

# Self-catalyzed GaAs and InAs nanowire growth (Monte Carlo simulation)

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**Abstract.** A new lattice Monte Carlo model of  $A^{III}B^V$  nanowire growth according to the vapor-liquid-solid mechanism is suggested. The peculiarities of this model and the procedure of energy parameters estimation for the InAs system are described. The characteristics of InAs and GaAs self-catalyzed nanowire growth are obtained using the suggested model. A comparison of InAs and GaAs self-catalyzed nanowire growth characteristics using the suggested Monte Carlo model is performed.

## 1. Introduction

Attention to nanowires (NWs) on the base of III-V materials can be attributed to their promising applications in opto- and nanoelectronics [1–3]. The first method of semiconductor NW formation is growth from catalyst drops according to the vapor-liquid-solid (VLS) mechanism [4]. For  $A^{III}B^V$  semiconductors self-catalyzed NW growth is promising when one of the elements composing the semiconductor – metal (In or Ga) is used as a catalyst [5–7].

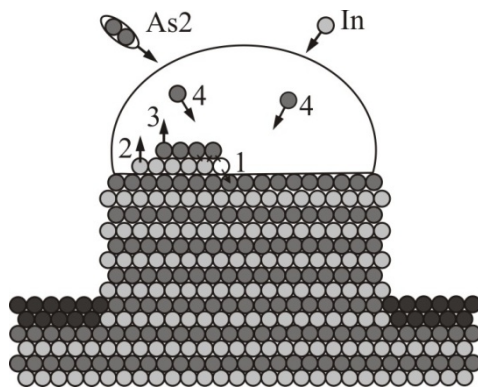
Theoretical works helped to explain some experimental results and revealed that self-catalyzed growth is more sensitive to the arsenic flux than the growth from golden droplets [8, 9]. Experimentally, it was demonstrated that InAs NWs had a narrower temperature range for growth in comparison with GaAs NWs [10]. Recently, it has been demonstrated that trials to extend the temperature range in a high temperature direction results in catalyst-free InAs nanowires growth [11]. There are only few works devoted to MBE growth of InAs NWs according to the VLS mechanism [6, 7]. Monte Carlo (MC) simulation can help in clearing up the details of nanostructure growth. Up to the present, only a number of articles have been devoted to MC simulation of nanowire growth according to the VLS mechanism [12, 13]. The results of MC simulation of GaAs NW growth with gold and gallium drops as catalysts were presented in [13]. In the present work a modified variant of the lattice MC model of self-catalyzed NW growth is suggested. The procedure of energy parameters estimation for the InAs system is described. The comparison of InAs and GaAs self-catalyzed nanowire growth characteristics is fulfilled using this model.

## 2. Monte Carlo model

Simulation was carried out using the program package SilSim3D [14]. The present MC model is similar to that presented in [13]. However, instead of the 6-component system suggested in [13], now we consider the 5-component system:  $As_2$ , As, Ga (In),  $Ga_{liq}$  ( $In_{liq}$ ) and  $M_r$ —molecular arsenic, atomic arsenic, gallium (indium) in solid and liquid phases and the film-mask material. In the modified model



liquid arsenic is excluded from consideration and the liquid phase is suggested only for gallium (indium). Following [13], the main processes included in the model are: Ga (In) and  $\text{As}_2$  adsorption, molecular arsenic dissociation and creation on the surface, gallium and arsenic surface diffusion,  $\text{As}_2$ , Ga (In),  $\text{Ga}_{\text{liq}}$  ( $\text{In}_{\text{liq}}$ ) desorption, transformation of solid gallium (indium) into the liquid state, atomic arsenic dissolution in liquid gallium (indium) and diffusion through a liquid drop,  $\text{Ga}_{\text{liq}}$  ( $\text{In}_{\text{liq}}$ ) crystallization at the drop-GaAs (InAs) interface. The processes considered in the drop and at the liquid-crystal interface are illustrated in figure 1.

