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Supporting Information for "Checked Patterned Elemental Distribution in AlGaAs Nanowire Branches via Vapor-Liquid-Solid Growth"

Giorgos Boras,[†,‖] Xuezhe Yu,[*,†,‖] H. Aruni Fonseka,[‡,‖] Dong Zhang,[§,‖] Haotian Zeng,[†] Ana M. Sanchez[‡] and Huiyun Liu[†]

[†]Department of Electronic and Electrical Engineering, University College London, London WC1E 7JE, United Kingdom

[‡]Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

[§]SKLSM, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China

1) Growth rate and volume of the branched nanowires

A useful conclusion from the statistical analysis of the dimensions of the NW trunks is the growth rate of the ternary structures. In order to estimate the values, it needs to be taken into account that the growth duration was the same (100 mins) for all the samples, regardless of their nominal composition. Additionally, as stated in the main article, As flux was kept stable at 2.7×10^{-6} Torr, whilst Ga flux was also fixed at a value corresponding to an As/Ga beam flux ratio of 15. This effectively signifies that Al supply was the main factor modifying the morphological characteristics of the branched AlGaAs NWs. From the statistical analysis that was conducted on 100 individual NWs from each sample, it can be viewed that the NW length alters significantly with Al content. Specifically, the average value of the NW axial length is found to be 8 μm, 6 μm, 5 μm and 4 μm for the samples with 10%, 20%, 30% and 40% Al, respectively. It is also noticed that the first 600 nm of the structures corresponded to bare GaAs stems that were grown for 10 mins prior to introducing Al in the reactor. From the above values it can be safely estimated that the axial growth rates for the samples with 10%, 20%, 30% and 40% nominal Al content are 1.23 nm/s, 0.9 nm/s, 0.73 nm/s and 0.57 nm/s, respectively. The above are illustrated in Fig. S1, in blue colour. This radical decrease of the axial growth rate at higher Al composition is anticipated due to two factors, namely: a) the low diffusion length of Al, which promotes lateral adherence rather than incorporation in the droplet and b) the suppression of the Ga diffusivity induced by the increasing Al supply.[1] The above renders preferential Ga adatoms to incorporate to the NW sidewall facets at higher Al contents, explaining the reduction of the axial growth rate and length of the NW trunks. This can be further supported by the statistical analysis of the diameter of the trunks, which is found to be 200 nm. 300 nm, 400 nm and 600 nm for the samples with 10%, 20%, 30% and 40% nominal Al composition, respectively, indicating a drastic increase of the diameters with increasing Al composition.

It is also interesting to mention that the NW volume is enhanced with increasing Al content, despite the reduced length, due to the enhancement of the diameter. Even though the exact calculations are

intricate, we can assume that the NWs have a perfectly cylindrical shape, which is a good approximation. Hence, the average volume of the structures can be calculated by using the formula $V=\pi r^2 h$, where r is the radius of the circle at the NW end and h is the NW height. From the data presented in Fig. 1 of the main text, we see that the average diameter of the samples with 10% Al content is 200 nm, thus the radius is 100 nm, while the height is 8 μm. The corresponding values for the radius of the rest of the samples are 125 nm, 150 nm and 200 nm for the NWs with 20%, 30% and 40% Al, respectively while the heights are 6 μm, 5 μm and 4 μm. Based on the presented formula and by replacing the aforementioned values, the average volume of the NWs can be estimated to be 0.2512 μm^3, 0.294375 μm^3, 0.35325 μm^3 and 0.5024 μm^3 for the samples with 10%, 20%, 30% and 40% Al, respectively. These results are presented in Fig. S1, depicted in red colour. Additionally, it is worth mentioning that the increased branches on the NW trunks at higher Al content signify a larger surface area and a longer carrier path in the structures. These factors are major advantageous features of branched NWs, rendering them promising candidates for energy storage and energy harvesting applications, including solar cells, supercapacitors and Li ion batteries.[2]

