Chemical potentials and growth rates of gold-catalyzed ternary InGaAs nanowires

J Grecenkov\textsuperscript{1}, V G Dubrovskii\textsuperscript{1,2,3}
\textsuperscript{1}St. Petersburg Academic University, Khlopina 8/3, 194021, St. Petersburg, Russia
\textsuperscript{2}Ioffe Physical Technical Institute RAS, Politekhnicheskaya 26, 194021, St. Petersburg, Russia
\textsuperscript{3}ITMO University, Kronverkskiy pr. 49, 197101 St. Petersburg, Russia

Abstract. By applying the Redlich-Kister polynomial model, we calculate chemical potentials of quaternary liquid alloys during the gold-catalyzed vapor-liquid-solid growth of ternary In\textsubscript{x}Ga\textsubscript{1-x}As nanowires. We then use these chemical potentials in the Zeldovich nucleation rate to obtain the nanowire axial growth rates versus the deposition conditions and indium compositions.

1. Introduction
Due to their ability to relax elastic strain on free sidewalls, nanowires are promising for monolithic integration of III-V optoelectronic materials with silicon electronic platform \cite{1,2}. III-V nanowires are usually grown by the gold-assisted vapor-liquid-solid (VLS) method wherein the III-V growth species are first transferred from vapor to liquid and then crystallize at the liquid-solid interface under the catalyst droplet \cite{3,4}.

Chemical potentials of Au-III-V liquid alloys play a crucial value in understanding the VLS growth and crystal structures of III-V nanowires. Previous works have shown that the analysis of chemical potentials of gold-assisted binary III-V nanowires allows for a delicate control over the VLS growth rates and wurtzite-zincblende polytypism within nanowires \cite{5-12}. In this work, we consider a more complex case of ternary gold-catalyzed InGaAs nanowires and study how chemical potentials affect the VLS growth rates under variable deposition conditions and indium compositions \cite{13}.

2. Chemical potential
In the mononuclear growth mode described by classical nucleation theory, the axial growth rate of a nanowire is given by the Zeldovich nucleation rate \cite{10}

\[ \frac{dl}{dt} = J_0 \exp \left( -\frac{p^2}{\Delta \mu_{\text{y}} T} \right) \]  

(1)

where \( J_0 \) is a prefactor, \( \Gamma \) is the effective surface, or edge energy of a two-dimensional island of a bilayer height, \( \Delta \mu \) is the difference of chemical potentials of a III-V pair (In\textsubscript{x}Ga\textsubscript{1-x}As) in the liquid and solid phases, \( T \) is the surface temperature and \( k_B \) is the Boltzmann constant. No vapor-solid contributions \cite{14} are considered in Eq. (1). Since the prefactor only weakly depends on the chemical potential and surface energy, the nucleation probability and consequently the nanowire growth rate is mainly determined by the Zeldovich exponent of the nucleation barrier in Eq. (1). The latter is
extremely sensitive to the chemical potential value and hence the $\Delta \mu$ needs to be determined as precisely as possible [11].

In the case of gold-catalyzed ternary III-V nanowires, we are dealing with quaternary Au-III-V liquid alloys such as Au-In-Ga-As. These chemical potentials can be calculated by applying the Redlich-Kister polynomial corrections to the Gibbs that take into account the interactions introduced by mixing the components. The Redlich-Kister polynomials have the form

$$G_{R-K} = \frac{1}{2} \sum_{i=1}^{4} c_i \sum_{m=0}^{n} L_{ij}^m (c_i - c_j)^m + \frac{1}{2} \sum_{i,j \neq k} c_i c_j c_k T_{ijk},$$

with $c_i$ denoting the concentrations of different elements in the liquid alloy and $L_{ij}^m$ are the interaction parameters between the atoms of different elements [15-21]. Once the Gibbs energy is calculated, the chemical potential of a given element is obtained as a derivative of the Gibbs energy with respect to the corresponding concentration

$$\mu_i = \frac{\partial G}{\partial c_i}.$$  \hspace{1cm} (3)

The liquid-solid chemical potential difference can be written down as

$$\Delta \mu = x(\mu_{\text{In}} + \mu_{\text{As}} - \mu_{\text{InAs}}) + (1-x)(\mu_{\text{Ga}} + \mu_{\text{As}} - \mu_{\text{GaAs}})$$  \hspace{1cm} (4)

under the central simplifying assumption on the identical indium content $x$ in liquid and solid phases. The quantities $\mu_{\text{In}}, \mu_{\text{Ga}}$ and $\mu_{\text{As}}$ denote chemical potentials of the indium, gallium and arsenic atoms in the liquid phase, while $\mu_{\text{InAs}}$ and $\mu_{\text{GaAs}}$ stand for chemical potentials of InAs and GaAs pairs in solid.

