S1. Specifications about the simulations

The model used for the simulation is based on the work of Mårtensson et al.\textsuperscript{1}, modified to treat nucleation and layer growth as two separate events. The model follows the mass transport of material through the seed particle over time; to achieve this, time is discretized into steps of $dt=1$ ms. Within each time step, the transfer of material between the vapor and liquid (catalyst) phases is treated, as well as any transfer of material from the liquid to the solid (nanowire) phase via either nucleation or layer growth.

The net vapor-liquid flow ($J_{net}$) is calculated using:

$$J_{net} = \frac{1}{\sqrt{2\pi m k_B T}} (P_{in} - \eta N P_{out})$$

Here, $m$ is the atomic mass of the species, $k_B$ is Boltzmann’s constant, $T$ is the growth temperature, $P_{in}$ is the pressure of the impinging growth species (chosen at the start of a simulation), $P_{out}$ is the vapor pressure of the species in the seed particle, $\eta$ is a factor describing the efficiency of the
evaporation set to 2x10^-4 after fitting, and N is the number of atoms per evaporation event (here 4 for As4 and 1 for Ga). The vapor pressure is calculated as:

\[ P_{out} = P_b \exp \left[ \left( \frac{\Delta H_{vap}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_b} \right) \right] \exp \left[ \frac{\mu - \mu_0}{kT} \right] \]

The pressure at which the element boils, \( P_b \), is first scaled from the boiling temperature (\( T_b \)) to the current temperature (420 °C) using the enthalpy of vaporization (\( \Delta H_{vap} \)), and the Clausius-Clapeyron relation. The vapor pressure is then adjusted to take the environment into consideration using the difference between the chemical potential of a pure species (\( \mu_0 \)) and that of the species in the seed particle (\( \mu \)). Values for \( P_b \), \( T_b \) and \( \Delta H_{vap} \) for Ga are easily found; however, since As sublimates under normal circumstances the values found in literature vary. Here, we used the lowest enthalpy of forming As4 in Ref.2 as an estimate. The boiling point was set to 36.2 bar at 1090 K for As. The net flow, \( J_{net} \), gives the net number of atoms per time and area and to get the net number of atoms which are incorporated into the seed, \( J_{net} \) is multiplied by dt and the area of the seed as in Ref.1. Since we do not take effects such as pyrolysis into consideration in the simulations, there will never be a one to one correlation between the simulation pressures and the experimental pressures. Because of this, the presented simulation pressures are scaled through multiplication with constants (1200 for As and 1.5 for Ga).

The chemical potentials needed are calculated from the molar Gibbs free energy (\( g \)) of a ternary alloy described by:

\[
g = \sum_{i=1}^{3} X_i \mu_{0,i} + \sum_{i=1}^{3} X_i RT \ln(X_i) + \sum_{i=1}^{2} \sum_{j=i+1}^{3} X_i X_j \sum_{v=0}^{2} L_{i,j,v} (X_i - X_j)^v
\]

The first term sums the unary chemical potentials based on the molar fraction of each species (\( X_i \)), the second term is the entropy of mixing (with R being the gas constant), and the third term takes binary interactions into account in the form of the Redlich-Kister expansion. For the As-Au-Ga
system, no ternary interaction parameter was found in literature, and for this reason it was not considered here. The temperature-dependent interaction parameters $L_{i,j,v}$ are taken from literature (As-Au$^{3,4}$, As-Ga$^5$, Au-Ga$^6$), and so are the expressions for the unary chemical potentials$^7$. The chemical potential for each species in the mixture is then calculated from the derivatives of $G$ as:

$$\mu_i = \frac{\partial G}{\partial N_i} , \quad G = g \sum_j N_j / N_{Av} , \quad X_i = \frac{N_i}{\sum_j N_j}$$

Here, $N_i$ represents the number of atoms of each component in the seed particle and $N_{Av}$ is Avogadro’s constant. This framework allows us to calculate the chemical potential for each species, which is needed for the vapor-liquid transfer.

Next, we can evaluate the energy barrier of forming a stable nucleus. From previous experiments$^8$, we assume that the experimentally grown nanowires were predominantly wurtzite (WZ), and for this reason we do not include the zinc blende (ZB) phase in the model. Because of the small radius of the nanowire (measured to be 16 nm), we chose to include the energy of the liquid phase into the nucleation model. The motivation to take the energy of the liquid seed into consideration is the depletion effect, as presented by in Dubrovskii.$^9$ This effect refers to the influence that removing III-V pairs to form or grow a nucleus has on the liquid seed particle, which becomes more significant as the seed particle becomes smaller. To describe the liquid to solid transition, we consider the Gibbs free energy ($G_{sys}$) of the liquid seed particle and a nucleus or a layer consisting of $i$ WZ pairs, which we describe as:

$$G_{sys}(N_{As}, N_{Ga}, i) = N_{As} \mu_{As} + N_{Au} \mu_{Au} + N_{Ga} \mu_{Ga} + i(\mu_{GaAs} + \psi) + \sqrt{i} \phi$$

