Supporting Information

Tailoring Lithiation Behavior by Interface and Bandgap Engineering at the Nanoscale

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Experimental Details

Materials synthesis

Ge nanowires were grown on Ge (111) surfaces in a cold wall CVD system (Atomate Inc.) according to the preparation and two-step growth procedures described elsewhere.[1] 40 nm diameter Au colloids were used to seed the nanowire growth for all samples. The pure Ge nanowire elongation proceeded at ~ 276 °C in GeH_4 (30 % in H_2) and GeH_4 partial pressure, $P_{i\text{-}GeH4}$ = 0.6 Torr. For the Ge/Si core/shell nanowires with extended Si segment atop, after the Ge nanowire elongation, the temperature was ramped from 276 °C to ~ 400 °C in GeH_4 flow at $P_{i\text{-}GeH4}$ = 0.15 Torr. The growth of the 1 nm Si shell and axial Si segment was carried out at ~ 440 °C for 1.5 min at $P_{i\text{-}SiH4}$ = 1.4 Torr. The Ge/Si core/shell nanowires with thicker Si shells used in the lithiation studies of the supplementary information used the same procedure to grow the Ge nanowire cores followed by the deposition of a low temperature Si blocking layer. SiH_4 flow was maintained as the temperature was ramped up to 500 °C where i-Si shell deposition took place at $P_{i\text{-}SiH4}$ =0.25 Torr for 25 min (3 nm Si shell), and 30 min (5 nm Si shell).[2]

Materials surface treatments

The Ge/Si core/shell nanowires were treated under oxygen plasma for about 3 minutes to oxidize the surface Si shell to SiO_x. For removal of the surface Si layer, after oxygen plasma treatment, the nanowires were dipped in 2% hydrogen fluoride (HF) acid for about 30 seconds, and followed by de-ionized water rinse for 3 times. The conformal carbon layer was coated on the Ge/Si core/shell nanowires with a sputter using a high purity (99.999%) graphite target (Kurt J. Lesker).

In-situ TEM electrochemical lithiation setup

A small piece of Ge wafer with Ge/Si core/shell nanowires (or Ge nanowires) was cleaved from a large Ge wafer substrate and glued onto an aluminum rod using conductive epoxy, which didn't break the contact between the nanowires and the substrate. This intact, as-grown contact ensured good electrical contact between the nanowires and the current collector. Fresh Li metal was scratched from a fresh cut Li metal surface with a tungsten rod inside a glove box filled with helium (O_2 and H_2O content < 1 ppm). Inside the same glove box, both the nanowire electrode and Li electrode were mounted onto a Nanofactory TEM-Scanning tunneling microscope (STM) holder, which was quickly transferred into the TEM column using a sealed bag with dry helium. During the transfer process, the Li metal was exposed in air for about 2 s and a naturally grown Li_2O formed on the surface of Li metal, which served as a solid-state electrolyte for Li ion transport. Inside the TEM (Tecnai F30, FEI), the Li_2O/Li electrode was driven to contact an individual Ge/Si nanowire (or Ge nanowire) to construct an electrochemical device. Lithiation experiments were conducted by applying a potential of -2 V on nanowire electrode against the Li counter electrode.[3, 4]

Energy band-edge simulations

The energy band-edge structure in Ge, Ge/Si core/shell, and Ge/Si/C core/multi-shell nanowires surrounded by a 2 nm Li metal layer were simulated using 3D Silvaco Atlas. A Poisson solver was employed for 62 nm diameter Ge cores, or 60 nm diameter Ge cores with a 2 nm Si shell. Both cases had a zero-biased Li metal shell with barrier heights cited in the text. For the case of Ge/Si/C core/multi-shell structure, a 5 nm thick carbon shell was used. The Fermi energy outside the nanowire can be determined from the difference in the work functions of Li and C and the chemical potential barrier for lithiation is governed by the properties of the C/Si interface.

1. Dayeh, S. A.; Picraux, S. T. *Nano Letters* **2010,** 10, (10), 4032-4039.
2. Dayeh, S. A.; Gin, A. V.; Picraux, S. T. *Applied Physics Letters* **2011,** 98, (16), 163112.
3. Liu, X. H.; Zheng, H.; Zhong, L.; Huang, S.; Karki, K.; Zhang, L. Q.; Liu, Y.; Kushima, A.; Liang, W. T.; Wang, J. W.; Cho, J.-H.; Epstein, E.; Dayeh, S. A.; Picraux, S. T.; Zhu, T.; Li, J.; Sullivan, J. P.; Cumings, J.; Wang, C.; Mao, S. X.; Ye, Z. Z.; Zhang, S.; Huang, J. Y. *Nano Letters* **2011,** 11, (8), 3312-3318.
4. Liu, X. H.; Wang, J. W.; Huang, S.; Fan, F.; Huang, X.; Liu, Y.; Krylyuk, S.; Yoo, J.; Dayeh, S. A.; Davydov, A. V.; Mao, S. X.; Picraux, S. T.; Zhang, S.; Li, J.; Zhu, T.; Huang, J. Y. *Nature Nanotechnology* **2012,** 7, (11), 749-756.

