Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

On-site Growth Method of 3D Structured Multi-layered Graphene on the SiO_2 Surfaces of Silicon Nanowires

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- **Standard conditions results of graphene growth on nanowires (NWs):**

Supplemental figures for Ni on SiO_2 on Si NW substrates annealed at 875 ^oC for 1.5 minutes under 30 sccm CH_4 and 100sccm He gas flow at 400 torr experiments for the purpose of growing multilayer graphene sheets in a NW shaped structure at the best-found conditions.

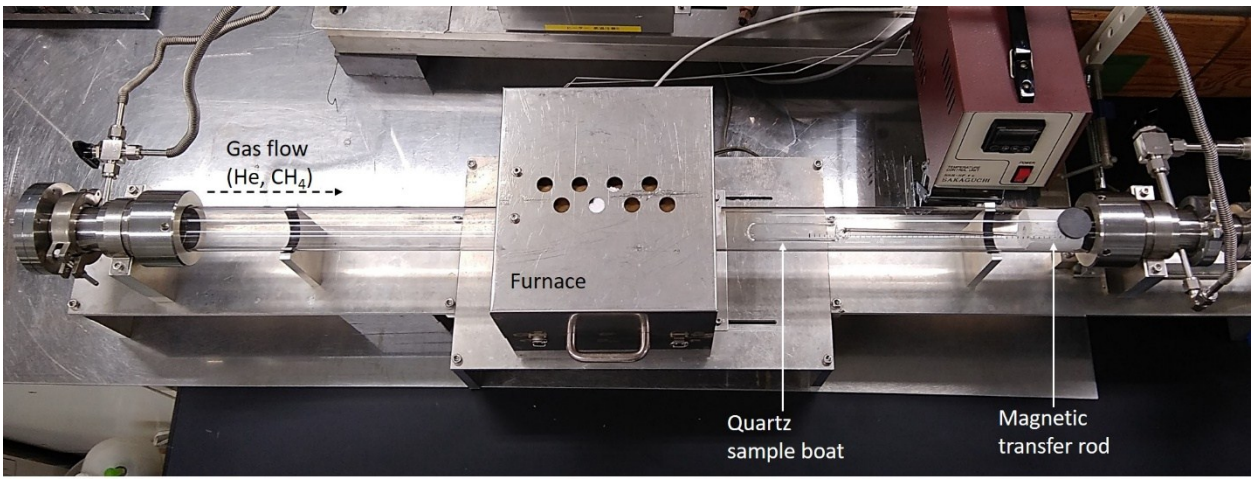

Figure S1. Custom-made quartz tube furnace CVD system. Picture of the multi-purpose furnace system that was used during the main portion of the described experiment where the samples were annealed at high temperature with a carbon source to form the graphene. The furnace reaches the target temperature of 875

°C in the center external of the tube as measured by a R-type thermocouple. Gases are mixed and introduced by individual flow meters into the chamber and removed by an attached vacuum pump. The sample is placed in the quartz boat visible in the image outside of the furnace hot zone. The attached quartz transfer rod is moved by an external magnet to quickly push the sample boat in and out of the hot zone.

