

Supplementary Information

Supplementary Information for “Diameter Modulation as a Route to Probe the Vapour-Liquid-Solid Growth Kinetics of Semiconductor Nanowires”

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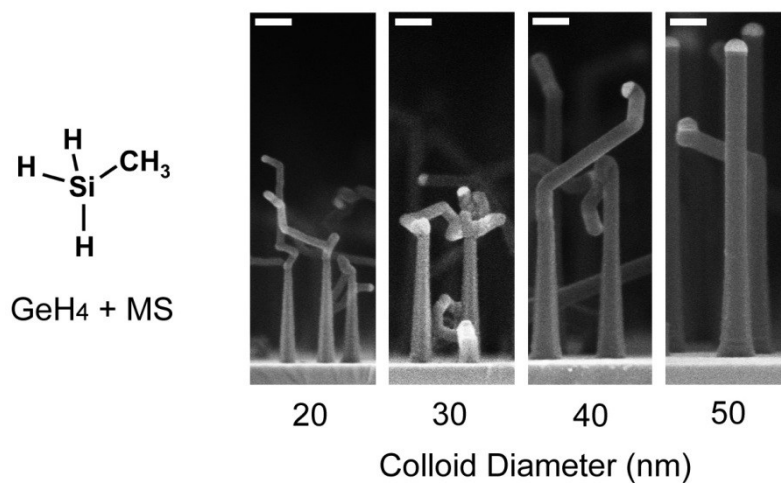


Fig. S1 Side view SEM images of Ge nanowires grown with a standard base as described in the main text and followed by 3 minutes with 0.28 Torr GeH₄ and 0.12 Torr SiH₃CH₃. 100, 96, 86, and 51 % of the nanowires kink at least once for 20, 30, 40, and 50 nm colloid, respectively. Scale bars, 100 nm.

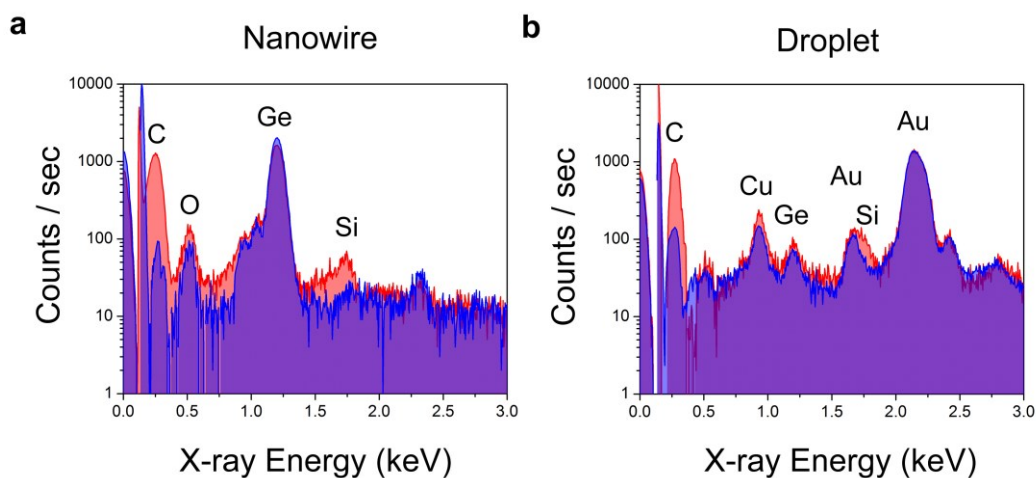


Fig. S2(a) EDX spectra of the upper segment for representative 50 nm Ge nanowires from the arrays in Fig. 1(a) (shown in blue) and Fig. 1(b) (shown in red). (b) EDX spectra of the catalyst droplet for representative 50 nm Ge nanowires from the arrays in Fig. 1(a) (shown in blue) and Fig. 1(b) (shown in red). Spectra in blue in (b) are scaled by 1/3. We note that EDX cannot distinguish between Si located in the bulk of or on the surface of the nanowire.

