

Surface Orientation Influence on the Langmuir Evaporation Characteristics of GaAs Substrates

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

¹Institute of Semiconductor Physics of SB RAS, 13 Lavrentiev aven., Novosibirsk, 630090, Russia

²Novosibirsk State Technical University, 20 K. Marx aven., Novosibirsk, 630073, Russia

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

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Abstract. The dependences of congruent evaporation temperature T_c and the desorption activation energies of GaAs components on the substrate surface orientation are analyzed using Monte Carlo simulation. On the vicinal surfaces with the (111)A orientation at temperatures exceeding T_c , the metal droplets start to grow at step edges, and, with the (111)B orientation, the droplets nucleate randomly on the terraces. The droplet concentration on the (111)B surface is higher than that on the (111)A surface. The droplet-crystal interface roughness is different for (111)A and (111)B orientations. The T_c of (111)B surfaces is lower than that of (111)A surfaces. For both surface orientations, T_c decreases when the vicinal surface terrace width is shorter than the double gallium diffusion length. The gallium and arsenic desorption activation energies dependence on the vicinal surface misorientation is demonstrated. A sharp increase in the arsenic desorption rate is observed with an increase of the (111)A surface coating with liquid gallium.

Introduction

High-temperature annealing, widely used to create clean flat silicon surfaces [1], is unsuitable for $A^{III}B^V$ semiconductors. Different volatilities of $A^{III}B^V$ semiconductor components result in the surface roughening and metal droplets formation during high-temperature annealing in vacuum. Liquid metal droplets are the basis of such technologies for nanostructures growth as droplet epitaxy technique [2] and self-catalyzed nanowire growth [3]. The ability of liquid gallium to etch GaAs substrates led to the creation of drop etching technology [4]. Recently it was demonstrated that the Ga droplets formed during high-temperature annealing also make microscale holes on the GaAs(001) substrate, acting as nanodrills [5]. The renewed interest in the growth of structures on GaAs(111) surfaces is due to the possibility of creating new types of devices for spintronics [6] and entangled photons [7]. Apart from the (001) orientation, (111) is the only orientation in which heavy- and light-hole states do not mix with each other [8]. The $A^{III}B^V$ nanowire growth, according to the vapor-liquid-solid mechanism, occurs on the substrates with surface orientation (111)B. The effect of the GaAs surface type (111)A or (111)B on surface characteristics, such as the etching rate [9] or adatom migration length [10], have been known for a long time. In [9] it was demonstrated that the GaAs(111)A facets etching rate in the special etchant is higher than that of GaAs(111)B facets.

The first experiments in the high-temperature GaAs annealing were carried out on the substrates with the (100) surface orientation [11]. Later it was experimentally demonstrated that the congruent Langmuir evaporation temperature depends on the surface orientation [12, 13]. There has been no detailed theoretical description of this phenomenon up-to-date. The thermodynamic models [14, 15] have been developed since the beginning of the $A^{III}B^V$ semiconductors production, and they provide the basis for the comprehension of the processes occurring in the material during annealing. Using thermodynamic steady-state calculations it was shown that, for temperatures slightly higher than the maximum temperature for the GaAs crystal congruent vaporization, the Ga droplet formation is the most stable state, compared to the formation of a liquid gallium film [16].

A detailed analysis of the processes occurring during the Langmuir evaporation of the $A^{III}B^V$ materials is possible using Monte Carlo (MC) simulation. MC simulation is the technique that allows analyzing surface morphological transformations at the atomic level. The examination of surface orientation influence on the $A^{III}B^V$ substrates Langmuir evaporation main characteristics is fulfilled in this work by simulation.

Monte Carlo Model and Simulation Results

The simulation of the GaAs high-temperature annealing is carried out using the program package SilSim3D on the base of kinetic lattice MC model [17]. The MC model of GaAs semiconductor Langmuir evaporation is close to the droplet epitaxial model [18]. Its main feature is a possibility to imitate the liquid phase in the lattice model. The basic processes considered in the model are: molecular arsenic creation and dissociation; Ga, As and As_2 diffusion; gallium melting; GaAs dissolution in liquid gallium and crystallization at a liquid-solid interface; gallium evaporation in the atomic form and arsenic evaporation in the molecular As_2 form. The probability of each event is determined by its activation energy. These energies are the model input parameters. The details of MC model realization and the choice of energy parameters can be found elsewhere [18–20].