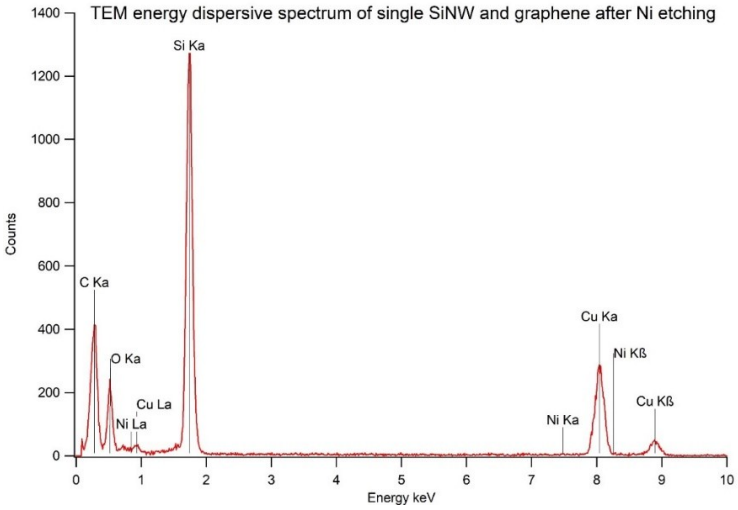

Figure S2. Elemental analysis of graphene on a single NW. EDS spectrum measured using TEM (on a TEM grid containing C and Cu) of single NW after nickel etching. The spectrum shows silicon, carbon, and oxygen as expected. Copper is also detected presumably from the TEM grid and is not seen in SEM-EDS results. Most important is the lack of clear nickel peaks. This shows that the etching process was effective enough to remove nickel to below detectable levels.

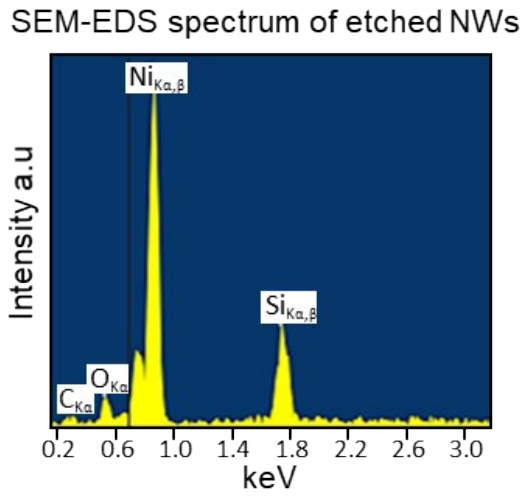

Figure S3. Elemental analysis before Nickel etching. EDS spectrum measured using SEM of multiple nanowires before nickel etching. Nickel is clearly the dominant signal before etching, illustrating the extent that it is reduced when compared to Figure 5 (c) and Figure S2

- **Results at alternative variable conditions:**

A series of experiments were conducted under different conditions to systematically test the dependency of the sample quality on these variables. The following samples were performed at all the same values as the standard conditions except for the value mentioned in the figure titles.

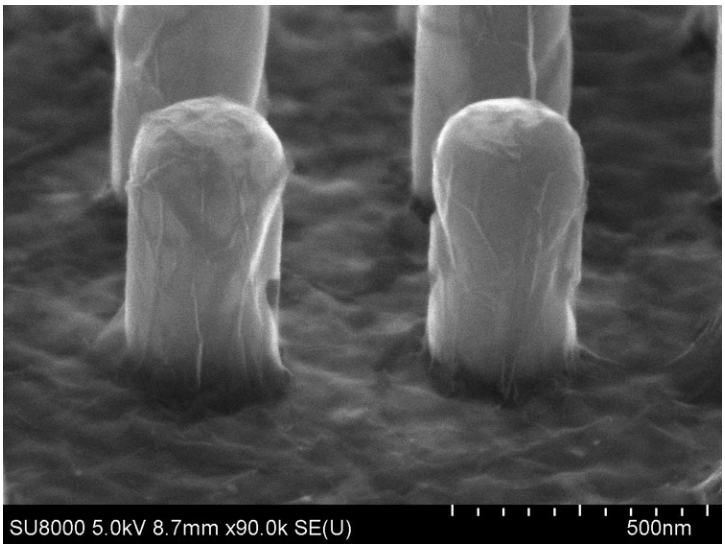

Figure S4. 900 ^{o}C anneal. SEM image of the sample annealed at 900 ^{o}C, after etching nickel. The sample experienced clear nickel dewetting behavior due to the high temperatures. Although a visible graphene sheet appears to be intact, the SiO_2 layer of most of the NWs are damaged through the removal of SiO_2 material and the formation of pores along the NW walls.

