Recipes for crystal phase design in Au-catalyzed III-V nanowires

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Abstract. We develop a kinetic model for the crystal structure of Au-catalyzed III-V nanowires which is capable of describing the wurtzite content as a function of the growth temperature, group V flux, and the nanowire elongation rate. The self-consistency condition with the correct pre-exponent in the Zeldovich nucleation rate allows us to estimate the actual group III concentration in the droplet which corresponds to a given elongation rate. Our model predicts a non-monotonic dependence of the wurtzite percentage on the group III concentration. We analyze relevant experimental data on the preferred crystal structure of Au-catalyzed GaAs nanowires obtained by three different epitaxy techniques and explain why the MBE-grown GaAs nanowires at near 550°C are predominantly wurtzite, while the MOCVD and HVPE-grown GaAs nanowires obtained with very high As fluxes and at very different temperatures (464°C and 715°C) are zincblende. Overall, the model provides some simple recipes for structural design of III-V nanowires by tuning the technologically controlled growth conditions such as temperature and fluxes.

1. Introduction
III-V semiconductor nanowires (NWs) offer a unique possibility of sophisticated design of their crystal structure. Stabilization of hexagonal wurtzite (WZ) crystal phase of III-V materials has only been observed in III-V NWs [1]. In the case of III-V NWs fabricated by the Au-catalyzed vapor-liquid-solid (VLS) method, the preferred crystal structure strongly depends on the growth conditions which influence the chemical potential of a liquid Au-III-V alloy in the droplet [2-6]. Recently, the synthesis of NWs containing heterostructures of the zincblende (ZB) and WZ crystal phases was demonstrated within a single nanowire [6-14]. The WZ/ZB superlattices in III-V NWs show very interesting optical properties [8]. In particular, insertions of a smaller bandgap ZB segments into the matrix of WZ III-V NWs yield a principally new type of quantum dots based on different crystal phases of same material rather than a combination of different materials [7]. These crystal phase heterostructures are achieved by tuning the growth parameters such as the group III or group V fluxes and the growth temperature. Such structural design requires advanced modeling of NW growth and the resulting crystal phase. VLS III-V NWs can be obtained not only by the Au-catalyzed VLS procedures but also with a group III metal (Ga) in the self-catalyzed approach [15-19]. For Ga-catalyzed VLS growth of GaAs NWs, it is known that the NW elongation rate is limited by the As flux [17-19], while the crystal structure is...
predominantly ZB due to the low surface energy of liquid Ga relative to Au [16]. Recently, Glas et al. presented a predictive model of Ga-catalyzed, molecular beam epitaxy (MBE) growth of GaAs NWs based entirely on the kinetics of As [19]. In this work, we try to extend this approach to a more complex case of Au-catalyzed III-V NWs. In Au-catalyzed VLS growth, the liquid Au-III-V alloy is ternary rather than binary and the growth rate is commonly believed to be limited by the kinetic of group III atoms, including those collected by the NW sidewalls [6,20]. We use the model of Ref. [21] to circumvent the uncertainty in the As chemical potential in the liquid phase by expressing it through the As flux and the NW elongation rate in the steady state. In the self-consistent approach where the transport-limited NW elongation rate is equated to the nucleation-mediated growth rate in the mononuclear mode [19,21,23], we include the Kashchiev’s renormalization for the pre-exponential factor in the Zeldovich nucleation rate. This allows us to estimate more precisely the actual Ga concentration in the droplet during growth which corresponds to a particular elongation rate. Finally, we consider the experimental data demonstrating predominantly WZ phase of Au-catalyzed GaAs NWs grown by molecular beam epitaxy (MBE) at 550°C [2,6], pure ZB phase of Au-catalyzed GaAs NWs grown by metal organic chemical vapor deposition (MOCVD) at 464°C [25,26] and Au-catalyzed GaAs NWs grown by hydride vapor phase epitaxy (HVPE) at 715°C [27]. These different crystal structures are explained very well within our model. We speculate that the pure ZB phase of VLS GaAs NWs obtained by chemical vapor epitaxies is due to a very high Ga content in the Au-Ga-As droplets where the necessary condition for the WZ phase formation the so-called triple phase line (TPL) nucleation [3] is suppressed on surface energetic grounds, as in the case of Ga-catalyzed GaAs NWs [16]. This large Ga concentration is required to ensure a high elongation rates (10 nm/s or more) and to compensate for a high As content which originates from a huge group V input in chemical vapor deposition methods compared to the MBE case.

