

Supporting information for:

Phase Engineering of GaAs Nanowires by Prolonging Growth  
Duration in MBE

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It has been well demonstrated in our previous study<sup>1</sup> that Ga concentration in the catalysts during GaAs nanowires growth is the sum of Ga atoms ( $N_N$ ) in the “neck” and Ga atoms ( $N_C$ ) in the post-growth catalyst detected by EDS:  $N_{Ga} = N_N + N_C$ . Since there is almost no Ga left in post-catalysts of three samples (**Fig. 3d-f**),  $N_C \sim 0$ . Therefore, Ga concentration during nanowires growth is estimated as  $N_N / (N_N + N_{Au})$  with  $N_{Au}$  being the number of Au atoms in the catalyst.

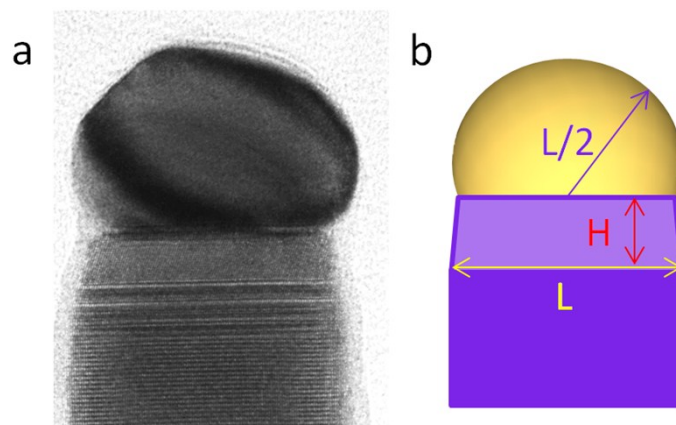
Since the “neck” region is zinc-blende structured GaAs, which contains 4 Ga atoms in a unit cell,  $N_N$  can be obtained by:

$$N_N = 4V_N / V_{U(GaAs)}, \quad (1)$$

where  $V_{U(GaAs)}$  is the volume of a unit cell of the zinc-blende structured GaAs, and  $V_N$  is the volume of the cylinder shaped “neck” region, which, according to **Fig. S1**, can be

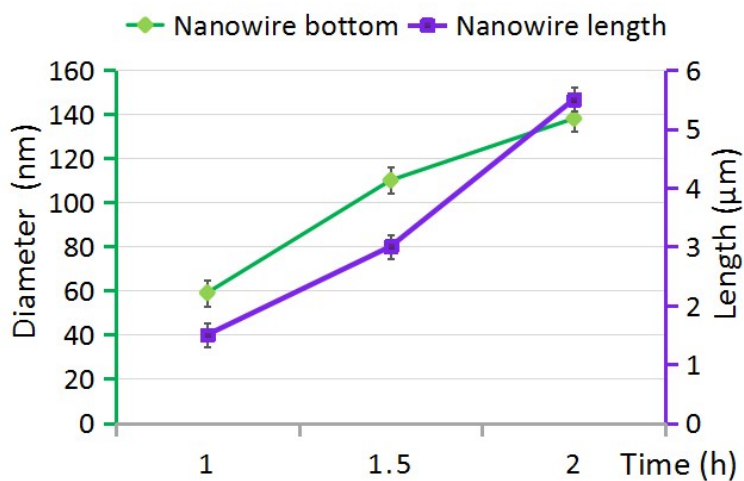
determined by  $V_N = \pi(\frac{L}{2})^2 H$  ( $L$  being the lateral dimension of the nanowire and  $H$  the height of the “neck” region). Similarly,  $N_{Au}$  can also be determined with Equation 1, by

replacing  $V_N$  with catalyst volume  $V_U = \frac{2}{3}\pi(\frac{L}{2})^3$  ( $L/2$  denotes the radius of the hemispheric catalyst, as illustrated in **Fig. 1Sb**); and  $V_{U(GaAs)}$  with unit cell volume of Au ( $V_{U(C)}$ ) with face-centered cubic structure:  $V_{U(C)} = a_c^3$  ( $a_c \approx 0.41$  nm, the lattice parameter).