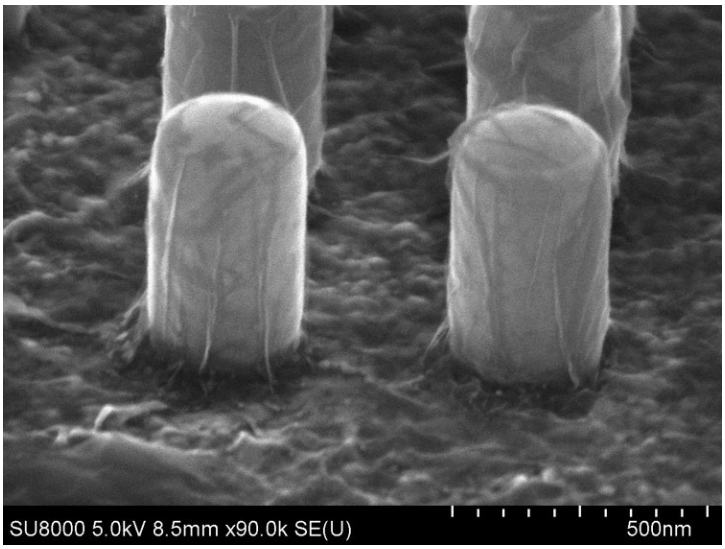

Figure S5. 850 °C anneal. SEM image of the sample annealed at 850 °C, after etching nickel. The sample is similar to the results at 875 °C except for an increase in contrast of spots on the NWs due to the different number of layers of graphene (either from folds or small graphene patches), and a less stiff appearance of the film. There is almost no visible damage to the SiO_2 layer of the NWs because of the lower temperature.

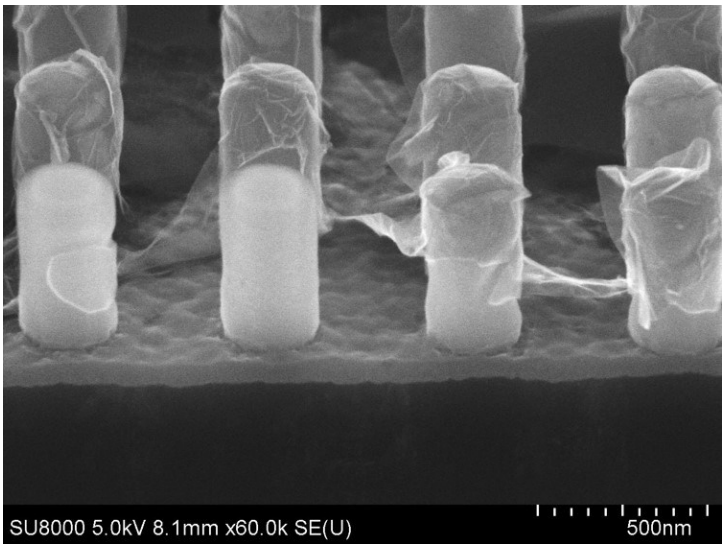

Figure S6. 2 minute anneal. SEM image of the sample annealed for 2 minutes, after etching nickel. The image is taken at the severed sample edge where the torn graphene layer is pulled off of some of the NWs. Similar to the anneal at 900 °C for 1.5 minutes, there is visible damage to the SiO_2 layer as now seen with the graphene layer removed. Despite the lower anneal temperature, the longer anneal at 875 °C still eventually resulted in destructive nickel dewetting behavior.

