in Fig. 3(b). Since the In evaporating fluxes from the (111)A and (111)B surfaces are equal (Fig. 3a); so, in Fig. 3(b), the increase in the total evaporating arsenic flux with the increasing temperature is shown. When the substrate surfaces become completely covered with a liquid metal film (at $T \geq 880$ K for InAs and $T \geq 1080$ K for GaAs), a noticeable increase of the As/Me ratio is observed. This increase is more pronounced for InAs. This fact is due to a higher InAs solubility in liquid indium than the GaAs solubility in liquid gallium [13]. Since the congruent evaporation temperatures for InAs and GaAs are different, to illustrate the above statement, we shift the As/Ga curve to lower temperatures by the value $\Delta T = T_c(\text{GaAs}(111)\text{A}) - T_c(\text{InAs}(111)\text{A}) = 240$ K. This curve 2' is marked with the open symbol in Fig. 3b. In all the temperature range under investigation, As evaporates intensively from InAs.

The InAs and GaAs substrates top views and cross-sections, at the temperature exceeding the T_c value by 220 K, are shown in Fig. 4. For InAs this temperature is equal to 860 K and 1080 K for GaAs. According to [1], the presence of liquid gallium enhances the arsenic evaporation rate from GaAs. More significant, the enhanced arsenic evaporation effect, in the presence of a liquid metal, is observed during the InAs annealing. Despite the fact that, at this temperatures, most of the GaAs

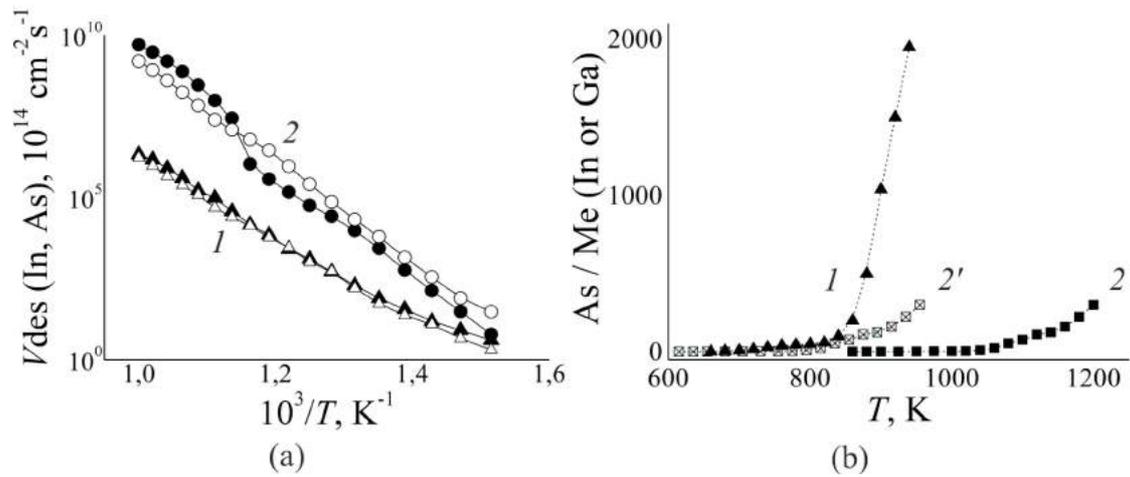


Fig. 3. a) The InAs substrate ($L = 20$ nm) evaporation rate temperature dependence: In – 1, As₂ – 2, solid symbols correspond to the (111)A surface, open symbols – to the (111)B surface; b) The As/Me ratio temperature dependences for the (111)A surface orientations: As/In – 1, As/Ga – 2; curve 2' is the curve 2 shifted along the temperature axis by $\Delta T = 245$ K.

surface is covered with liquid metal and only separate drops appear on the InAs surface (Fig. 4), the As/In ratio is higher than the As/Ga ratio (Fig. 3b). The model surface cross-sections demonstrate that the In drop penetrates deeper into the substrate, pumping more arsenic from the InAs crystal.

