Study of the geometrical parameters of In nanostructures during droplet epitaxy on the As-stabilized GaAs(001) surface

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Abstract. The droplet epitaxy of indium on the As-stabilized GaAs(001) surface is investigated using theoretical model and experimental studies. The model is developed on the basis of a combination of the nucleation thermodynamic theory and kinetic Monte Carlo algorithm. The surface density of droplets is observed to decrease with increasing temperature whereas both the droplet diameter and height increases because of the intensive attachment of In adatoms to larger, i.e. more stable, islands. At the same time, the droplet aspect ratio demonstrates a nonmonotonic temperature dependence. Although a general tendency for the aspect ratio with increasing temperature is falling, there is a temperature at which the aspect ratio is maximal both for simulations and experiments. This is caused by the temperature balancing between the wetting of the substrate and the formation of islands with near-spherical shape. The simulation results are in good agreement with obtained experimental data in a wide range of substrate temperatures.

1. Introduction
The use of nanostructures opens wide prospects for the realization of nanolasers, photonic integrated circuits, quantum computers and other novel devices. III–V semiconductor materials are of particular interest due to their optoelectronic properties and technological capabilities \cite{1-6}. However, precise control of the geometrical characteristics of nanostructures is necessary to ensure required device parameters. The Stranski-Krastanov growth mode is commonly used to obtain an array of self-organized quantum dots in a lattice-mismatched material system, such as Ge/Si \cite{7,8} or InAs/GaAs \cite{9,10}. However, the impossibility to fabricate quantum dots in lattice-matched systems and to exercise an independent control of their size and surface density imposes a number of shortcomings on the Stranski-Krastanov growth method as compared with droplet epitaxial formation of quantum dots \cite{11-17}. The latter method has been actively used for last three decades to fabricate nanostructures with different shape and size, including InAs/GaAs quantum dots of segmental shape \cite{18-20}. The influence of the substrate temperature on the characteristics of nanostructures has been investigated during both stages of droplet epitaxy: formation of metallic droplets \cite{16,21} and their crystallization in the flux of group V molecules \cite{20,22}. Nevertheless, mechanisms of nucleation and growth of metallic nanostructures still remain unclear. One of important issues is a balance between the formation of an island and the substrate wetting.

In the present work, we carry out a complex investigation of geometrical parameters during In/GaAs(001) droplet epitaxy on the As-stabilized surface. We use the combination of analytical theory and kinetic Monte Carlo method to compare the experimental results with the simulation and to
analyze the microscopic processes. This approach allows combining productivity of the analytical model and versatility of Monte Carlo simulations [23-27].

2. Description of the model
The model used in the current work was previously developed and applied to the droplet epitaxial growth on the Ga- and As-stabilized GaAs surfaces [11,28]. It is based on the (1+1)-dimensional approach with calculation of interatomic binding energies using the expression of the Lennard–Jones potential. Deposition, desorption and diffusion of atoms through six nearest sites are implemented with the probability defined by the Arrhenius equation. The probability determines a waiting time for a certain event and put into a queue in the general time scale.

We previously validated the model by the experiments in a wide range of growth temperatures [11]. The studies demonstrated nonmonotonic dynamics of the adatom supersaturation and island critical size as well as formation of the wetting layer with thickness depending on the substrate temperature. In this work, we use the As-stabilized GaAs substrate with the (001) orientation to study the dependence of the droplet geometrical parameters, such as surface density, curvature radius, height and aspect ratio, on the growth temperature. A linear size of the simulation area equal to 200 nm is considered to be sufficient for the low-temperature growth (below 300 °C) to estimate the characteristics of nanostructures.

3. Experiment
The samples were grown on the GaAs(001) epi-ready substrates using the the SemiTEq STE 35 molecular beam epitaxy system with solid state sources. First, we carried out a standard procedure of the oxide removal and deposited a 400-nm thick GaAs buffer at a substrate temperature of 580°C. Then we closed the arsenic source and cooled the substrate down to the growth temperature at which the droplet epitaxy studies were carried out. The substrate temperature was varied from 150 to 350°C in 50°C increments. We preliminarily calibrated the indium growth rate by the growth of InGaAs ternary compounds. A growth rate of 0.5 ML/s and an equivalent deposition thickness of 4 ML were used for all samples. After the In droplets had been formed, we quenched the samples and transferred to the SEM characterization.

![Image](image1.png)

**Figure 1.** SEM images of the droplet arrays after deposition of 4 ML of indium at $T = 150°C$ (a) and $T = 250°C$ (b).

The results of experimental studies demonstrated that the droplets have a shape of spherical segments with an acute contact angle (Figure 1). The droplet arrays are not spatially ordered, but the size distribution is quite uniform. Tiny droplets are practically not observed which is due to the fact that small islands of subcritical size are not stable and tend to decompose rapidly according to the
classical nucleation theory [29,30]. During the period while the substrate is being quenched the processes of Ostwald ripening and island stabilization occur.

