Electronic Supplementary Material (ESI) for ChemComm.

Temperature Induced Diameter Variation of Silicon Nanowires via a Liquid-Solid Phase Transition in the Zn Seed

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Supporting Information

Experimental

Zn Electrodeposition

The Zn coated SS substrates were prepared using previously reported procedure.[1] A Keithley 2400 was used as a power-source for the electrodeposition process. A 0.1 mm thick SS 316 sheet (99.999%, Kurt J. Lesker) was used as the substrate. The sheet surface was roughened on one side using 500 grit sandpaper to increase the surface area for enhanced NW growth. The plating solution used consists of $ZnCl_2$, methanesulfonic acid (MSA) and NaOH which where all purchased from Sigma Aldrich. The substrate was plated galvanostatically at a current density of 60 mA/cm^2 for 8 seconds. After deposition, the substrates were washed using deionized water and allowed to dry in air.

Reaction setup

NW synthesis was carried out in a round bottom flask to which 4 mL of squalane was added. The Zn-coated SS substrates were secured in a steel rack and placed horizontally facing down at the centre of the flask bulb. A stainless-steel cap as inserted into the flask to redirect the refluxing liquid and minimize it coming into contact with the growth substrate and induce unwanted temperature changes. The flask was attached to a water condenser and placed inside a 3-heating zone type furnace. To ensure that all moisture was removed from the system, the furnace was ramped up to 150 °C while a vacuum of 300 mTorr was applied through a Schlenk line for 30 minutes and then switched to Ar before being ramped up to the reaction temperature.

VLS NW Growth

The reaction temperature was set to 470 °C. 0.75 mL of phenylsilane (97%, GM Chemical) was then injected into the system through the septum cap on the condenser. Following this, 0.05 mL of a 2 M $LiBH_4$ in Tetrahydrofuran solution (purchased from Sigma Aldrich) was injected into the system to reduce any oxides present on the catalysts surface. The reaction was then allowed to proceed for 1.5 h.

VSS NW Growth

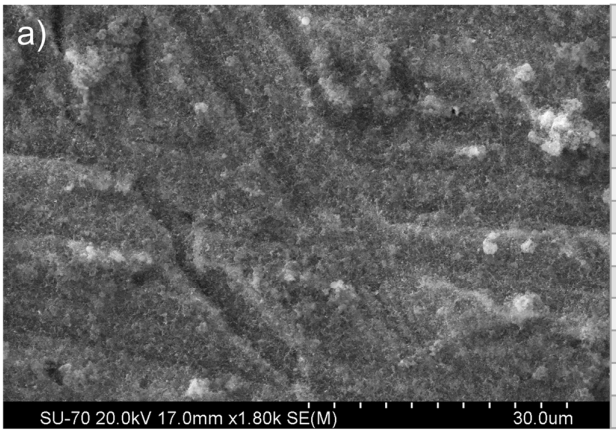
The reaction temperature was set to 340 °C. 0.75 mL of phenylsilane (97%, GM Chemical) was then injected into the system through the septum cap on the condenser. After 25 minutes, 0.05 mL of a 2 M $LiBH_4$ in Tetrahydrofuran solution (purchased from Sigma Aldrich) was injected into the system to lower the decomposition temperature of PS and reduce any oxides present on the catalysts surface. A further 0.05 mL of $LiBH_4$ was injected every 20 minutes until the reaction was terminated after 1.5 h.

