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# Influence of GaAs substrate properties on the congruent evaporation temperature

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**Abstract.** High-temperature annealing of GaAs(111)A and GaAs(111)B substrates under Langmuir evaporation conditions was studied using Monte Carlo simulation. The maximal value of the congruent evaporation temperature was estimated. The congruent evaporation temperature was demonstrated to be dependent on the surface orientation and concentration of surface defects.

## 1. Introduction

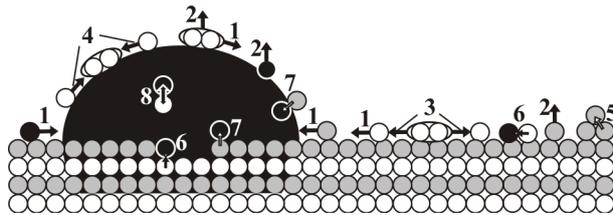
High-temperature substrate annealing in vacuum is called free or Langmuir evaporation. Depending on the temperature range, evaporation can be congruent, with equal numbers of A<sup>III</sup> and B<sup>V</sup> desorbed atoms, and non-congruent, when particles of group V evaporate more intensively, and the excess atoms of group III are assembled into clusters and form droplets on the surface. The transition from one evaporation mechanism to the other occurs at the temperature referred to as congruent. The renewal of interest in Langmuir evaporation of A<sup>III</sup>B<sup>V</sup> materials is associated with the formation of group III metal drops on the surface. Liquid metal droplets are used in the implementation of a number of technologies for nanostructure growth. It is known that metal droplets can act as a growth catalyst for semiconductor nanowires [1]. Metal droplets are the basis of droplet epitaxy. When crystallizing such droplets in an arsenic flux, nanostructures of various morphologies can be obtained [2]. Drops of liquid metal found their application in plasmonics as an active medium [3]. Langmuir evaporation of GaAs substrates has been studied for a long time [4–7]. It was experimentally shown that the congruent evaporation temperature depends on the surface orientation [5, 7]. However, the literature data on the congruent evaporation temperature are ambiguous. For example, the congruent evaporation temperature of Ga(001) was found to be 663° C in [5] and only 630° C in [7]. A detailed analysis of the processes occurring during Langmuir evaporation of A<sup>III</sup>B<sup>V</sup> materials is possible using Monte Carlo simulation. In this paper, the Monte Carlo model for Langmuir evaporation of GaAs substrates is described. Using this model, the reasons for the ambiguous determination of the congruent temperature are analyzed.

## 2. Monte Carlo Model

The simulations were carried out using the SilSim3D program package [8]. A four-component system was considered in the modeling of GaAs high-temperature annealing: Ga(*s*), Ga(*l*), As, As<sub>2</sub> (gallium in solid and liquid states, and atomic and molecular arsenic, respectively). The possible elementary events included in the model and schematically presented in figure 1 are: diffusion of components



over the surface, Ga(s), Ga(l), and As<sub>2</sub> desorption from the surface, As<sub>2</sub> dissociation and formation, phase transformations (melting, dissolution, crystallization), and As dissolution and diffusion in a liquid metal. The probability of any of these events depends on the temperature in accordance with the expression  $P = A \cdot \exp(-E_{\text{act}}/k_{\text{B}}T)$ , where  $A$  is the pre-exponential factor,  $E_{\text{act}}$  is the activation energy of the process,  $k_{\text{B}}$  is the Boltzmann constant,  $T$  is the temperature.



**Figure 1.** Schematic representation of elementary events of the model: 1 – particle diffusion along the surface; 2 – Ga and As<sub>2</sub> desorption; 3 – As<sub>2</sub> dissociation; 4 – As<sub>2</sub> formation; 5 – Ga melting; 6 – Ga crystallization; 7 – Ga dissolution; 8 – As dissolution in a liquid metal and diffusion through a liquid drop. As is marked in white, Ga(s) in gray, and Ga(l) in black; As<sub>2</sub> is shown in an ellipse.

