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Supporting information

Long catalyst-free InAs nanowires grown on silicon substrate by HVPE

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I] Kinetics and thermodynamics calculations

The growth model is the replica of the model developed for GaAs growth by HVPE, thoroughly described in reference [SI-1]: general description of the growth model for reversible and irreversible vapor phase epitaxy complex processes, namely HVPE and MOVPE; and in reference [SI-2]: specific application of the reversible model for GaAs growth by HVPE. Initially, the model considers a growing surface made of terraces and steps where incorporation of the crystal units occurs, aiming at modeling layer by layer growth after island nucleation on exact surfaces, or a regular array of surface steps on vicinal substrates. In complex chemical systems, one has to take into account adsorption and desorption of precursor materials (reactions (2) and (3) for the present study), decomposition frequency (dechlorination according to reaction (4)) and diffusion of ad-species on the surface before being incorporated into the crystal:

$$2As_{2(g)} \rightleftarrows As_{4(g)} \qquad (1)$$

$$4V + As_{4(g)} \rightleftarrows 4\,As \qquad (2)$$

$$As + InCl_{(g)} \rightleftarrows AsInCl \qquad (3)$$

$$AsInCl + \frac{1}{2}H_{2(g)} \rightleftarrows InAs_{(c)} + HCl_{(g)} \quad (4)$$

It is shown that for reversible processes where a complex species (B=AsInCl) acts as source for the crystal unit (A=InAs), the growth rate of crystal A can be reduced to the growth rate expression for direct condensation in a one-particle system, when the desorption frequency of the source species B (that occurs here through the desorption of InCl according to reverse reaction (3)), is much higher than the dechlorination frequency (reaction (4)) [SI-2]. As a matter of fact, in (As, IIICl) systems with III=Ga or In, the adsorption/desorption flux ratio for As is greater than one for temperature up to 800°C, but it is not the case for the volatile IIICl molecules. Desorption of IIICl starts to be an issue for temperature around 600°C, that is why III/V ratio greater than one are used in HVPE to compensate the strong desorption of element III precursors. The physics of desorption prevails over reaction (4), so that the surface density of the source precursors B=AsInCl is uniform governed by reaction (3) all over the surface, and diffusion fluxes vanish.

The classical expression for direct condensation R_{DC} in one-particle systems is:

$$R_{DC} = \Omega_{InAs}\gamma_{InAs}\upsilon_{-4}c_{InAs} \quad (5)$$

where Ω_{InAs} is the molecular volume of InAs, υ_{-4} is the chlorination frequency of InAs according to reverse reaction (4), c_{InAs} is the surface concentration of InAs. c_{InAs} depends on the detailed description of the intermediate steps (reactions (1) to (3)) involved in the growth of the InAs crystal unit (reaction (4)), as described in the following.

Introducing the chlorination flux (reverse reaction (4)) J_{-4}:

$$J_{-4} = \upsilon_{-4}c_{InAs} \quad (6)$$

R_{DC} is written as:

$$R_{DC} = \Omega_{InAs}\gamma_{InAs}J_{-4} \quad (7)$$

The net adsorption fluxes of ad-species i per unit time and surface $J_i = J_{+i} - J_{-i}$, where J_{+i} is the adsorption flux and J_{-i} the desorption flux of species i, are written for chemical reactions (2), (3) and (4) as:

$$J_{As} = J_2 = J_{+2} - J_{-2} = 4\,k_{+2}\theta_V\,[As_{4(g)}] - k_{-2}\frac{\theta_{As}^4}{\theta_V^3} \qquad (8)$$

$$J_{AsInCl} = J_3 = J_{+3} - J_{-3} = k_{+3}\theta_{As}\,[InCl_{(g)}] - k_{-3}\theta_{AsInCl} \qquad (9)$$

$$J_{InAs} = J_4 = J_{+4} - J_{-4} = k_{+4}\theta_{AsInCl}\,[H_{2(g)}]^{1/2} - k_{-4}\theta_{InAs}\,[HCl_{(g)}] \qquad (10)$$

where $k_{\pm i}$ are temperature-dependent pre-factors involving activation energies ε_i, $[i_{(g)}]$ is the partial pressure of gaseous species i and θ_i is the surface coverage of ad-species i. The calculation of the pre-factors $k_{\pm i}$ is thoroughly described in reference [SI-2]. Namely, k_{+i} are the kinetic constants corresponding to the adsorption of As (reaction (2)), InCl (reaction (3)) and H_2 onto AsInCl ad-species that leads to dechlorination (reaction (4)). k_{+i} are written with the Ernst-Knudsen flux expression. k_{-i} are the kinetic constants corresponding to the reverse desorption processes of reactions (2), (3) and (4); they are written as products of the partition functions of the species involved.