The experiments show that the surface density of droplets is low, as compared with other material systems, such as Ga/GaAs or Ga/AlGaAs [12,31-33]. This is due to the higher mobility of In adatoms and smaller diffusion length of Ga adatoms [34]. The high diffusivity of In adatoms on the GaAs substrate is an advantage of this system which allows achieving a sufficient distance between nanostructures and eliminate undesirable quantum-mechanical interactions.

Figure 1 demonstrates that an increase of the substrate temperature leads to an increase in the average droplet size and to a decrease in the surface density of droplets. This phenomena is not unexpected since it was observed in a number of growth systems, including droplet epitaxy [16,21]. The reason of this behavior is the decomposition of unstable nuclei and surface diffusion of released atoms towards the most stable ones as a result of the mobilization connected with an increase in the growth temperature.

4. Simulation results and discussion

The simulation was carried out for the experimental temperature range with the same deposition thickness and annealing during 5 seconds. Morphology of droplets at the substrate temperature \( T = 150 \, ^\circ \text{C} \) and \( T = 250 \, ^\circ \text{C} \) is presented in Figure 2. The islands nucleate randomly on the surface of the substrate, grow and take a shape of non-ideal spherical segment. The wetting layer with thickness exceeding 1 monolayer is formed on the surface. In contrast to the Ga-stabilized surface, on which formation of the wetting layer is suppressed almost completely [28], the wetting layer is formed on the As-stabilized surface and its thickness decreases with increasing temperature, which is confirmed by our previous study [11]. This behavior is explained by the fact that binding energy of metallic atoms (In and Ga atoms) between each other is lower than the covalent bond between In and As atoms. The larger barrier is needed to be overcome to start the nucleation. Consequently, the wetting layer of larger thickness remains on the surface.

![Figure 2](image2.png)

**Figure 2.** Morphology of In droplets after deposition of 4 monolayers of indium on the As-stabilized GaAs(001) surface at \( v = 0.5 \, \text{ML/s} \) and \( a) \ T = 150 \, ^\circ \text{C}, \ b) \ T = 250 \, ^\circ \text{C} \). The simulation area is 300 nm long.

One can see that the islands vary in geometrical parameters depending on the growth temperature. The surface density of droplets decreases twice with the temperature increasing from 150 \( ^\circ \text{C} \) to 250 \( ^\circ \text{C} \). At the same time, an increase in the droplet diameter is also observed. Figure 3 shows the quantitative difference between the geometrical characteristics of In nanostructures obtained at different substrate temperatures. A good agreement of the simulation results with the experiments in a wide range of temperatures is observed. A slight discrepancy is explained by the specifics of the experiments.
Figure 3. Temperature dependence of the droplet diameter and density ($H = 4$ ML, $v = 0.5$ ML/s). Filled figures – experiments, open figures – simulation.

Figure 4. Temperature dependence of the droplet height and aspect ratio ($H = 4$ ML, $v = 0.5$ ML/s). Filled figures – experiments, open figures – simulation.

Figure 4 demonstrates that the droplet height increases with increasing temperature which is also connected with the intensification of the surface diffusion. However, the average aspect ratio of a droplet expressed as a ratio of the droplet diameter to the droplet height does not change monotonically. It is known that the wetting of the substrate by the liquid phase becomes better with increasing temperature [35], but we reveal that there is a maximum value of the aspect ratio which does not correspond to the minimal value of the temperature. Although there is no precise coincidence of the simulation results with the experiments, there is a common regularity concerning the temperature dependence of the aspect ratio. Our model takes into account the fact that at low temperatures adatoms are not as mobile as at high temperatures. They have a larger energetic barrier to detach from the substrate and form a droplet with larger contact angle. The presence of the peak in the temperature dependence of the aspect ratio is a consequence of the temperature balance between the substrate wetting and the mutual attraction between In atoms.

5. Conclusion
In summary, we carried out the experimental and theoretical study of geometrical parameters of In nanostructures during droplet epitaxial growth on the As-stabilized GaAs(001) surface. The analytical–Monte Carlo model we used in the present study demonstrated a good agreement with the experiments in a wide range of growth conditions. It was observed that the surface density of droplets decreases with increasing temperature whereas the average droplet diameter and height increases. We revealed that the temperature dependence of the droplet aspect ratio has a maximum value at $T = 200$ °C which is explained by the fact that the contact angle cannot increase continuously at low temperatures. The location of the peak is determined by the balance between the substrate wetting and the detachment of adatoms from the surface to form a droplet with a large contact angle.