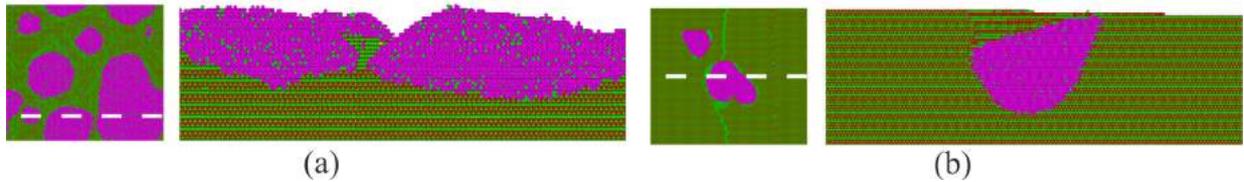


Fig. 4. Top views and cross-sections of GaAs (a, b) and InAs (a, b) model substrates (111)A after the annealing at $T = T_c + 220$ K: $T = 1080$ K (a, b), $T = 860$ K (a, b).

In Fig. 5 is the liquid indium layer formation kinetics during the InAs(111)A annealing at a high temperature. At first separate In drops are formed on the surface. Since etching rate of InAs by liquid indium is maximal for the (111)A facet [15], the etching rate in the vertical direction is high at the initial annealing stage. As A-facets destruct with time, the etching rate in the vertical direction slows down and indium drops grow in all directions. With time, drops merge and liquid indium layer covers the surface. For each temperature, when a steady-state desorption rate is reached, there is a certain thickness h of the liquid metal layer on the surface. We estimated this liquid indium layer thickness h at $T = 1000$ K ($T = T_c + 350$) and that of the liquid gallium layer at $T = 1220$ K. The liquid metal stationary thickness at $T = T_c + 350$ over GaAs was found to be 2 times smaller than that over the InAs substrate.

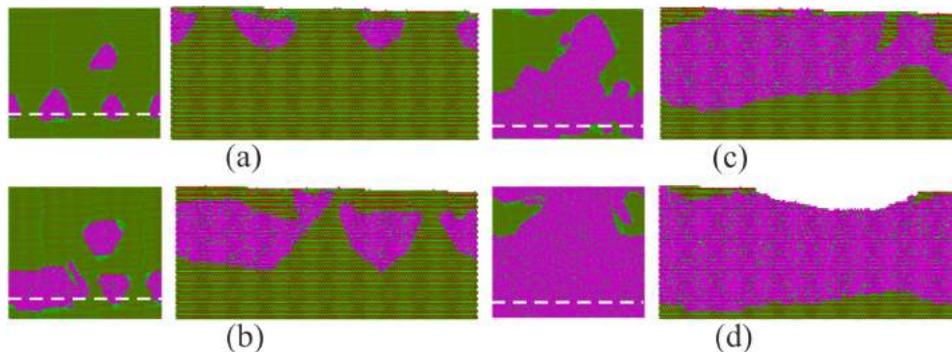


Fig. 5. Top views and cross-sections of InAs(111)A model substrates after the annealing at $T = 1000$ K during: $t = 1 \cdot 10^{-3}$ s (a), $2.5 \cdot 10^{-3}$ s (b), $3.5 \cdot 10^{-3}$ s (c), $4.5 \cdot 10^{-3}$ s (d).

We have previously demonstrated that T_c depends on the vicinal surface terrace width [14]. This fact is illustrated in Fig. 6. The lower the terrace width L is, the lower the congruent evaporation temperature is. T_c corresponds to the minimal temperature when metal droplets are created on the surface. On ideal singular surfaces, the adatom source is the vacancy islands (island edges) created on the surface during high-temperature annealing. The vacancy island density is determined by temperature. The average distance between the islands on the (111)A surface is approximately equal to the double Ga (In) diffusion length before evaporation $\lambda_{\text{dif}}(\text{Ga}, \text{In})$. In Fig. 6a the maximal T_c corresponds to the congruent evaporation temperature on a singular surface. When terrace width L becomes lower than $2 \cdot \lambda_{\text{dif}}(\text{Ga}, \text{In})$ the T_c value decreases, since step edges supply additional Ga atoms on the terrace and droplets can be nucleated at a lower temperature. So, from the plots in Fig. 6a, $\lambda_{\text{dif}}(\text{Ga}, \text{In})$ can be estimated: $\lambda_{\text{dif}}(\text{Ga}) \sim 60 \text{ nm}$, $\lambda_{\text{dif}}(\text{In}) \sim 130 \text{ nm}$. The adatom diffusion length before the evaporation from the (111)A surface can be estimated using the standard expression $\lambda_{\text{dif}} \sim a_0 \cdot \exp((E_{\text{des}} - E_{\text{dif}})/(2kT))$, where a_0 is the distance between atoms on the crystal surface. At $T = 1000 \text{ K}$ – $\lambda_{\text{dif}}(\text{Ga}) \sim 80 \text{ nm}$ and at $T = 870 \text{ K}$ – $\lambda_{\text{dif}}(\text{In}) \sim 200 \text{ nm}$. Both estimates show that, at the congruent evaporation temperature, $\lambda_{\text{dif}}(\text{In})$ is approximately equal to twice $\lambda_{\text{dif}}(\text{Ga})$.

