

Supporting information

Be, Te and Si doping of GaAs nanowires: theory and experiment

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1. Equations (3) of the main text

Let us first comment Eqs. (3) of the main text:

$$\frac{dL}{dt} = v_3 \left(\frac{2}{1+\cos\beta} + \frac{2\lambda_3}{R} \right) (1 - e^{\mu_3 - \mu_3^v}), \quad (3a)$$

$$\frac{dL}{dt} = \frac{4v_{5(2)}}{1+\cos\beta} (1 - e^{2\mu_5 - \mu_{5(2)}^v}), \quad (3b)$$

$$\frac{dL}{dt} = h\pi R^2 \eta J(\Delta\mu). \quad (3c)$$

These equations are valid under the steady state regime of VLS growth where the atomic influxes of group III and group V atoms into the droplet are exactly equalized by their reverse diffusion onto the NW sidewalls and desorption (for group III adatoms) or only desorption (for group V atoms), and the sinks due to NW growth. Equation (3b) is clear – it assumes that that group V atoms arrive to and desorb from the droplet in the form of dimers such as As₂, and that thermodynamic equilibrium for group V atoms in vapor and liquid occurs when $2\mu_5 = \mu_{5(2)}^v$, as in Refs. [S1] and [S2]. Equation (3c) gives the nucleation-mediated NW growth rate in the mononuclear mode [S1,S2], with $\Delta\mu = \mu_3 + \mu_5 - \mu_{35}^P$ as the chemical potential difference per III-V pair in liquid and solid.

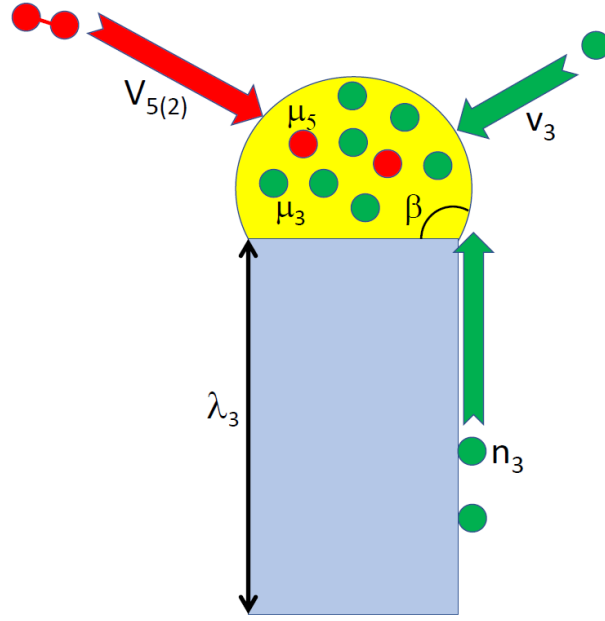


Figure 1. Schematics of the VLS growth process with surface diffusion of group III adatoms.

Let us now derive Eq. (3a). We consider a simplified form of the diffusion flux on the NW sidewalls such that the group III adatom concentration n_3 equals n_l at the liquid-solid boundary below the droplet and n_f at distance λ_3 from the droplet (see Fig. 1). We now solve the simple diffusion equation with these boundary conditions:

$$\frac{d^2 n_3}{dz^2} = 0, \quad n_3(z = L) = n_l, \quad n_3(z = L - \lambda_3) = n_f, \quad (\text{S1})$$

and use the standard expression for the diffusion-induced NW growth rate [S3]

$$\left(\frac{dL}{dt}\right)_{diff} = -2 \frac{D_3}{R} \Omega_{35} \left(\frac{dn_3}{dz}\right)_{z=L}, \quad (\text{S2})$$

with D_3 as the diffusion coefficient of group III adatoms on the NW sidewalls and Ω_{35} as the elementary volume per III-V pair in solid. The result is given by:

$$\left(\frac{dL}{dt}\right)_{diff} = 2 \frac{D_3}{R} \Omega_{35} \frac{(n_f - n_l)}{\lambda_3}. \quad (\text{S3})$$

We note that in the steady state regime $n_f = \varphi_3 I_3 \tau_3$, with φ_3 as a geometrical coefficient which depends on the epitaxy technique, I_3 as the arrival rate of group III atoms per unit area of the surface (measured in $\text{nm}^{-2}\text{s}^{-1}$) and τ_3 as their mean lifetime on the NW sidewalls. Using $\Omega_{35} I_3 = v_3$ and $D_3 \tau_3 = \lambda_3^2$, we have

$$\left(\frac{dL}{dt}\right)_{diff} = \frac{2\lambda_3}{R} \varphi_3 v_3 \left(1 - \frac{n_l}{n_f}\right). \quad (S4)$$

The ratio n_l/n_f can equivalently be presented as $n_l/n_f = \exp(\mu_3 - \mu_f)$, where μ_3 is the chemical potential of group III atoms in liquid and μ_f is the chemical potential of group III adatoms at distance λ_3 from the droplet. Without radial growth on the sidewalls, the latter should equal chemical potential of group III atoms in vapor: $\mu_f = \mu_3^v$. In VPE deposition techniques, $\varphi_3 = 1$. Therefore, we obtain

$$\left(\frac{dL}{dt}\right)_{diff} = \frac{2\lambda_3}{R} v_3 (1 - e^{\mu_3 - \mu_3^v}). \quad (S5)$$

Combining it with the contribution to the NW growth rate due to the direct exchange with vapor (in VPE technique),

$$\left(\frac{dL}{dt}\right)_v = \frac{2v_3}{(1+\cos\beta)} (1 - e^{\mu_3 - \mu_3^v}), \quad (S6)$$

we arrive at Eq. (3a). Note that this NW growth rate cancels at $\mu_3 = \mu_3^v$ corresponding to equilibrium for group III species in vapor and liquid.

