Supporting information: In-situ observations of size effects in GaAs nanowire growth

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SI-1: Description of the model

As shown by Maliakkal et.al [1] the step-flow is sensitive to the changes in AsH_3 supply. Based on their experimental data it is therefore possible to approximate the layer propagation to be inversely proportional to the net flux of As atoms across the liquid-vapour (LV) interface:

$$t_{SF} \propto \frac{1}{J_{As,\,LV}}$$

Where t_{SF} is the step-flow time and $J_{As,\,LV}$ is the As atom flux across the LV interface. The net flux can be further expanded on using the Hertz-Knudsen equation, which allows us to approximate the step-flow time as a balance between the As pressure in the vapour and liquid phase as seen below:

$$t_{SF} = \frac{A_{LS}\sqrt{2RM_{As}T\pi}}{A_{LV}N_A\left(P_{As,Vapour} - P_{As,Liquid}(r)\right)} \cdot \frac{h}{\Omega_{GaAs}}$$

Where, A_{LS}, A_{LV} are the liquid-solid (LS) and liquid-vapour (LV) interface areas, respectively. The A_{LS} was calculated by approximating the interface as a circle. The liquid-vapour area, A_{LV}, was calculated by approximating the droplet as a spherical cap. The LS area for different diameters was calculated extrapolating from a fit applied to areas calculated from 3 on axis nanowires where we measured diameter and height of the cap. Height of a GaAs bilayer is h, GaAs Ω_{GaAs} is the volume of a GaAs atom pair, $P_{As,Vapour}$ and $P_{As,Liquid}$ is the As pressure in the vapour and liquid phase, respectively. The As pressure in the vapour phase was set to be constant and calculated by assuming no desorption from the nanowire for the 26 nm diameter nanowire and using experimentally measured value for the corresponding step-flow.

Additionally, R is the ideal gas constant, M_{As} is the Arsenic molar mass and T is the temperature in Kelvin. In this simplistic model we assume the sticking coefficient to be unity. This means that all As atoms present in the vapour phase are absorbed into the liquid phase. Since the supplied AsH_3 amount during growth is kept constant and $A_{LS}, A_{LV} \propto r^2$ the step-flow time, within this framework, will depend only on the diameter dependent liquid phase vapour pressure. In order to incorporate the diameter dependence $P_{As,Liquid}$ is expressed using the Kelvin equation. Kelvin equation describes increase of vapour pressure for curved LV interfaces, such as those of liquid droplets. Expressing the As pressure in the liquid using Kelvin equation leads to the following expression:

$$t_{SF} = \frac{A_{LS}\sqrt{2RMT\pi}}{A_{LV}N_A\left(P_{As,Vapour} - \eta \exp\left(\frac{2\gamma_{LV}V_L}{rRT}\right)\right)} \cdot \frac{h}{\Omega_{GaAs}}$$

Where, γ_{LV} is the liquid-vapour interface surface energy, V_L, is the molar volume and η is a fitting parameter used to describe the As pressure of a flat liquid surface. The value of surface energy was extracted using data reported by Tornberg et.al [2] at a constant contact angle of 100°. It is worth noting that changes in surface energy will lead to shifts in the model curve which could improve the fit significantly, however, since the contact angle dynamically changes a typical average value was selected. For molar volume Au molar volume at room temperature and 1 atm was used [3].

SI-2: Droplet contact angle as a function of nanowire diameter

Droplet contact angle at the LS interface was measured for nanowires that were observed with the LS interface parallel to the electron beam. The results of these measurements can be seen in the graph in Fig. 1. The measurement of the contact angle was conducted during incubation process and was not found to correlate with nanowire diameter in a meaningful way. Additionally, for nanowires of very similar diameter the contact angle was found to vary on a similar to scale to the variation observed across the investigated diameter span, see Fig. 1 (c-e). Contact angles also sometimes differed slightly between the two sides of the nanowire, and varied somewhat for the same nanowire as it grew. This suggests that any small changes that nanowire diameter could induce might be small compared to the natural variation from nanowire to nanowire. It is also worth noting that the range in which contact angle was observed to vary in our study is small compared to theoretical predictions of where the contact angle might affect nanowire growth [2].