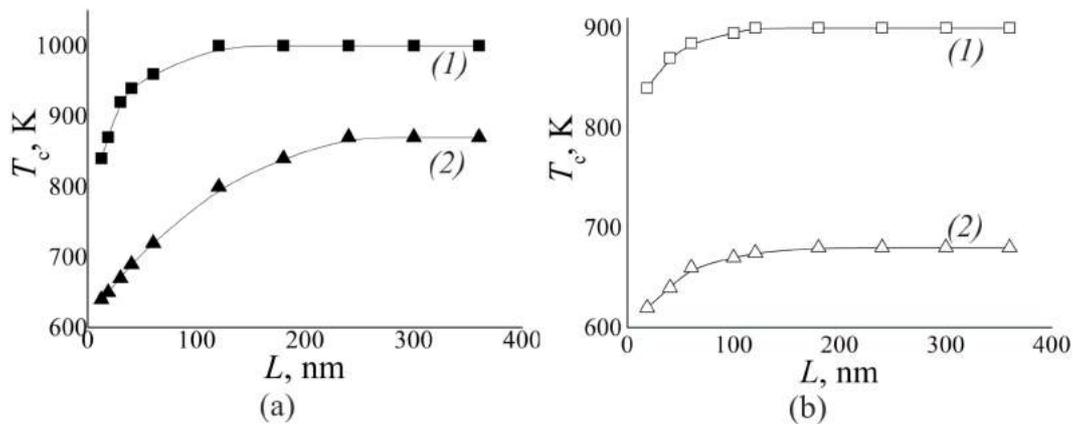


Fig. 6. The congruent evaporation temperature of GaAs (1) and InAs (2) versus terrace width L for (111)A (a) and (111)B (b) surface orientations.

A similar $T_c(L)$ dependence was obtained for the (111)B substrate surface orientation (Fig. 6b). The T_c values on the (111)B surface are smaller than those on (111)A, because, on the As-terminated surface at $T < T_c$ a high vacancy island concentration is created. The distance between the islands on the (111)B surface is determined by the arsenic diffusion rate, which is smaller than the gallium (indium) diffusion rate. For example, from the density of the vacancy islands, formed on the (111)B surface during the GaAs substrates annealing at temperature $T = 820 \text{ K}$ ($T < T_c$), the arsenic diffusion length before evaporation was estimated: $\lambda_{\text{dif}}(\text{As}) \sim 10 \text{ nm}$. The presence of a large number of vacancy islands on the (111)B surface increases the adatom concentration and leads to a decrease in the T_c value. As is evident from Fig. 6b, the T_c value ceased to depend on the terraces width L starting from $L \geq 100 \text{ nm}$ for GaAs (111)B and from $L \geq 180 \text{ nm}$ for InAs(111)B. These L values greatly exceed the arsenic diffusion length before evaporation. We believe that the minimal L value, corresponding to the maximal T_c in Fig. 6b, again, is determined by the double Ga (In) diffusion length before evaporation, in this case along the (111)B surface. The comparison of Fig. 6a and Fig. 6b shows that the adatom diffusion length along the (111)B surface is smaller ($\lambda_{\text{dif}}(\text{Ga}) \sim 50 \text{ nm}$, $\lambda_{\text{dif}}(\text{In}) \sim 90 \text{ nm}$) than that along the (111)A surface. The metal adatom evaporation during the migration along the As-terminated surface, in addition to elementary diffusion hops and evaporation acts, includes the acts of adatom incorporation into numerous vacancies on the surface. So, the description of the metal atom evaporation from the (111)B surface is more complicated and a simple expression for the λ_{dif} estimation is invalid.