VLS-VSS Transition NWs

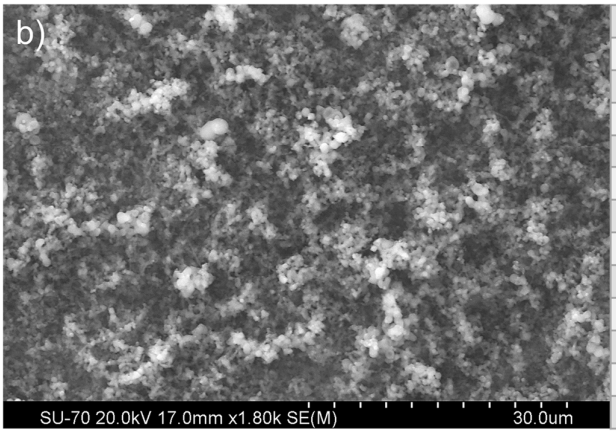
The reaction temperature was set to 470 °C. 0.75 mL of phenylsilane (97%, GM Chemical) was then injected into the system through the septum cap on the condenser followed by 0.15 mL of a 2 M $LiBH_4$ in Tetrahydrofuran solution (purchased from Sigma Aldrich). The reaction was then allowed to proceed for 45 minutes. The reaction temperature was then set to 340°C and the furnace was fully opened to accelerate cooling process. Once the furnace cools to 340°C (after approximately 5 minutes) the furnace was closed again and the reaction was left to proceed for 15 minutes before being terminated. For producing NWs with VLS-VSS-VLS transitions, the furnace was ramped back up to 470 °C and allowed to proceed for another 10 minutes before terminating the reaction.

Materials Characterisation

Scanning electron microscopy (SEM) analysis was performed using a Hitachi SU-70 and operated between 5 and 20 kV. The samples were untreated prior to SEM analysis. For transmission electron microscopic (TEM) analysis, the NWs were removed from the substrate by sonicating them in 0.4 mL of toluene for 30 sec and drop cast on a Cu grid (mesh 200 lacey carbon film). The TEM used for analysis was a JEOL JEM-2100F field transmission microscope equipped with a Gatan Ultrascan CCD camera and EDAX genesis EDS detector and operated at 200 kV. Statistical analysis including size distributions for VLS and VSS synthesised NWs, Zn-seed:NW diameter ratios and the diameter increase for VLS-VSS transitions where obtained by manually measuring the width of 100 different NWs using the Gatan Digital Micrograph software.



Element	Weight%	Atomic%
C K	26.34	52.58
O K	9.05	13.56
Si K	14.01	11.96
S K	0.54	0.40
Cr K	8.68	4.00
Mn K	0.69	0.30
Fe K	33.12	14.22
Ni K	4.62	1.89
Zn K	2.95	1.08
Totals	100.00	



Element	Weight%	Atomic%
C K	39.77	60.72
O K	14.29	16.38
Si K	24.01	15.68
S K	0.31	0.18
Cr K	3.89	1.37
Mn K	0.37	0.12
Fe K	13.26	4.36
Ni K	1.51	0.47
Zn K	2.58	0.72
Totals	100.00	

Figure S1. Low magnification SEM image of as-grown Zn-seeded Si NW and corresponding quantitative EDS at 470°C (a) and 340°C (b).