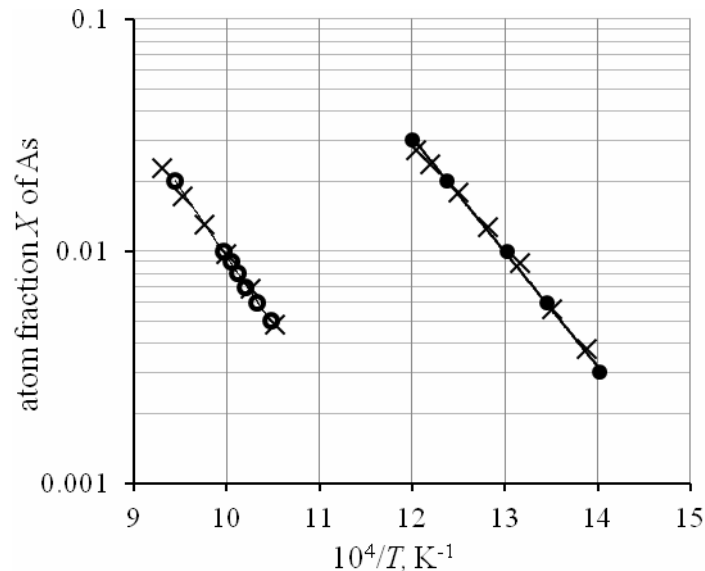


**Figure 1.** A scheme of the model system and the processes considered in the drop and drop-crystal interface: crystallization (1) and dissolution (2) of Ga (In), As dissolution (3) in the a liquid drop, As diffusion through a metal drop (4). The catalyst material  $\text{Ga}_{\text{liq}}$  ( $\text{In}_{\text{liq}}$ ) is marked in white, Ga (In) - in light gray, As - in gray, the material mask - in black colors.

The liquid phase in the lattice model of VLS NW growth is imitated similar to the model of droplet epitaxy growth [15]. The drop surface tension is controlled by covalent binding energies between liquid atoms and wetting – by the binding energies between drop and substrate atoms. The catalytic action of liquid indium or liquid gallium on the growth process was realized by decreasing the energy barrier for molecular arsenic dissociation on the Ga (In) drop surface. The activation energy values of elementary events for the GaAs system were chosen according to [13, 15]. The value of liquid In surface tension of  $0.5 \text{ J/m}^2$  is 1.3 times less than the liquid Ga surface tension being of  $0.7 \text{ J/m}^2$  [16]. The same relation is chosen for the covalent binding energy of indium and gallium atoms:  $E_{\text{Ga-Ga}} = 1.3 E_{\text{In-In}}$ . The energy barrier for In desorption was estimated by fitting the simulation results with the experimental data of temperature dependence of equilibrium In pressure above liquid indium [17]. According to this fitting, we obtained  $E_{\text{sub(In)}} = 0.7 \text{ eV}$ , where  $E_{\text{sub}} = E_{\text{des}} - E_{\text{dif}}$  (desorption energy  $E_{\text{des}}$  in the model is equal to  $E_{\text{des}} = E_{\text{dif}} + E_{\text{sub}}$ ). The important parameters that determine  $\text{A}^{\text{III}}\text{B}^{\text{V}}$  nanostructure growth are activation energies of molecular arsenic dissociation and creation on the surface. The first approximation values of these energies, as well as the  $\text{As}_2$  desorption barrier for InAs, are the same as for GaAs NW growth. Only on the liquid drop surface, the energy barriers for molecular arsenic dissociation are assumed to be different for In and Ga. In this manner we imitate a different catalytic role of indium and gallium drops.