**Fig. S1.** (a) A HRTEM image showing the top region of a typical GaAs nanowire grown for 2 h. (b) A schematic model showing the nanowire top containing a hemisphere catalyst, a cylinder disk-shaped “neck” region and the nanowire section.

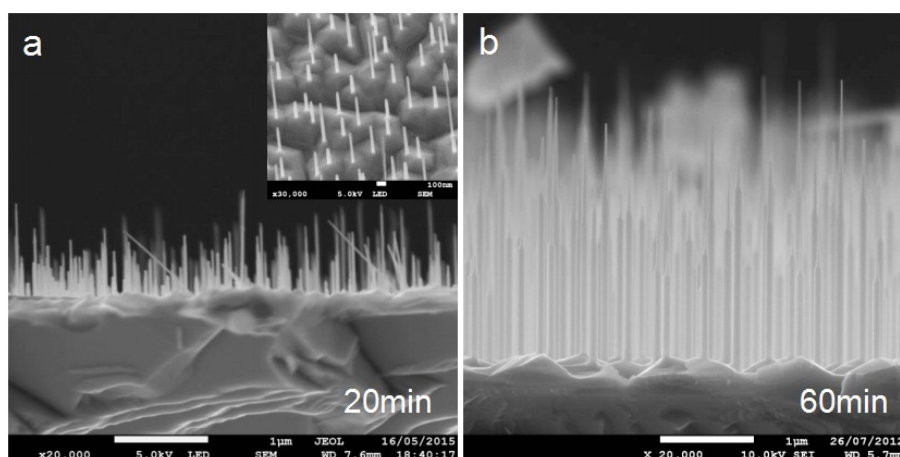
**Fig. S2** shows the statistical measurements of GaAs nanowires lengths and corresponding lateral dimension at nanowires bottom regions with the growth durations. As can be noted, the average length of 1h grown nanowires is  $\sim 1.5 \mu\text{m}$ , while 1.5h and 2h grown nanowires have  $\sim 3 \mu\text{m}$  and  $\sim 5.5 \mu\text{m}$  in length respectively, suggesting that nanowire axial growth increases with the growth duration. The corresponding nanowires diameters at the bottom regions are  $\sim 60 \text{ nm}$ ,  $110 \text{ nm}$  and  $140 \text{ nm}$ , suggesting the nanowire lateral dimension increases with increasing the growth duration as well.



