Supporting Information for:

Plateau-Rayleigh crystal growth of nanowire heterostructures: Strain-modified surface chemistry and morphological control in 1, 2 and 3 dimensions

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Materials and Methods

Periodic Shell Nanowire Synthesis. Si core nanowire growth: Au nanoparticle catalysts (20, 30, 50, 80, and 100 nm; Ted Pella) were diluted 1 to 100 by volume in water and subsequently dispersed on an oxidized Si growth substrate (p-type Si, 0.005 Ω cm, 600 nm oxide; Nova Electronic Materials) functionalized with 0.1% w/v poly-L-lysine (150,000 – 300,000 g/mol; Sigma Aldrich) in water. After rinsing in deionized water and drying with nitrogen, the substrates were placed into a home-built chemical vapor deposition reactor and the system was evacuated to a base pressure of ~5 mTorr. Si core nanowires were grown via the Au nanoparticle catalysed growth mechanism (S1) for ~10-60 minutes at 465 °C and a total pressure of 40 Torr with 1 standard cubic centimeters per second (sccm) silane (SiH_4;100%; Voltaix) and 60 sccm hydrogen (H_2; 99.999%; Matheson) flow rates. Ge shell growth: Following Si core growth, the furnace temperature was ramped to 480-560 °C. At this temperature, shells were grown for 0.25 - 80 minutes at ~0.3 Torr with gas flow rates of 1-40 sccm GeH_4 and 0-200 sccm H_2. Ge core nanowire growth: Germanium core nanowires were typically synthesized from 30-50 nm diameter Au nanoparticle catalysts at a total pressure of 300 Torr with 200 sccm H_2 and 20 sccm germane (GeH4; 10% in H2; Voltaix) flow rates. Ge cores were nucleated for 5 minutes at 330°C and grown for another 50 minutes at 270°C. Si shell growth: Following Ge core growth, the furnace temperature was ramped to 680 °C. At this temperature, shells were grown for 20 – 30 minutes at ~0.3 Torr with gas flow rates of 0.8 sccm SiH_4 and 60 sccm H_2.

Nanowire Characterization. Scanning electron microscopy (SEM, Zeiss Ultra Plus field emission SEM) images of periodic shell nanowires were recorded directly from the as-synthesized growth wafers and after nanowires were transferred to Si_3N_4-coated Si wafers (200

nm Si_3N_4, 100 nm SiO_2 on p-type Si, 0.005 Ω cm; Nova Electronic Materials). Energy dispersive X-ray spectroscopy (EDS) maps were collected at 512 x 400 resolution using a 400 ms dwell time per pixel in commercial EDAX Genesis software on a Hitachi Spherical Aberration Corrected STEM/SEM HD-2700.

Anti-correlated non-conformal Ge shell growth and one-sided growth. Anticorrelated patterns are observed for our growths on larger cores and for others on top-down fabricated substrates, where Ge shell islands self-organize on opposites sides of a straight NW substrate in an alternating pattern. The formation of one Ge island relieves stress by elongating Si at the interface and bending the substrate, which encourages subsequent growth to occur in an axially adjacent but radially opposite position. For our 1D NWs with 20-30 nm diameter cores, Ge lies on the same side of a curved substrate. We suggest this key difference results from the freestanding ultra-compliant nature of small diameter NWs, which are attached to a substrate at only one end and can thus expand and deform unimpeded at their free end. In contrast, the aforementioned top-down 1D substrates are attached at both ends; one-sided growth would lead to substrate expansion at the surface and a global substrate bending with stress at these fixed ends, which opposes additional bending. This has been shown for 2D Si nanomembranes with four fixed edges where deposition only on the top surface lead to one-sided growth. (S2)

We propose that a 'critical' amount of strain must be achieved for one-sided growth to occur. If this 'critical' amount of strain is not obtained before random or anticorrelated nucleation/growth occurs, then strain from initial shell growth will be opposed and one-sided growth will not proceed. For smaller NW cores, a smaller Ge shell (in terms of absolute size)

should be required to reach this ‘critical’ level of strain because (i) strain increases as shell thickness approaches the core diameter, and (ii) the bending stiffness of the core scales inversely with core diameter. Thus, we suggest that smaller, freestanding 1D substrates have higher likelihood of obtaining one-sided growth, and moreover, that long diffusion lengths and slow nucleation rates increase this likelihood.