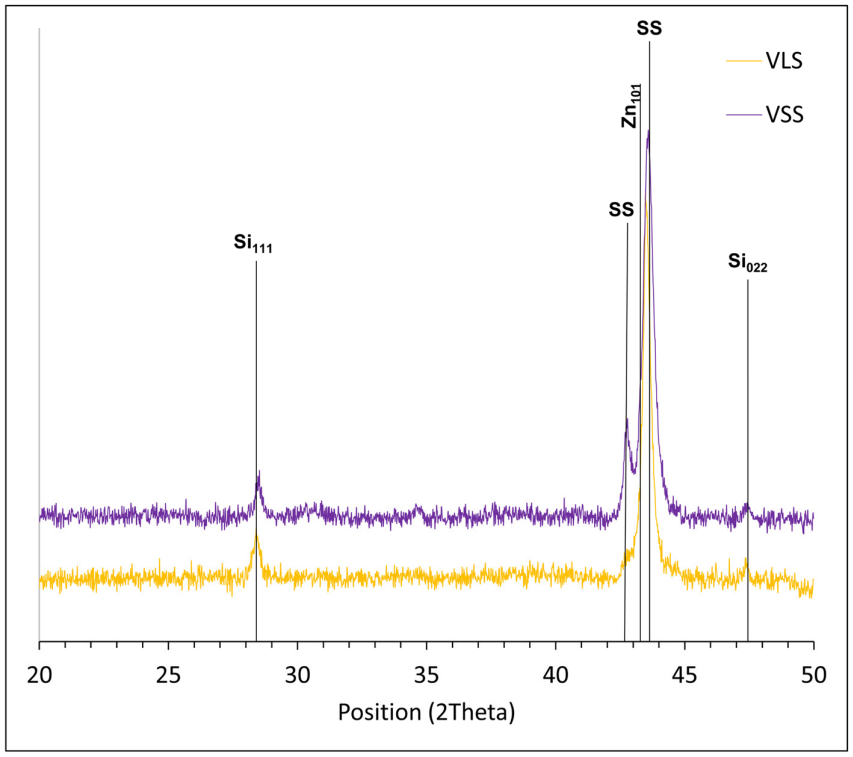


Figure S2. XRD of the as grown Zn-seeded Si NWs synthesised via the VLS mechanism at 470°C (yellow) and the VSS mechanism at 340°C (purple).

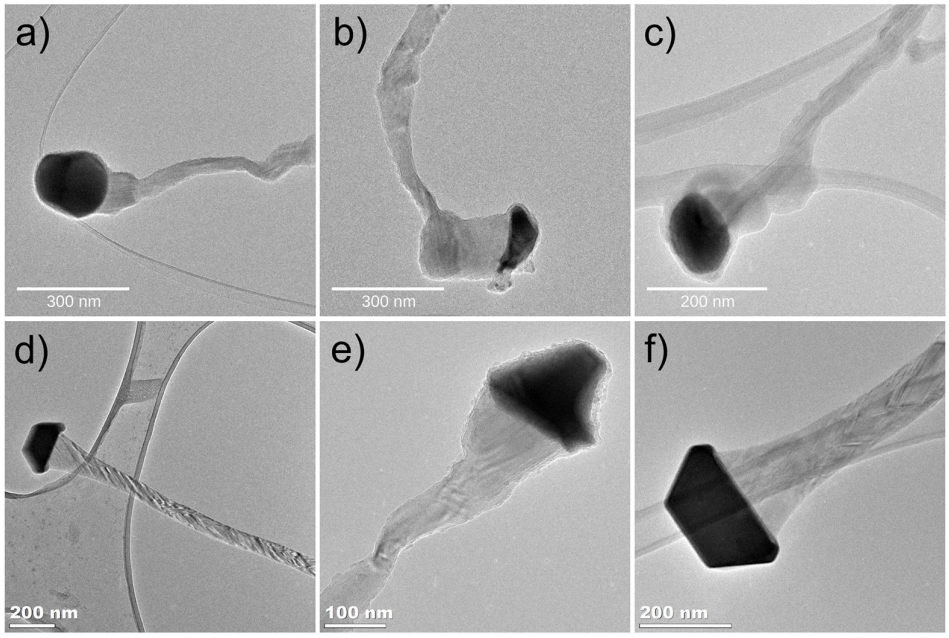


Figure S3. TEM imaging of Si NWs synthesised at 470°C via the VLS mechanism showing a diameter increase near the Zn seed.

