Supplementary Information

Crystal structure transfer in core/shell nanowires

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S1. Fabrication of Si nanotubes

The fabrication of Si nanotubes requires three main steps: GaP nanowire growth, Si shell growth and GaP etch. The GaP nanowires have been grown via the standard Vapor-Liquid-Solid (VLS) growth method using gold as a catalyst. Substrate conformal imprint lithography allows for the fabrication of a hexagonal array of Au dots on a GaP (111)B substrate (*1*). The dots have a diameter of 90 nm and an interdistance of 1 µm. Prior to growth, a chemical treatment with piranha etch (H_2SO_4:H_2O_2:H_2O) and a thermal anneal at 700 °C were used for the preparation of the substrate. The nanowires were grown in a Metal-Organic Vapor Phase Epitaxy (MOVPE) reactor. GaP superlattice structures can be grown by adding Zn to the gas phase during growth. Different Ga-precursor partial pressures, ranging from $2.3x10^{-4}$ up to $4.6x10^{-3}$ mbar, were used in order to control the segment length of the superlattice structure at a constant temperature of 550 °C and Zn partial pressure of $1.4*10^{-2}$ mbar (*2*). Pure wurtzite GaP nanowires were grown at 630 °C without the addition of any dopant.

The Si shell was grown at 550 °C using Si_2H_6 as a precursor with a partial pressure of 3.4 mbar. The growth parameters for Si have been chosen such that VLS growth is suppressed, whereas diffusion-mediated surface growth is facilitated, resulting in Si shell with a thickness of a few nm. The VLS growth of Si is delayed using a growth interruption method. Just after the GaP core nanowire growth, the temperature is lowered to 200 °C for the AuGa eutectic to solidify.

The sample is then heated up to 550 °C under a constant flow of Si_2H_6, where (radial) Si shell growth takes place, and (axial) VLS growth of Si is suppressed.
The GaP-Si core-shell nanowires are then dipped for 1 minute in a hot, 80 °C, aqua regia solution ($HCl:HNO_3:H_2O$). First, the Au particle is removed by the etchant solution, and then the GaP core is selectrively etched with respect to the Si shell. As a result, Si nanotubes are left behind (fig. S.1).

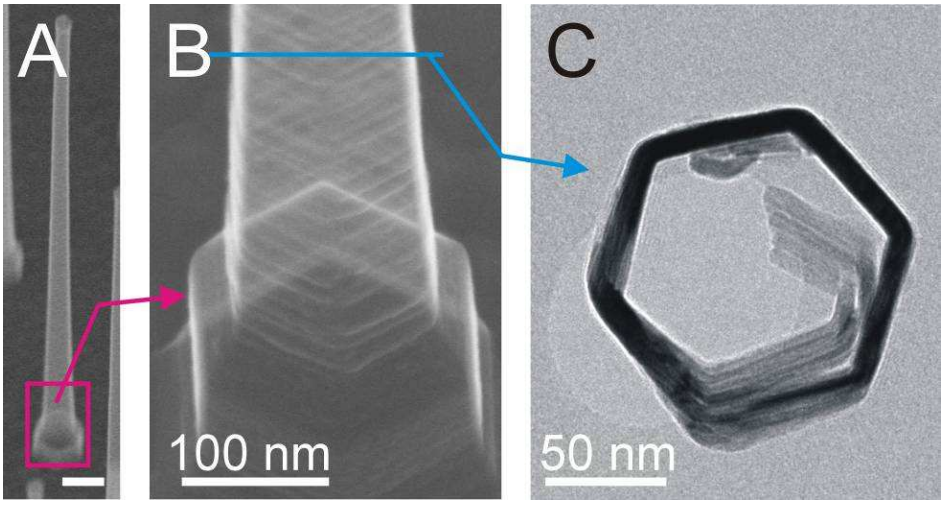

fig. S1. SEM image (tilt 30 °C) of one Si nanotube (A) overview of the nanowire (scale 100 nm) and (B) zoom-in of the basis. The nanotube is transparent for electrons and has a hexagonal cross section. (C) Bright field TEM view of a fragment of a nanotube. The view is aligned with the axis of a broken nanotube. The nanotube has a perfect hexagonal shape.