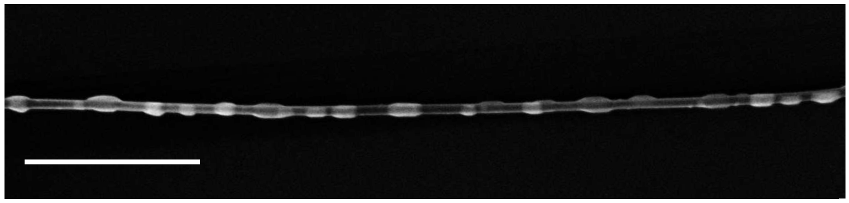

Figure S1. PR crystal growth of Ge periodic shells on 50 nm diameter Si NW cores. SEM after single-step shell synthesis of Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 2.5 min. Scale bar: 1 µm.

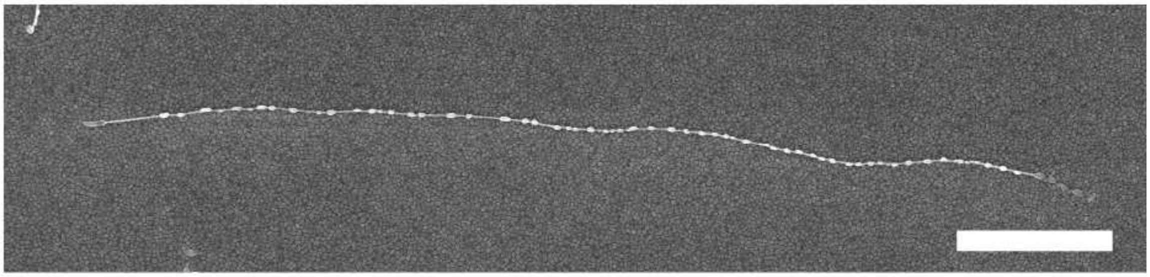

Figure S2. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 3 minutes. SEM of an approximately straight NW morphology after Ge deposition at 520 °C with a GeH_4 flow rate of 40 sccm (19 mtorr) for 3 minutes. Scale bar: 3 μm. SEM of curved and mixed-type morphologies are shown in Figure 3.