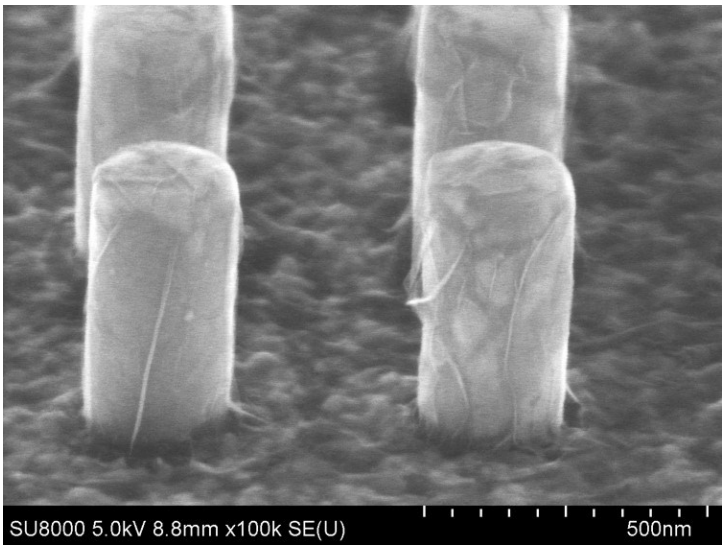

Figure S7. 1 minute anneal. SEM image of the sample annealed for 1 minute, after etching nickel. Similar to the results at 850 ^{o}C, there are thinly visible graphene films and a lack of visible damage. The shorter anneal time therefore also limits the extent of the graphene growth.

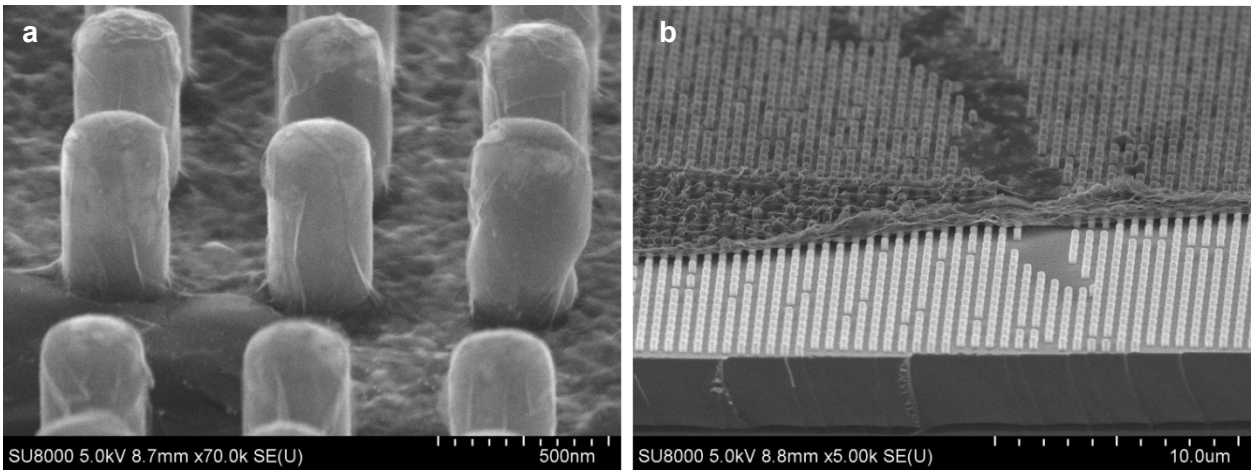

Figure S8. 40 sccm CH_4 anneal. (a) SEM image of the sample annealed with 40 sccm CH_4 after etching nickel. There is no visible damage to the NWs but the graphene appears to be thick due to the large concentration of carbon precursors. (**b)** a lower magnification image of the severed sample edge showing the graphene layer peeling off of a large number of NWs along the entire edge. The increase in stiffness makes it easier to pull the graphene off the NWs as a single continuous film.