**Fig. S2** Plot of nanowires lengths and diameters in the bottom regions with the growth durations.

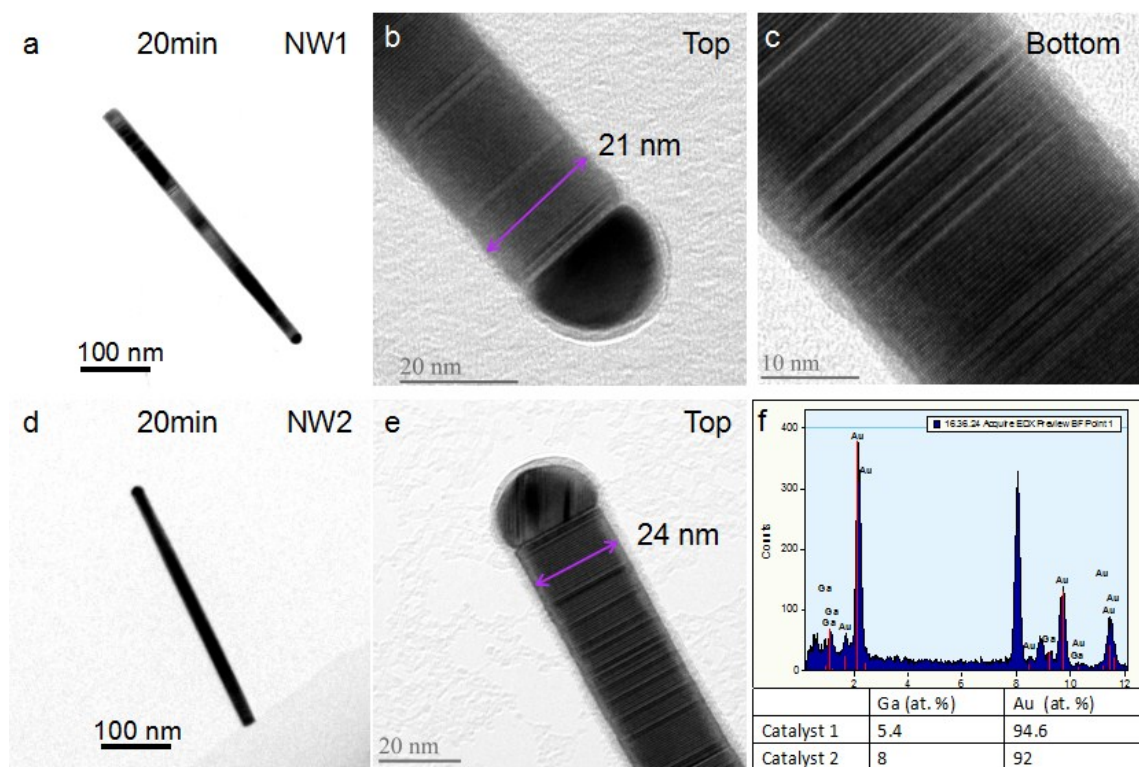
To further confirm the impact of growth duration on nanowire growth behavior and phase purity, we repeated the growth with different growth parameters (growth temperature of 400°C, a thinner Au film deposition (1100°C, 10s), growth duration of 20min and 60min, respectively). (**Fig. S3-S5**)

**Fig. S3a,b** shows the typical side-view images of the grown sample, suggesting the similar nanowire density and the major nanowire growth orientation is perpendicular to the substrate surface. The average length of nanowires grown for 20min is ~500 nm, while nanowires grown for 60min are as ~2 μm high. Additionally, it can be noted that the diameter of 20min grown nanowires is uniform along the nanowire (see the inset in **Fig. S3a**), while nanowires grown for 60min formed the shoulders.



**Fig. S3** (a,b) Typical side-view SEM images of GaAs nanowires grown for 20min and 60min at 400°C. The inset in (a) is corresponding 30°-tilted SEM image.