S2. Control of the Si nanotube wall thickness with Si growth time

The TSL nanotubes wall thickness increases from 2 nm, for a growth time of t_{Si} = 2 min, to 11 nm for t_{Si} = 20 min. In the case of WZ nanotubes, the growth rate is much lower as shown in figure S2a. The growth rate for the Si shell in the TSL diamond crystal structure is 0.6 nm/min, whereas it is only 0.25 nm/min for the WZ crystal structure.

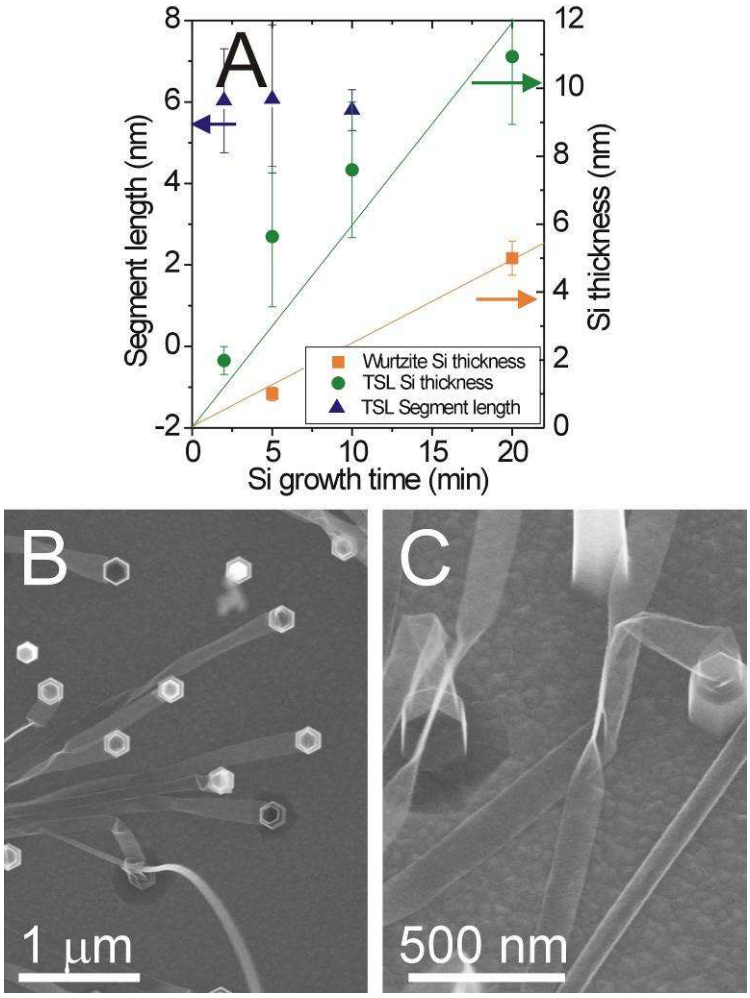

fig. S2. (A) Graph displaying the evolution of both TSL segment length and Si thickness with the growth time. The nanotube wall thickness increases with the Si growth time, whereas the TSL segment length value is constant. The WZ Si shell grows at a slower rate than the diamond phase Si shell. SEM pictures (B) top view and (C) tilted of ultra thin Si nanotubes (thickness ~1-2 nm), showing their flexibility.