The simulations were fulfilled on the vicinal GaAs substrates with (111)A and (111)B surface orientations in the temperature range of 800–1200 K. At temperatures lower than congruent evaporation temperature T_c , the layer-by-layer evaporation was observed at equal arsenic and gallium evaporation rates. Liquid gallium droplets are created on the surface at $T > T_c$. On the (111)B surface the droplets are formed chaotically over the whole substrate surface and, on (111)A, the drops nucleation starts near the steps (Fig. 1(a,b)). The Ga droplets concentration is appreciably higher on the (111)B surface than that on the (111)A surface. On the GaAs(111)B surface, the droplet nucleation starts on the vacancy defects formed on the terraces due to the high arsenic volatility. The model T_c value for the (111)A orientation is higher than that for (111)B according to the experimental data [12, 13]. The droplet-crystal interface roughness is different for (111)A and (111)B surfaces. For the GaAs(111)B orientation the interface is practically flat and, for the GaAs(111)A, the interface roughness evolves with temperature rise. The difference in the droplet-substrate interfaces on the (111)A and (111)B surfaces is preserved at high temperatures. The cross-sections and a top view of the GaAs (111)A and (111)B model substrates after the annealing at $T = 1000$ K and $T = 1200$ K are shown in Fig. 1.

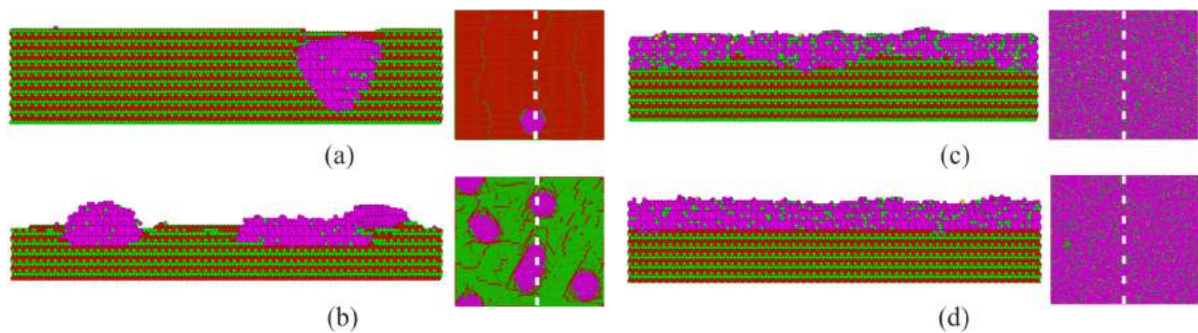


Fig. 1. Cross-sections and top views of GaAs model substrates (111)A (a, c) and (111)B (b, d) after the annealing at $T = 1000$ K (a, b) and $T = 1200$ K (c, d). Liquid gallium is marked in pink, solid Ga – in red, As – in green. The same coloration corresponds to the figures below.

At $T = 1000$ K separate Ga drops are created on both surfaces. The substrates are completely covered with a liquid gallium layer at $T = 1200$ K. A smooth droplet-substrate interface is preserved on the GaAs(111)B surface and, on GaAs(111)A, the interface roughness is developing. This is due to the GaAs etching rate dependence on the surface orientation: the (111)A surfaces are etched with liquid gallium more actively than (111)B. The simulation revealed that congruent evaporation temperature T_c , Ga and As_2 desorption activation energies E_{des} depend on the vicinal surface misorientation that is on terrace width L . The L decrease results in the T_c lowering and E_{des} increase.