3. VLS growth rate

We can now exploit Exp. (1) to estimate the growth rates of gold-catalyzed InGaAs nanowires under different conditions. For simplicity, that the nucleation process occurs in the centre of the liquid-solid interface rather than at the triple phase line, we can use the expression for the surface energy of a newly formed island in the form [10]

$$\Gamma = x\Gamma_{\text{In}} + (1-x)\Gamma_{\text{Ga}},$$

with $\Gamma_{\text{In}}$ being the surface energy of an InAs island in an Au-In droplet (the influence of arsenic on the surface energy can be neglected due to its low concentration inside the catalyst droplet) and respectively $\Gamma_{\text{Ga}}$ in the same value for a GaAs island in an Au-Ga droplet. We take $\Gamma_{\text{Ga}} = \Gamma_{\text{Ga}}(c_{\text{Ga}})$ and $\Gamma_{\text{In}} = \Gamma_{\text{In}}(c_{\text{In}})$ as the linear interpolations between pure gold and group III metal droplets [11].

The prefactor in the Zeldovich nucleation rate can be calculated using the expression of Ref. [22]

$$J_0 = 3^{1/4} D_3 \left( \frac{h}{\Omega_{35}} \right)^2 e^{\mu_{\text{As}}^S \Delta \mu^{1/2}}.$$  \hspace{1cm} (6)

Here, $D_3$ is the diffusion coefficient of the arsenic adatoms through the liquid, $\Omega_{35}$ is the elementary volume of a III-V pair, $h$ is the height of a bilayer and $\mu_{\text{As}}^S$ is the averaged value of chemical potential of a III-V pair in the solid phase. Equations (1) to (6) constitute the complete system for computing the VLS growth rates of gold-catalyzed ternary nanowires versus temperature and droplet composition.

4. Results and discussion

Figure 1 shows the VLs growth rate of gold-catalyzed In$_x$Ga$_{1-x}$As nanowires versus the indium composition at 750 K, for a fixed arsenic concentration $c_3=0.05$ and three different total group III concentrations $c_3=0.3, 0.5$ and $0.7$. Quite interestingly, we observe a non-monotonic dependence of $dL/dt$ on $x$ for $c_3=0.3$, while for larger $c_3$ the growth rate gradually increases with $x$. Figure 2 shows the chemical potentials in quaternary Au-In-Ga-As alloy with respect to solid In$_x$Ga$_{1-x}$As,
computed for the same parameters as in Fig. 1. Clearly, these chemical potentials increase monotonically with $x$ and hence the non-monotonic behavior of $dL/dt$ on $x$ at $c_3=0.3$ is due to a combined effect of chemical potential and surface energy.

![Figure 1. Growth rates of gold-catalyzed In$_x$Ga$_{1-x}$As nanowires versus $x$ at a fixed temperature of 750 K, arsenic concentration of 0.05 and three different total concentrations of group III atoms in the droplet $c_3 = c_{ln} + c_{Ga}$.

Since both chemical potential and surface energy enter the Zeldovich exponent, even the slightest changes in them result in a dramatic effect on the VLS growth rate. In particular, our results show that In$_x$Ga$_{1-x}$As nanowires of the same composition $x$ grow at very different rates depending on the total group III concentration (determined by the V/III ratio). For example, low total group III flux may stop completely the VLS growth for small enough $x$, while at higher group III fluxes same nanowires would continue growing normally.

![Figure 2. Chemical potentials versus $x$ for the same parameters as in Fig. 1.]
5. Conclusion
The model presented is capable of describing the VLS growth rates of gold-catalyzed ternary InGaAs nanowire based on classical nucleation theory involving the macroscopic Zeldovich nucleation rate and quaternary chemical potentials. The latter has been calculated using the Redlich-Kister polynomials. The results show that changing the In/Ga as well as the total V/III flux ratio under otherwise fixed experimental conditions may cause an abrupt growth stop within a plausible range of parameters. We now plan to extend our approach for predicting the crystal structures of InGaAs nanowires and to apply this approach to other ternary nanowires based on both group III and group V intermixing.

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