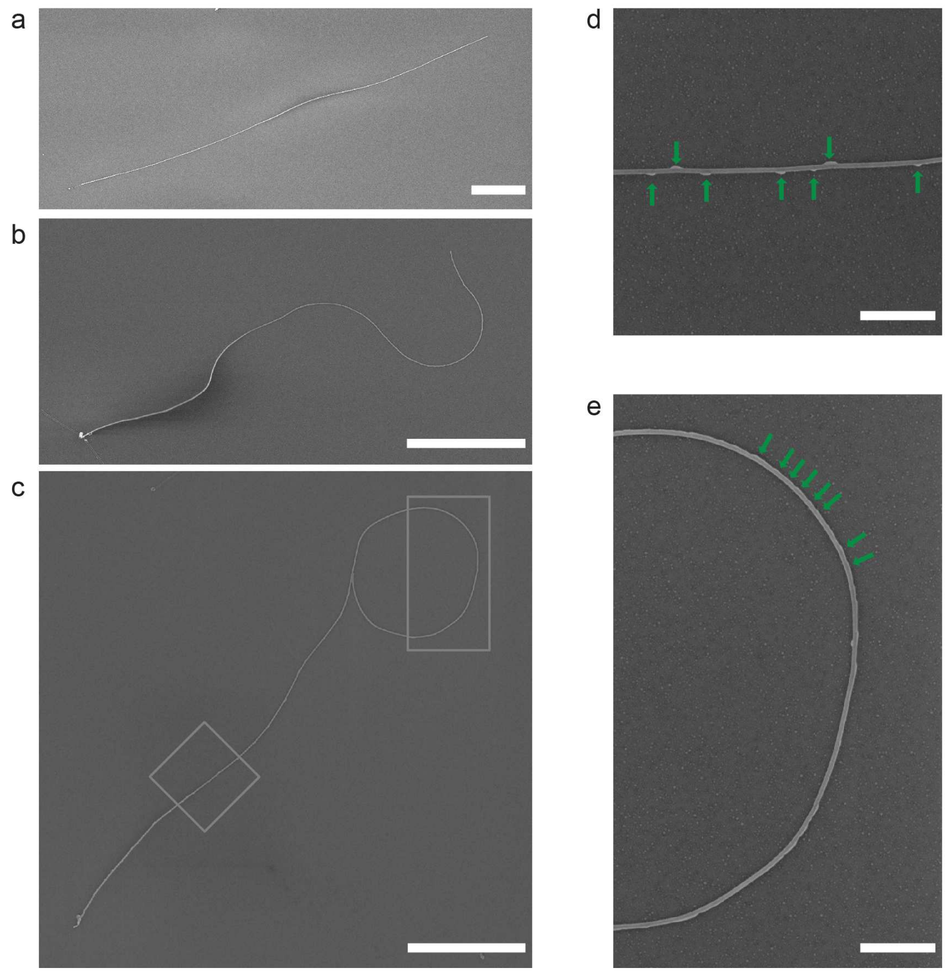

Figure S3. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 15 seconds. (a-c) SEM of straight (a), curved (b), and mixed-type (c) NW morphologies after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 15 seconds. Scale bars: 3 µm. (d, e) SEM images of 'straight' (d) and 'curved' (e) portion of the mixed-type NW morphology from left and right rectangular boxes, respectively, in (c). Green arrows are guides to the eye to indicate position of Ge shells. Scale bars: 500 nm

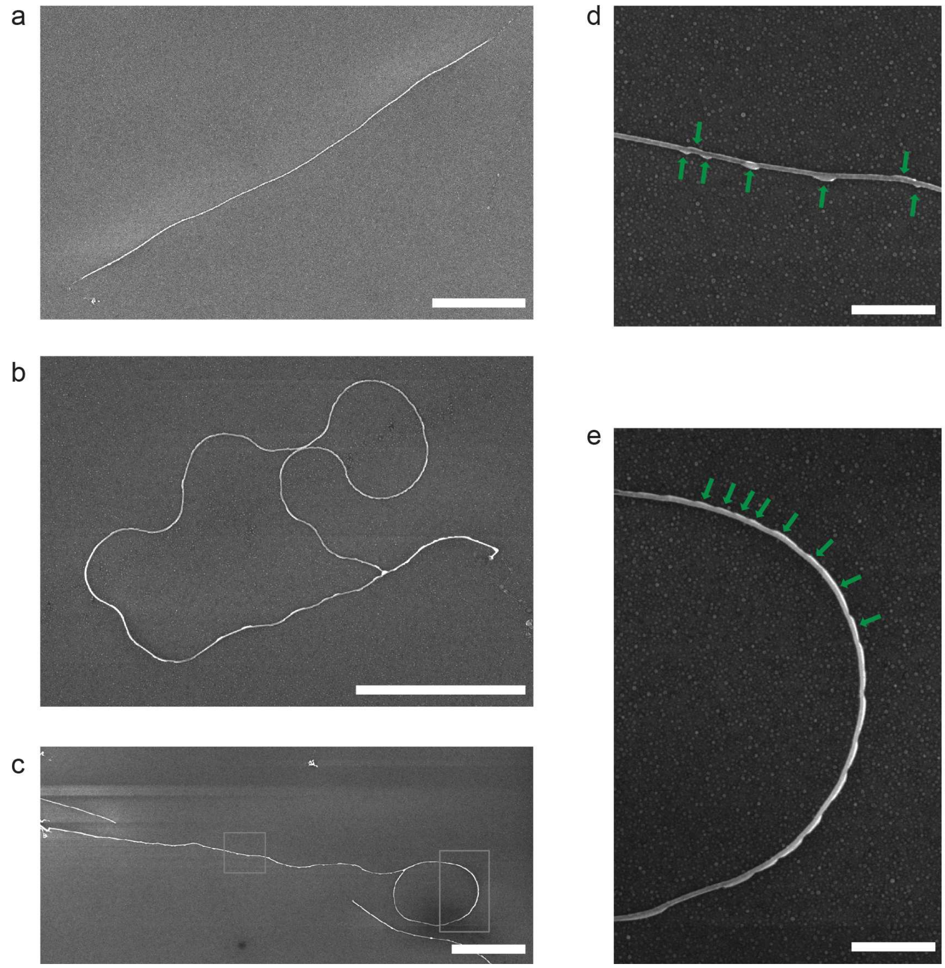

Figure S4. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 30 seconds. (a-c) SEM of straight (a), curved (b), and mixed-type (c) NW morphologies after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 30 seconds. Scale bars: 3 µm. (d, e) SEM images of 'straight' (d) and 'curved' (e) portion of the mixed-type NW morphology from left and right rectangular boxes, respectively, in (c). Green arrows are guides to the eye to indicate position of Ge shells. Scale bars: 500 nm