Supporting Figures and Table

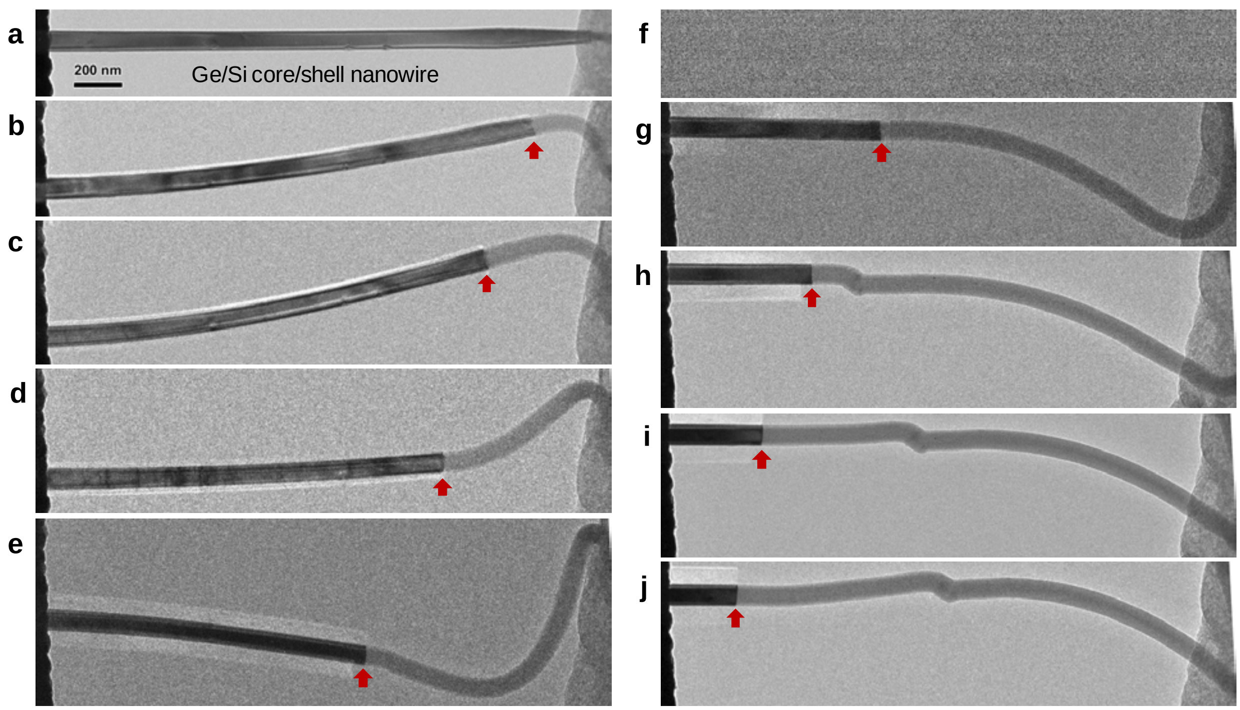

Figure S1. Unchanged axial lithiation behavior of Ge/Si core/shell nanowire under different beam dosage rates. (a) Pristine nanowire contacted with Li_2O/Li electrode. (b-e) Gradual decrease of the beam intensity by changing the spot size upon lithiation, shows an axial lithiation behavior. (f) Beam blank (i.e. without electron beam irradiation). (g-j) Gradual increase of the beam intensity by changing the spot size upon lithiation, still shows an axial lithiation behavior. The reaction fronts are marked by the red arrow heads. The corresponding spot size and beam dosage rate to each image are listed in Table S1.

Table S1. The spot size and beam dosage rate corresponding to the images shown in Figure S1.

Panel # in Figure S1	a	b	c	d	e	f	g	h	i	j
Spot size	2	2	4	6	8	Beam blank	8	6	4	2
Dosage rate (A/m^2)	47.2	47.2	17.9	6.95	1.67	0	1.67	6.95	17.9	47.2

