Kinetic Monte Carlo simulation of the indium droplet epitaxy on the Ga-terminated GaAs(001) surface

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Abstract. Model of In/GaAs(001) molecular beam epitaxial growth is developed to study the processes of droplet epitaxy on the Ga-terminated surface. The model allows computation of significant geometrical characteristics of nanostructures on a large scale and estimating a phase of material by the crystal density. The nucleation and growth mechanisms in a range of indium near-melting temperatures are investigated. Average size of islands is shown to increase with rising substrate temperature whereas the island density demonstrates an inverse relationship between these parameters. An increase of the growth rate intensifies the nucleation processes and leads to an increase in the droplet surface density and decrease in the average droplet diameter. The deposition thickness is observed to have an influence on the island size, but not impact on the surface density of islands.

1. Introduction
Ample opportunities for application of AIIIBV nanostructures in nanoelectronic and photonic devices lead to the necessity of better controlling their parameters. Therefore, methods of the formation of nanostructures with specified characteristics have been actively developed. One of these methods is droplet epitaxy which allows the formation of nanostructure arrays with either ultralarge or ultrasmall surface density, a wide range of sizes and in a wide range of technological parameters.

Although AlGaAs droplet epitaxial system has been successfully investigated for a long time [1–3], there is a lack of studies on InAs/GaAs nanostructures formed by this method. Because of difficulties in simulation of InAs/GaAs growth processes, theoretical works on the droplet epitaxy of InAs on the GaAs substrate are rare or absent at all. Experimental studies made it possible to examine basic nucleation, growth and crystallization processes [4–6] and determine the dependences of diffusion parameters and geometrical characteristics on the growth conditions [4,5,7,8]. However, in all these works the growth was carried out on As-terminated surfaces because obtaining Ga-stabilized conditions (especially under low growth temperatures) is a challenge. At the same time, droplet nucleation on the metal-terminated surfaces is expected to occur without wetting layer formation which could be useful for many applications.

In the present work, kinetic Monte Carlo method is used to simulate the MBE growth of indium on the Ga-terminated GaAs(001) surface. This technique permits to reproduce the growth process on a large time and dimensional scale and consider many relevant microscopic processes and features of the material system [9,10].
2. Description of the model

2.1. Crystal

The simulation area represents a two-layered square lattice with a lateral period of 0.2 nm and 0.14 nm in vertical direction. The nearest sites are located diagonally to each other so that the distance between two layers of the simulation lattice is equal to 0.2 nm. Thus, the (1+1)-dimensional approach of the crystal simulation is used [1] and the zinc blende structure of GaAs is taken as a basis.

Each atom in the lattice is bound to atoms belonging to seven coordination spheres characterizing distances between sites. The distance \( r \) between an atom and its neighbour enters into the expression of the Lennard–Jones potential [11]:

\[
U(r) = \epsilon \left( \frac{r_m^{12}}{r^{12}} - 2 \frac{r_m^6}{r^6} \right)
\]

where \( r_m \) is the distance at which the potential reaches its minimum, \( \epsilon \) is the interaction energy of a pair of atoms at the distance \( r_m \). Values for \( r_m \) are taken to be average inter-atomic distances in the substance to which a pair of atoms belongs. The binding energy of all pairs “atom–neighbour” amounts to the total binding energy of an atom in a certain environment.

Before the growth starts, the simulation lattice is filled with atoms of the GaAs substrate. The upper layer is set to be gallium monolayer implying that Ga-terminated conditions are created on the surface. This situation can be achieved by appropriate simultaneous control of the substrate temperature and arsenic flux before cooling down the sample. Low temperatures (100–200°C), at which the simulations are carried out in this work, allow maintaining these conditions.

2.2. Microscopic processes on the surface

Atoms on the substrate can occupy each site of the lattice, even in case they do not fit in the starting zinc blende structure. The deposition is implemented as an appearance of an atom in a random site next layer above the substrate or the growing layer. Deposited atoms are considered to be adsorbed immediately. The probability of depositing a new indium atom is predefined by the growth rate.

A deposited atom, then, can diffuse in one of empty site of the 1\(^{st}\) or 2\(^{nd}\) coordination sphere. Therefore, six directions for the atom migration are available. In order to estimate the activation barrier for the diffusion, the difference between binding energies with initial and final neighbourhoods is calculated. The probabilities obtained for each possible direction are summed up and normalized to unity. The direction is selected by a random number distributed uniformly over the interval (0–1). If a site where an atom can move to is occupied by a neighbouring atom, the probability of the migration in this direction goes to zero because atom exchange is impossible.

The desorption of In atoms is neglected since the growth temperature under consideration is low.

2.3. Kinetic Monte Carlo procedure

The algorithm is based on the traditional kinetic Monte Carlo technique [12]. The activation energy \( E_i \) for an event \( i \) defines its probability expressed by the Arrhenius equation [13,14]:

\[
p_i = n_0 \exp \left( E_i / k_B T \right)
\]

where \( n_0 \) is the attempt frequency, \( k_B \) is the Boltzmann constant, \( T \) is the growth temperature.