2. Derivation of Eq. (4) for the NW growth rate

According to Ref. [S2], solution to Eqs. (3a) to (3c) have the form

$$\mu_3 = \mu_3^v + \ln\left(1 - \frac{1}{V_3} \frac{dL}{dt}\right), \quad \mu_5 = \frac{1}{2} \mu_{5(2)}^v + \frac{1}{2} \ln\left(1 - \frac{1}{V_5} \frac{dL}{dt}\right), \quad (S7)$$

and

$$\frac{dL}{dt} = \frac{V_5}{1+V_5/V_3} \frac{1}{1+i_c/W(y)}, \quad y = \frac{(1+V_5/V_3)}{V_5} V_{35} i_c. \quad (S8)$$

Here, V_3 , V_5 , V_{35} and i_c are given by the corresponding expressions of the main text. $W(y)$ is the Lambert function such that $W \exp(W) = y$. To further simplify Eq. (S8), we note that the term with $i_c/W(y)$ limits the VLS growth only if it is large compared to unity, which occurs when $W(y) \ll 1$. In this case, $W(y) \cong y$ and we can use the simple approximation

$$\frac{i_c}{W(y)} \cong \frac{i_c}{y} = \frac{V_5}{(1+V_5/V_3)V_{35}}. \quad (S9)$$

Using this in Eq. (S8), we arrive at Eq. (4) of the main text.

3. Derivation of Eq. (8) for V_{35}

The nucleation-limited NW growth rate is generally given by Eq. (3c) at $\Delta\mu = \Delta\mu_v$ [S2]:

$$V_{35} = h\pi R^2 \eta J_*(\Delta\mu_v) \exp\left(-\frac{a^2}{4\Delta\mu_v}\right), \quad (\text{S10})$$

where a is a constant related to the surface (edge) energy of 2D island and pre-exponential factor J_* weakly depends on $\Delta\mu_v$. Chemical potential of vapor $\Delta\mu_v$ depends on the material fluxes according to

$$\Delta\mu_v = \Delta\mu_v^0 + \ln(v_3/v_3^0) + \frac{1}{2}\ln(v_{5(2)}/v_{5(2)}^0). \quad (\text{S11})$$

Using this in Eq. (S10) and assuming that the chemical potential variation $\ln(v_3/v_3^0) + \frac{1}{2}\ln(v_{5(2)}/v_{5(2)}^0)$ is much smaller than $\Delta\mu_v^0$, we can write approximately:

$$V_{35} = h\pi R^2 \eta J_*(\Delta\mu_v^0) \exp\left[-\frac{a^2}{4\Delta\mu_v^0 \left(1 + \frac{\ln(v_3/v_3^0) + (1/2)\ln(v_{5(2)}/v_{5(2)}^0)}{4\Delta\mu_v^0}\right)}\right] \cong h\pi R^2 \eta J(\Delta\mu_v^0) \exp\left[\frac{a^2}{4(\Delta\mu_v^0)^2} \ln\left(\frac{v_3}{v_3^0} \left(\frac{v_{5(2)}}{v_{5(2)}^0}\right)^{1/2}\right)\right]. \quad (\text{S12})$$

Noting that $i_c = \left[a^2/4 (\Delta\mu_v^0)^2\right]$, we obtain Eq. (8) of the main text.

4. Derivation of Eqs. (10) for the doping levels

Comparing Eqs. (1) and (2) of the main text, we obtain

$$x = x_n \exp(\mu_* - \mu_*^v + \mu_5 - \mu_{5(2)}^v/2 - \varepsilon_{5*} + \varepsilon_{5*}^n),$$

$$y = y_n \exp(\mu_* - \mu_*^v + \mu_3 - \mu_3^v - \varepsilon_{3*} + \varepsilon_{3*}^n),$$

where the values ε_{5*} and ε_{3*} are generally different for nominal doping of thin films and for VLS NWs due to different compensation ratios. Using Eqs. (S7) and Eq. (4) of the main text, we arrive at

$$x = x_n \left(\frac{V_5/V_3 + V_5/V_{35}}{1 + V_5/V_3 + V_5/V_{35}}\right)^{1/2} \exp(\mu_* - \mu_*^v - \varepsilon_{5*} + \varepsilon_{5*}^n),$$

$$y = y_n \left(\frac{1 + V_5/V_{35}}{1 + V_5/V_3 + V_5/V_{35}}\right) \exp(\mu_* - \mu_*^v - \varepsilon_{3*} + \varepsilon_{3*}^n). \quad (\text{S13})$$

At $\varepsilon_{3*} = \varepsilon_{3*}^n$ and $\varepsilon_{5*} = \varepsilon_{5*}^n$, this is reduced to Eqs. (10) of the main text. At $\mu_* = \mu_*^v$, this is further reduced to Eqs. (6) of the main text.

▪ References

- [S1] Glas, F.; Ramdani, M. R.; Patriarche, G.; Harmand, J. C. Predictive modeling of self-catalyzed III-V nanowire growth. *Phys. Rev. B* **2013**, 88, 195304.
- [S2] Dubrovskii, V. G. Group V sensitive vapor-liquid-solid growth of Au-catalyzed and self-catalyzed III-V nanowires. *J. Cryst. Growth* **2016**, 440, 62.
- [S3] Dubrovskii, V. G.; Hervieu, Yu. Yu. Diffusion-induced growth of nanowires: Generalized boundary conditions and self-consistent kinetic equation. *J. Cryst. Growth* **2014**, 401, 431-440.