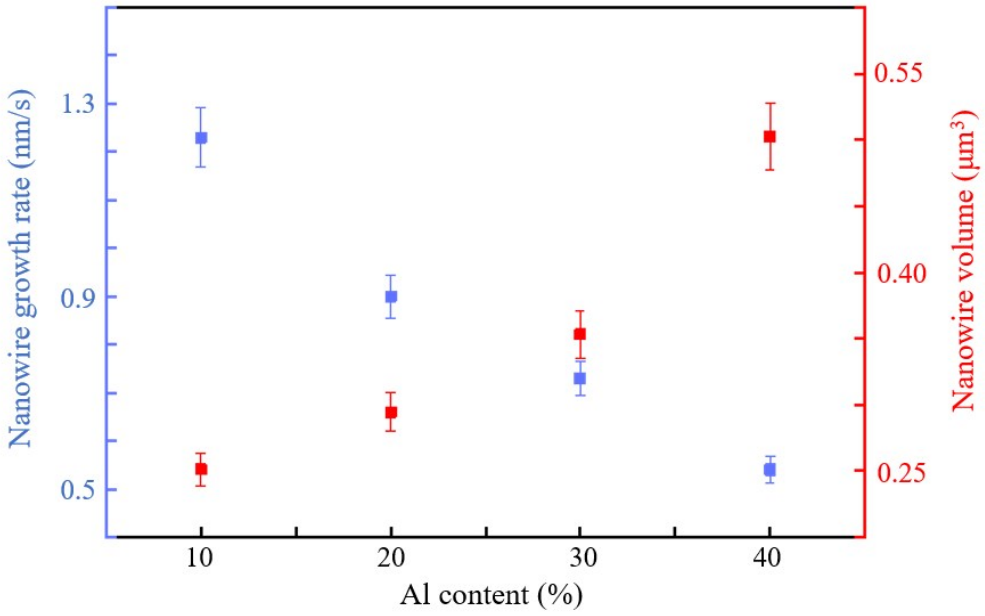

Figure S1: Graph of the NW growth rate (blue) and NW volume (red), as a function of the Al content.

2) Additional scanning electron microscopy analysis

Scanning electron microscopy (SEM) measurements that were studied in the main text provided us with a detailed insight of the morphological characteristics of the nanowires (NWs). The realization of the AlGaAs branches is confirmed, whilst their vertical orientation with respect to the Si substrate is validated. This effectively signifies that the NW trunks are elongated along the <111> direction. For a direct inspection, we present the SEM image of Fig. 1d again in Fig. S2a. It is conspicuous that three branches are nucleated from the NW trunk, with hierarchical structure being evident. Furthermore, it can be seen that the branches form an angle of roughly 90° with respect to the trunk. In order to define the growth direction of the NW branches, top-view SEM images were acquired. A representative example is demonstrated in Fig. S2b, where a single NW trunk with three nucleated NW branches can

be distinctly viewed and are pointed by white arrows. As indicated in the same figure, the branches are spaced at an angle of roughly 60° with each other. The adopted orientation of the branches corresponds to a 6-fold symmetry, if we also consider the extension of the directions on both sides of the trunk. It is noted that this can be safely assumed, even though no structures with 6 branches nucleated on the same trunk could be spotted. The geometrical features of the top-view SEM are consistent with branch growth along the <112> direction. Additionally, when the trunk is imaged in the <110> zone axis, the branches, which are also located in the same zone due to the epitaxial nature of the growth, are presented to be vertical to the trunk. From the relationship between angles of crystallographic planes in the ZB crystal, the direction that is perpendicular to both <111> and <110> is <112>. Hence, it is inferred that the branches that nucleate on the NW trunks are elongated along <112> direction.