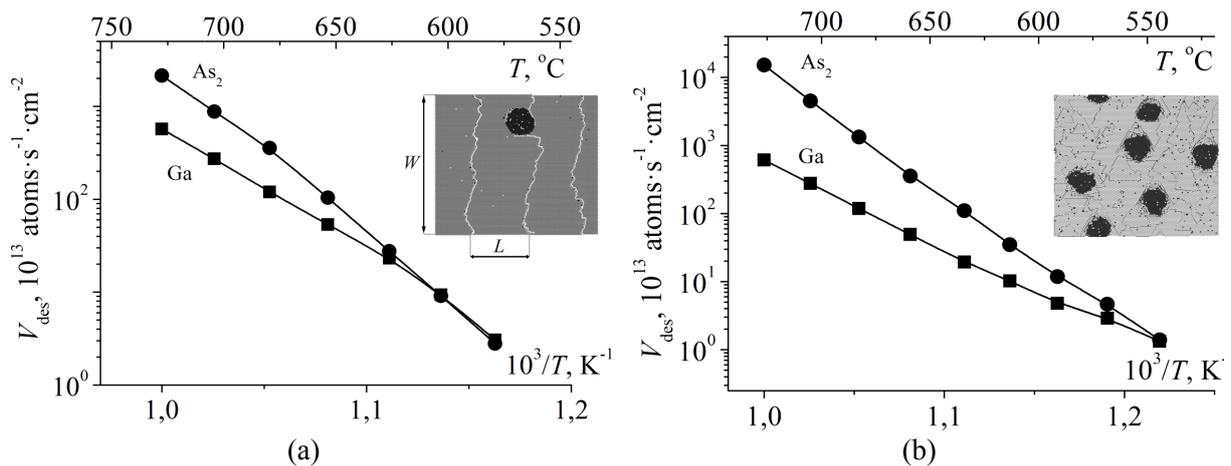
The energy parameters of the model were chosen on the basis of available literature data and special computational experiments. When choosing the energies of covalent interaction of particles, the correlation between the binding energy of atoms and the melting point of the material was taken into account [9]. The single-bond energy values were estimated by an empirical calculation, taking into account the electronegativity of the metal and As atoms [10]. The diffusion activation energy in liquid Ga of 0.7 eV was taken according to the experiment [11]. The activation energies of Ga dissolution in a liquid drop and Ga crystallization at a drop-crystal interface in the form of GaAs were chosen by fitting the simulated and experimental solubility of GaAs in liquid Ga [12]. By fitting the model and experimental [13] temperature dependences of the equilibrium gallium pressure over the Ga(l)-As solution surface, it was possible to estimate the liquid gallium desorption characteristics: the energy barrier for sublimation  $E_{\text{sub}}$  and the covalent interaction energies responsible for the gallium droplet surface tension. The model takes into account the decrease in the surface tension of a metal drop when atomic arsenic is dissolved in it. The equilibrium pressure of molecular arsenic depends on its concentration on the surface and on the As<sub>2</sub> desorption rate. The same characteristics determine the Langmuir evaporation rate. The molecular arsenic concentration is determined by the rates of As<sub>2</sub> decomposition and formation, that is, by the activation energies of these reactions. The activation energies of the reactions were estimated from the agreement of the model and experimental results of such processes as epitaxial growth, evaporation under equilibrium conditions and Langmuir evaporation. The parameters characterizing the As<sub>2</sub> desorption rate were chosen from the agreement of these calculation results with the experiment. A more detailed justification for choosing the values of energy parameters can be found elsewhere [14].

The simulation of high-temperature annealing of GaAs substrates was performed with the following values of energy parameters: the binding energy between atoms  $E_{\text{Ga-As}} = 0.9$  eV,  $E_{\text{As-As}} = 0.7$  eV,  $E_{\text{Ga-Ga}} = 0.6$  eV; the activation energies of gallium dissolution and crystallization  $E_{\text{dis}} = 1.25$  eV,  $E_{\text{cr}} = 1.2$  eV; the activation energy of molecular arsenic formation and decay  $E_{\text{form}} = 3.0$  eV;  $E_{\text{dec}} = 1.2$  eV.