2. Experimental data

The Au-catalyzed GaAs NWs described in detail in Ref. [26] were grown by MOCVD on GaAs(111)B substrates from trimethylgallium (TMGa) and arsine (AsH₃) at a system pressure of 100 Torr, constant surface temperature of 464°C and with V/III ratio of 70. The measured NW elongation rate was found to be radius-independent and equalled approximately 10 nm/s. Transmission electron microscopy (TEM) studies revealed the pure ZB crystal structure of these GaAs NWs regardless of their radius from 80 nm down to 12 nm, as shown in Figs. 1 (a1) and (a2). The NWs were oriented along <111> crystallographic direction, their shape was regular hexahedral, with the side facets defined by six equivalent (211) planes.

Figure 1 (b) shows the TEM image of the body of a GaAs NW obtained by the Au-assisted MBE [2]. These NWs (usually 20-60 nm in radius) show the predominant WZ structure (although with some twins and stacking faults) in the temperature window 530 – 600°C, V/III fluxes ratios of about 3 and typical equivalent planar growth rates of the order of 0.2-0.3 nm/s. The NW shown in Fig. 1 (b) was obtained at 550°C and was found to have WZ side facets. In contrast to the MOCVD case, the NW elongation rate in MBE strongly depends on the NW radius: the typical length-radius correlation is decreasing as in the diffusion-induced growth mode [20]. Collection of sidewall adatoms increases the elongation rate of thinnest NWs up to 1 nm/s. However, this does not change the prevalence of the WZ structure. Similar findings for Au-catalyzed, MBE-grown GaAs NWs are published, e.g., in Refs. [3,20,21] and show the prevalence of the WZ structure. In accordance with experiments [2,3] the model of Ref. [3] shows that the ZB phase can be present in MBE-grown, Au-catalyzed GaAs NWs only at the transient growth steps at the beginning and at the end of growth where the Ga concentration in the droplet is lower than in the steady state. Figures 1 (c1) and (c2) show the defect-free ZB structure of a 60 nm radius GaAs NWs obtained by the Au-catalyzed HVPE from GaCl and As₄ vapors on Au-coated 4-misoriented GaAs(100) substrates in a hot wall
Figure 1. TEM (a1) and high resolution TEM (HRTEM) (a2) images of a \( <111> \)-oriented, 12 nm radius GaAs NW grown by the Au-catalyzed MOCVD at 464\(^\circ\)C, with the corresponding selected area electron diffraction (SAED) pattern in the insert of (a1) showing its ZB phase [26]. HRTEM image of a WZ GaAs NW grown by MBE at 550\(^\circ\)C, with the insert showing the SAED pattern (b) [2]. HRTEM image of a \( <111> \)-oriented, 60 nm radius GaAs NW obtained by HVPE at 715\(^\circ\)C (c1), SAED patterns viewed in different zone axes (c2) demonstrate the defect-free ZB structure [27].

These NWs are typically obtained at 715\(^\circ\)C with a partial pressure GaCl of 300 Pa, a partial pressure of As\(_4\) of 70 Pa and with a H\(_2\) vector gas of 3000 SCCM including additional HCl flow used to tune the supersaturation of the vapor phase. These NWs grow in \( <111> \) direction and are defined predominantly by (211) side facets. Very importantly, the radius-independent elongation rate of GaAs NWs obtained by Au-catalyzed VLS HVPE reaches the record value of the order of 30 nm/min. Therefore, the Au-catalyzed GaAs NWs grown by MOCVD and HVPE at rather low (464\(^\circ\)C) and high (715\(^\circ\)C) surface temperatures have the ZB crystal structure, while the MBE-grown GaAs NWs obtained at intermediate temperatures (550\(^\circ\)C) are predominantly WZ. Therefore, the growth temperature is not the sole key factor determining the phase, as commonly assumed [6]. The NW radii in these experiments are also close, while the structure is different, so size-dependent effects on the preferred crystal structure [4] should not be important. Hence, the observed difference in the resulting crystal structure must originate from the main features of chemical vapor epitaxies versus MBE. Obviously, MOCVD and HVPE involve much higher amounts of materials deposited per unit time (yielding much larger elongation rates), and huge values of V/III ratios compared to MBE. It is the aim of the foregoing theoretical analysis to attribute the
WZ phase of Au-catalyzed MBE-grown GaAs NWs and ZB phase of MOCVD and HVPE-grown GaAs NWs to these differences in the growth techniques.