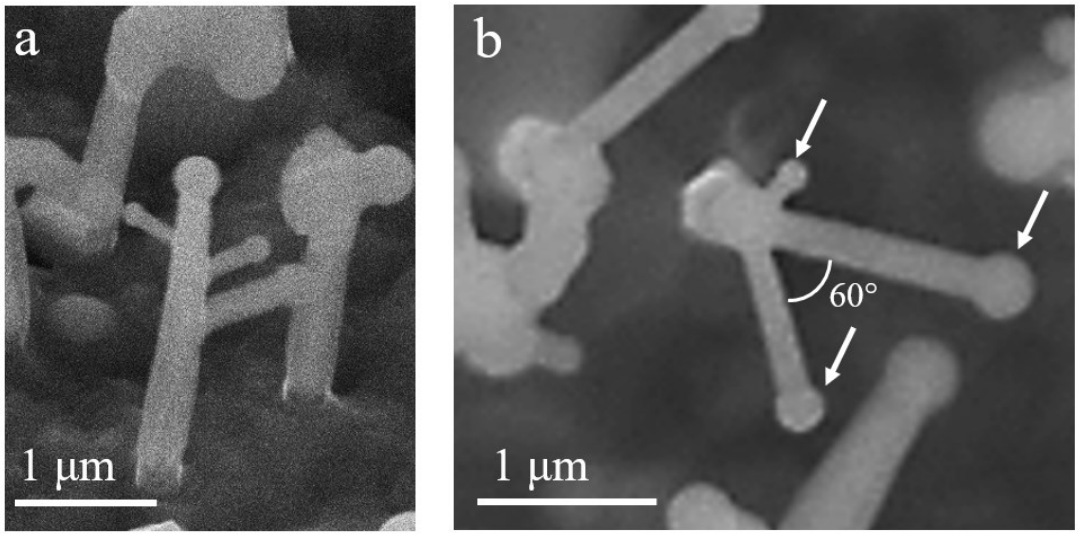

Figure S2: a) SEM image of an individual NW with three branches. The same SEM was presented in Fig. 1d of the main text and is presented here for a direct inspection of the directionality of the branches. b) Top-view SEM image of the branched NW with three branches spaced at 60° from each other, whose configuration is indicative of <112> direction.

3) Computational details for ab initio calculations

Vienna ab initio software package (VASP) was employed for the ab initio calculations that were performed to determine the spatial preference of Ga and Al adatoms in the branched NWs. The calculations were performed using the Perdiew-Burke-Ernzerhof (PBE) functional and the generalized gradient approximation (GGA) within the density functional theory for the exchange-correlation energy. We adopted the projected augmented wave (PAW) pseudopotentials and set the kinetic cutoff energy at 560 eV. The Monkhorst Pack reciprocal k-points grid is sampled by sums over 1x1x13. Besides, as the lattice constants of AlGaAs and GaAs compounds are almost identical, the surface relaxation was only performed in the pristine GaAs branched NWs, for simplicity.

The selected configurations are purposely designed to maintain the same stoichiometry. Specifically, in order to mimic the NW samples, the models built had the same geometric configurations, where only the Al composition and the Al location is important to our comparison, as other factors including the surface conditions and quantum confinement effect related to the diameter are equivalent. Using the

above configurations, we were able to determine the variation in the formation energies as a function of the number of Al atoms doped at different positions of the structure. The calculations were performed using the following equations:

$$\delta\Delta = E_n - E_0 - xE_\Delta,$$

$$E_n = (90-x)E_{Ga} + xE_{Al} + 90E_{As} + \Delta_n$$

where, E_{Ga}, E_{Al} and E_{As} are the total energies of single Ga, Al and As atoms, respectively. Δ_n is the formation energy of the "n" branched NW model, x is the number of Al atoms and E_0 is the total energy of pristine GaAs. $E_\Delta = E_{Al} - E_{Ga}$ is a term representing the total energy difference in vacuum, which was introduced to eliminate energy differences which might arise from the unequal number of Al adatoms in the models. Based on this, $\delta\Delta$ is solely determined by the various positions taken by Ga and Al atoms in the model, regardless of the number of atoms that are doped. The results are described in the main text (Fig. 3h).

4) Energy Dispersive X-Ray Scanning

Energy Dispersive X-Ray (EDX) measurements have been employed in the radial direction of the NW trunks, revealing the spontaneous formation of a shell. That is shown in Fig. S3, where a representative example of a radial EDX line scan is presented. The TEM image above depicts the area of the scanning, while the arrow shows the scan direction. It is conspicuously viewed that Al presents clear peaks, corresponding to dips in Ga, at the external facets of the NW. Such observations signify core/shell configuration. As mentioned in the main text, the spontaneous core/shell formation has been systematically reported in AlGaAs NWs, due to the short diffusion length of Al, which leads to Al atoms being preferentially incorporated at the external regions close to the NW base. The formation of the Al-rich, AlGaAs shell is the driving force for the initiation of the branched structures, as elucidated in the main text. It is noted that this phenomenon was distinguished only in the trunks of the NWs, since after TEM inspection of the branches, no core/shell configuration was revealed in this part of the structures.