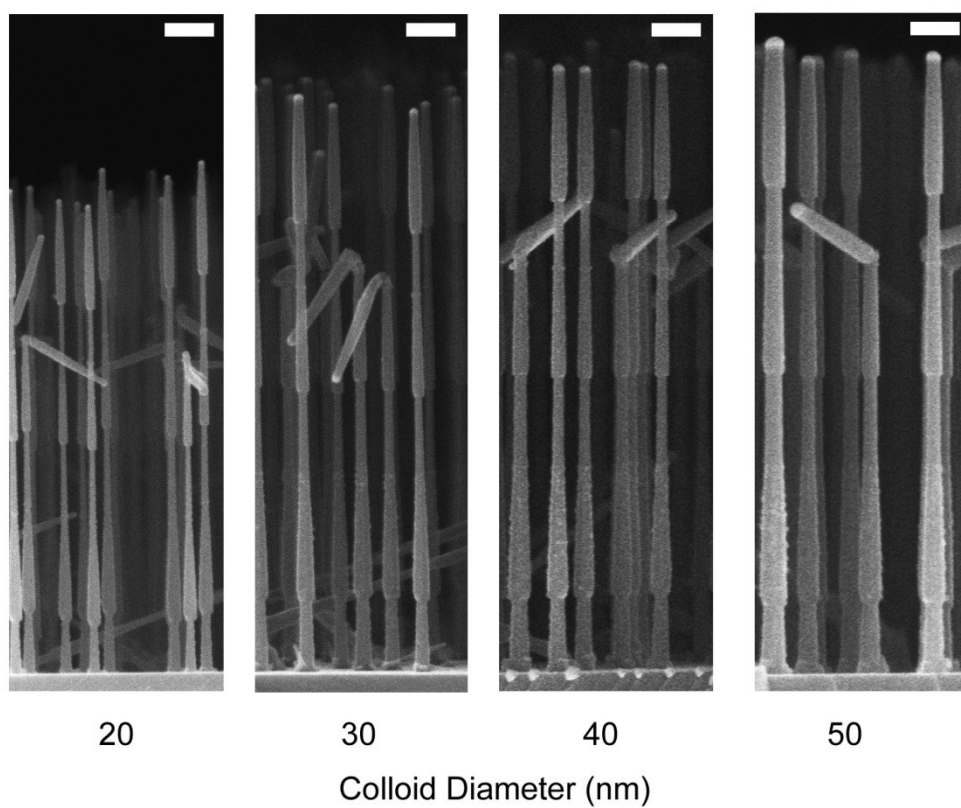


Fig. S3 Additional side view SEM images of the samples in Fig. 5 showing kinking for segments grown at 300 °C. Scale bars, 200 nm.

Model Discussion

We fit our data to the recently reported model by N. Li et al,¹ but emphasize that the use of this model is largely illustrative of the fitting made possible by the rapid and accurate extraction of nanowire growth rate. The model assumes that nucleation at the liquid-solid interface is rate limiting and leads to the following expression for growth rate

$$dL/dt = \alpha \exp\left(-\frac{\beta}{d_s}\right), \quad (S1)$$

with

$$\alpha = c^L \sqrt{\pi C_0^S \lambda^S} \omega \exp\left(-\frac{\pi \lambda^S \Omega^S \gamma_{LS}^2}{2 \left(kT \ln\left(\frac{c^L}{c_{eq}^L}\right)\right)^2} \ln\left(\frac{c^L}{c_{eq}^L}\right)\right), \quad (S2)$$

$$\beta = \frac{\pi \lambda^S (\Omega^S)^2 \gamma_{LS}^2}{kT \left(kT \ln\left(\frac{c^L}{c_{eq}^L}\right)\right)^2} \left(\frac{\Omega^S \gamma_{VS} - 2\Omega^L \gamma_{VL} \sin(\theta)}{\Omega^S}\right), \quad (S3)$$