3. Chemical potentials

As shown in Ref. [21], if the group V (As) concentration in the liquid Au-Ga-As droplet remains constant during growth, the chemical potential of GaAs in the ternary liquid alloy with respect to the stoichiometric ZB solid state (as defined in Ref. [22]) is given by

$$\Delta \mu = \mu^L_{G} + \frac{k_B T}{n} \ln \left( \frac{\omega_5 v_5 (1 + \varepsilon) - \omega_3 dL/dt}{v_5^0} \right)$$

(1)

with

$$v_5^0 = \frac{2\omega_3}{1 + \cos(\beta)} \frac{n\Omega_3 k_5 P^0_{5(n)}}{\sqrt{2\pi m_{5(n)} k_B T}}$$

(2)

Here, $\mu^L_{G}(c_3, T)$ is the chemical potential of Ga atoms in the alloy, which is determined primarily by the Ga concentration in the droplet and the surface temperature and is not expected to be strongly dependent of the As concentration $c_3$ in view of $c_5 << c_3$ , $k_B$ is the Boltzmann constant, $n$ is the number of As atoms in an $\text{mathtext As}_n(X)$ molecule in vapor, $v_5 = I_5\Omega_3$ , $I_5$ is the direct atomic As flux, $\Omega_3 = 0.0452 \text{nm}^3$ is the elementary volume per a GaAs pair in the solid state, $\varepsilon$ is the As re-emission coefficient $\{17,19\}$ in MBE and 1 for chemical vapor deposition, $\omega_3 = 1$ for MBE and $(1 + \cos(\beta))/2$ for chemical vapor deposition (with $\beta$ being the contact angle of the droplet at the NW top), $dL/dt$ is the nanowire elongation rate, and $\mu^L_{55}$ is the chemical potential of a GaAs pair in the ZB solid state. In Eq. (2), $k_5$ is the Knudsen adsorption coefficient for As $(k_5 \cong 1)$ and $m_{5(n)}$ is the mass of an $\text{As}_n(X)$ molecule in vapor, while the temperature-dependent $P^0_{5(n)}$ is defined as

$$\mu^L_{5(n)} = k_B T \ln \left( \frac{P_{5(n)}/P^0_{5(n)}}{\Omega_{As} k_5} \right)$$

(3)

where $\mu^L_{5(n)}$ is the chemical potential of an $\text{mathtext As}_n(X)$ perfect gas at the pressure $P_{5(n)}$. According to Refs. [3,4], the prevalence of the WZ phase over ZB in VLS NWs occurs when the $\Delta \mu$ is larger than the two critical chemical potentials. The first one corresponds to the equality of the nucleation barriers for the WZ and ZB nuclei at the TPL and the second to the equality of the nucleation barrier of the WZ nucleus at the TPL and the ZB nucleus in the center (C) of the liquid-solid interface under the droplet. Consequently, the WZ structure forms when

$$\Delta \mu > \max\{\Delta \mu_{TPL}; \Delta \mu_{C}\}$$

(4)