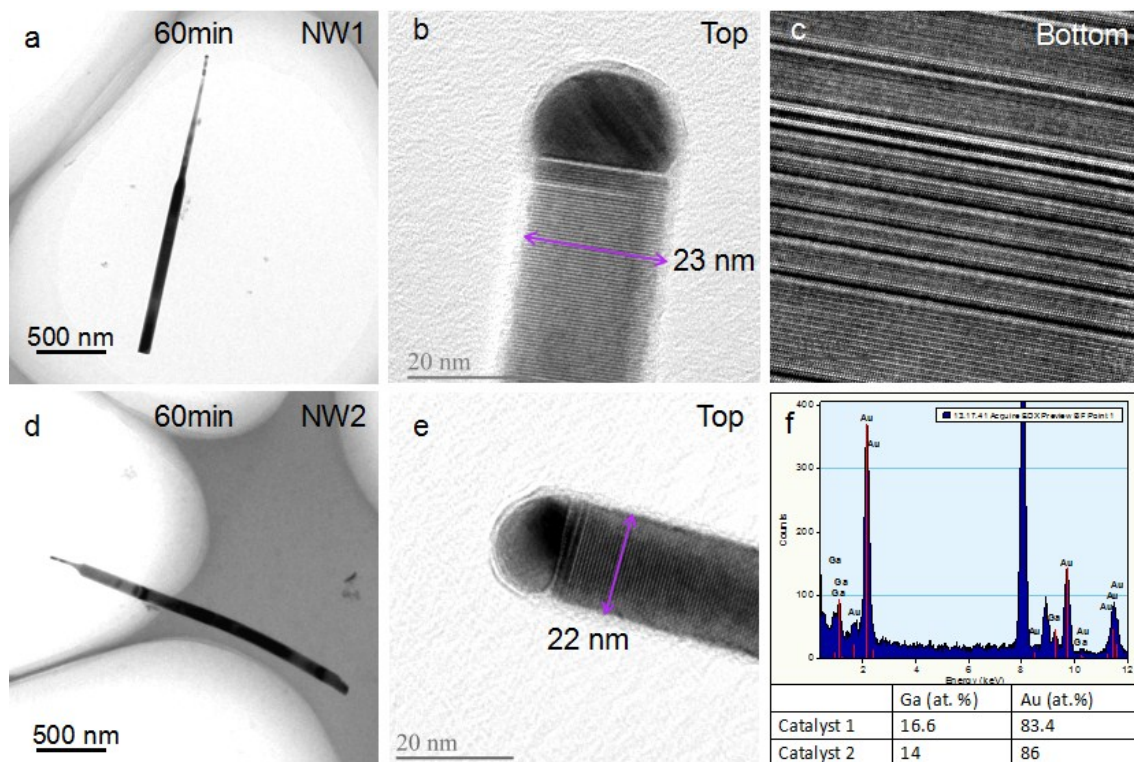
**Fig. S4** shows the TEM analyses of the 20min-grown nanowires sample. **Fig. S4a** shows BF TEM image of a typical grown nanowire and **Fig. S4b,c** is corresponding HRTEM images of the nanowire top and bottom regions, indicating the defected structure along the whole nanowire, which is confirmed by the our statistical analysis of this nanowire sample, as shown by the BF TEM image (**Fig. S4d**) of another typical grown nanowire and the corresponding HRTEM image (**Fig. S4e**) from the nanowire top. **Fig. S4f** shows a typical EDS point analysis profile taken from the catalyst and a table summarizing the catalysts composition containing 5-8 at% Ga of nanowires shown in **Fig. S4a,b**.



**Fig. S4** BF (a) and (b,c) HRTEM images of a typical 20min-grown GaAs nanowire and its top and bottom regions. BF (d) and (e) HRTEM images of another typical nanowire and its top region. (f) EDS point analysis profile taken from a typical catalyst and the table show the catalysts composition of (a,d).

**Fig. S5** shows the TEM analyses of the 60min-grown nanowire sample. **Fig. S5a** is the BF TEM image of a typical nanowire, which has shoulder morphology. **Fig. S5b,c** is corresponding HRTEM images of the nanowire top and bottom regions, where the bottom region is defected as the 20min-grown nanowire is, but the top region is defect-free. This phenomenon is further confirmed by our statistical analyses on this sample, as typically depicted in **Fig. S5d,e**. **Fig. S5f** shows a typical EDS point analysis profile taken from the catalyst and a table summarizing the catalysts composition containing 14-17 at% Ga of nanowires shown in **Fig. S5a,b**, which is higher than the Ga concentration in the

catalysts of the 20min grown nanowires.



**Fig. S5.** BF (a) and (b,c) HRTEM images of a typical 60min-grown GaAs nanowire and its top and bottom regions. BF (d) and (e) HRTEM images of another typical nanowire and its top region. (f) EDS point analysis profile taken from a typical catalyst and the table show the catalysts composition of (a,d).

## References

- 1 C. Zhou, K. Zheng, Z. Lu, Z. Zhang, Z. Liao, P. Chen, W. Lu and J. Zou, *J. Phys. Chem. C*, 2015, **119**, 20721-20727.