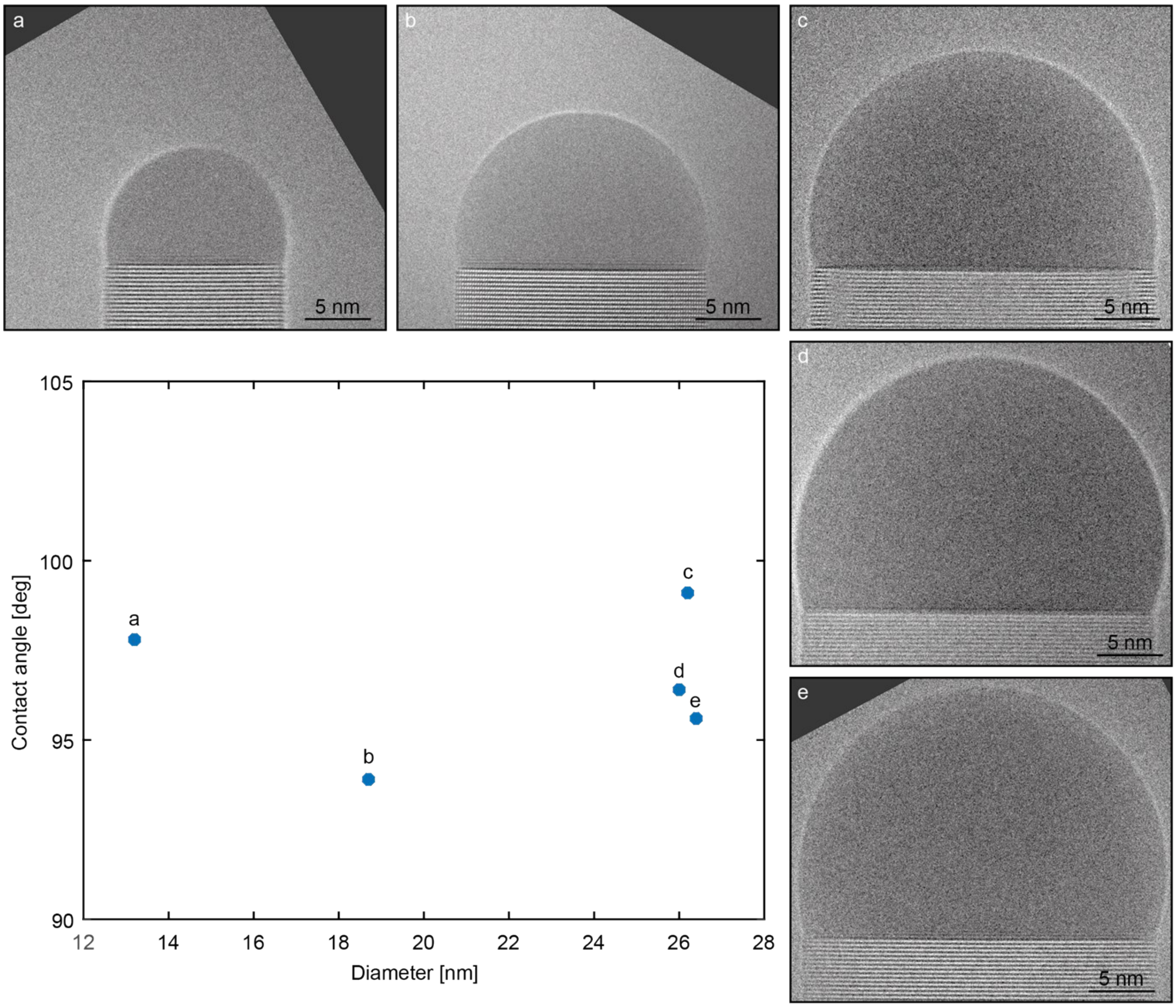

Fig. 1*: Droplet contact angle as a function of nanowire diameter.* (a-e) Au-seeded GaAs nanowires of various diameters imaged when the liquid-solid interface was parallel to the viewing direction. The plotted graph shows the measured contact angle from images (a-e) as a function of nanowire diameter.

SI-3: Faceting of the bilayer during the step-flow process

The newly forming bilayer during the step-flow process can be observed to shift between straight-edged, convex and concave configurations as previously observed by Harmand et al. [4]. In Fig. 2 the different configurations are demonstrated in TEM images and schematically.