with $\Psi_{WZ}$ being the bulk energy difference between WZ and ZB structures. The effective surface energies of nuclei at the TPL positions are given by [3]: $\Gamma_{ZB} = (\gamma_{ZB} - \gamma_{LV}\sin(\beta))x + \gamma_{SL}(1 - x)$; $\Gamma_{WZ} = (\gamma_{WZ} - \gamma_{LV}\sin(\beta))x + \gamma_{SL}(1 - x)$. The $\gamma_{ZB}$, $\gamma_{WZ}$ are the surface energies of relevant ZB and WZ NW sidewall facets, $\gamma_{LV}$ is the liquid-vapor surface energy of the droplet, $\gamma_{SL}$ is the surface energy of the lateral solid-liquid interface of a two-dimensional island, and $x$ is the fraction of the island perimeter at the TPL. In the stationary model, we do not consider possible variations of the contact angle $\beta$ during growth [28]. The critical chemical potentials obtained from Eqs. (4) are shown in Fig. 2 for the following parameters of Au-catalyzed GaAs NWs: $\Psi = 24 \text{meV/pair}$ [29], $\gamma_{WZ} = 1.30 \text{J/m}^2$ for the lowest energy (1100) WZ side facets and $\gamma_{ZB} = 1.543 \text{J/m}^2$ for the lowest energy (110) ZB side facets and $\gamma_{ZB} = 1.79 \text{J/m}^2$ for the
Figure 2. Critical chemical potentials, obtained from Eqs. (4): black curves - $\Delta \mu_{TPL}$ for (100) and (211) ZB side facets, light blue curves - $\Delta \mu_C$ at 715°C (solid line) and 550°C (dotted line), these critical curves show a negligible temperature dependence (1); violet curve - with the Kashchiev renormalization, dark blue curve - $\Delta \mu_{TPL}$ with the Kashchiev renormalization (2). The WZ phase is prevalent in the top-left corner, while the ZB structure forms below the critical curves. Red, magenta and green lines correspond to the chemical potentials in Au-Ga-As droplets for GaAs NWs by HVPE at 715°C, MBE at 550°C, and MOCVD at 464°C, calculated from Eq. (1) for the parameters listed in Table 1. Dots show the actual Ga concentrations during growth, obtained from the self-consistency condition. GaAs NWs obtained by HVPE and MOCVD form at high Ga concentrations larger than 0.67, where the WZ phase is suppressed on surface energetic grounds (the TPL nucleation becomes unfavorable). MBE-grown GaAs NWs are formed at a much lower Ga concentrations and hence their preferred crystal structure is WZ. More energetic (211) side facets [30], $\beta = 110^\circ$, and a triangle island ($x = 0$ or 1/3). The dependence $\gamma_{LV}(c_3)$ is taken as the linear approximation between pure liquids ($\gamma_{Ga} = 0.663 \text{ J/m}^2$, $\gamma_{Au} = 1.215 \text{ J/m}^2$ at 715°C and $\gamma_{Au} = 1.248 \text{ J/m}^2$ at 550°C (Ref. [31])). The is the linear approximation between 1.0 J/m² at $c_3 = 0$ (Ref. [3]) and 0.123 J/m² for a pure Ga droplet (at $c_3 = 1$) [19]. It is seen that the critical chemical potentials are almost temperature-independent (due to a slow temperature dependence of the liquid and solid surface energies). Consequently, we have a temperature-independent WZ corner in the top-left part of the plane, and the WZ phase forms when the liquid chemical potential during growth enters this corner. Very importantly, the ZB phase should form for all $c_3 > 0.67$ actually regardless of the growth conditions such as the arsenic flux and the NW elongation rate. We also note that the first principle calculations by Rosini and Magri [32] and Pankoke et al. [33] give much lower values for the sidewall surface energies and compared to those used in Fig. 2, which could lead to a very different predictions regarding the preferred crystal structure. This will be studied in detail elsewhere. The increasing curves in Fig. 2 show the dependences of the chemical potentials on the Ga concentration, calculated for the growth parameters listed in Table 1, with the Ga chemical potential obtained from the model of Glas [22]. It is seen that the first ZB-to-WZ transition occurs at low Ga concentration within the range of approximately 0.1-0.2 depending on the facet type, growth temperature and the model used for $\Delta \mu_{TPL}$. This transition takes place due to a lower surface energy of WZ nuclei relative to ZB nuclei at the TPL, and is explained within the original model.
of Glas et al. [3]. The reverse WZ-to-ZB transition, discussed earlier by Dubrovskii [21], occurs abruptly when the Ga concentration in the Au-Ga-As droplets exceeds the critical value of 0.67, and is due to the energetic suppression of the TPL nucleation in droplets having low surface energy. Therefore, the preferred crystal structure now depends on the actual Ga concentration during the VLS growth, which will be studied in the foregoing sections.

Table 1. Growth parameters of Au-catalyzed GaAs

| Growth method | T (°C) | As vapor | dL/dt (nm/s) | v5 (nm/s) | ε | v50 (nm/s) | µ35 (meV) | P0 β (Pa) |
|---------------|--------|----------|-------------|----------|---|-------------|------------|-----------|
| MOCVD         | 464    | AsH3     | 10          | 2.1 × 10^4 | 3.25 | 367         | -1520    | 0.51      |
| MBE           | 550    | As2      | 1           | 9.0       | 3.25 | 1.1 × 10^4 | -1615    | 16        |
| HVPE          | 715    | As4      | 28          | 6.2 × 10^4 | 3.25 | 8.5 × 10^4 | -1820    | 2800      |

