Contact angle stability of gold droplets on top of GaAs nanowires in the non-stationary case

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Abstract. A kinetic model for contact angle stability is introduced for the non-stationary case with time-dependent fluxes in a molecular-beam epitaxy chamber. We present numerical simulations for different regimes of the nanowire growth process.

1. Introduction
Studies of formation processes and physical properties of semiconductor nanowires (NW) are currently of great interest. NW is a non-planar semiconductor crystal with a diameter of several nanometers and a length 10-100 times greater than the diameter [1]. One of the major advantages of fabricating III-V NWs is the low density of structural defects on substrates (such as silicon substrates) without lattice mismatch [2]. NWs are grown by the vapor-liquid-solid (VLS) mechanism in the presence of an external catalyst, in most cases gold [3, 4]. The metal droplet in this process acts as a reservoir for group III and V atoms. It is also known that nucleation and growth processes are quicker in the liquid than in the solid phase. According to [5, 6], the contact angle of a catalyst droplet on the NW top is one of the main parameters defining the phase structure type (zincblende (ZB) or wurtzite (WZ)) of the resulting NW crystal. In [7], it is shown that the contact angle of the droplet depends on the fluxes of group III and V atoms in the stationary case, i.e. the fluxes are constant throughout the growth time. We here present a kinetic model describing contact angle stability in the non-stationary case.

2. Model
Here we propose a system of kinetic equations for understanding the contact angle evolution in the case with instant switching between fluxes of group III and V atoms. Let the total number of atoms in an Au droplet be denoted via the volume of a ternary Au-III-V droplet on the NW top:

\[ N_3(t) + N_5(t) + N_{Au} = \frac{\pi R^3(t)}{3\Omega_L} f[\beta(t)], \]

where \( N_3(t), N_5(t), N_{Au} \) stand for the number of group III, group V and Au atoms, respectively; \( \Omega_L \) is the elementary volume in the liquid phase; \( \beta(t) \) is the droplet contact angle and \( f(x) = (1 - \cos(x))^2 (2 + \cos(x))/\sin^3(x) \). We assume here that the NW radius is constant, so \( R(t) = \text{const} = R \).

The time evolution of the number of group III and V atoms in a catalyst droplet can be expressed in the following form [5, 7–9]:

\[ N_3(t) = \frac{\pi R^3(t)}{3\Omega_L} f[\beta(t)], \]

\[ N_5(t) = \frac{\pi R^3(t)}{3\Omega_L} g[\beta(t)], \]

\[ N_{Au}(t) = \frac{\pi R^3(t)}{3\Omega_L} h[\beta(t)], \]

where \( f[\beta(t)], g[\beta(t)], h[\beta(t)] \) are functions depending on the contact angle.
\[
\frac{dN_i(t)}{dt} = k_0 \left[ \chi_i(t)v_i(t) + \frac{2v_i(t)\lambda_\alpha \sin(\alpha)}{R} - J(t) \right], \quad (2)
\]
\[
\frac{dN_i(t)}{dt} = k_0 \left[ \chi_i(t)v_i(t) - \frac{2}{1+\cos[\beta(t)]}v_5^0 e^{i\phi} - J(t) \right] \quad (3)
\]
with \( k_0 = \pi R^2 / \Omega_3 \). Here \( \chi_k \) are the geometrical factors dependent on the growth method (\( \chi_k = \sin^{-2} [\beta(t)] \) for molecular beam epitaxy (MBE) or \( \chi_k = 2 / (1 + \cos[\beta(t)] \) for metal organic vapor phase epitaxy (MOVPE)) \((k = 3, 5)\); \( v_k \) are the atomic fluxes; \( \Omega_3 \) is the elementary volume of a III-V pair in the solid phase, which is 0.0452 nm\(^3\) for a GaAs pair. The first terms of equations (2) – (3) describe the direct impingement fluxes of the \( k \)-th group in the droplet. The second term in (2) describes the diffusion of Ga adatoms from NW sidewalls to the catalyst droplet, where \( \lambda_3 \) stands for the effective diffusion length of Ga adatoms, and \( \alpha \) is the flux inclination angle relative to the substrate normal. The second term in (3) describes the desorption of group V atoms from the droplet, where \( v_5^0 \) is the temperature-dependent desorption constant and \( i = 2 \) for As\(_2\) as in [6].