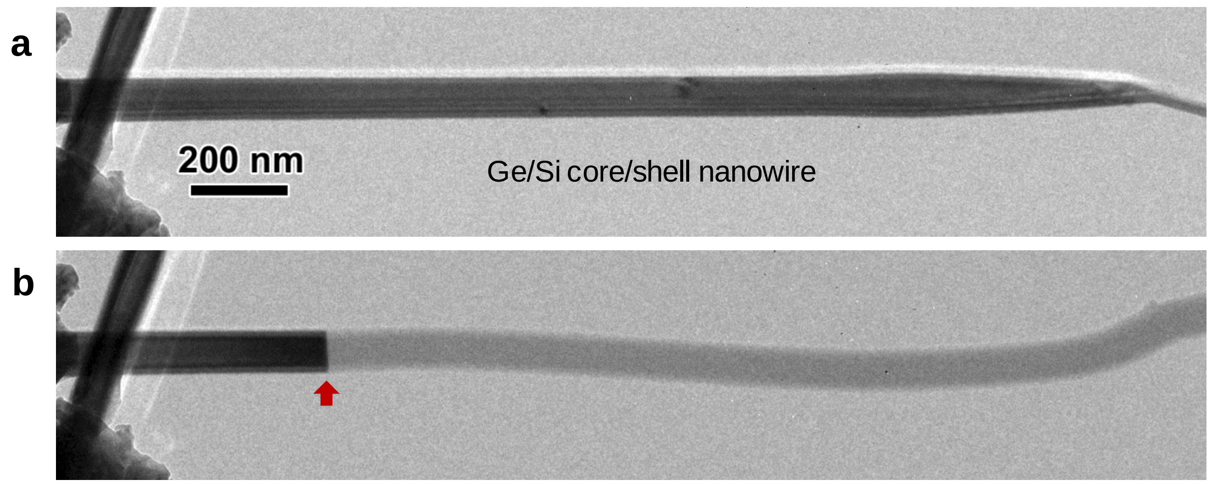

Figure S2. Axial lithiation behavior of Ge/Si core/shell nanowire without electron beam illumination (Beam blank). (a) Pristine Ge/Si core/shell nanowire. After it was contacted with Li_2O/Li electrode to construct a nanobattery, the electron beam was blanked and a potential of -2V was applied on nanowire electrode to initiate the lithiation. (b) After five minutes, the applied potential was turned off and the electron beam was turned back on for imaging the resulting structure. It is clear that the reaction front marked by the red arrow head lies on the cross section of the nanowire and the nanowire does not show any swelling, but only elongation, indicating an axial lithiation behavior, which is the same as the lithiation behavior with electron beam on. The beam blank experiment along with the lithiation experiment under different beam intensity shown in Figure S1 can safely exclude the possible beam effects on our discussion and conclusions in this work.

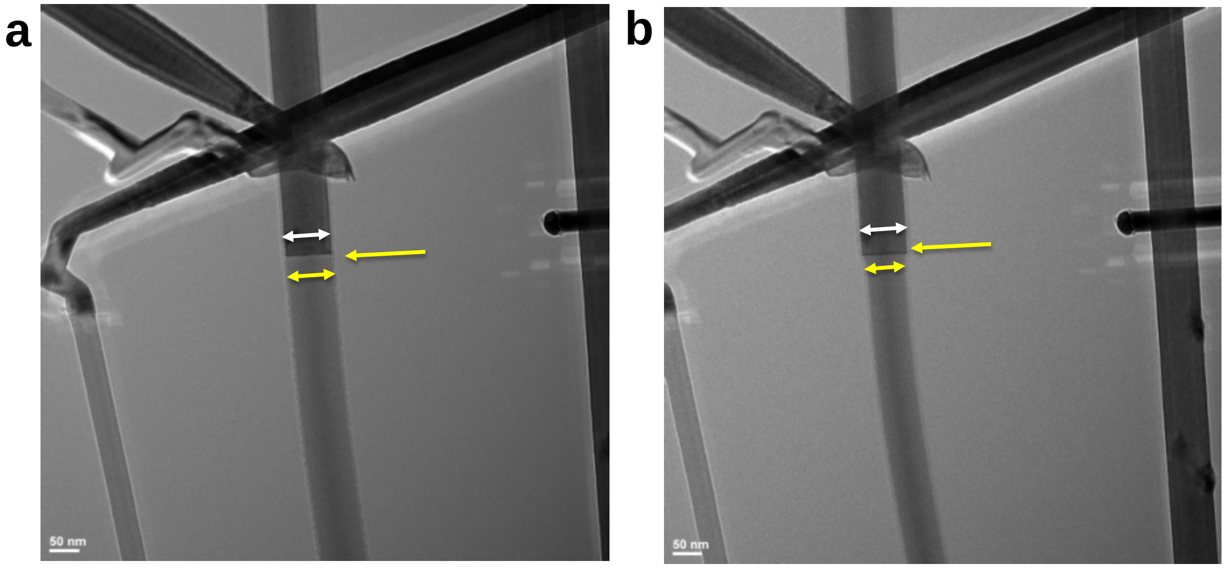

Figure S3. Electron beam induced delithiation and shrinkage of the lithiated LixGe segment. (a) Image recorded immediately after lithiation, showing the same diameter of the nanowire on both sides of the reaction front. (b) Image recorded after taking a few images at high magnifications (Figure 1i is one of the images), where the diameter of the lithiated Li_xGe segment became smaller due to the electron beam induced delithiation.