4. Zeldovich nucleation rate and Kashchiev renormalization

In their modeling of MBE-grown, Ga-catalyzed GaAs NWs, Glas et al. [19] used the following classical expression [34] for the Zeldovich nucleation rate:

\[ J = A_{c5} \Delta \bar{\mu}^{1/2} \exp \left( -\frac{a^2}{4\Delta \bar{\mu}} \right) \]  \hspace{1cm} (5)

Here, \( c_5 \) is the As atomic concentration in the liquid Au-Ga-As alloy, \( \Delta \bar{\mu} = \Delta \mu / (k_B T) \) is the dimensionless chemical potential of GaAs in the droplet in thermal units,

\[ a = 2 \times 3^{3/4} (\Omega_{35} h)^{1/2} \Gamma \sqrt{T} \]  \hspace{1cm} (6)

is the surface energy constant for a regular triangle island (with \( \Gamma \) as the effective surface energy of the island lateral surface for a given nucleation scenario, \( \Gamma = \gamma_{SL} \) in the case of Ga-catalyzed GaAs NWs), \( h=0.326 \) nm is the height of a GaAs monolayer and \( A \) is a certain pre-factor which may depend on temperature but neither on \( c_5 \) nor on \( \Delta \bar{\mu} \). It was found that the experimental data on the NW growth rate dependence on temperature and As flux are best fitted at a temperature-independent \( A = 7 \) nm s\(^{-1}\) and \( \gamma_{SL} = 0.123 \) J/m\(^2\) (within the temperature window 580 – 640°C) [19]. Our analysis involves the so-called Kashchiev re-normalization of the nucleus formation energy [24] which has been used extensively in general studies [35,36] but overlooked in modeling of VLS NWs. In brief, Kaschiev proposed to change the equation for the macroscopic formation energy of a nucleus consisting of \( i \) monomers (GaAs pairs in our case) \( F(i) \) to \( F(i) - F(1) \) in order to ensure that the quasi-equilibrium distribution \( n(i) = n_1 \exp[-F(i)] \) gives correctly the monomer concentration at \( i = 1 \). Under the assumption of the ballistic growth mode for near-critical nuclei, this yields the re-normalized expression for the pre-factor \( A \) in Eq. (5) of the form (a more detailed analysis will be presented elsewhere):

\[ A = \frac{3^{3/4}}{\sqrt{\pi}} \left( \frac{h}{\Omega_{35}} \right)^2 D_5 \exp(\mu_{35}^0 + a) \]  \hspace{1cm} (7)

for a triangle island. Here, \( D_5 \) is the diffusion coefficient of As in liquid. This shows the validity of the Glas assumption [19]: for Ga-catalyzed VLS growth, \( A = A(T) \) indeed depends only on temperature. However, in the more general case of ternary Au-Ga-As alloy in the droplet, the value would depend on the Ga concentration \( c_3 \) via the surface energy \( \Gamma \) in the constant \( a \) [Eq. (6)] and also through the As diffusion coefficient \( D_5 = D_5(T, c_3) \). When the Kashchiev renormalization of the formation energy and the corresponding modification of the nucleation barrier are included, the elongation rates \( dL/dt \) for NWs having different crystal structures...
contain the exponential terms $\exp[-a^2/(4\bar{\mu})] - a$ rather than just $\exp[-a^2/(4\bar{\mu})]$ in the Glas model [3]. This modifies the Glas conditions given by Eqs. (4) to

$$\frac{a_{WZ}^2}{4(\bar{\mu} - \bar{\Psi})} - a_{WZ} < \frac{a_{ZB}^2}{4(\bar{\mu} - \bar{\Psi})} - a_{ZB}$$

(8)

with $\bar{\Psi} = \Psi/(k_B T)$, for the two possible ZB scenarios [(ZB,TPL) and (ZB,C)]. This gives a rather different behavior of the critical chemical potentials compared to $\Delta \mu_C = \Psi/[1 - (a_{WZ}/a_{ZB})^2]$ in the case of Au-catalyzed VLS growth, because both $a_{WZ}$ and $a_{ZB}$ depend on $c_3$ via the surface energies $\Gamma_{WZ}$, $\Gamma_{ZB}$ and $\gamma_{SL}$ entering Eq. (6). The modified liquid chemical potentials are shown in Fig. 2 and give a wider WZ region, where the WZ phase formation at intermediate Ga concentrations becomes much easier (since it requires a much lower chemical potentials during growth). A more detailed analysis of these new features will be presented elsewhere. We note, however, that the Kashchiev renormalization does not change significantly the abrupt transition to the ZB structure at high Ga concentrations ($c_3 > 0.67$ for our model parameters).