When all events are processed and unnecessary ones are rejected, the expectation time for each event is calculated as follows:

\[
\tau_i = -\frac{1}{p_i} \ln \delta
\]

where \( \delta \) is a random number distributed uniformly over the range (0–1).

After an event is executed, its expectation time is added to the total growth time (settled-life time). An event with the minimal settled-life time is executed during each iteration.
3. Results and discussion
Using the model, the MBE growth of indium on the GaAs(001) substrate in a range of the indium near-melting temperatures (100–200 °C) is investigated. The simulation results show that all indium atoms conglomerate into islands of near-segmental shape (figure 1). A wetting layer does not form on the surface. However, because of the attractive force of the substrate the island shape is far from semispherical and the contact angle is small.

In figure 1, the difference between the crystal densities in different regions of the island can be discerned. In some regions atoms are located closer to each other and some regions are more rarefied. In the framework of the zinc blende-based lattice, it is impossible to simulate the ideal structure of the solid indium. However, the density of atoms in a part of an island allows approximate estimating the substance phase. At \( T = 150 \, ^\circ\mathrm{C} \) (which is 6.6 °C below the indium melting temperature) the aggregate state of islands is expected to be solid. However, a quantity of experimental works is evidence of the liquid droplet formation in a range of temperatures from 100 to 200 °C and more which can be attributed to the dimensional effect. As figure 1 demonstrates, the crystal in larger islands is denser as well as in the depth of an island. This observation confirms the fact that nanometer islands can be liquid under the melting temperature due to the dimensional effect.

![Figure 1](image1.png)

**Figure 1.** Morphology of In droplets after deposition of 3 monolayers of indium on the Ga-terminated GaAs(001) surface at \( T = 150 \, ^\circ\mathrm{C} \): a) \( v = 0.5 \, \text{ML/s} \), B) \( v = 1 \, \text{ML/s} \), C) \( v = 2 \, \text{ML/s} \).

Figure 2 shows the dependences of the droplet array characteristics on the growth rate \( v \) and temperature \( T \). An increase of the droplet density is observed both with decreasing substrate temperature (figure 2a) and increasing growth rate (figure 2c). This behavior is attributed to the enhancement and suppression of the surface diffusion of In adatoms, respectively. It is known [15,16] that geometry of MBE grown islands strongly depends on the migration of metal atoms on the surface. Since the critical island size falls with increasing supersaturation, the average island size is observed to decrease at the same time (figures 2b and 2d). At \( T = 100 \, ^\circ\mathrm{C} \) and \( v = 1 \, \text{ML/s} \), the droplet density is equal to \( 6 \times 10^{10} \, \text{cm}^{-2} \) and average size is about 8 nm, whereas these values are \( 8 \times 10^{8} \, \text{cm}^{-2} \) and 80 nm, respectively, at \( T = 200 \, ^\circ\mathrm{C} \) and \( v = 0.25 \, \text{ML/s} \). The simulation values are in good agreement with experimental data [8,17].
An increase of the growth rate leads to the gradual saturation of the temperature dependence of the droplet density. This phenomenon can be explained by the fact that the concentration of indium nuclei on the GaAs(001) surface cannot reach the adatom concentration or even the doublet concentration according to Frenkel’s theory [18]. There is a critical size under which an indium cluster is unstable and exposed to the decay.

The growth rate dependence of the droplet diameter (figure 2d) is observed to become stronger when the temperature exceeds the indium melting point (156.6 °C). The most probable reason of this behaviour is the exponential growth of the island diameter with increasing temperature. However, the island crystal phase or shape dynamics could have a significant influence on this dependence too.

![Figure 2](image1.png)

**Figure 2.** Temperature (a, b) and growth rate (c, d) dependences of the In/GaAs(001) nanostructure surface density (a, c) and average diameter (b, d).

The possibility to control island characteristics by altering the deposition thickness is also found. As figure 3 shows, the average size of droplets steadily increases with increasing amount of the deposited material whereas the island density remains almost steady. This means that the deposition thickness does not have an impact on the nucleation processes and only leads to the island growth and shape transformation. Therefore, the average size of In/GaAs nanostructures can be adjusted while maintaining their density with a value defined by the other technological parameters.
4. Conclusion
In summary, the low-temperature droplet epitaxy of indium on the Ga-terminated GaAs(001) surface was investigated using the kinetic Monte Carlo model. Using the simulations, we considered the significant microscopic processes on the surface and the crystal phase of growing material and calculated the geometrical characteristics of In/GaAs(001) nanostructures. The average island size was found to increase with rising substrate temperature and decreasing growth rate whereas the island surface density is exposed to the opposite influence. It was shown that the size of nanostructures can be adjusted by varying the deposition thickness without changing the island density. As the simulations results are in good agreement with experimental data, the model is applicable to the description of the initial stage of the AIII BV nanostructure formation and is intended to be developed to consider the processes of the droplet crystallization and formation of nanostructures on modified surfaces with complicated morphology.

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