S3. GaP WZ nanowire

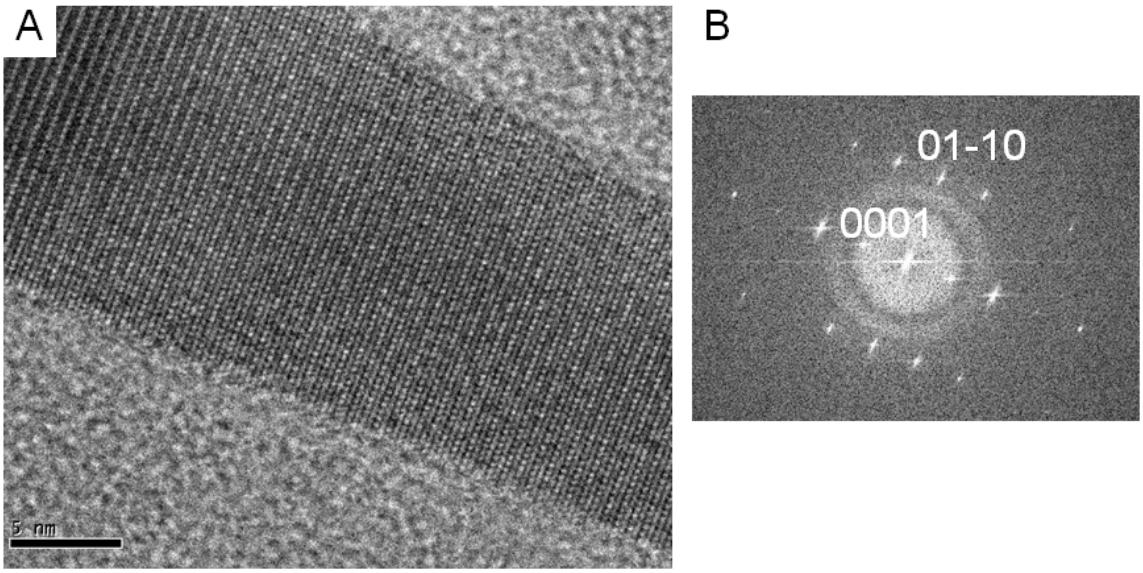

fig. S3. (A) HRTEM image of a defect-free WZ GaP nanowire with the hexagonal crystal structure imaged along the [2-1-10] zone axis (B) FFT of image (A).

S.4 HRTEM observation of WZ Si

In Figure S4 high-resolution TEM images are shown of a GaP/Si core nanowire along the [2-1-10] (figure S4A) and [01-10] (Figure S4C) zone axis, and their corresponding FFT patterns. It is important to image along two independent zone axes, since stacking faults only appear along one of them. In the left FFT image, streaking in the horizontal direction can be observed, indicating lateral relaxation of the Si lattice. From these images the lattice parameters have been determined.