### 3. Simulation results

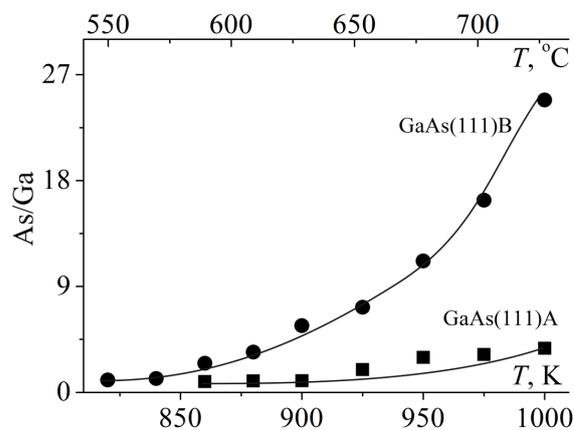
The simulation of Langmuir evaporation of GaAs substrates was carried out on vicinal surfaces with two surface orientations: (111)A and (111)B. In the annealing temperature range below  $T_c$ , layer-by-layer or congruent evaporation was observed; that is, arsenic and gallium evaporated at the same rate. In this temperature range, the evaporation rate is limited by the gallium evaporation rate. At temperatures above  $T_c$ , molecular arsenic evaporated more intensively than gallium atoms. The calculated temperature dependences of Ga and As<sub>2</sub> desorption rates at high-temperature annealing of

GaAs substrates are shown in figure 2. The excess of metal atoms on the surface at  $T > T_c$  leads to the formation of metal clusters, which causes the droplet nucleation. On the GaAs (111)A surface, gallium droplets were formed near the steps because of the maximum concentration of Ga atoms in this region. On the GaAs (111)B surface, the droplet nucleation starts on the point vacancy defects formed due to the high volatility of arsenic. The Ga desorption rate is the same during annealing of GaAs (111)A and GaAs (111)B substrates, in contrast to the  $\text{As}_2$  desorption rate.



**Figure 2.** Temperature dependences of Ga and  $\text{As}_2$  desorption rates in the Langmuir evaporation of GaAs(111)A (a) and GaAs(111)B (b) substrates. The inserts show the top views of model surfaces at  $T = 1000$  K,  $L = 20$  nm,  $W = 40$  nm.

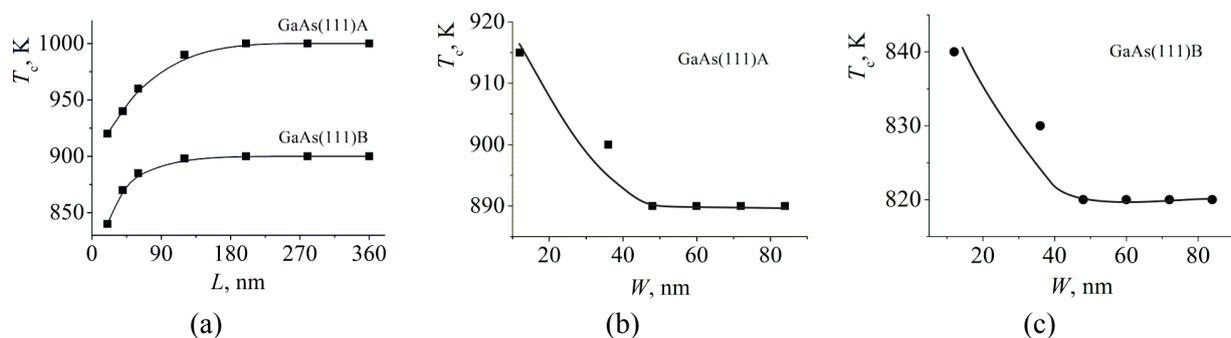
Figure 3 shows the temperature dependence of the ratio of evaporating arsenic to gallium fluxes. It can be seen that, at temperatures below  $T_c$  (850 K for GaAs (111)B and 920 K for GaAs (111)A), Ga and As atoms are removed from the surfaces in equal amounts. With an increase in the annealing temperatures ( $T > T_c$ ), the arsenic evaporation increases more intensively on the (111)B surface than on (111)A. This is explained by the crystallographic structure of substrates (the upper layer of GaAs(111)B consists of arsenic atoms) and the volatile properties of  $\text{As}_2$ .



**Figure 3.** Temperature dependence of the evaporating As/Ga flux ratio during annealing of GaAs(111)A and GaAs(111)B substrates;  $L = 20$  nm,  $W = 40$  nm.