These values cease to change when $L/2$ exceeds the gallium diffusion length before evaporation. A comparison of the model values of T_c and E_{des} with the experimental ones is presented in Table 1. The L increase from 20 nm to 360 nm leads to an equality of the gallium desorption activation $E_{\text{des}}(\text{Ga})$ values in the model and experiment, and approach of the model $E_{\text{des}}(\text{As}_2)$ values to the experimental ones. The L influence on the T_c value is more pronounced for the (111)A surface. It is worth noting that the model T_c value on the (111)A surface for $L = 360$ nm is higher than the experimental one. This discrepancy may be due to the model substrate perfection. T_c decreases when introducing the point defects on the (111)A surface. T_c for the (111)B surface is insensitive to the point defects concentration. This difference can be explained by different volatilities of gallium and arsenic. On the ideal (111)B surface the high point defects concentration is created spontaneously during the initial annealing stage, and an additional defects introduction does not change the characteristics of Langmuir evaporation. The difference between simulated (for $L = 360$ nm) and experimental results can be explained by the lack of surface defects in the model, that are presented on the real surface.

Table 1. The main GaAs Langmuir evaporation parameters

Parameter	T_c , [K] (111)A	T_c , [K] (111)B	$E_{\text{des}}(\text{Ga})$, [eV] (111)A	$E_{\text{des}}(\text{Ga})$, [eV] (111)B	$E_{\text{des}}(\text{As}_2)$, [eV] (111)A	$E_{\text{des}}(\text{As}_2)$, [eV] (111)B
Simulation ($L = 20$ nm)	930	890	2.52	2.50	3.37	3.84
Simulation ($L = 360$ nm)	1000	900	2.50	2.47	3.21	3.25
Experiment	950 [12] 930 [13]	900 [12] 890 [13]	2.5 [12]	2.4 [12]	3.0 [12]	3.2 [12]

For the GaAs(111)A surface at some definite temperatures T^* , the arsenic evaporation rate temperature dependence demonstrates a change in the E_{des} . The temperature dependence of evaporating As to the Ga fluxes ratio is shown for two surface orientations in Fig. 2(a), and for the (111)A orientation and two L values in Fig. 2(b). At $T > T_c$ this ratio > 1 . For temperatures lower than some critical value T^* , the As evaporation increases more intensively on the (111)B surface than that on (111)A, since the upper GaAs(111)B layer consists of arsenic atoms, and As is more volatile than Ga. However, with the temperature rise, the surface part covered with liquid gallium increases. It was demonstrated experimentally [11] that the GaAs evaporation rate increases when the GaAs surface is covered with liquid gallium. So, liquid gallium acts as a pump for arsenic. At $T = T^*$ the fluxes, evaporating from the GaAs(111)A and GaAs(111)B substrates, are equal. At $T > T^*$, when an appreciable surface fraction is covered with liquid gallium, the As/Ga fluxes ratio on the (111)A surface exceeds this ratio on the (111)B surface. This phenomenon is due to different etching rates of the (111)A and (111)B surfaces.

The surface morphology influence on the GaAs decomposition during Langmuir evaporation was pointed out in [21]. It was predicted that a larger local miscut gives a lower local T_c . It means that the Langmuir evaporation characteristics should depend on the vicinal surface terrace width. The gallium desorption rate dependence on the vicinal surface terrace width L for different temperatures is shown in Fig. 3(a) and the arsenic desorption rate dependence – in Fig. 3(b). The desorption rates increase with the L decrease. Since step edges are the main adatoms source for a following evaporation, such dependence is expected. In Fig. 3 the $V_{\text{des}}(L)$ dependence can be approximated by a power function of the form $V_{\text{des}} = V_0 \cdot L^{-\beta}$, with parameter β depending on the temperature. For $T < 980$ K, parameter $\beta \sim 1$, and that means that the evaporation rate is approximately proportional to the step density. Such dependence was predicted in [21] only for the As evaporation rate. At high temperatures $\beta < 1$, since Ga droplets start to play the crucial role in the evaporation process. It should be noted that at $T > 1000$ K, the Ga droplets were present on the surface with any deviation from a singular surface and, at $T < 1000$ K, only on surfaces with small L values (large miscut).