The third term in relations (2) and (3) stands for the axial NW growth as a function of the liquid-solid chemical potential difference per III-V pair [7]:

\[
J(t) = J_0 \exp \left( -\frac{A}{\Delta \mu(t)} \right) \quad (4)
\]
\[
\Delta \mu(t) = \mu_3(t) + \mu_5(t) - \mu_5^0 \quad (5)
\]
\[
\mu_3(t) = \mu_3^0 + \ln \left[ C_3(t) \right] + \omega_{3, A_5} \left[ 1 - C_3(t) \right]^2 + \left[ \omega_{3, A_5} + \omega_{3, A_6} - \omega_{3, A_5} \right] C_3(t) \left[ 1 - C_3(t) \right] \quad (6)
\]
\[
\mu_5(t) = \mu_5^0 + \ln \left[ C_5(t) \right] + \omega_{5, C_3} \left[ 1 - C_3(t) \right]^2 + \left[ \omega_{5, A_5} + \omega_{5, A_6} - \omega_{5, A_5} \right] C_3(t) \left[ 1 - C_3(t) \right] \quad (7)
\]
where \( J_0 = \text{const} \sim \pi R^2 h \), \( h \) is the height of a III-V monolayer (0.326 nm for <111>-oriented GaAs NWs). \( C_3(t), C_5(t) \) are the atomic concentrations of Ga and As atoms in the droplet, respectively, and \( C_3(t) = N_3(t) / [N_3(t) + N_5(t) + N_{A_5}] \). We assume that \( C_3(t) \ll 1 \). The described set of equations (1) – (7) is a self-consistent system.

3. Results

The major difference of this paper from the recent studies is that we solve the system of kinetic equations (1) – (7) in the non-stationary case. We use a numerical solution because it is hard to derive an analytical solution for this system in the non-stationary case. Kinetic simulations in MATLAB were performed with the following model parameter values: \( \lambda_3 = 750 \) nm, \( \mu_{35}^0 = 11.8 \) eV/pair, \( A = 14.6 \), \( J_0 = 23000 \) nm\(^2\), \( v_5^0 \exp(2\mu_5^0) = 37000 \) nm/s, \( \omega_{3, A_5} = -9.517 \), \( \omega_{3, A_6} = 1.101 \), \( \omega_{3, A_5} = -4.488 \). Figure 1 shows that under a fixed value of group III flux it takes less time to get a steady-state value of the contact angle for a NW with a small top radius. On the other hand, increasing the group III flux while fixing the III-V flux imbalance results in a sharp decrease in the time required to achieve a steady state.
Figure 1. (a) Contact angle dependence on time for different values of the NW top radius and a constant value of the flux imbalance of $v_3 - v_5 = 3$ nm/s. The solid and dashed lines demonstrate different group III fluxes: $v_3 = 0.05$ nm/s and $v_3 = 1.5$ nm/s, respectively. (b) Qualitative sketch of a NW with a gold droplet on the top facet; the droplet contact angle is equal to $\beta_0$.

We have also modeled a situation where the fluxes of group III and V atoms suddenly switch to a different value. Figure 2 shows that increasing the group V flux from 8.5 nm/s to 19.5 nm/s for 40 seconds reduces the contact angle of the catalyst droplet by ~4 degrees. We can observe the same effect when the Ga flux is decreased from 4.5 nm/s to 0.5 nm/s in 86 seconds. We also clearly see that an increase in the gallium flux from 4.5 nm/s to 6.5 nm/s results in an increase in the droplet contact angle of ~3 degrees. At the same time, a decrease in the group V flux from 8.5 nm/s to 6 nm/s produces larger values for the droplet contact angle.

Figure 2. Contact angle time evolution. The initial values of group III and V fluxes are 4.5 nm/s and 8.5 nm/s, respectively. The top radius of NWs is $R = 20$ nm.
4. Conclusion
The droplet composition and contact angle versus the material fluxes can be described by our model in the VLS growth of gold-catalyzed GaAs NWs under non-stationary conditions. MOVPE growth can be modelled using the same equations but with different geometrical factors. These results may be useful for understanding and controlling the droplet compositions, which affect the morphology and polytypism of VLS III-V NWs grown using different epitaxy techniques.

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