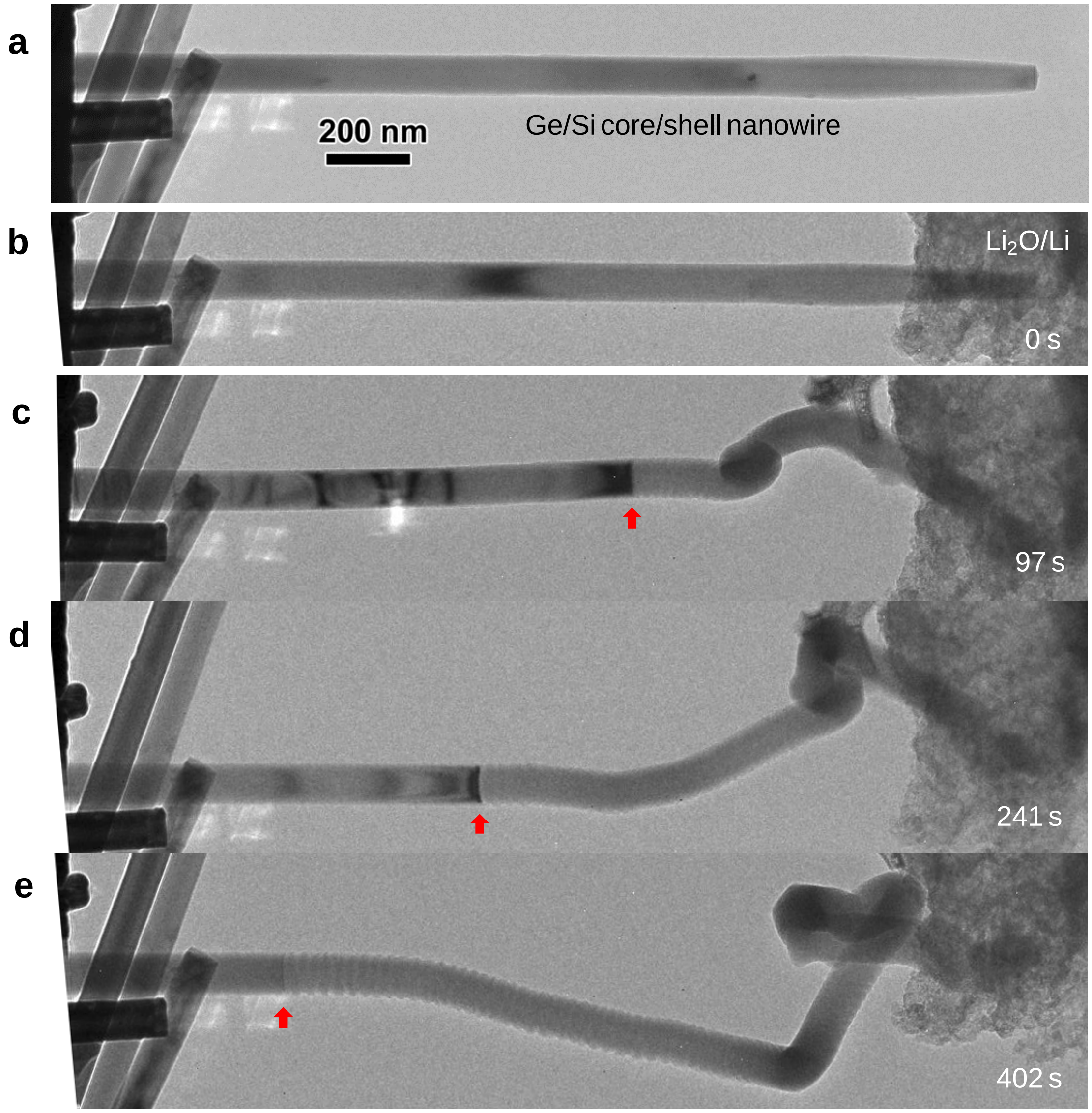

Figure S4. Axial lithiation behavior of Ge/Si core/shell nanowire without the top Si segment. (a) The pristine Ge/Si core/shell nanowire after the top Si segment was mechanically removed. (b) The nanowire was contacted with Li_2O/Li electrode to construct an electrochemical device. (c-e) Structure evolution of the nanowire upon lithiation, showing the axial lithiation behavior. The reaction fronts are marked by the red arrow heads.