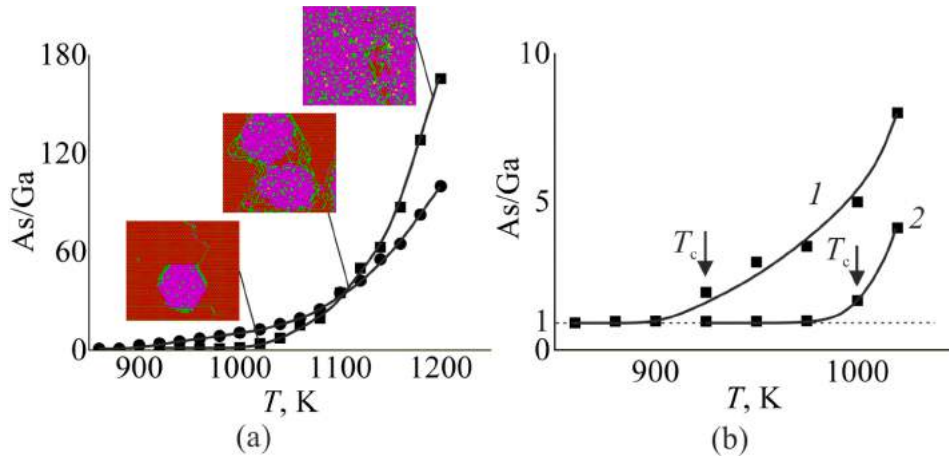


Fig. 2. The temperature dependences of the evaporated As/Ga ratio for: (a) two surface orientations with $L = 360$ nm, and (b) different terrace width $L = 20$ nm – 1, $L = 360$ nm – 2 for the (111)A surface; (111)A – squares, (111)B – circles. The top views of the model (111)A surface in (a) correspond to $T < T^*$, $T = T^*$ and $T > T^*$.

At high temperature, when the entire surface is covered with liquid gallium, Ga and As evaporation rates are independent of L . The reason for the evaporation rate dependence deviation from that inversely proportional to L is similar for gallium and arsenic. When gallium droplets appear on the surface a droplet becomes the main source of evaporating Ga atoms. The occurrence of liquid gallium significantly increases the arsenic evaporation from the surface, thereby reducing the steps role in the arsenic evaporation process, too.

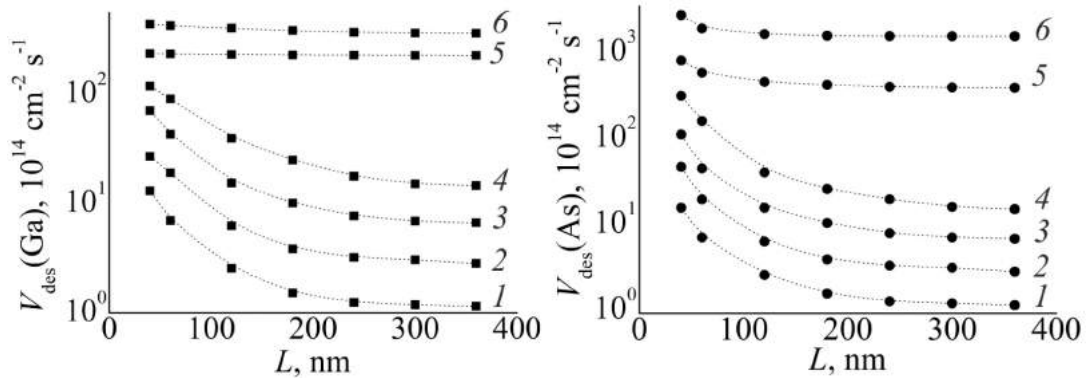


Fig. 3. Gallium (a) and arsenic (b) evaporation rates from the GaAs(111)A substrate *versus* terrace width L for different temperatures: 1 – $T = 920$ K, 2 – $T = 940$ K, 3 – $T = 960$ K, 4 – $T = 980$ K, 5 – $T = 1000$ K, 6 – $T = 1020$ K.

The different etching rates of GaAs (111)A and (111)B by liquid gallium affect the GaAs annealing kinetics. The total amount kinetic dependences of the evaporating GaAs substance at temperatures 1000 K and 1200 K are shown in Fig. 4. It can be seen that this dependence is nonlinear, indicating a change in the desorption rate with time. This fact was noted in the experimental work on the InAs Langmuir evaporation at high temperatures [22], where the material evaporation rate ceased to depend on time only after the entire surface had been covered with a liquid metal film. At the initial annealing stage, the evaporation is not stationary. As the surface relief develops and the gallium droplets size increases, the evaporating fluxes from the GaAs substrates begin to grow linearly with time. At $T = 1000$ K, the GaAs evaporation from the (111)B surface is more intense than that from (111)A (Fig. 4a). The main source of the evaporating matter from GaAs(111)B, along with steps of the vicinal surface are the vacancy islands on the terraces, and, from GaAs(111)A, it is the gallium droplets surface. Although there are more Ga droplets on the (111)B surface, their influence on the As evaporation rate is less significant than that on the (111)A surface, since the GaAs dissolution rate in liquid gallium for the (111)B orientation is