A cardinal change (in comparison with [13]) has been realized with a description of the processes in the liquid drop and at the energy barriers drop/crystal interface since we excluded liquid arsenic. Now arsenic dissolution and diffusion through a liquid drop are described by the unified exchange reaction:  $\text{Ga}_{\text{liq}} (\text{In}_{\text{liq}}) + \text{As} \rightarrow \text{As} + \text{Ga}_{\text{liq}} (\text{In}_{\text{liq}})$ . The reactant neighbourhood specifies the process: dissolution in liquid metal or exchange diffusion through the drop. The activation energy barrier of arsenic dissolution rate higher than the energy barrier of diffusion through the drop can be reached by increasing the activation energy of exchange reaction at the liquid-crystal interface. The presence of solid gallium (indium) at the interface ensures this increase of activation energy barrier. Overestimation of the energy parameters responsible for the phase transformation was required after the model modification. The diffusion activation energy value of  $0.3 \text{ eV}$  in liquid In and of  $0.7 \text{ eV}$  in liquid Ga are taken according to the experiment [18] and [19], respectively. The activation energies of Ga (In) dissolution in the liquid drop and Ga (In) crystallization at the drop-crystal interface in the form of GaAs (InAs) are chosen fitting the simulated and experimental solubility of GaAs (InAs) in liquid Ga (In) [20]. The results of such fitting are shown in figure 2. The activation energy of Ga (In)

crystallization is found to be equal to 1.2 (1.5) eV and 1.7 (1.85) eV for Ga (In) dissolution. Using the specified energy parameters, the self-catalyzed growth of InAs and GaAs nanowires was carried out.

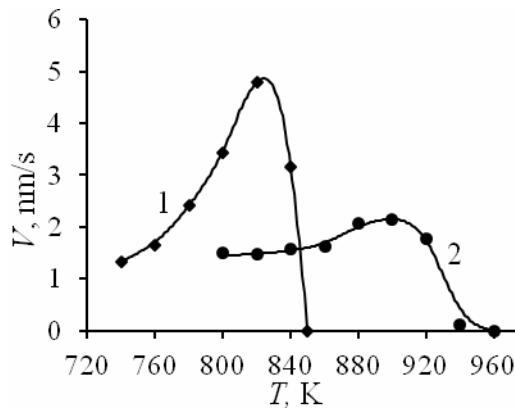


**Figure 2.** Temperature dependence of equilibrium arsenic concentration in liquid metal (In – solid circles, Ga – open circles from experimental data [20], crosses - simulation results).

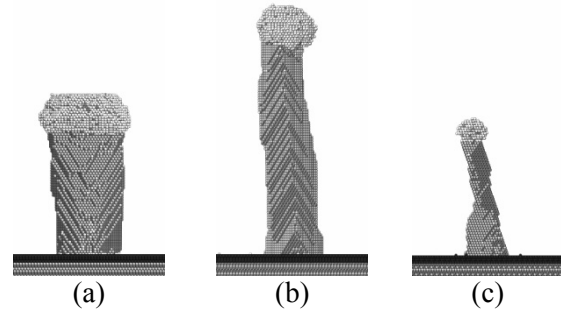
### 3. Simulation results

The initial substrate is a semi-infinite InAs or GaAs crystal with the (111)B surface orientation covered with a film mask having a round through-hole containing an In or Ga drop. The temperature range for growth is chosen according to experimental works [6, 21]: for InAs  $T = 740 - 840$  K and for GaAs  $T = 800 - 950$  K. The reported data about flux intensities are worthless since our model surface is much smaller than the real one. That means that the Ga diffusion component of NW growth in the experiment is higher than that in simulation. So, the intensities of gallium and indium fluxes in the simulation are chosen higher than those in the experiment. A small model surface size means a significant readsorption effect for the NW growth rate [22]. The input flux intensities ranges used for modelling are:  $F_{In} = (0.3-0.7)$  monolayer per second (ML/s),  $F_{Ga} = (0.1-0.5)$  ML/s and fluxes ratio  $F_{As_2}/F_{In} = 0.7-1.7$ . InAs and GaAs NW growths are carried out at the same  $As_2$  flux. The NW growth rate dependences on temperature, In (Ga) and  $As_2$  fluxes are obtained.