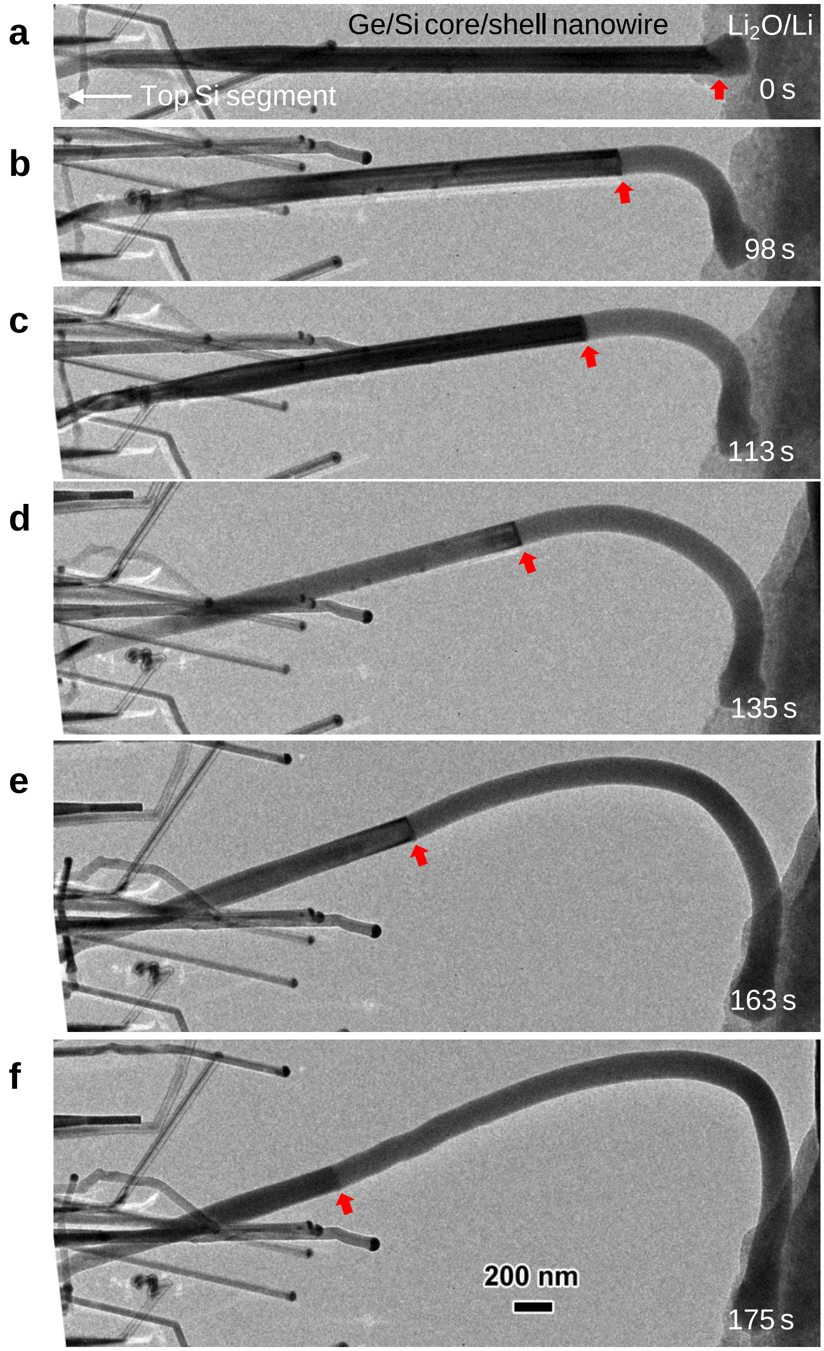

Figure S5. Axial lithiation behavior of Ge/Si core/shell nanowire which was lithiated from Ge segment. (a) The Ge segment was contacted with Li_2O/Li electrode, where the lithiation was initiated. (b-f) Morphology evolution of the Ge/Si core/shell nanowire upon lithiation, showing the axial lithiation behavior. The reaction fronts are marked by the red arrow heads. In this case, the polarity of build-in electric field from the axial Ge/Si junction was changed.