We know that the average trunk length for the samples with 40% Al is roughly 4 μm. Additionally, we know that the growth duration for the AlGaAs NWs was 100 mins. However, we should consider that the first 600 nm corresponded to the GaAs bare stems (this was added in the revised manuscript in paragraph 4). As a result, the length of the AlGaAs part is 3400 nm averagely, corresponding to a growth rate of 0.57 nm/s. Using the structure of Fig. 1d as a representative example, the first branch nucleates at a height of 2664 nm. Considering that the first 600 nm are the GaAs stem, 2064 nm are grown until the branching occurs. For an axial growth rate of 0.57 nm/s, this corresponds to a duration of 60.35 mins. As a result, the remaining growth duration is 39.65 mins.

The total length of the first branch (which is also the longest, in line with the hierarchy anticipated) is 1.35 μm. Considering the two conventions that we accept, namely that a) the growth of the branch began when the NW trunk reached the point of the nucleation and b) the growth of the branch was terminated at the same time as the NW trunk, the growth rate of the branch is roughly 0.57 nm/s, which corresponds to a growth of 3.42 nm at 6 seconds. This value is in close proximity to the periodicity of 3.6 nm that was observed in the TEM data.

Following this, we repeated the procedure for the second branch, which nucleated at 3422 nm. So excluding the GaAs stem at 2822 nm height, corresponding to a growth duration of 82.5 mins, the remaining growth time is 17.5 nm. The length of the branch is 660 nm, meaning that the growth rate is

0.62 nm/s. This corresponds to a growth of 3.72 nm at 6 seconds, which is also close to the periodicity that was observed in the TEM data.

Finally, the third branch was nucleated at a height of 3000 nm (excluding the initial 600 nm of bare GaAs). The growth time at this point was 87.7 mins, so the remaining time was 12.3 mins. The total length of the NW branch was just 480 nm (as expected by the hierarchy of the structure). This corresponds to a growth rate of 0.65 nm/s, which means that at 6 seconds the NW would have grown by 3.9 nm, which is still not a large deviation from the periodicity.

Despite the assumptions that were taken into consideration for the procedure described above, it can be seen from the representative calculations that the rough estimations showed a growth length of the branches during a period, that corresponded to periodicity within the frame of acceptable error, with respect to the 3.6 nm that was analysed in the manuscript.