5. Self-consistent determination of Ga concentrations

In order to find the actual Ga concentration during the VLS NW growth at a given set of the growth conditions, we write the self-consistency equation in the form

$$\frac{dL}{dt} = \frac{3\sqrt{3}}{2} R^2 h \sum_{k=1}^{3} \eta_k J_k; \quad J_k = A_k c_5 (\Delta \bar{\mu} - \Psi_k)^{1/2} \exp\left(-\frac{a_k^2}{4(\Delta \bar{\mu} - \Psi_k)}\right)$$

(9)

The left-hand side is the transport-limited NW elongation rate which was directly measured for each set of the experimental data discussed later on. The right-hand side gives the nucleation-mediated elongation rate of a hexahedral NW with side $R$ in the mononuclear mode [3,4,19,23] in three possible nucleation scenarios $k=(WZ,TPL)$, (ZB,TPL) and (ZB,C) relating to different $\Gamma_k$ in Eq. (6) and different $\bar{\Psi}_k = \Psi/(k_B T)$ for the WZ structure and 0 for ZB structure. The $\eta_k = 2r_c^{(k)}/R$ for the TPL nucleation position, with $r_c^{(k)} = (1/3^{1/4})(\Omega_{35}/h)^{1/2}[a/(\Delta \bar{\mu} - \Psi_k)]$ as the critical radii, are the geometrical factors in the TPL nucleation scenarios which account for the reduction of the available nucleation area to the TPL ring of the critical radius [4]. We ignore the pulsed fluctuations of the liquid chemical potential in mononuclear growth [36-39] by averaging the NW elongation rate over a sufficiently long time interval consisting of many monolayer pulses.

Figure 3. WZ contents versus Ga concentration for the three growth methods; dots correspond to the actual Ga concentrations obtained from the actual Ga concentrations obtained from the self-consistent model with the Kashchiev renormalization of the nucleation barriers.
We then use Eq. (1) for the chemical potentials in which the Ga contribution is computed by means of the Glas model [22] for each temperature and the growth conditions listed in Table 1, as in Fig. 2. After that, Eq. (9) contains only one unknown (in both sides): the Ga concentration, which is obtained by numerically solving Eq. (9) for each set of the growth parameters. The corresponding Ga concentrations during growths are shown by dots in Fig. 2. Figure 3 shows the WZ content versus Ga concentration for each set of the growth conditions, obtained simply by

$$p_W = \frac{(dL/dt)_{WZ,TPL}}{dL/dt}$$

where \((dL/dt)_{WZ,TPL}\) is the term in the right-hand side of Eq. (9) corresponding to the WZ phase formation via the (WZ,TPL) nucleation scenario. These graphs were obtained with the parameters of Table 1 and NWs with 20 nm radius. In calculations, we assumed the same diffusion coefficients at 550 and 715°C (based on the data of Ref. [19] which reveal a temperature-independent coefficient \(A = 7 \text{ nm-2s}^{-1}\) in Eq. (5) for temperatures 580 – 640°C), and the ten times lower diffusivity of As at 464°C. It is seen that the HVPE and MOCVD-grown GaAs NWs should be pure ZB regardless of their radius, although the growth temperatures are very different. Prevalence of the ZB structure in these NWs is due to the high Ga concentrations in the droplets, the effect which decreases the liquid-vapor surface energy and suppresses the TPL nucleation on surface energetic grounds, as in the case of Ga-catalyzed GaAs NWs [16,40]. High Ga content originates from very large input amounts of both growth species in HVPE and MOCVD, yielding large values of the NW elongation rates (10-30 nm/s). This benefit of high growth rates for the phase purity has been discussed earlier by Ren et al. [26] and Joyce et al. [41]. For Au-catalyzed GaAs NWs grown by MBE with modest fluxes of Ga and As, the elongation rate is much lower, which yields a low Ga content corresponding to the WZ corner. This prevalence of WZ structure in Au-catalyzed, MBE-grown GaAs NWs is quite stable and cannot be changed by the achievable variations in the fluxes or growth temperatures within the growth window (usually 500 – 600°C [36]). Hence, the ZB phase can be present in these NWs only at the transient growth steps at the beginning and at the end of MBE growth where the Ga concentration in the droplet is lower than in the steady state [2,3], or when the upper parts of the NWs are grown by MBE at very high temperatures about 630°C [6]. All these conclusions of the model are consistent with the experimental data [2,3,25-27]. Summarizing, we have developed a model for the VLS growth and crystal structure of Au-catalyzed GaAs and other III-V NWs obtained by different epitaxy techniques. Our model accounts for the complete set of the growth parameters: temperature, As flux, V/III flux ratio and NW elongation rate. Some of the key elements of the model (such as the pre-exponent in the Zeldovich nucleation rate, the modified critical chemical potentials for the WZ-ZB phase transitions, the dependence of As diffusivity in the liquid phase on temperature and Ga concentration) still need to be developed. However, the model represents very well the main structural trends of Au-catalyzed GaAs NWs obtained by different growth techniques. Our results can be used for tuning the crystal structure of Au-catalyzed III-V NWs by changing the technologically controlled growth parameters, e.g., by alternating the flux of group V element. This brings about some new and useful ways for fabrication of the crystal phase heterostructures and quantum dots in III-V NWs. This work was supported by scientific program 21 of the Russian Academy of Sciences, grants 13-02-12405 and 13-02-00662 of the Russian Foundation for Basic Research, and the FP7 projects NANOEMBRACE (Grant agreement 316751) and FUNPROB (Grant agreement 269169).