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References
[1] Ageev O A, Smirnov V A, Solodovnik M S, Rukomoikin A V and Avilov V I 2012 *Semiconductors* **46** 1616–1621
[2] Klimin V S, Solodovnik M S, Smirnov V A, Eskov A V, Tominov R V and Ageev O A 2016 Proceedings of SPIE 10224 1022412

[3] Mokkapati S and Jagadish C 2009 Mater. Today 12 22–32

[4] Ageev O A, Klimin V S, Solodovnik M S, Eskov A V and Krasnoborodko S Y 2016 J. Phys.: Conf. Ser. 741 012178

[5] Avilov V I, Ageev O A, Smirnov V A, Solodovnik M S and Tsukanova O G 2015 Nanotech. in Russia 10 214-219

[6] Ageev O A, Solodovnik M S, Balakirev S V, Eremenko M M and Mikhailin I A 2016 J. Phys.: Conf. Ser. 741 012012

[7] Brehm M and Grydlík M 2017 Nanotechnology 28 392001

[8] Santalla S N, Kanyinda-Malu C and Cruz R M 2003 J. Cryst. Growth 253 190–197

[9] Grundmann M, Stier O and Bimberg D 1995 Phys. Rev. B 52 11969

[10] Yamaguchi K, Yurobo K and Kaizu T 2000 Jpn. J. Appl. Phys. 39 L1245–L1248

[11] Balakirev S V, Solodovnik M S and Ageev O A 2018 Phys. Status Solidi B 255 1700360

[12] Solodovnik M S, Balakirev S V, Eremenko M M, Mikhailin I A, Avilov V I, Lisitsyn S A and Ageev O A 2017 J. Phys. Condens. Matt. 19 176223

[13] Somaschini C, Bietti S, Koguchi N and Sanguinetti S 2010 Appl. Phys. Lett. 97 203109

[14] Somaschini C, Bietti S, Koguchi N and Sanguinetti S 2009 Nano Lett. 9 3419–24

[15] Mano T, Watanabe K, Tsukamoto S, Fujioka H, Oshima M and Koguchi N 1999 Jpn. J. Appl. Phys. 38 L1009–11

[16] Lee J H, Wang Z M and Salamo G J 2007 J. Phys. Condens. Matt. 19 176223

[17] Lee J H, Wang Z M, Kim E S, Kim N Y, Park S H and Salamo G J 2009 Nanoscale Res. Lett. 5 308–14

[18] Mano T, Watanabe K, Tsukamoto S, Imanaka Y, Takamasu T, Fujioka H, Kido G, Oshima M and Koguchi N 2000 Jpn. J. Appl. Phys. 39 4580–3

[19] Lee J, Wang Z and Salamo G 2009 IEEE Trans. Nanotechnol. 8 431–436

[20] Noda T, Mano T and Sakaki H 2011 Crystal Growth & Design 11 726–8

[21] Kim J S and Koguchi N 2004 Appl. Phys. Lett. 85 5893–5895

[22] Noda T and Mano T 2008 Appl. Surf. Sci. 254 7777

[23] Ageev O A, Solodovnik M S, Balakirev S V and Eremenko M M 2016 J. Vac. Sci. Technol. B 34 041804

[24] Balakirev S V, Solodovnik M S, Eremenko M M, Mikhailin I A and Ageev O A 2017 J. Phys. Condens. Matt. 19 176223

[25] Ageev O A, Solodovnik M S, Balakirev S V and Mikhailin I A 2016 Technical Physics 61 971–977

[26] Reyes K, Smereka P, Nothern D, Millunchick J M, Bietti S, Somaschini C, Sanguinetti S and Frigeri C 2013 Phys. Rev. B 87 165406

[27] Ageev O A, Solodovnik M S, Balakirev S V and Mikhailin I A 2016 J. Phys. Condens. Matt. 19 176223

[28] Balakirev S V, Solodovnik M S, Eremenko M M, Mikhailin I A and Ageev O A 2017 J. Phys. Condens. Matt. 19 176223

[29] Dubrovskii V G 2014 Nucleation Theory and Growth of Nanostructures (Berlin: Springer) p 601

[30] Kelton K and Greer A L 2010 Nucleation in Condensed Matter: Applications in Materials and Biology (Amsterdam: Elsevier) p 756.

[31] Ageev O A, Solodovnik M S, Balakirev S V and Eremenko M M 2016 Phys. Solid State 58 1045

[32] Somaschini C, Bietti S, Sanguinetti S, Koguchi N and Fedorov A 2010 Nanotechnology 21 125601

[33] Lee C D, Park C, Lee H J, Park S, Lee K S, Park C, Noh S and Koguchi N 1998 Jpn. J. Appl. Phys. 37 7158.

[34] Ageev O A, Solodovnik M S, Balakirev S V, Mikhailin I A and Eremenko M M 2017 J. Cryst.
Growth 457 46

[35] Zhang H, Chen Y, Zhou G, Tang C and Wang Z 2012 Nanoscale Res. Lett. 7 600