Summary

Using Monte Carlo simulation the Langmuir evaporation characteristics of GaAs and InAs were analyzed. The gallium and indium desorption activation energies E_{des} of the GaAs and InAs Langmuir evaporation have been determined. The congruent evaporation temperature T_c for both materials with the (111)A and (111)B surface orientations has been obtained. The T_c value dependence on the terrace width has been demonstrated. The Ga and In diffusion lengths before evaporation vicinal surface at congruent temperatures have been estimated. It has been demonstrated that $\lambda_{\text{dif}}(\text{In}) \geq 2 \cdot \lambda_{\text{dif}}(\text{Ga})$. The calculated T_c and E_{des} values obtained for GaAs are in agreement with the experimental data, and, for InAs they are the predictions of the model.

References

- [1] C.Y. Lou, G.A. Somorjai, Studies of the vaporization mechanism of gallium arsenide single crystals, *J. of Chem. Phys.* 55 (1971) 4554-4565.
- [2] B. Goldshtein, D.J. Stozak, V.S. Ban, Langmuir evaporation from the (100), (111A) and (111B) faces of GaAs, *Surf. Sci.* 57 (1976) 733-740.
- [3] S. Kanjanachuchai, C. Euaruksakul, Self-Running Ga Droplets on GaAs (111)A and (111)B Surfaces, *ACS Appl. Mater. Interfaces* 5 (2013) 7709-7713.
- [4] Ju. Huhryanski, L. Veremjanina, I. Kombarova, I. Nikishina, O. Sysoev, Kinetics of Langmuir evaporation of indium phosphide and arsenide components, *J. Phys. Chem.* 71 (1997) 870-874.
- [5] S. Kanjanachuchai, P. Photongkam, Dislocation-guided self-running droplets, *Cryst. Growth Des.* 15 (2015) 14-19.
- [6] J. Jian-yun Shen, C. Chatillon, Thermodynamic calculations of congruent vaporization in III-V systems; Applications to the In-As, Ga-As and Ga-In-As systems, *J. Cryst. Growth* 106 (1990) 543-552.
- [7] M. Panish, J. Arthur, Phase equilibria and vapor pressures of the system In+P, *J. Chemical Thermodynamics* 2 (1970) 299-318.
- [8] A.N. Nesmeyanov, The vapor pressure of the chemical elements, Moscow, 1961, pp. 204-206 (in rus.).
- [9] C. Pupp, J. Murray, R. Pottie, Vapour pressures of arsenic over InAs(c) and GaAs(c). The enthalpies of formation of InAs(c) and GaAs(c), *J. Chem. Thermodynamics* 6 (1974) 123-134.
- [10] A. Zverev, C. Zinchenko, N. Shwartz, Z. Yanovitskaja, A Monte Carlo simulation of the processes of nanostructures growth: The time-scale event-scheduling algorithm, *Nanotech. in Russia* 4 (2009) 215-224.
- [11] A.A. Spirina, A.G. Nastovjak, S.V. Usenkov, N.L. Shwartz, Lattice Monte Carlo model of Langmuir evaporation of $A^{\text{III}}B^{\text{V}}$ semiconductors: submitted to *Journal Computational Technologies* (in russian) (2018).
- [12] M. Vasilenko, I. Neizvestny, N. Shwartz, Formation of GaAs nanostructures by droplet epitaxy — Monte Carlo simulation, *Comput. Mat. Sci.* 102 (2015) 286-292.
- [13] R.N. Hall, Solubility of III-V compound Semiconductors in column III liquids, *J. Electrochem. Soc.* 110 (1963) 385-388.
- [14] A.A. Spirina, A.G. Nastovjak, N.L. Shwartz, Influence of GaAs substrates properties on the congruent evaporation temperature, *J. Phys.: Conf. Ser.* 993 (2018) 012011.
- [15] H.C. Gatos, M.C. Lavine, Characteristics of the {111} Surfaces of the III-V Intermetallic Compounds, *J. Electrochem. Society*, 107 (1960) 427-433.