References
[1] A.I. Persson, M.W. Larsson, S. Stengstrom, B.J. Ohlsson, L. Samuelson, and L.R. Wallenberg, Nature Mater. 3, 677 (2004)
[2] I.P. Soshnikov, G.E. Cirlin, A.A. Tonkikh, Y.B. Samsonenko, V.G. Dubrovskii, V.M. Ustinov, O.M. Gorbenko, D. Litvinov, and D. Gerthsen, Phys. Sol. State 47, 2213 (2005)
[3] F. Glas, J.C. Harmand, and G. Patriarche, Phys. Rev. Lett. 99, 146101 (2007)
[4] V.G. Dubrovskii, N.V. Sibirev, J.C. Harmand, and F. Glas, Phys. Rev. B 78, 235301 (2008)
[5] H. Shtrikman, R. Popovitz-Biro, A. Kretinin, and M. Heiblum, Nano Lett. 9, 215 (2009)
[6] V.G. Dubrovskii, N.V. Sibirev, G.E. Cirlin, A.D. Bouravleuv, Yu.B. Samsonenko, D.L. Dheeraj, H.L. Zhou, C. Sartel, J.C. Harmand, G. Patriarche, and F. Glas, Phys. Rev. B 80, 205305 (2009)
[7] N. Akopian, G. Patriarche, L. Liu, J.C. Harmand, and V. Zwiller, Nano Lett. 10, 1198 (2010)
[8] D. Spirloska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M.H. Gass, A.L. Bleloch, S. Estrade, M. Käniher, J. Rossler, F. Peiro, J.R. Morante, G. Abstreiter, L. Samuelson, and A. Fontcuberta i Morral, Phys. Rev. B 80, 245325 (2009)
[9] D.L. Dheeraj, A.M. Munshi, M. Scheffler, A.T. J van Helvoort, H. Wenman, and B.O. Finland, Nanotechnology 24, 015601 (2013)
[10] K.A. Dick, C. Thelander, L. Samuelson, and P. Caroff, Nano Lett. 10, 3494 (2010)
[11] S. Lehmann, D. Jacobsson, K. Deppert, and K. Dick, Nano Research 5, 470 (2012)
[12] S. Lehmann, J. Wallentin, D. Jacobsson, K. Deppert, and K.A. Dick, Nano Lett. 13, 4099 (2013)
[13] P. Krogstrup, M.H. Madsen, H. Wen, K. Miwa, J. Nygrd, T. Masamitu, and R.K. Feidenhans, Appl. Phys. Lett. 100, 093103 (2012)
[14] A. Fakhr, Y.M. Haddara, and R.R. LaPierre, Nanotechnology 21, 165601 (2010)
[15] C. Colombo, D. Spirloska, M. Frimmer, G. Abstreiter, and A. Fontcuberta i Morral, Phys. Rev. B 77, 155326 (2008)
[16] V.G. Dubrovskii, G.E. Cirlin, N.V. Sibirev, F. Jabeen, J.C. Harmand, and P. Werner, Nano Lett. 11, 1247 (2011)
[17] M.R. Ramdani, J.C. Harmand, F. Glas, G. Patriarche, and L. Travers, Cryst. Growth Des. 13, 91 (2013)
[18] G. Priante, S. Ambrosini, V.G. Dubrovskii, A. Franciosi, and S. Rubini, Cryst. Growth Des. 13, 3976 (2013)
[19] F. Glas, M.R. Ramdani, G. Patriarche, and J.C. Harmand, Phys. Rev. B 88, 195304 (2013)
[20] G.E. Cirlin, V.G. Dubrovskii, N.V. Sibirev, I.P. Soshnikov, Yu.B. Samsonenko, A.A. Tonkikh, and V.M. Ustinov, Semiconductors 39, 557 (2005)