lower. At $T = 1000$ K, the gallium drops occupy only a small substrates surface fraction. At a higher annealing temperature ($T = 1200$ K Fig. 4(b)); when both GaAs substrates are rapidly completely covered by liquid gallium, the flux As/Ga ratio changes (Fig. 2(a)) and a more intensive evaporation occurs from the GaAs(111)A surface.

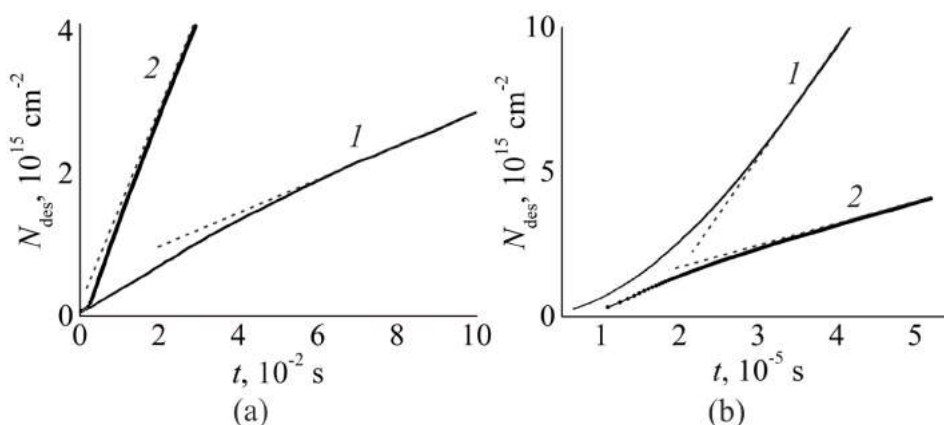


Fig. 4. The kinetic dependence of the vaporizing GaAs from the (111)A (1) and (111)B (2) surfaces under Langmuir evaporation conditions at (a) $T = 1000$ K and (b) $T = 1200$ K; dotted lines approximate stationary evaporation.

Summary

The dependence of the main GaAs Langmuir evaporation characteristics on the substrate surface orientation was examined by Monte Carlo simulation. The Ga droplets are easier created on the (111)B surface than on (111)A: the congruent evaporation temperature T_c is lower and the droplet concentration is higher. For the (111)A substrate orientation, the drop-crystal interface is rougher than that for (111)B. The congruent evaporation temperature was demonstrated to be the function of vicinal surface terrace width L . The change in the slope of As_2 evaporation rate temperature dependence for the (111)A surface orientation is revealed. This slope variation takes place at temperatures when an appreciable part of the GaAs surface is covered with liquid gallium. Liquid gallium acts as a pump increasing the arsenic evaporation from the (111)A surface. The features associated with the surface orientation can be explained by different Ga and As_2 volatilities and different rates of the (111)A and (111)B surface etchings by liquid gallium.

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References

- [1] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, S.I. Stenin, Transformations on Clean Si(111) stepped surface during sublimation, *Surf. Sci.* 213 (1989) 157-169.
- [2] K. Reyes, P. Smereka, D. Nothorn, J.M. Millunchick, S. Bietti, C. Somaschini, S. Sanguinetti, C. Frigeri, A unified model of droplet epitaxy for compound semiconductor nanostructures: experiments and theory, *Phys. Rev. B.* 87 (2013) 165406.
- [3] C. Colombo, D. Spirkoska, M. Frimmer, G. Abstreiter, A. Morral, Ga-assisted catalyst-free growth mechanism of GaAs nanowires by molecular beam epitaxy, *Phys. Rev. B* 77 (2008) 155326.
- [4] Z.M. Wang, B.L. Liang, K.A. Sablon, G.J. Salamo, Nanoholes fabricated by self-assembled gallium nanodrill on GaAs(100), *Appl. Phys. Lett.* 90 (2007) 113120.
- [5] S. Li, J. Wu, Z. Wang, Z. Li, Y. Su, Z. Wu, Y. Jiang, G.J. Salamo, Thermal etching process of microscale pits on the GaAs(001) surface, *Phys. Status Solidi RRL* 6 (2012) 25-27.