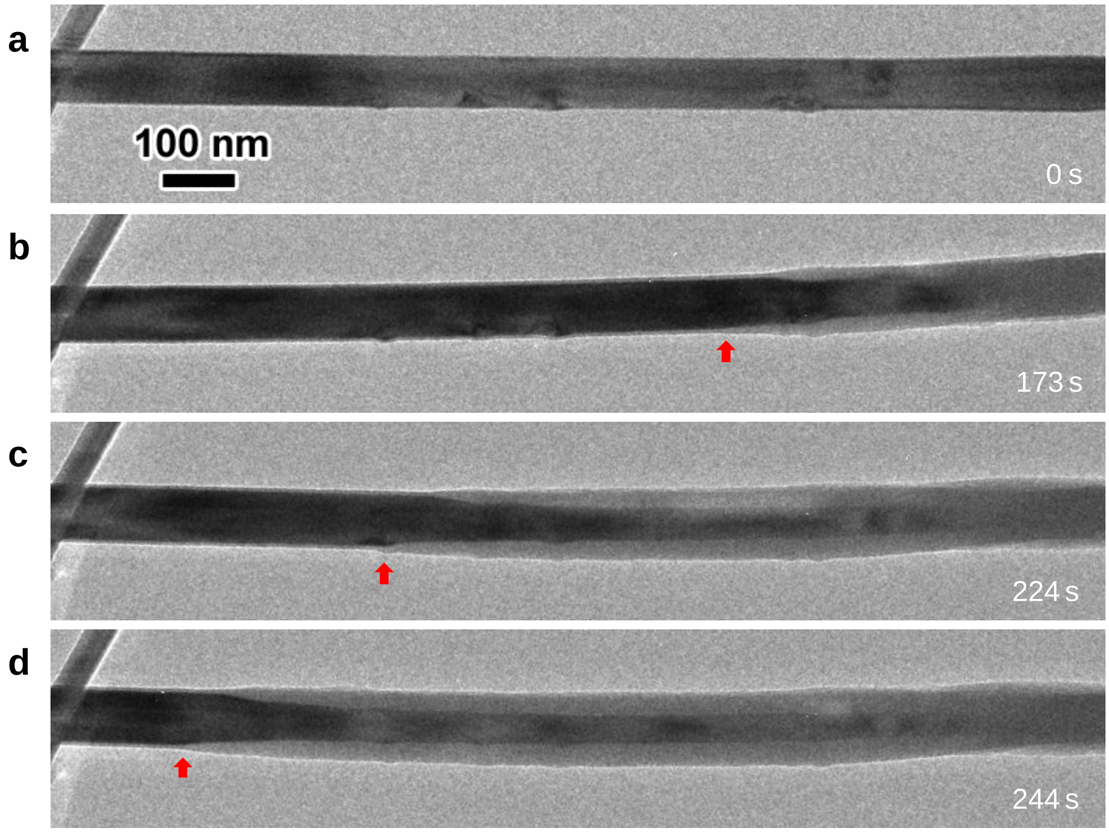

Figure S6. Core-shell lithiation behavior of Ge/Si core/shell nanowire after surface oxidation by a treatment of oxygen plasma. The reaction fronts are tapered in shape, as marked by red arrow heads.

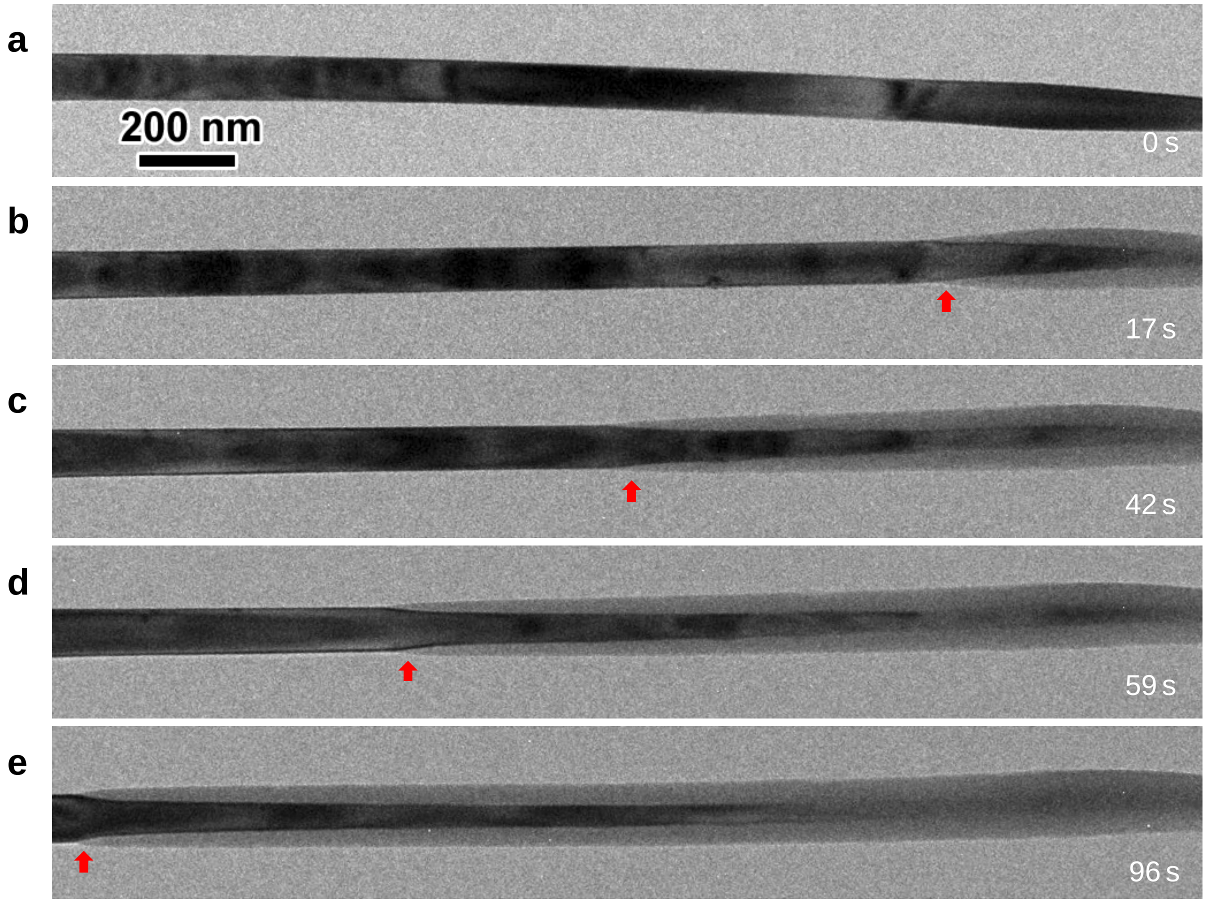

Figure S7. Core-shell lithiation behavior of Ge/Si core/shell nanowire after the removal of the surface Si shell. The reaction fronts are marked by the red arrow heads.