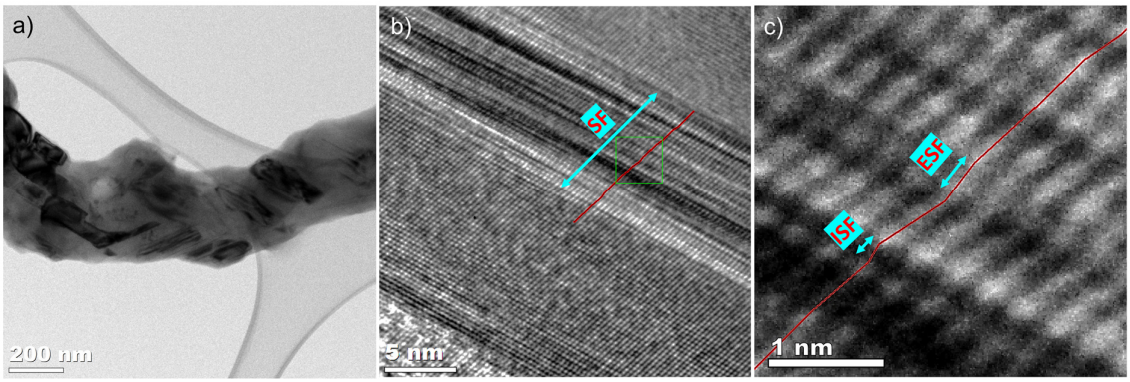


Figure S4. (a) Low magnification TEM imaging of a VSS grown Si NW. (b) TEM showing defects in VSS grown Si NW. (c) Higher resolution TEM imaging of section indicated by green square in (b) showing evidence intrinsic stacking faults (ISF) and extrinsic stacking faults.

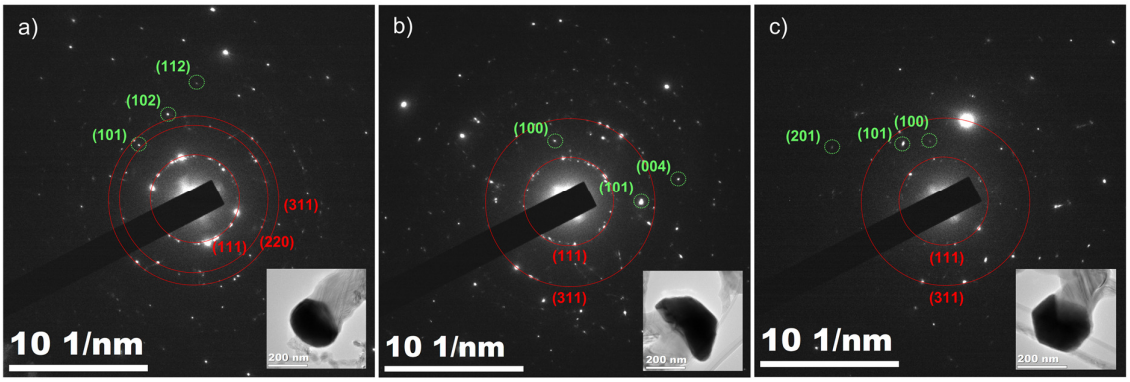


Figure S5. SAED's of different seed types shown in Figures 3 including spherical (a), Trapezoidal (b) and Hexagonal (c). The spots highlighted in green represent the phases for metallic Zn with the overlayed Si diffraction pattern shown in red.

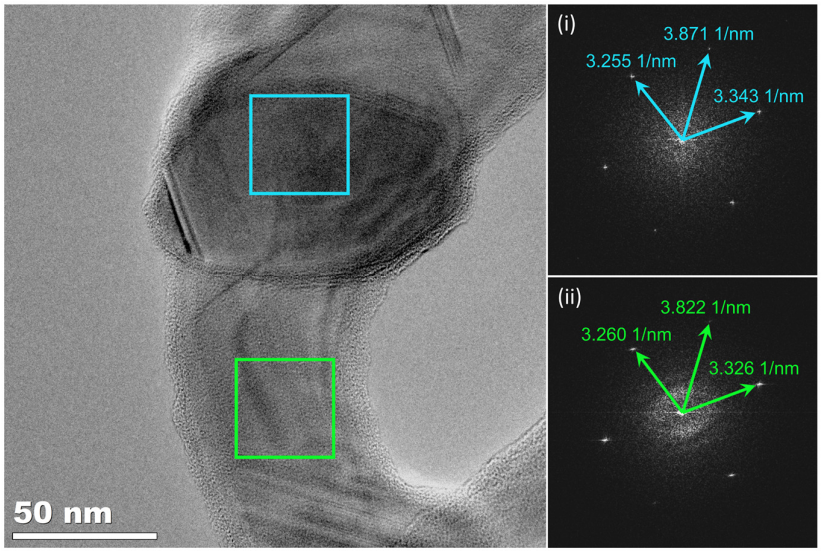


Figure S6. Higher magnification TEM imaging of region with diameter transition of NW shown in Figure 4b. FFTs obtained from both the VLS (i) and VSS (ii) segments indicated by a green and blue square respectively, show that no phase changes occur during the diameter transition.