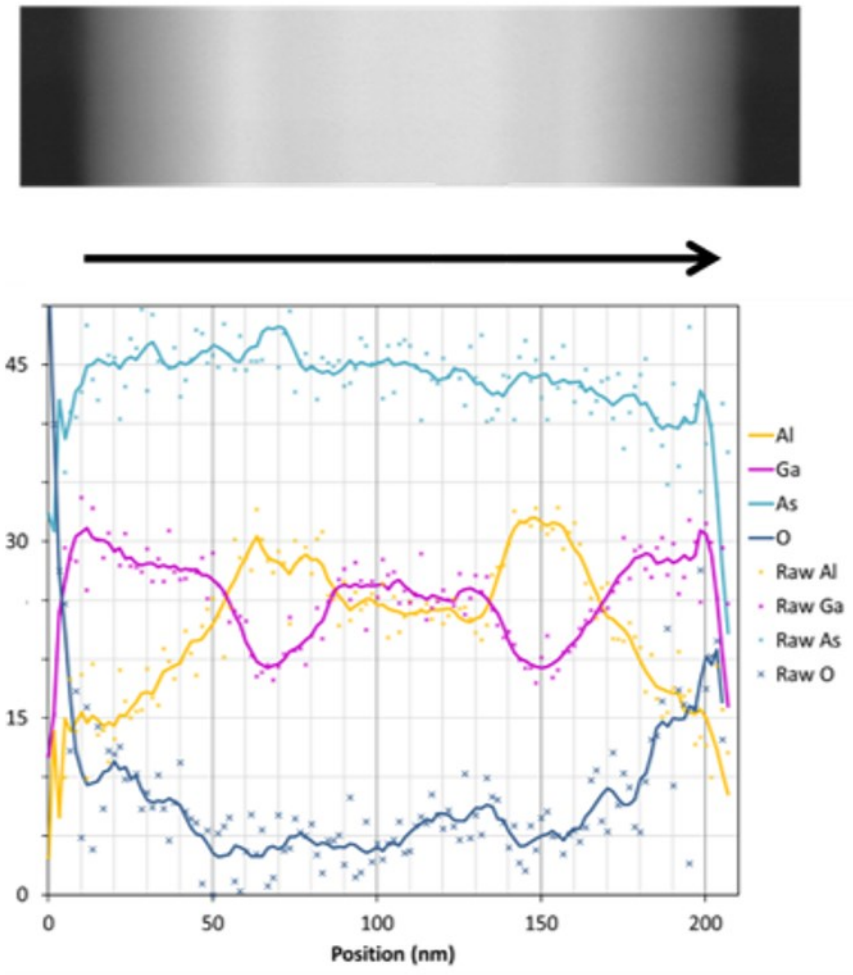

Figure S3: Radial EDX scanning of the NW trunk. The TEM image above shows the area of the scanning along the direction of the black arrow. The graph below shows the atomic percentages for Al, Ga, As and O at different positions across the NW. The peaks in Al (and dips in Ga) signify the spontaneous formation of an Al-rich shell.

5) Calculations on the periodicity of the perpendicular bright stripes

The periodicity of the perpendicular bright stripes was confirmed by the intensity profile along the branch growth direction, presented in Fig. 4c of the main text. As thoroughly described, the periodic bright stripes are anticipated to stem from the rotation of the sample within the growth chamber, which is in line with the shadowing effect and affects the compositional distribution of the non-vertical NW components. In order to further verify this phenomenon, calculations were performed for a representative NW with 40% Al content, where branching was more promoted. The calculations were performed on the AlGaAs NW presented in the SEM of Fig. S2a. The aim of the calculations is to find the length of the branch that is grown during a full rotation of the sample (which is 6 seconds considering the rotation speed of 10 rpm). This value should correspond to the periodicity measured, which is 3.6 nm. It is important to mention that the calculations are rough, as two conventions needed to be taken into account, namely that a) the growth of the branches began when the NW trunk reached the point of the nucleation and b) the growth of the branch was terminated at the same time as the WN trunk. However, the results are strong indicators of the validity of the interpretation regarding the perpendicular bright stripes.

The average trunk length for the samples with 40% Al is roughly 4 μm (as established by the statistical analysis presented in Fig. 1f). However, it should be taken into account that the initial 600 nm corresponded to the GaAs bare stems. As a result, the average length of the AlGaAs part is 3400 nm averagely, whilst it is also known that the growth duration of the samples was 100 mins. The above information correspond to a growth rate of 0.57 nm/s. Using the structure of Fig. S2a as a representative example of multiple branching events, the closest branch to the NW base nucleates at a height of 2664 nm. As the first 600 nm are the GaAs stem, 2064 nm are grown until the first branching event occurs. For an axial growth rate of 0.57 nm/s, this corresponds to a duration of 60.35 mins. As a result, the remaining growth duration is 39.65 mins. The total length of the first branch, which is also the longest as anticipated by the hierarchy of branched NWs, is 1.35 μm. Considering the two aforementioned conventions, the growth rate of the branch is roughly 0.57 nm/s, which corresponds to a growth length of 3.42 nm at 6 seconds. This value is in close proximity to the periodicity of 3.6 nm that was observed in the TEM data.

Following this procedure, we repeated the calculations for the second branch, which nucleated at 3422 nm. Hence, excluding the GaAs stem, 2822 nm are grown prior to the nucleation, corresponding to a growth duration of 82.5 mins. The remaining growth time is 17.5 mins. The length of the branch is 660 nm, signifying a growth rate of 0.62 nm/s. This corresponds to a growth length of 3.72 nm at 6 seconds, which is also close to the value of the measured periodicity.

Finally, the last branch, closer to the NW tip, nucleated at a height of 3600 nm, which means that 3000 nm of AlGaAs NW were grown prior to the nucleation (excluding the initial GaAs stem). The growth time at this point was 87.7 mins. Thus, the remaining time was 12.3 mins. The total length of the NW branch was just 480 nm, which is also in line with the expected hierarchy of the structures. This corresponds to a growth rate of 0.65 nm/s, meaning that at 6 seconds the NW would have grown by 3.9 nm, which is still not a large deviation from the observed periodicity.

Despite the fact that the conventions considered above could lead to deviations, it can be seen that the approximate computations showed a growth length of the branches during a full rotation that corresponded to the periodicity observed, within the frame of acceptable error. As a result, this strongly indicates the validity of the proposed mechanism interpreting the formation of the perpendicular bright stripes.

References

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