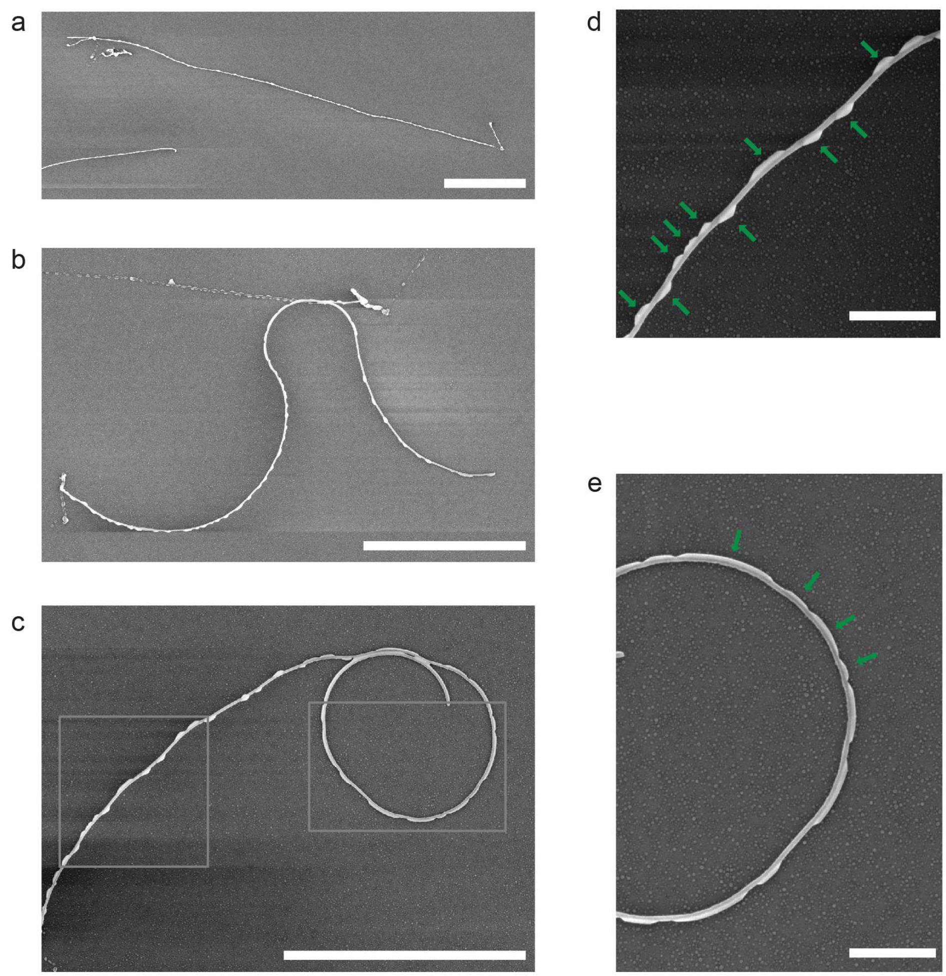

Figure S5. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 1 minute. (a-c) SEM of straight (a), curved (b), and mixed-type (c) NW morphologies after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 1 minute. Scale bars: 3 µm. (d, e) SEM images of 'straight' (d) and 'curved' (e) portion of the mixed-type NW morphology from left and right rectangular boxes, respectively, in (c). Green arrows are guides to the eye to indicate position of Ge shells. Scale bars: 500 nm