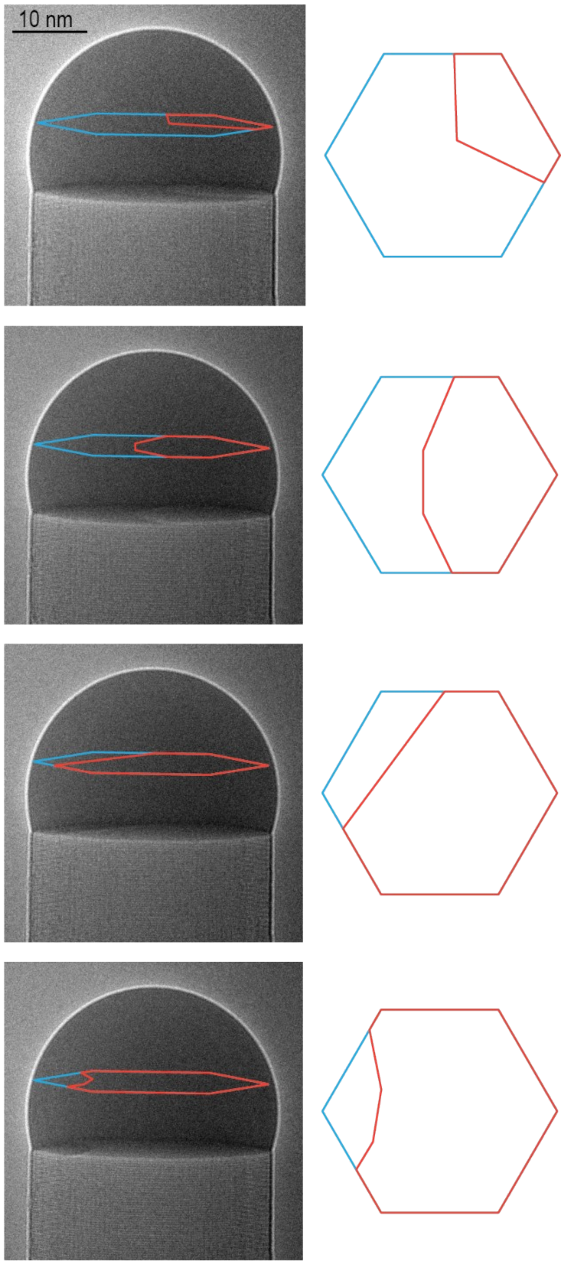

Fig. 2: Faceting of a bilayer during the step-flow process. Top to bottom image sequence of a nanowire during the step-flow process. The nanowire cross-section is assumed to be hexagonal (schematically shown in blue). The faceting of the advancing bilayer can be observed to shift between straight edged, convex and concave configurations.

SI-4: Video treatment procedure for supporting information

Following steps were taken to convert the acquired in-situ dataset video that was acquired at 202 FPS at 1024x1024 pixel resolution to .avi video of nanowire growth for supporting information using DigitalMicrograph (version 3.43.3213.0) and ImageJ (version 1.52a):

DigitalMicrograph:

- Video was binned by 2 reducing resolution to 512x512 pixels;
- 10 frame sum with 10 frame skip was applied to increase signal to noise ratio;
- Hanning double window filter was used to drift correct the video;
- Video was extracted as .avi file.

ImageJ:

- The .avi file extracted from DigitalMicrograph was opened in ImageJ as a stack;
- Video was rotated and surrounding background was cropped;
- Timestamps and scale bar was overlaid with each video frame;
- Stack was saved as .avi by applying JPEG compression.

References

1 C. B. Maliakkal, E. K. Mårtensson, M. U. Tornberg, D. Jacobsson, A. R. Persson, J. Johansson, L. R. Wallenberg and K. A. Dick, *ACS Nano*, , DOI:10.1021/acsnano.9b09816.

2 M. Tornberg, C. B. Maliakkal, D. Jacobsson, K. A. Dick and J. Johansson, *J. Phys. Chem. Lett.*

3 R. DeHoff, *Thermodynamics in materials science*, CRC Press, 2006.

4 J. Harmand, G. Patriarche, F. Glas, F. Panciera, I. Florea, J. Maurice, L. Travers and Y. Ollivier, *Phys. Rev. Lett.*, 2018, **121**, 166101.