In a wide range of arsenic fluxes, the InAs NW growth rate was found to be linearly dependent on arsenic flux intensity that is typical for the self-catalyzed growth [23]. The temperature dependences of InAs and GaAs NW growth rates are demonstrated in figure 3. The maximal growth rate of InAs NWs corresponds to 820 K and that of GaAs NW – to 900 K. This result is mainly due to the different arsenic solubility in liquid gallium and indium and different In and Ga volatility. The stable growth of InAs and GaAs NWs was observed around these optimal temperatures. At a lower temperature, the growth rate slows down since the temperature decelerates all processes responsible for NW growth, such as In(Ga) and  $As_2$  desorption, arsenic diffusion through the drop, crystallization at the drop-crystal interface, diffusion of all species along the surface. The NWs at temperatures lower than the optimal temperature are thicker and, at  $T < 740$  K, In drops are formed at NW side walls resulting in the following NW branching. At temperatures higher than the optimal one, the growth rate decrease is due to the enhanced In(Ga) and arsenic desorption. At temperatures higher than 850 K (950 K), the NW growth stopped because of indium (gallium) drop evaporation. The morphology of NWs grown at different temperatures is demonstrates in figure 4.

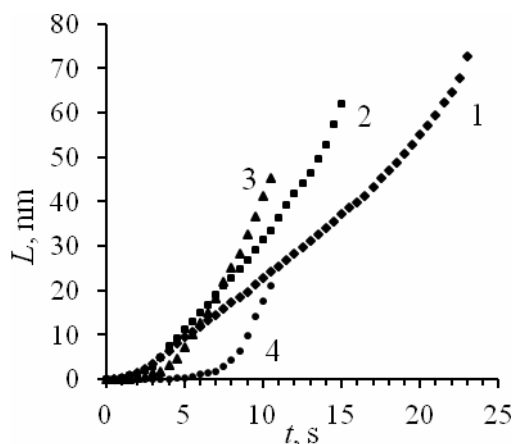


**Figure 3.** Temperature dependences of NW growth rate: for InAs (1), GaAs (2);  $F_{\text{As2}} = 0.5 \text{ ML/s}$ ,  $F_{\text{Ga}} = 0.3 \text{ ML/s}$ ;  $F_{\text{In}} = 0.5 \text{ ML/s}$ .

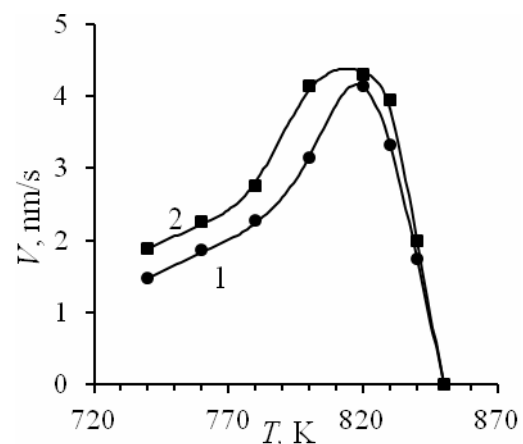


**Figure 4.** Cross-sections of InAs NWs at the same growth time ( $t = 10 \text{ s}$ ) at different temperatures:  $T = 760 \text{ K}$  (a),  $T = 800 \text{ K}$  (b) and  $T = 840 \text{ K}$  (c). As is marked in gray, In – in light gray,  $\text{In}_{\text{liq}}$  – in white, film – in black colors.

It is worth noting that the growth rate presented in figure 3 corresponds to the average growth rate determined for a certain deposition time. The dependence of NW length on deposition time for different growth temperatures is shown in figure 5. For all temperatures one can single out three time intervals. The first interval corresponds to drop gathering (the incubation period), the second interval corresponds to stable growth with a practically constant growth rate and the third interval – with the increasing growth rate. This growth rate increase during the third time interval is associated with the metal drop size decrease. The growth rate decrease in the high temperature region in figure 3 may be due to the untimely metal drop consumption or to the prolonged incubation period. In our model system, with a significant readsorption effect, the In(Ga) drop is rapidly consumed by the enlarged arsenic flux due to readsorption at high temperatures. In figure 6 one can see the difference in the average growth rate values calculated at the same time of growth (curve 1) and at the moment of In drop consumption (curve 2).