The obtained congruent evaporation temperatures of model GaAs(111)A and GaAs(111)B substrates turned out to be smaller than the experimental values ( $T_c = 950$  K for (111)A,  $T_c = 900$  K for (111)B [5] and  $T_c = 930$  K for (111)A,  $T_c = 890$  K for (111)B [7]). The difference between the model and experimental  $T_c$  may have multiple explanations. The influence of the model surface sizes on the

congruent temperature was analyzed. To realize this, the simulation was carried out on vicinal substrates with different widths  $W$  (step lengths) and length  $L$  of terraces (distance between steps). With an increase in the terrace length, the congruent temperature increased (figure 4(a)). With increasing  $L$ , the step density on the substrate surface decreased. A decrease in the step density leads to a decrease of Ga adatom concentration and, as a result, the droplets are formed at a higher temperature. When the distance between the steps reached the double gallium diffusion length before the evaporation, the steps stopped interacting with each other and  $T_c$  ceased to change. Under these conditions, surface vacancy islands were formed on the terraces during annealing. A decrease in the length of steps  $W$  leads to an increase in the congruent temperature (figure 4(b, c)). Such a dependence of  $T_c$  on the step length was observed at  $W < 40$  nm. To eliminate the influence of the geometric factor on the simulation results, the calculations were carried out at  $W > 40$  nm. As can be seen in figure 4(a), a noticeable decrease in the congruent evaporation temperature is observed when the surface deviates from the (111) direction at an appreciable angle (more than  $0.1^\circ$ ), and the annealing of surfaces close to the singular ones points to an overestimated  $T_c$  value ( $T_c = 1000$  K for GaAs(111)A and  $T_c = 900$  K for GaAs(111)B), in comparison with the experiment.

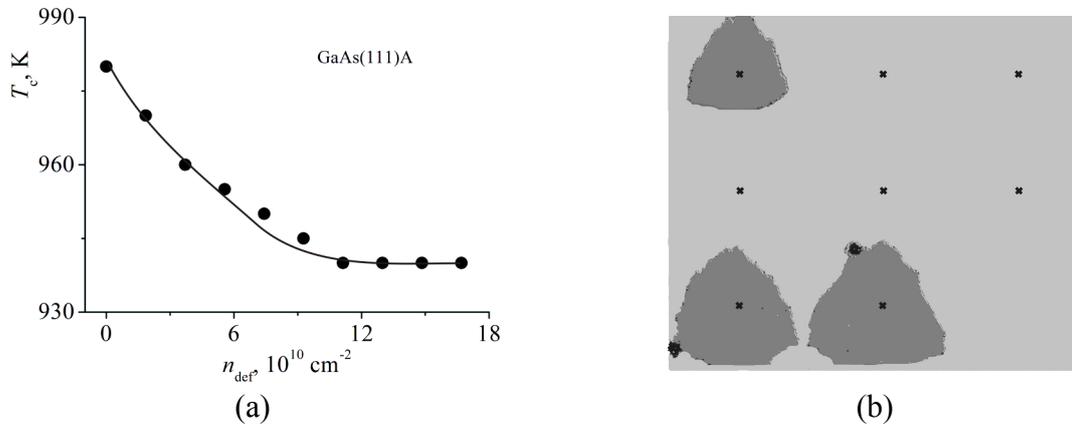


**Figure 4.** The congruent evaporation temperature *versus* terrace length (a) and the terrace width (b, c) of vicinal GaAs(111)A and GaAs(111)B surfaces.

The discrepancy between the experimental and calculated  $T_c$  may be due to the presence of defects on the real surface. Surface defects should lead to an increase in the concentration of gallium adatoms and, consequently, to an increase in the probability of drop formation. Therefore, when considering the ideal model surface, the congruent evaporation temperature is likely to be slightly overestimated. Figure 5(a) shows the congruent temperature as a function of the concentration of point surface defects. It is seen that  $T_c$  initially decreases with the increasing defect concentration, but when  $n_{\text{def}}^*$  reaches a certain concentration,  $T_c$  ceases to depend on  $n_{\text{def}}$ . Point defects provoke the formation and the subsequent enlargement of vacancy islands that increase the concentration of gallium adatoms on the surface. However, for high defect concentration, when the average distance between them becomes less than the gallium and arsenic diffusion lengths, some of the islands are built up by embedding of Ga and As atoms in the vacancy island steps, and the original defect disappears from the surface. The model surface image with the initial density of point defects  $n_{\text{def}} > n_{\text{def}}^*$  after annealing is shown in figure 5(b). One can see that out of eight original point defects, there are only three that resulted in the formation of triangular vacancy islands, and the number of drops on the surface is even smaller (two).