where d_s – nanowire diameter, C^L – Ge atom concentration in the droplet, C_{eq}^L – Ge atom concentration in the catalyst droplet at equilibrium with the Ge solid assuming a flat liquid-solid interface, C_0^S – volumetric atom density in the solid, λ^S – solid layer thickness, ω – capture rate of Ge atoms by growing island, Ω^S – solid Ge atom volume, Ω^L – liquid Ge atom volume, γ_{LS} – liquid-solid interface energy, γ_{VS} – vapour-solid interface energy, γ_{VL} – vapour-liquid interface energy, k – Boltzmann's constant, T – absolute temperature, θ is the catalyst droplet contact angle to the liquid-solid interface plane. The assumptions that $kT \ln(C^L/C_{eq}^L) \gg 2(\Omega^S \gamma_{VS} - 2\Omega^L \gamma_{VL} \sin(\theta))/d_s$ and $\Omega^S \approx \Omega^L$ allow the terms dependent in nanowire diameter to be collected, which should be valid when far from the critical diameter.²

The diameter and volume of the catalyst droplet, assuming a spherical shape, are related via $d_L = [(24V/\pi)(1+\cos(\theta))^2(2-\cos(\theta))^{-1}]^{1/3}$. The diameter of the liquid catalyst droplet (d_L) and solid nanowire (d_s) beneath can be related via $d_s = d_L \sin(\theta)$. V is the actual volume of the catalyst droplet and can be expressed as $V = d_{colloid}^3(\pi/6)/(1-C^L\Omega^L)$, assuming an ideal solution, where

d_{colloid} (nm) is the original diameter of the, assumed spherical, Au colloid nanoparticle. Substituting these relationships into the above equations provides growth rate as a function of Au colloid diameter

$$dL/dt = \alpha' \exp\left(-\frac{\beta'}{d_{\text{colloid}}}\right) P_{\text{GeH}_4}, \quad (\text{S4})$$

with

$$\alpha' = K \sqrt{\pi C_0^S} \lambda^S \omega \exp\left(-\frac{\pi \lambda^S \Omega^S \gamma_{\text{LS}}^2}{2(kT)^2 \ln\left(\frac{K P_{\text{GeH}_4}}{C_{\text{eq}}^L}\right)}\right), \quad (\text{S5})$$

$$\beta' = \frac{\pi \lambda^S (\Omega^S)^2 \gamma_{\text{LS}}^2}{kT \left(kT \ln\left(\frac{K P_{\text{GeH}_4}}{C_{\text{eq}}^L}\right)\right)^2} \left(\frac{\Omega^S \gamma_{\text{VS}} - 2\Omega^L \gamma_{\text{VL}} \sin(\theta)}{\Omega^S}\right) \frac{(1+\sin(\theta))^{2/3} (2-\sin(\theta))^{1/3}}{\sin(\theta)} \left(\frac{1-K P_{\text{GeH}_4} \Omega^L}{4}\right)^{1/3}, \quad (\text{S6})$$

where $K = C^L/P_{\text{GeH}_4}$ is a temperature-dependent equilibrium constant, assuming crystallization is rate limiting and P_{GeH_4} is the partial pressure of GeH_4 (Torr). Based on the data shown in Fig. 4, the pressure dependence appears nearly first order (1.00 ± 0.02). Clearly, almost every unknown variable comprising the lumped parameters (i.e., α' and β') varies with temperature. Thus, we determine, via fitting of our data, the functional form of the overall T dependence for each parameter using a minimum number of free variables. α' and β' exhibit a $\exp(A \times T)$ and $B \times T - C$ relationship, respectively, where A, B, and C are positive empirical constants. These dependencies lead to the following final rate expression

$$dL/dt = \exp(AT) \exp\left(-\frac{BT-C}{d_{\text{colloid}}}\right) P_{\text{GeH}_4}. \quad (\text{S7})$$

We plot our data as $\ln(\Delta L/\Delta t/P_{\text{GeH}_4})$ as a function of $1/d_{\text{colloid}}$, as shown in Fig. S4(a), to extract α' and β' from the slope and y-intercept, respectively. We find that $A = 1.01 \times 10^{-2}$, $B = 1.18 \times 10^{-1}$, and $C = 6.64 \times 10^1$ when using data collected at all the temperatures shown in Fig. 5.