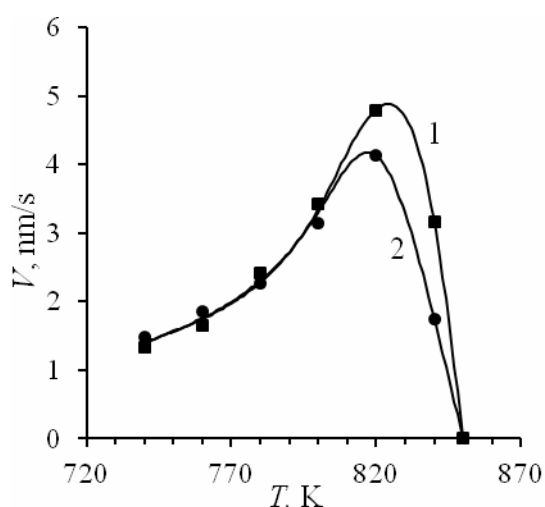


**Figure 5.** Dependence of NW length on time for different growth temperatures:  $T = 780 \text{ K}$  – (1),  $T = 800 \text{ K}$  – (2),  $T = 820 \text{ K}$  – (3),  $T = 840 \text{ K}$  – (4).

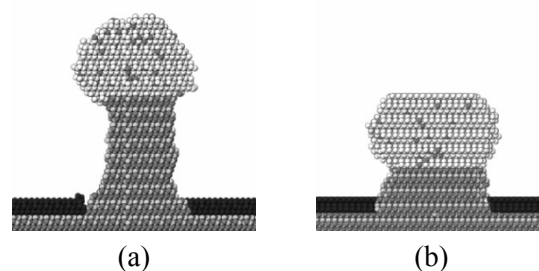


**Figure 6.** Temperature dependence of InAs NW growth rate determined at  $t = 10 \text{ s}$  (1) and at the moment of drop consumption (2)  $F_{\text{As2}} = 0.5 \text{ ML/s}$ ,  $F_{\text{In}} = 0.5 \text{ ML/s}$ .

We analyzed the influence of catalytic indium drop properties on the temperature dependence of NW growth rate. We considered two different energy barriers for molecular arsenic dissociation on the liquid indium drop surface. The first variant – catalytic influence of liquid indium on  $\text{As}_2$  dissociation is assumed to be equal to the influence of liquid gallium (curve 1 in figure 7). The second variant – molecular arsenic dissociates on the liquid indium surface that is more difficult than on the liquid gallium surface (curve 2). The reduction of growth rate for curve 2 is predominately due to the enhanced  $\text{As}_2$  evaporation. This statement is illustrated in figure 8. Here one can see the cross-sections of InAs NWs at the initial growth stage. The growth time is equal for both NWs, but the NW grown according to curve 1 (figure 8 (a)) is longer and that indicates a higher arsenic inflow at the drop-vapor interface.



**Figure 7.** Temperature dependence of InAs NW growth rate:  $\text{As}_2$  dissociation on the  $\text{In}_{\text{liq}}$  surface is easier for curve 1 in comparison with curve 2;  $F_{\text{As}_2} = 0.5 \text{ ML/s}$ ,  $F_{\text{In}} = 0.5 \text{ ML/s}$ .



**Figure 8.** InAs NWs cross-sections at the initial stage of growth ( $t = 4 \text{ s}$ ) at  $T = 820 \text{ K}$ ;  $\text{As}_2$  dissociates on the liquid indium surface is easier in (a) than in (b).

The optimal temperature value depends on arsenic to gallium (indium) flux ratio. The increase of  $\text{As}_2/\text{Ga}(\text{In})$  flux ratio results in the optimal temperature shift to the low temperature region.

#### 4. Conclusions

A modified version of the lattice Monte Carlo model of NW growth according to the vapor-liquid-solid mechanism was presented. The characteristics of self-catalyzed indium arsenide and gallium arsenide nanowire growth on (111)B substrates were analyzed using Monte Carlo simulation. The dependence of NW morphology on growth conditions was demonstrated. The temperature dependence of axial NW growth rate was analyzed. The influence of catalytic properties of the metal drop on the NW growth rate was demonstrated. The difference in optimal conditions for InAs and GaAs NWs self-catalyzed growth is due to different gallium and indium volatility and different arsenic solubility in liquid gallium and indium.

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