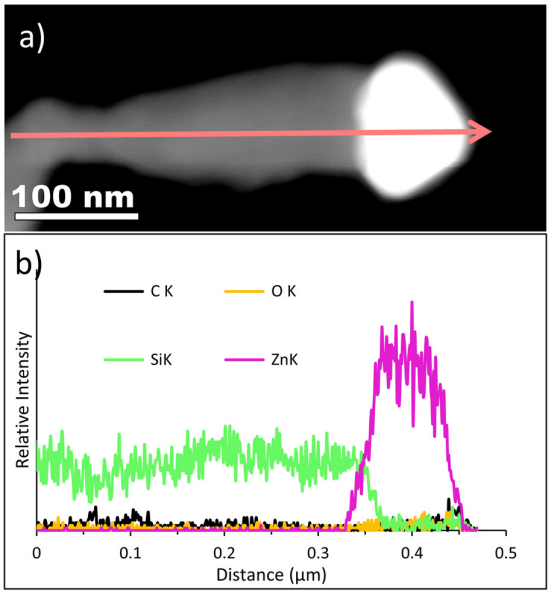
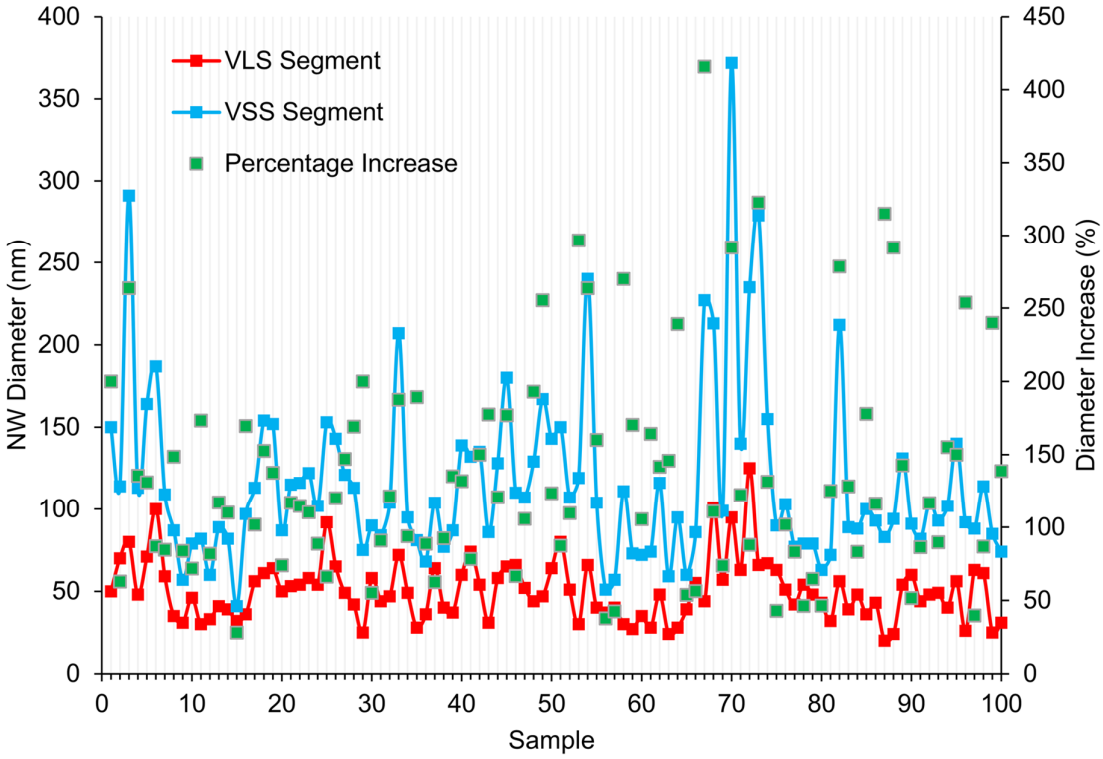