The model, when fitted to our data, suggests diameter-independent growth will occur at 290 °C; however, it's clear that our 300 °C data remains diameter-dependent. If we assume that the morphological and trend differences observed for growth at 300 °C are attributable to catalyst

droplet phase change, then a fit without data at this temperature is warranted. This possibility is explored in Fig. S4(b), which shows the experimental data and model prediction when excluding the 300 °C data in the fit. We find $A = 1.01 \times 10^{-2}$, $B = 1.47 \times 10^{-1}$, and $C = 8.57 \times 10^1$ for this case. Importantly, this fit results in the prediction of an inverse diameter-dependence at temperatures below 310 °C that results from a sign change for β' . Such behaviour is known for other nanowire systems,³⁻⁵ but its significance here, if any, requires additional investigation.

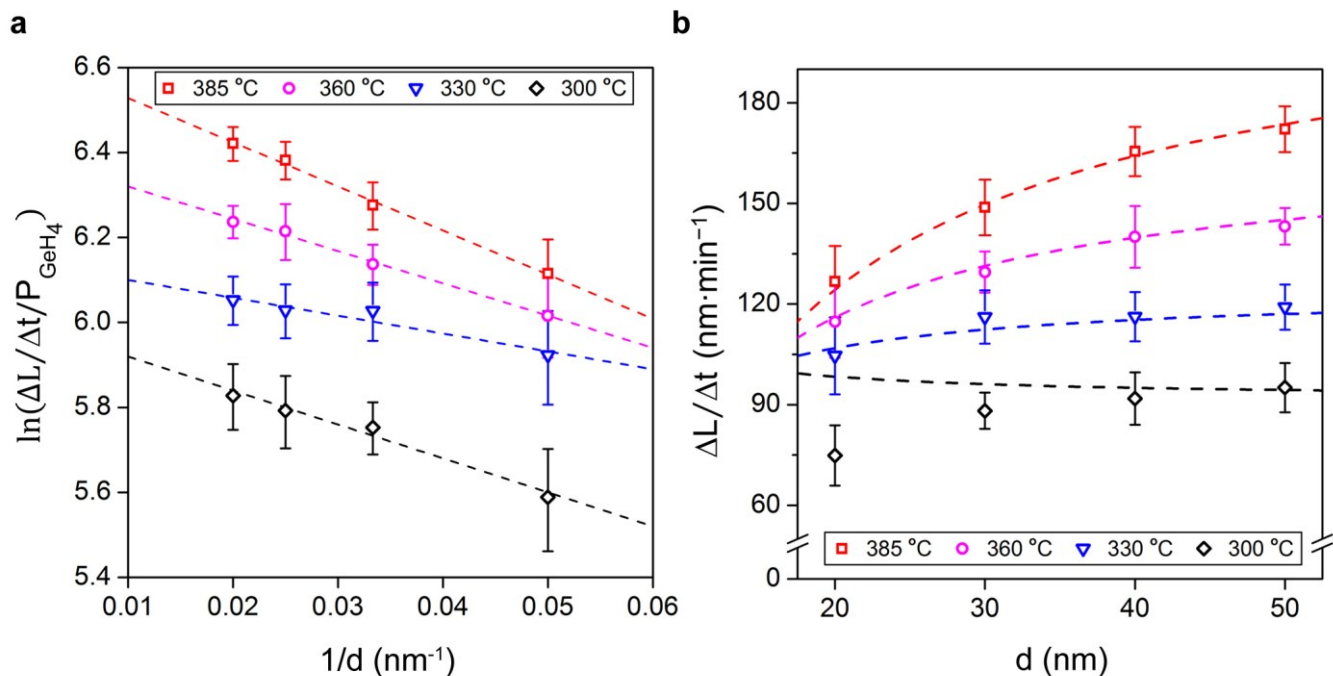


Fig. S4 (a) Linearization of data shown in Fig. 5, given the functional form of Equation 1. Open shapes correspond to experimental data, while dashed lines are linear fits to each temperature. (b) Axial elongation rate ($\Delta L/\Delta t$) plotted as a function of gold colloid diameter and substrate temperature. The dashed curves for each temperature result from a fit to the data based on Equation 1, only using temperatures in the range 330 – 385 °C.

Notes and references

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