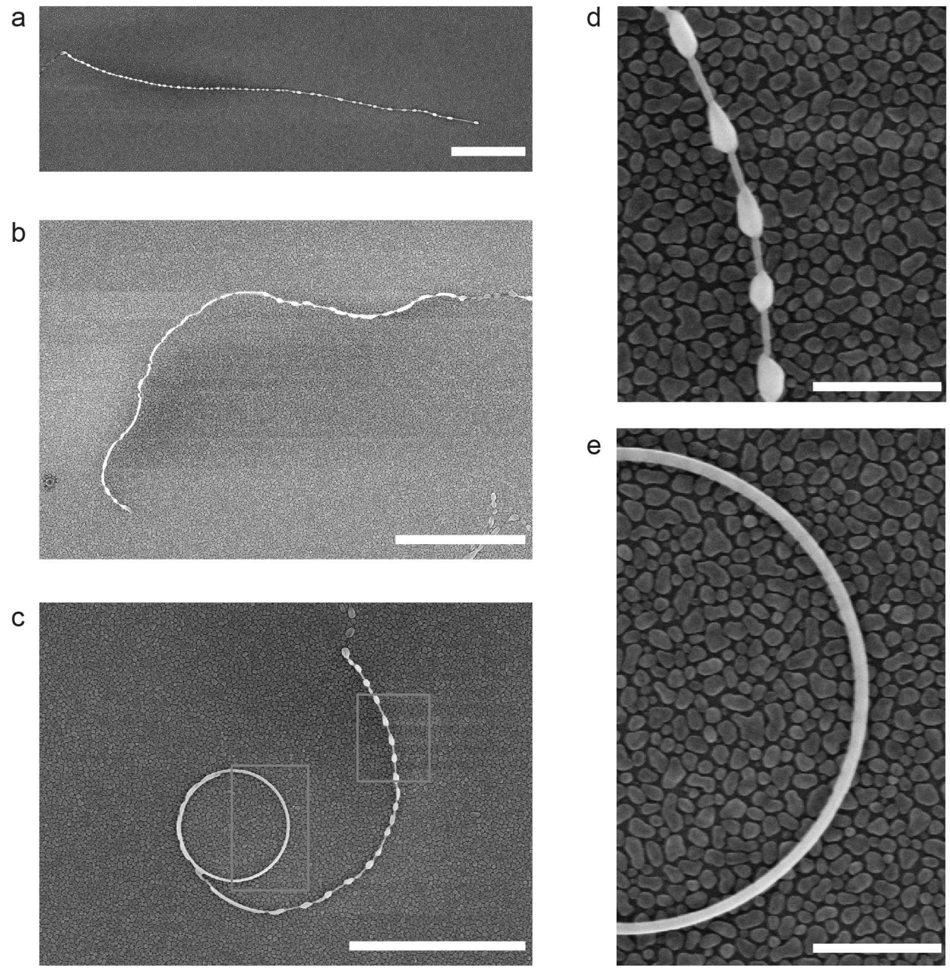

Figure S6. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 4 minutes. (a-c) SEM of straight (a), curved (b), and mixed-type (c) NW morphologies after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 4 minutes. Scale bars: 3 μm. (d, e) SEM images of 'straight' (d) and 'curved' (e) portion of the mixed-type NW morphology from right and left rectangular boxes, respectively, in (c). Scale bars: 500 nm