Figure S7. (a) STEM imaging and corresponding EDX linescan (b) showing elemental composition of 2-segment NW and Zn seed.



Figures S8. Plot of diameter increase observed for 100 NWs with a VLS-VSS transition and percentage increase.

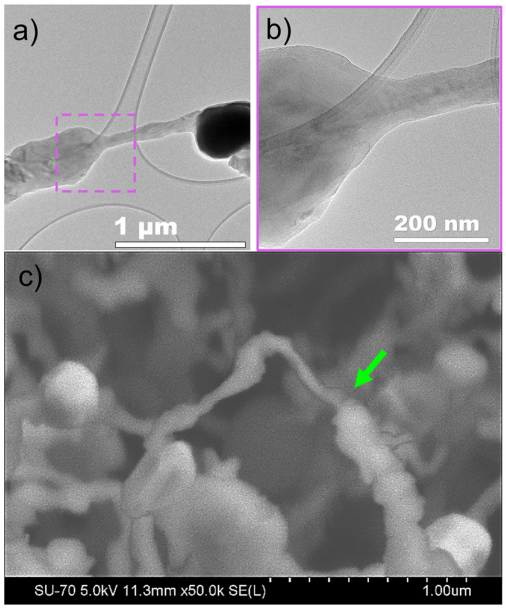


Figure S9. (a) BF-TEM imaging NW temperature induced VSS-VLS transition. (b) Higher magnification TEM image of diameter transition in (a). (c) SEM image NW with VSS-VLS segment with transition indicated by green arrow.

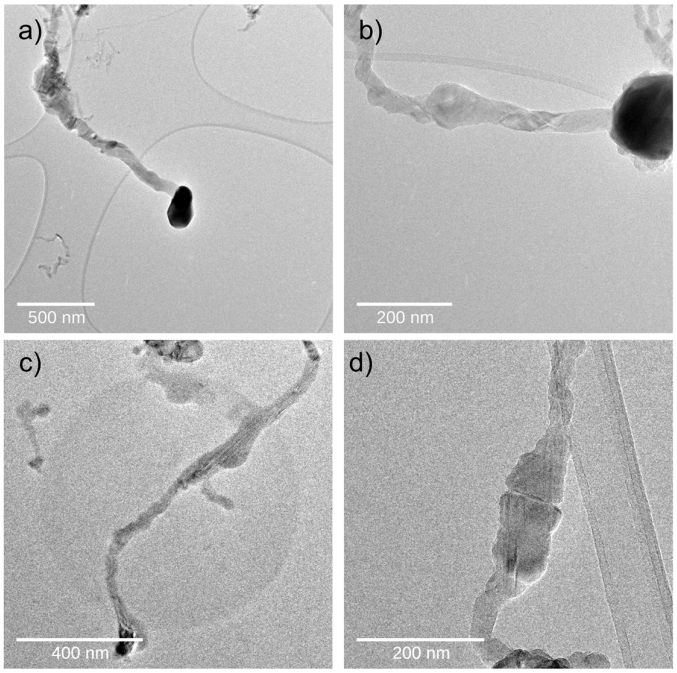


Figure S10. (a-d) BF-TEM imaging of other 3-segment Si NWs with VLS-VSS-VLS transition.

1. Kilian, S., et al., *Direct Growth of Si, Ge, and Si–Ge Heterostructure Nanowires Using Electroplated Zn: An Inexpensive Seeding Technique for Li-Ion Alloying Anodes.* Small, 2021. **17**(10): p. 2005443.