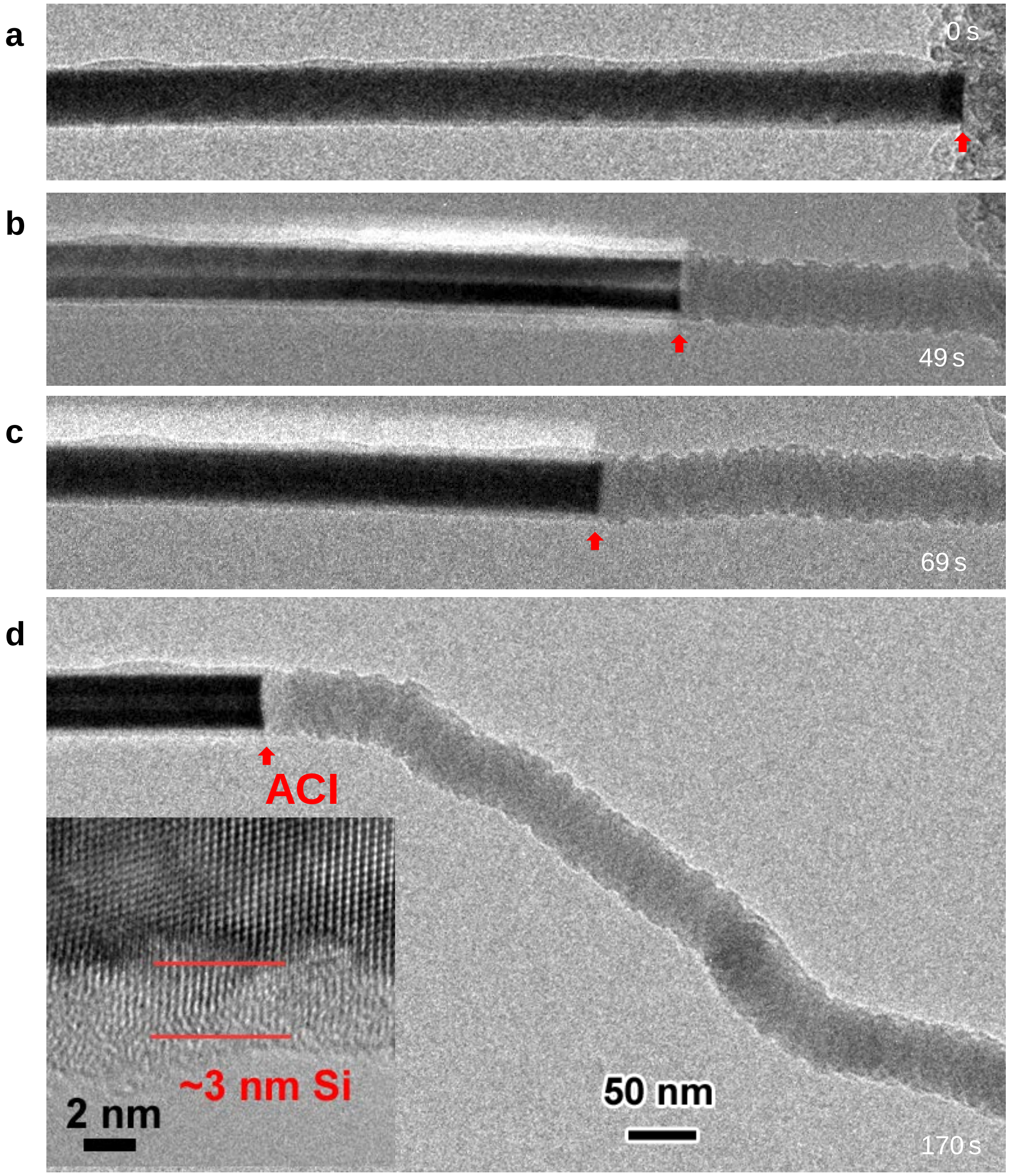

Figure S8. Axial lithiation behavior of a typical Ge/Si core/shell nanowire with a 3 nm thick Si shell. (a-d) Structure evolution of the nanowire upon lithiation, showing the axial lithiation behavior. The amorphous-crystalline interface (ACI), i.e. reaction fronts are perpendicular to the axial direction and are marked by red arrow heads. Insert image in (d) is a high resolution TEM image showing the surface 3 nm thick Si layer.