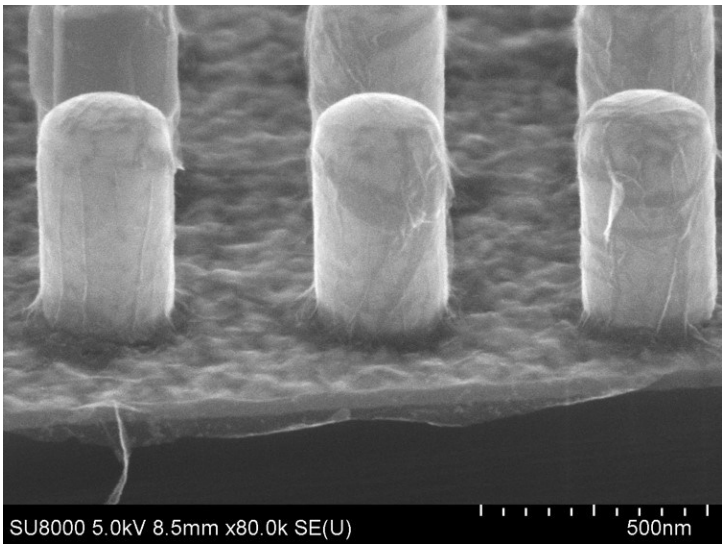

Figure S9. 25 sccm CH_4 anneal. SEM image of the sample annealed with 25 sccm CH_4, after etching nickel. The results with the low CH_4 concentration are visually similar to the lower temperature and shorter anneal time, again pointing to a reduction in graphene growth.

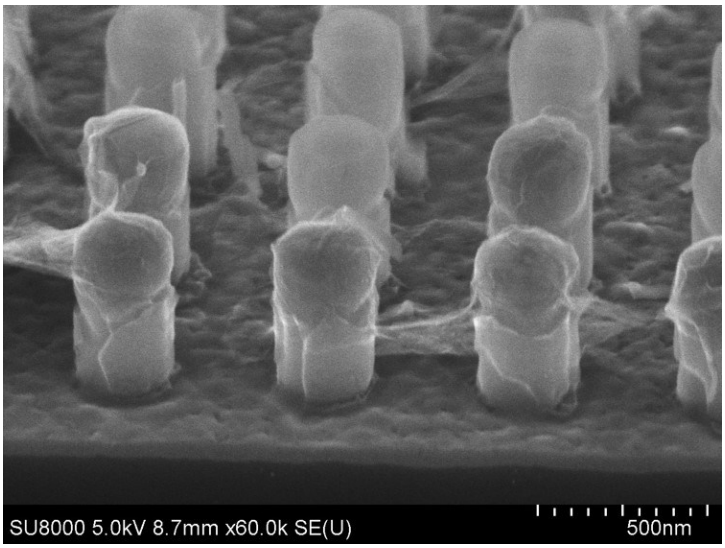

Figure S10. 50 torr anneal. SEM image of the sample annealed at 50 torr, after etching nickel. There is a large amount of visible damage to the NWs due to nickel dewetting at this lower pressure compared to the higher pressure experiments despite being performed at the same temperature and annealing time. The graphene growth is also very poor and segmented perhaps due to a reduction in the density of carbon precursors at low pressure.

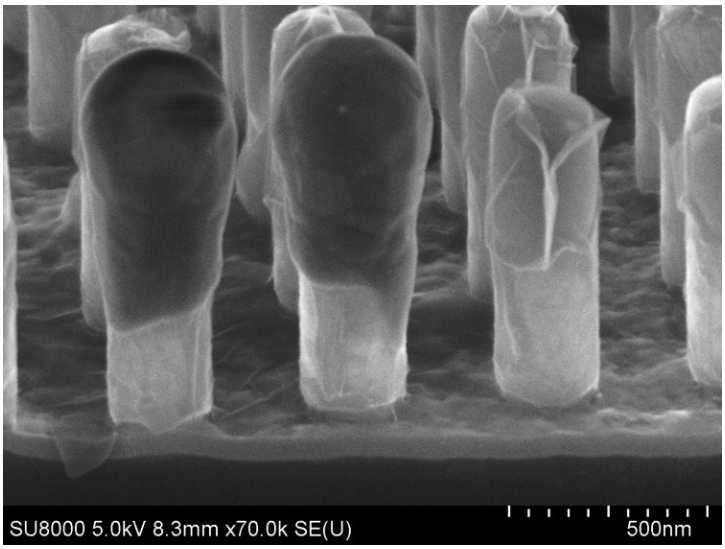

Figure S11. Longer and densely spaced NW substrate. SEM image of 700 nm long NWs at 500 nm periods annealed under normal annealing conditions, after etching nickel. The longer and denser NWs make it more difficult to sputter a consistent thickness of nickel over the entire NW, leading to thinner nickel towards the bottoms which can dewet more quickly. The graphene quality is mostly the same as the shorter and more widely spaced NWs, but not all of the nickel is etched away due to drastic dewetting making it difficult for the etchant to access the isolated nickel on all of the NWs. Where the nickel is removed, the graphene has a loose bag-like shape due to the distorted nickel catalyst.