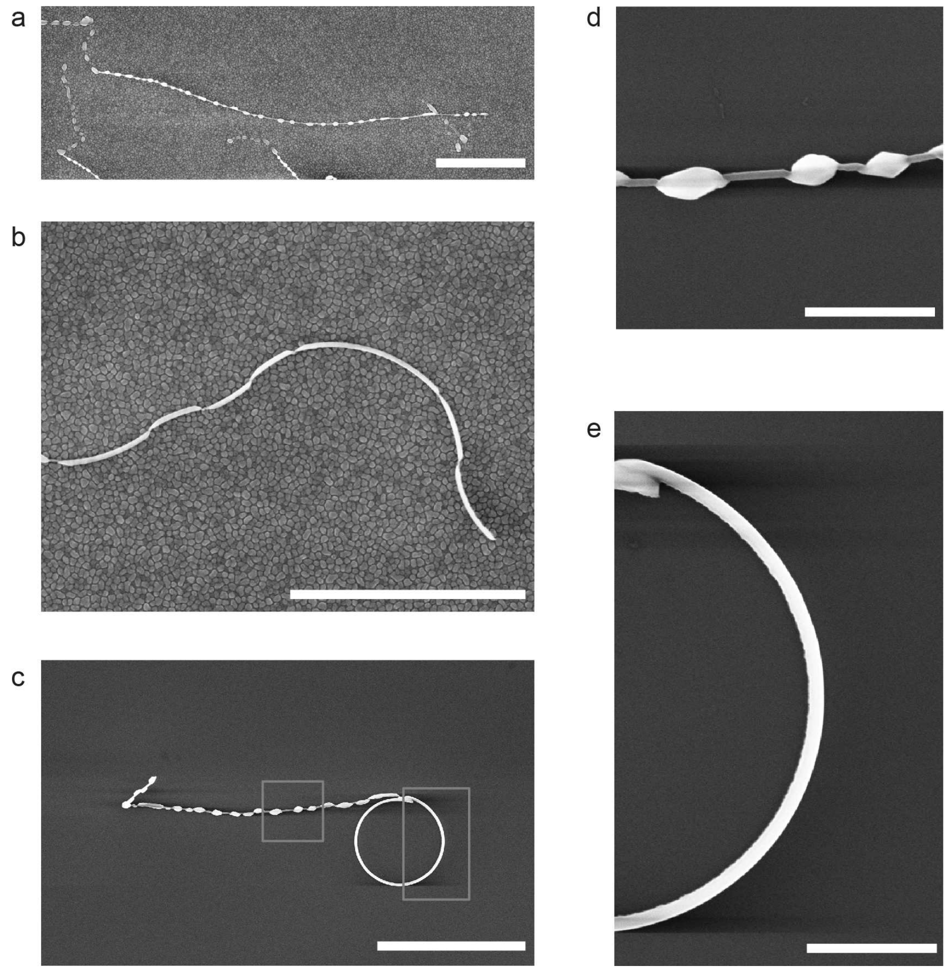

Figure S7. PR crystal growth of Ge periodic shells on 30 nm diameter Si NW cores after 5 minutes. (a-c) SEM of straight (a), curved (b), and mixed-type (c) NW morphologies after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 5 minutes. Scale bars: 3 μm. (d, e) SEM images of 'straight' (d) and 'curved' (e) portion of the mixed-type NW morphology from left and right rectangular boxes, respectively, in (c). Scale bars: 500 nm.

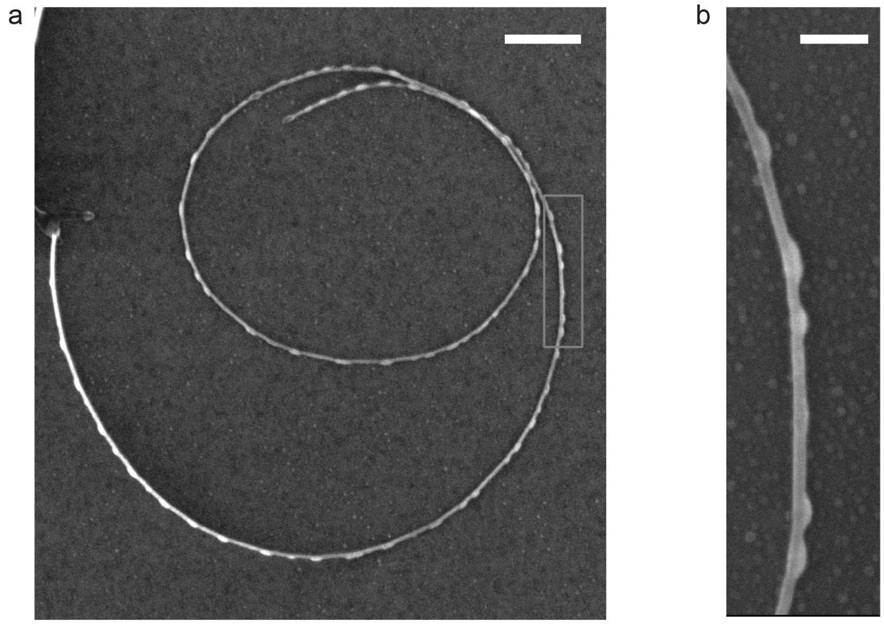

Figure S8. PR crystal growth of Ge periodic shells on 20 nm diameter Si cores. SEM of NW structure after Ge deposition at 520 °C with GeH_4 flow rate of 40 sccm (19 mtorr) for 15 sec. Scale bar: 200 nm. (b) SEM image from right rectangular box in (a). Scale bar: 50 nm. Ge shells form on primarily one side of the 20 nm diameter Si core to form a 2D loop structure.