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- [6] C. Zhao, J. Li, Y. Yu, H. Ni, Z. Niu, X. Zhang, Observation of the in-plane spin-dephasing anisotropy in [111]-grown GaAs/AlGaAs quantum well, *Appl. Phys. Lett.* 104 (2014) 052411.
- [7] E. Stock, T. Warming, I. Ostapenko, S. Rodt, A. Schliwa, J.A. Töfflinger, A. Lochmann, A.I. Toropov, S.A. Moshchenko, D.V. Dmitriev, V.A. Haisler, D. Bimberg, Single-photon emission from InGaAs quantum dots grown on (111) GaAs, *Appl. Phys. Lett.* 96 (2010) 093112.
- [8] M. Jo, T. Mano, M. Abbarchi, T. Kuroda, Y. Sakuma, K. Sakoda, Self-Limiting Growth of Hexagonal and Tri-angular Quantum Dots on (111)A, *Cryst. Growth & Des.* 12 (2012) 1411-1415.
- [9] M.S. Abrahams, C.J. Buiocchi, Etching of Dislocations on the Low-Index Faces of GaAs, *J. Appl. Phys.* 36 (1965) 2855-2863.
- [10] T. Takebe, M. Fujii, T. Yamamoto, K. Fujita, T. Watanabe, Orientation – dependent Ga surface diffusion in molecular beam epitaxy of GaAs on GaAs patterned substrates, *J. Appl. Phys.* 81 (1997) 7273-7281.
- [11] C. Lou, G. Somorjai, Studies of the vaporization mechanism of gallium arsenide single crystals, *J. Chem. Phys.* 55 (1971) 4554-4565.
- [12] B. Goldshtein, D. Stozak, V. Ban, Langmuir evaporation from the (100), (111A) and (111B) faces of GaAs, *Surf. Sci.* 57 (1976) 733-740.
- [13] S. Kanjanachuchai, C. Euaruksakul, Self-running Ga droplets on GaAs (111)A and (111)B surfaces, *ACS Appl. Mater. Interfaces* 5 (2013) 7709-7713.
- [14] J.R. Arthur, Vapor pressures and phase equilibria in the Ga-As system, *J. Phys. Chem. Solids* 28 (1967) 2257-2267.
- [15] 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. Crystal Growth* 106 (1990) 543-552.
- [16] C. Chatillon, D. Chatain, Congruent vaporization of GaAs(s) and stability of Ga(l) droplets at the GaAs(s) surface, *J. Cryst. Growth* 151 (1995) 91-101.
- [17] 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.
- [18] N. Shwartz, M. Vasilenko, A. Nastovjak, I. Neizvestny, Concentric GaAs nanorings formation by droplet epitaxy – Monte Carlo simulation, *Comput. Mat. Sci.* 141 (2018) 91-100.
- [19] M. Vasilenko, I. Neizvestny, N. Shwartz, Formation of GaAs nanostructures by droplet epitaxy – Monte Carlo simulation, *Comput. Mat. Sci.* 102 (2015) 286-292.
- [20] A.A. Spirina, A.G. Nastovjak, N.L. Shwartz, Influence of GaAs substrates properties on the congruent evaporation temperature, *J. of Phys.: Conf. Ser.* 993 (2018) 012011.
- [21] J. Tersoff, D.E. Jesson, W.X. Tang, Decomposition Controlled by Surface Morphology during Langmuir Evaporation of GaAs, *Phys. Rev. Lett.* 105 (2010) 035702.
- [22] Yu.P. Khukhryanskii, L.N. Veremjanina, I.V. Nikishina, O.I. Sisoiev, Kinetics of Langmuir evaporation of indium phosphide and arsenide components, *J. Phys. Chem.* 71 (1997) 870-874 (in rus.)