The first three terms give the energy of the liquid phase, with $N_{Au}$ set to an estimated value of 600000 atoms and $N_{As}, N_{Ga}$ dynamically changing over time. The last two terms give the energy of the nucleus or incomplete layer of the WZ phase. The chemical potential of the solid WZ phase is calculated by first calculating the chemical potential of ZB, $\mu_{GaAs}$, using the data in Ref.$^{10}$, and the difference in bulk cohesive energy between ZB and WZ, $\psi$, which is taken as 23.1 meV/pair$^{11}$. 
The chemical potentials are in units of J/atom for the species and J/pair for the binary. Here, $\phi$ is the average surface energy of the nucleus and is calculated as $\phi = C\Gamma \sqrt{\Omega_s h}$. The constant $C$ relates to the shape of the nucleus, and is given by the ratio of the perimeter to the square root of the surface area of the top of the nucleus. For a triangular shape assumed here, $C$ is approximately 1.86. The factors $\Omega_s$ (volume of a GaAs pair in the solid) and $h$ (height of a bilayer) are assumed to be the same for both crystal phases and are calculated from bulk ZB values. The effective surface energy of the perimeter, $\Gamma$, is based on the model by Glas et al. of triple phase line nucleation, and is calculated as $\Gamma = (1 - x) * \gamma_{SL} + x(\gamma_{SV} - \gamma_{LV} \sin \beta)$, using the interface energies for the solid-liquid $\gamma_{SL}$ fitted to be 0.1 J/m$^2$, the solid-vapor taken from Tornberg et al. and the liquid-vapor times the sine of the contact angle as described in Ref. The variable $x$ refers to the fraction of the nucleus which is in contact with the vapor, and for a triangular nucleus this equates to 1/3. However, since the expression for the effective surface energy is used to describe both the initial nucleus and the subsequent growth of the bilayer (which in the end form a complete layer where the entire perimeter is in contact with the vapor), the value of $x$ was chosen to vary linearly with the coverage of the nucleus from 1/3 at the initial nucleation to 1 at a complete layer.

With the energy of the system described above, the change in Gibbs free energy of adding a new GaAs pair is given by:

$$\Delta G^+ (N_{As}, N_{Ga}, i) = G_{sys}(N_{As} - 1, N_{Ga} - 1, i + 1) - G_{sys}(N_{As}, N_{Ga}, i)$$

We note here that many variables used to calculate $G_{sys}$ depend on the number of Ga and As atoms in the seed particle (such as the chemical potentials), and these variables are re-calculated after removing a Ga-As pair from the liquid.

In the incubation periods, we are interested in the rate at which a stable nucleus is formed, which depends on the size at which it is favorable for a nucleus to grow. The critical size of the nucleus
\( \Delta G^* \) is defined as the smallest \( i \) where \( \Delta G^{+1}(N_{As} - i, N_{Ga} - i, i) < 0 \). This gives the effective nucleation barrier as:

\[
\Delta G^* = \sum_{i=0}^{i^*-1} \Delta G^{+1}(N_{As} - i, N_{Ga} - i, i)
\]

From this, the nucleation rate is calculated as per the classical nucleation theory as:

\[
\omega = \omega_0 \exp \left( -\Delta G^*/kT \right)
\]

where \( \omega_0 \) is the pre-exponential factor which was set to \( 10^9 \) s\(^{-1} \). The value for the pre-exponential factor was fitted to give a variance of the incubation times in the As series of a similar scale as measured in the experiments. For determining whether or not a successful nucleation occurred in the current time step, the rates were converted to probabilities using the cumulative exponential distribution function, and the outcome was chosen using random numbers as described in Ref.\(^1\). When a successful nucleation occurs, the time is noted, and \( i^* \) Ga-As pairs are removed from the liquid and added to a now stable, growing new bilayer.

The simulation changes to layer growth mode once a stable nucleus has formed. At this stage, we assume that the liquid is always in equilibrium with the nucleus, meaning that the attachment rate of GaAs pairs to the nucleus is not limited by kinetic considerations in the liquid. In each time interval, the composition of the seed is first updated based on the impingement as before. Then, to find how much the layer grows, the inequality \( \Delta G^{+1}(N_{As}, N_{Ga}, i) < 0 \) is considered. If this inequality holds, it is energetically favorable for the layer to grow, and one Ga-As pair is removed from the liquid \( (N_{As/Ga} \rightarrow N_{As/Ga} - 1) \) and added to the nucleus \( (i \rightarrow i + 1) \), which lowers the supersaturation of the liquid seed particle. This layer growth is repeated until the inequality no longer holds, at which point the system moves on to the next time interval. This iterative process is carried out until a complete layer has formed. Once the layer is completed, the time is noted and
the simulation resets \((i \rightarrow 0)\) and goes back to incubation mode and tries to grow the next layer. The times at which nucleations occurred and layers were completed were then used to calculate the mean and standard deviation of the incubation and layer completion times presented in the main text.

**S2. Kinetics as a function of temperature**

![Graph showing incubation and layer completion times as a function of growth temperature at fixed precursor flows.](image)

Fig. S1. Incubation and layer completion times as a function of the growth temperature at fixed precursor flows.

The effect of temperature on the nanowire growth kinetics is shown in Fig. S1. In the measured range (440-500 °C) the incubation time increases with temperature, while there is no clear trend seen in the layer completion time. There are numerous factors related to the growth that may depend on temperature, such as precursor decomposition, As evaporation rate, Ga surface diffusion on the nanowire sidewalls, flow patterns in the growth cell and surface energies. A straightforward explanation of the observed trend is not possible, and would require a much larger dataset to fully analyze, which is beyond the scope of this article.
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