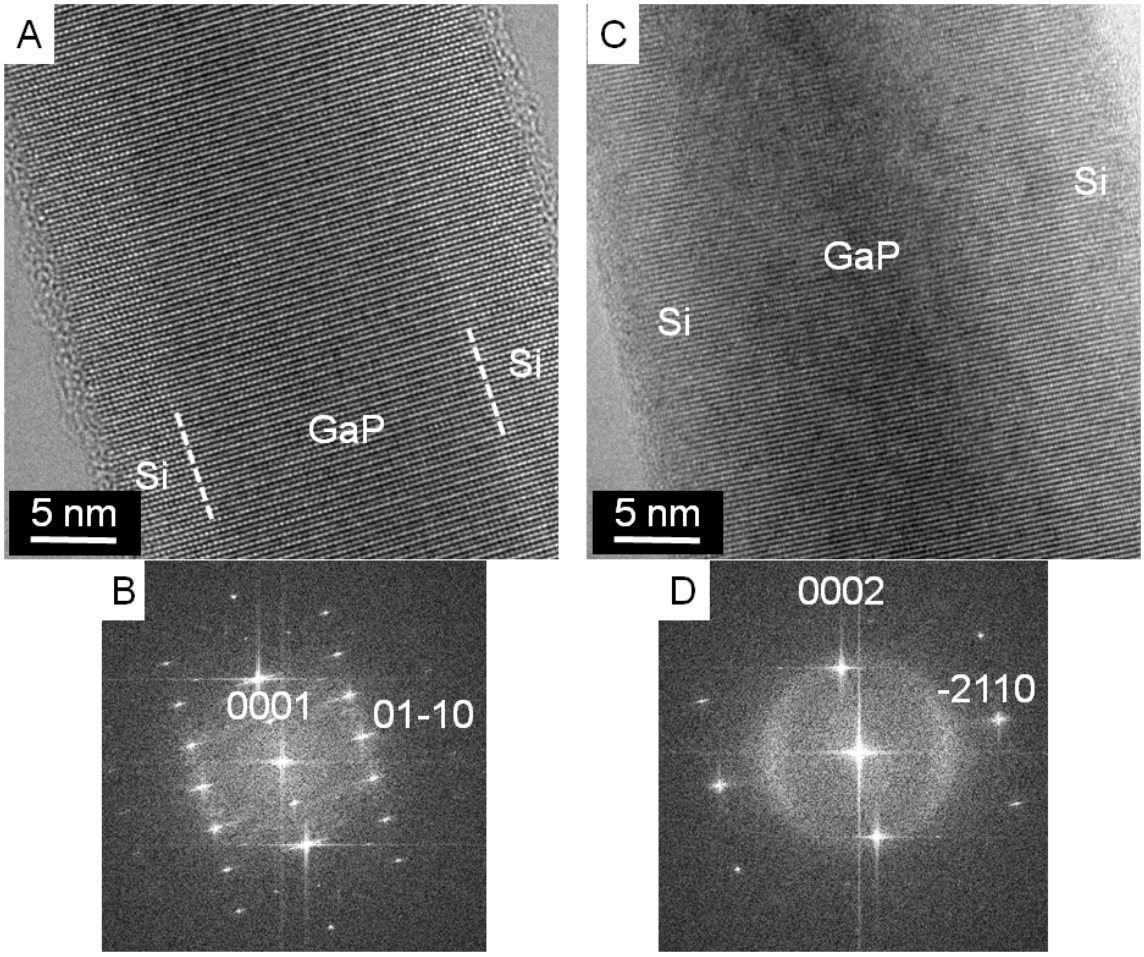

fig. S4. HRTEM image of a GaP/Si core-shell nanowire along two independent zone axes: A) [2-1-10] and corresponding (B) FFT pattern, (C) HRTEM image along [01-10] zone axis, and (D), corresponding FFT pattern.

S.5 Raman scattering experiments on GaP/Si core/shell structure and Si nanotubes

Raman spectroscopy was realized in the backscattering configuration on the as grown samples. The 514.5 nm line of an Ar^+ laser or the 647.1 nm line of a Kr^+ laser were used for excitation. The beam was focused with a 100x microscope objective with numerical aperture of 0.95. The laser spot size varies between 550 and 700 nm, depending on the excitation wavelength. Therefore, only few nanowires or nanotubes were probed. The power of the incident light was about 150 μW, in order to avoid heating effects. The scattered light was collected by an

XY Raman Dilor triple spectrometer with a multichannel charge-coupled device detector. The sample was positioned on a XY piezo-stage.

The downshift of the TO/LO mode of the Si TSL nanotubes can be addressed mainly to phonon confinement since its amount changes with the Si TSL nanotubes thickness.

Raman spectra of WZ GaP/Si nanowires are shown in Fig S5. The red spectrum is obtained from the core/shell structure. The peak at 390 cm^{-1} originates from the core WZ GaP, the peak at 521 cm^{-1} from the diamond Si at the top of the wires, due to the axial VLS growth (see text S1), and the peaks at about 510 cm^{-1} and 495 cm^{-1} correspond to the modes of the hexagonal Si shell. These two modes are still observed when the core is etched away (black spectrum in fig. S5) but are slightly shifted due to partial strain relaxation.

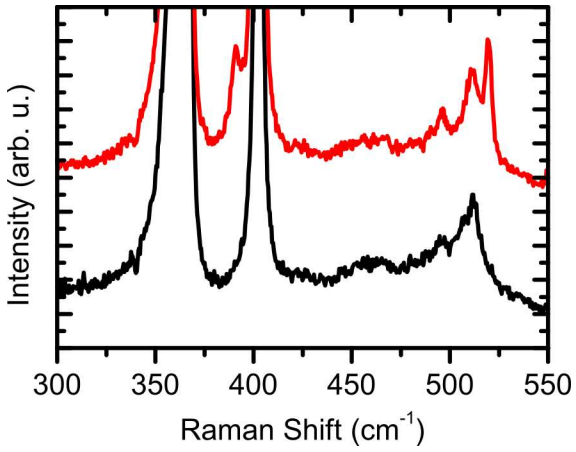

fig. S5. Typical Raman spectra of WZ GaP/Si core/shell nanowires (red solid line) and of the wurtzite Si lattice after etching the GaP core (black solid line).

References

[1] A. Pierret *et al., Nanotechnology* **21**, 0653051 (2010).

[2] Algra *et al.,* The role of surface energies and chemical potential during nanowire growth ‘, submitted .