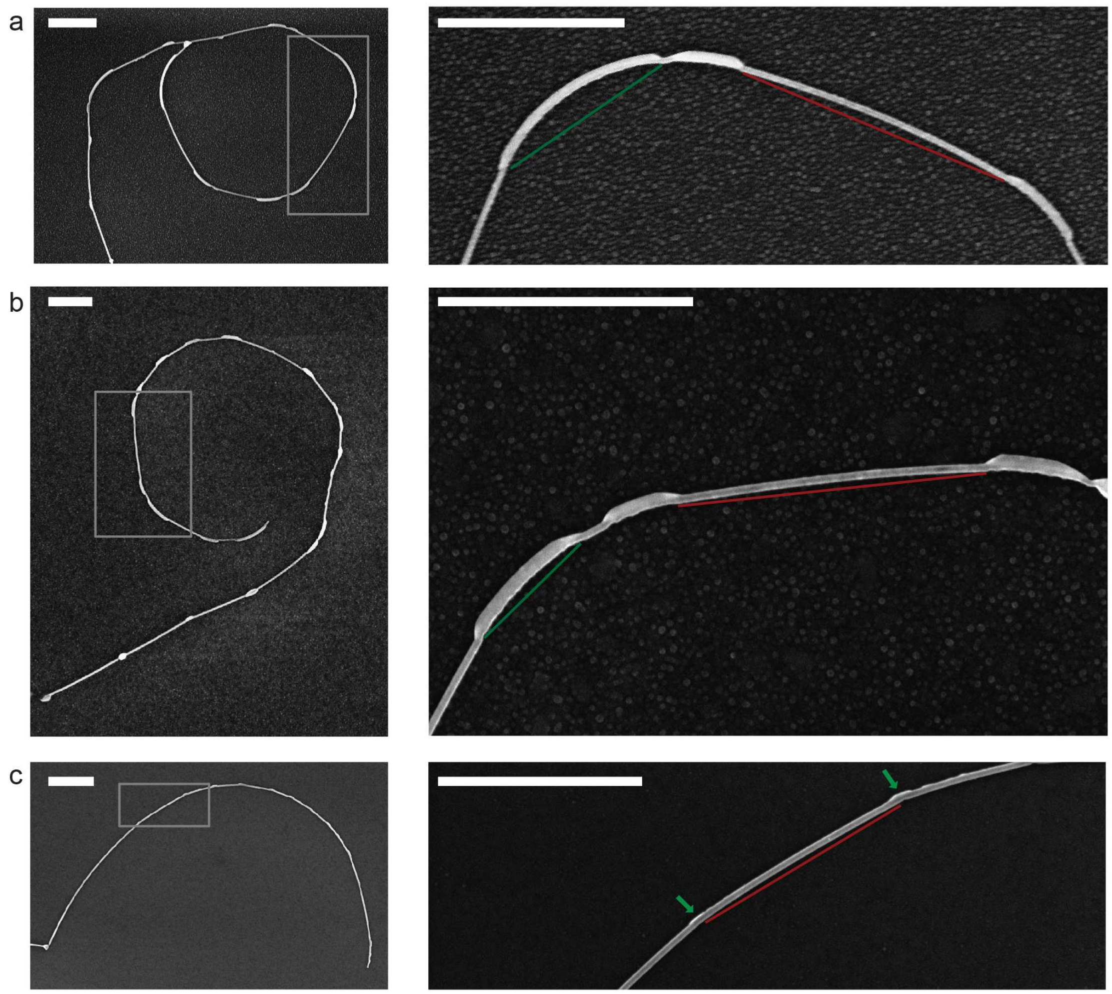

Figure S9. Lower pressure P-R crystal growth of Ge periodic shells on 30 nm diameter Si NW cores. (a-c) Left: SEM images of NWs with 'closed' (a) and 'open' (b,c) 2D morphologies after Ge was deposited on 30 nm diameter Si NW cores at 520 °C and 1 sccm (0.48 mtorr) for 30 (a,b) and (c) 5 minutes. Right: Higher magnification SEM images from the rectangular boxes in (a), (b), and (c). Lines are guides to the eye to indicate the local curvature of the NW at the Si/Ge interface (green) and the global curvature of the NW between two shells (red). Green arrows are guides to the eye to indicate position of Ge shells. Scale bars: 1 μm.

Supplementary References

S1. Cui, Y. et al. Diameter-controlled synthesis of single-crystal silicon nanowires. *Appl. Phys. Lett.* **2001**, *78*, 2214-2216.

S2. Deneke, C.; Malachias, A.; Rastelli, A.; Merces, L.; Huang, M.; Cavallo, F.; Schmidt, O. G.; Lagally, M. G. *ACS Nano* **2012**, *6*, 10287-10295.