The surface coverage of vacant surface sites is defined as:

$$\theta_V = 1 - \theta_{As} - \theta_{AsInCl} - \theta_{InAs} \qquad (11)$$

or

$$\frac{1}{\theta_V} = \left[1 + \frac{\theta_{As}}{\theta_V} + \frac{\theta_{AsInCl}}{\theta_V} + \frac{\theta_{InAs}}{\theta_V}\right] \qquad (12)$$

with

$$\frac{\theta_{As}}{\theta_V} = \sqrt{2}\left(\frac{k_{+2}^{1/4}}{k_{-2}^{1/4}}\right)[As_{4(g)}]^{1/4} = A(T, \varepsilon_2)\,[As_{4(g)}]^{1/4} \qquad (13)$$

$$\frac{\theta_{AsInCl}}{\theta_V} = \frac{k_{+3}}{k_{-3}}[InCl] \times A(T, \varepsilon_2)[As_{4(g)}]^{1/4} = B(T, \varepsilon_2,\varepsilon_3)\,[InCl_{(g)}][As_{4(g)}]^{1/4} \qquad (14)$$

$$\frac{\theta_{InAs}}{\theta_V} = \frac{k_{+4}}{k_{-4}}([H_{2(g)}]^{1/2}/[HCl_{(g)}]) \times B(T, \varepsilon_2, \varepsilon_3)\,[InCl_{(g)}][As_{4(g)}]^{1/4} \tag{15}$$

$$\frac{\theta_{InAs}}{\theta_V} = C(T, \varepsilon_2, \varepsilon_3, \varepsilon_4)\,[InCl_{(g)}][As_{4(g)}]^{1/4}[H_{2(g)}]^{1/2}/[HCl_{(g)}] \tag{16}$$

The activation energies ε_i are determined after fitting experimental data. θ_V is plotted and the growth rate R_{DC} can be finally plotted as a function of θ_V:

$$R_{DC} = \kappa \times \gamma_{InAs} \times \theta_v \tag{17}$$

with $\kappa = \Omega_{InAs} k_{-4}\, C(T,\varepsilon_2,\varepsilon_3,\varepsilon_4)\,[InCl][As_4]^{1/4}[H_2]^{1/2}$.

This section is dedicated to the calculation of the supersaturation related to the formation of indium droplets from gaseous InCl. The reaction is given by the equation:

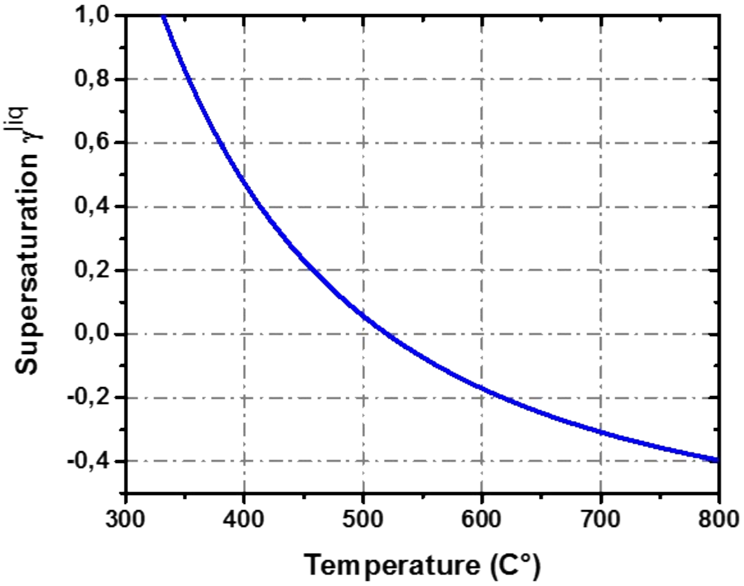
$$InCl_{(g)} + \frac{1}{2}H_{2(g)} \rightleftharpoons In_{(l)} + HCl_{(g)}$$

The Van't Hoff relation allows to calculate the equilibrium constant of the reaction as a function of the Gibbs energy difference between the reactants and the products:

$$K_{In}^{eq}(T) = \exp\left(- \frac{\Delta G(T)}{RT} \right)$$

Then we can determine the supersaturation γ_{In}^{liq} defined as:

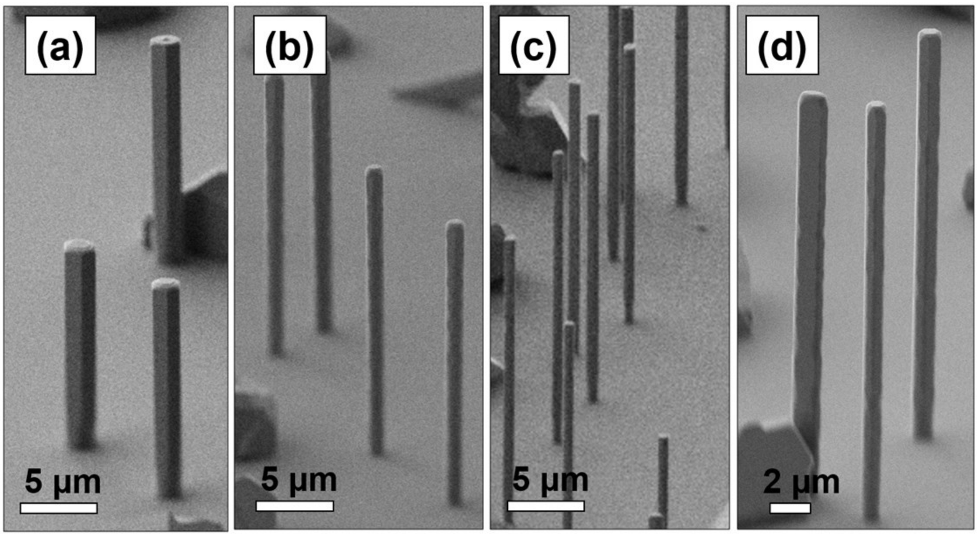
$$\gamma_{In}^{liq} = \frac{[InCl][H_2]^{1/2}}{[HCl]K_{In}^{eq}} - 1$$



One can observe that the supersaturation becomes negative at a temperature of 520°C. This means that for growth temperature above 520°C the formation of an indium droplet is not favourable. The supersaturation was calculated here with the partial pressures that are the most favourable for the formation of indium droplets (III/V =18 in this study).

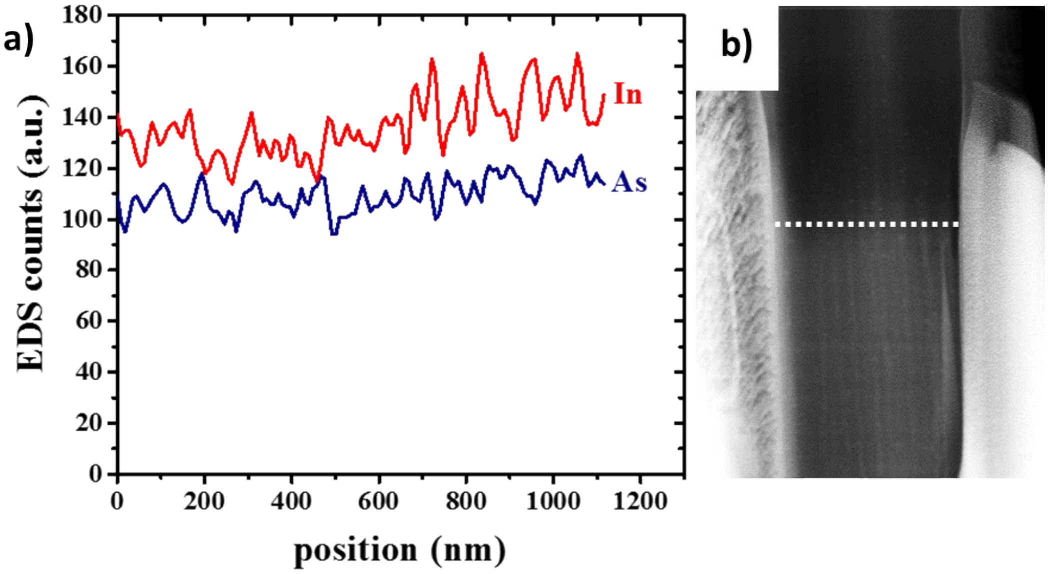
II] Characterizations

SEM images of InAs nanowires for different III-V ratios (a) 6, (b) (12) at fixed InCl and (c) 6, (d) 12 at fixed AsH_3.



The growths were performed at 680°C.

EDS linescan performed on InAs nanowire grown at 680°C. III/V ratio was 6.



References

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[SI-2] Gil-Lafon E.; Napierala J.; Pimpinelli A.; Cadoret R.; Trassoudaine A.; Castelluci D, *J. Cryst. Growth* 2003, **258**, 14-25.