[21] V.G. Dubrovskii, Appl. Phys. Lett. 104, 035130 (2014)
[22] F. Glas, J. Appl. Phys. 108, 073506 (2010)
[23] V.G.Dubrovskii and N.V.Sibirev, Phys. Rev. E 70, 031604 (2004)
[24] D. Kashchiev, Nucleation: Basic Theory with Applications. Butterworth-Heinemann, Oxford, 2000
[25] H. Huang, X. Ren, X. Ye, J. Guo, Q. Wang, Y. Yang, S. Cai, and Y. Huang, Nano Lett. 10, 64 (2010)
[26] X. Ren, H. Huang, V.G. Dubrovskii, N.V. Sibirev, M.V. Nazarenko, A.D. Bolshakov, X. Ye, Q. Wang, Y. Huang, X. Zhang, J. Guo, and X. Liu, Semicond. Sci. Technol. 26, 014034 (2011)
[27] M.R. Ramdani, E. Gil, C. Leroux, Y. Andre, A. Trassoudaine, D. Castellucci, L. Bideux, G. Monier, C. Robert-Goumet, and R. Kupka, Nano Lett. 10, 1836 (2010)
[28] V.G. Dubrovskii, I.P. Soshnikov, G.E. Cirlin, A.A. Tonkikh, Yu.B. Samsonenko, N.V. Sibirev, and V.M. Ustinov, Phys. Stat. Sol. (b) 241, R30 (2004)
[29] C.-Y.Yeh, Z. W. Lu, S. Froyen, and A. Zunger, Phys. Rev. B 46, 10086 (1992)
[30] N.V. Sibirev, M.A. Timofeeva, A.D. Bolshakov, M.V. Nazarenko, and V.G. Dubrovskii, Phys. Solid State 52, 1531 (2010)
[31] J.J. Jasper, J. Phys. Chem. Ref. Data 1, 841 (1972)
[32] M. Rosini and R. Magri, Nano Letters 10, 6021 (2010)
[33] V. Pankoke, P. Kratzer, and S. Sakong, Phys. Rev. B 84, 075455 (2011)
[34] I. Markov, Crystal growth for beginners. 2nd Edition. World Scientific, New Jersey London Singapore Hong Kong (2003)
[35] V.G. Dubrovskii and M.V. Nazarenko, J. Chem. Phys. 132, 114507 (2010)
[36] V.G. Dubrovskii, Nucleation theory and growth of nanostructures. Springer, Heidelberg New York Dordrecht London, 2014
[37] C.-Y. Wen, J. Tersoff, K. Hillerich, M.C. Reuter, J.H. Park, S. Kodambaka, E.A. Stach,and F. M. Ross, Phys. Rev. Lett. 107, 025503 (2011)
[38] F. Glas, J.C. Harmand, and G. Patriarche, Phys. Rev. Lett. 104, 135501 (2010)
[39] V.G. Dubrovskii, Phys. Rev. B. 87, 195426 (2013)
[40] G.E. Cirlin, V.G. Dubrovskii, Yu.B. Samsonenko, A.D. Bouravleuv, K. Durose, Y.Y. Proskuryakov, Buddhak Mandal, L. Bowen, M. A. Kaliteevski, R.A. Abram, and Daguo Zeze, Phys. Rev. B 82, 035302 (2010)
[41] H.J. Joyce, Q. Gao, H.H. Tan, C. Jagadish, Y. Kim, M.A. Fickenschier, S. Perera, T.B. Hoang, L.M. Smith, H.E. Jackson, J.M. Yarrison-Rice, X. Zhang, and J. Zou, Nano Lett. 9, 695 (2009)