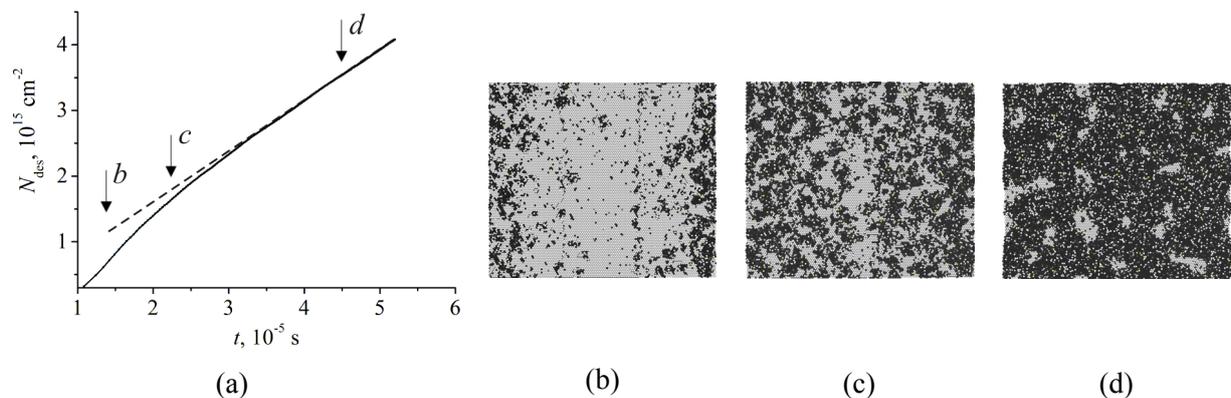
It should be noted that the desorption rate can vary with time. Figure 6(a) demonstrates the dependence of the total number of atoms (gallium and arsenic) evaporating from the vicinal GaAs(111)B surface on the annealing time. It can be seen that this dependence is nonlinear, indicating a change in the desorption rate with time. This fact was noted in the experimental work on the InAs Langmuir evaporation [15], where the material evaporation rate ceased to depend on time only after the entire surface had been covered with a liquid metal film. Figures 6(b-d) show the surface images at different moments of the annealing process. These moments are indicated in figure 6(a) by the arrows.

It can be seen that the desorption rate becomes practically constant when almost all the surface is covered with liquid Ga.



**Figure 5.** (a) The congruent evaporation temperature of the singular GaAs (111)A substrate as a function of the concentration of point surface defects; (b) top view of the GaAs(111)A surface after annealing at  $T = 970$  K; the crosses mark the positions of original defects.

The analysis of simulation results showed that the dispersion in congruent temperature values in different experiments can be related not only to inaccuracy in measuring the substrate temperature, but also to the substrate itself: the degree of deviation from the singular surface and the concentration of surface defects. In addition, measuring the desorption rate at the initial annealing stage, before the surface is completely covered by a liquid metal, can also lead to inaccuracy in determining  $T_c$ .



**Figure 6.** (a) Dependence of the total number of evaporating gallium and arsenic atoms from the GaAs(111)B surface on the annealing time at  $T = 1200$  K; (b-d) the model surface top views after different annealing times.

#### 4. Conclusions

The processes of high-temperature annealing of GaAs(111)A and GaAs(111)B substrates under Langmuir evaporation conditions were studied using Monte Carlo simulations. The congruent and noncongruent evaporation temperature ranges were determined. The maximum congruent evaporation temperature was estimated. The formation of metal droplets on the (111)A surface began near the steps of the vicinal substrates and, on the (111)B surface, the droplets were formed and randomly distributed over the entire substrate surface. The desorption rate dependence on the annealing time and

the kinetics of the surface morphological evolution during noncongruent evaporation were analyzed. It was found that the congruent temperature value depends on the substrate orientation, step density on the vicinal surface and point defect concentration on the singular surface.

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