- **Anchoring ability of NW structure:**

When graphene is grown on flat catalyst surfaces and then etched, the graphene will usually be washed away from the original substrate. The NWs in the experiment show a unique ability to keep the graphene in its original position after wet etching, making on-site synthesis possible.

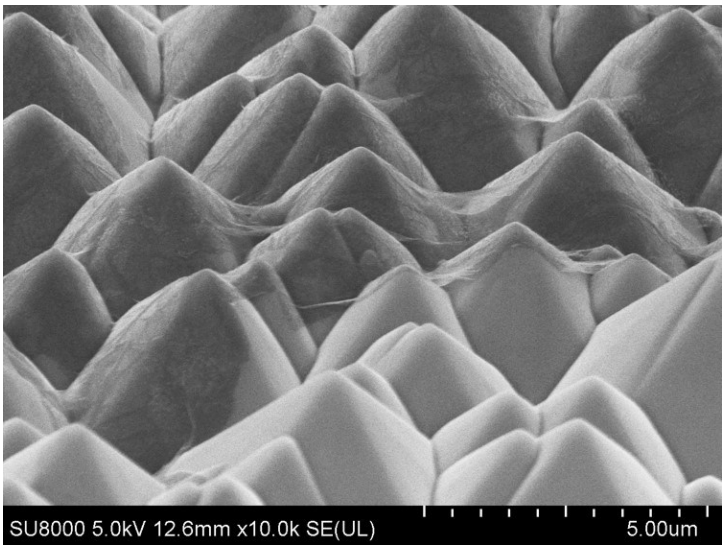

Figure S12. Pyramid structure results. SEM image of multilayer graphene partially remaining on nanopyramid array, after etching nickel. The pyramidal structure was able to create a graphene layer with a 3D shaped structure, but the silicon pyramids cannot anchor the graphene during etching. As a result, almost all the graphene was washed away and the image here represents only an extremely small section where some graphene remained as seen in the upper half of the image.

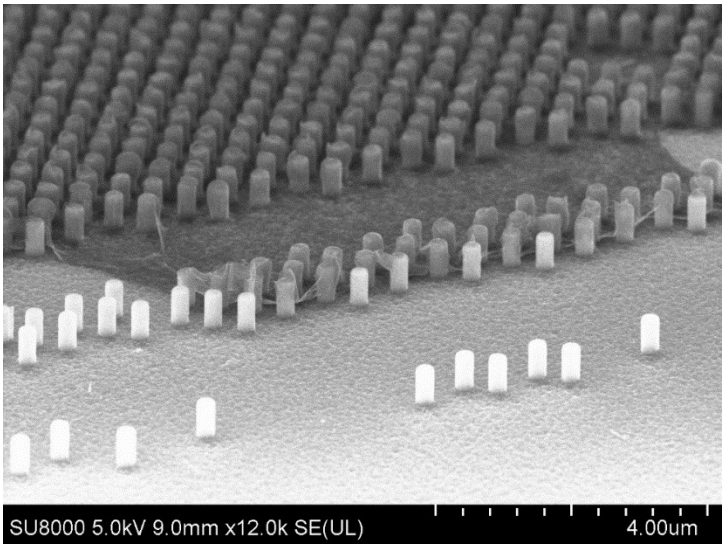

Figure S13. NW and planar section boundary. SEM image demonstrating the limits of multilayer graphene anchoring by NWs. Graphene on the clustered together NWs stay on-site after wet etching, while graphene on the planar areas is ripped and washed away. Isolated NWs on the bottom portion of the image cannot retain the graphene layer either. But, small enough planar sections between clusters of NWs can be kept in place such as is the middle of the image.