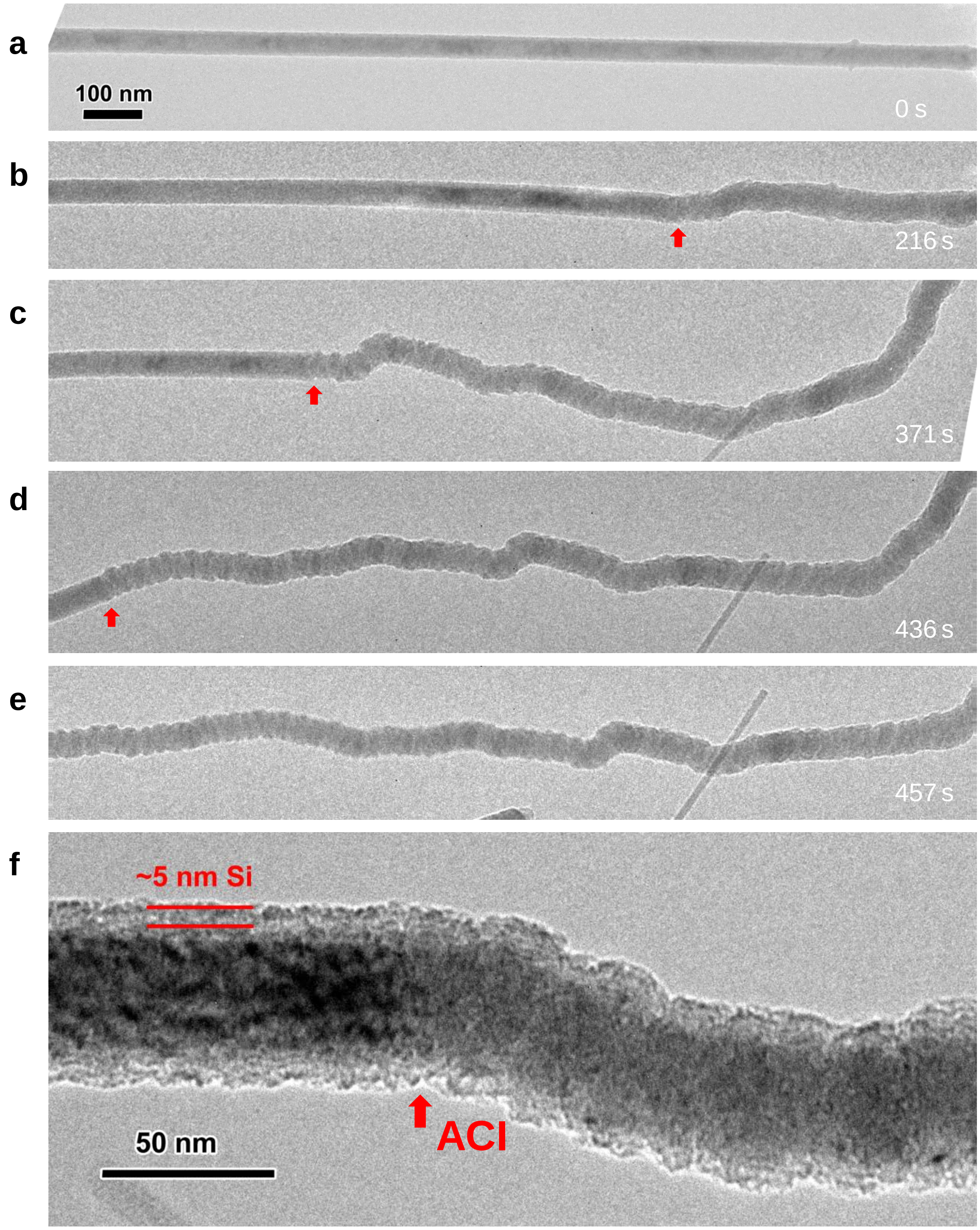

Figure S9. Axial lithiation behavior of a typical Ge/Si core/shell nanowire with a 5 nm thick Si shell. (a-e) Morphology evolution of the nanowire upon lithiation. The reaction fronts are perpendicular to the axial direction and are marked by red arrow heads, showing axial lithiation. (f) Close view of the reaction front area in lithiation. The ACI, i.e. reaction front, is marked by red arrow head.

Supporting Movies

Movie S1.

File name: nl4027549_si_002.mov

Lithiation of a pure Ge nanowire, showing the core-shell lithiation behavior. The movie was recorded at 2 frames/second and is played at 5x speed.

Movie S2

File name: nl4027549_si_003.mov

Lithiation of a Ge/Si core/shell nanowire, showing the axial lithiation behavior. The movie was recorded at 2 frames/second and is played at 20x speed.

Movie S3

File name: nl4027549_si_004.mov

Lithiation of a Ge/Si core/shell nanowire after the removal of surface Si shell showing the core-shell lithiation behavior. The movie was recorded at 2 frames/second and is played at 20x speed.

Movie S4

File name: nl4027549_si_005.mov

Lithiation of a Ge/Si core/shell nanowire with surface carbon coating showing the core-shell lithiation behavior. The movie was recorded at 2 frames/second and is played at 5x speed.