Supplementary Information

Revealing anisotropic lithiation control in silicon nanowires via a novel in situ TEM-based cross-sectional characterization method

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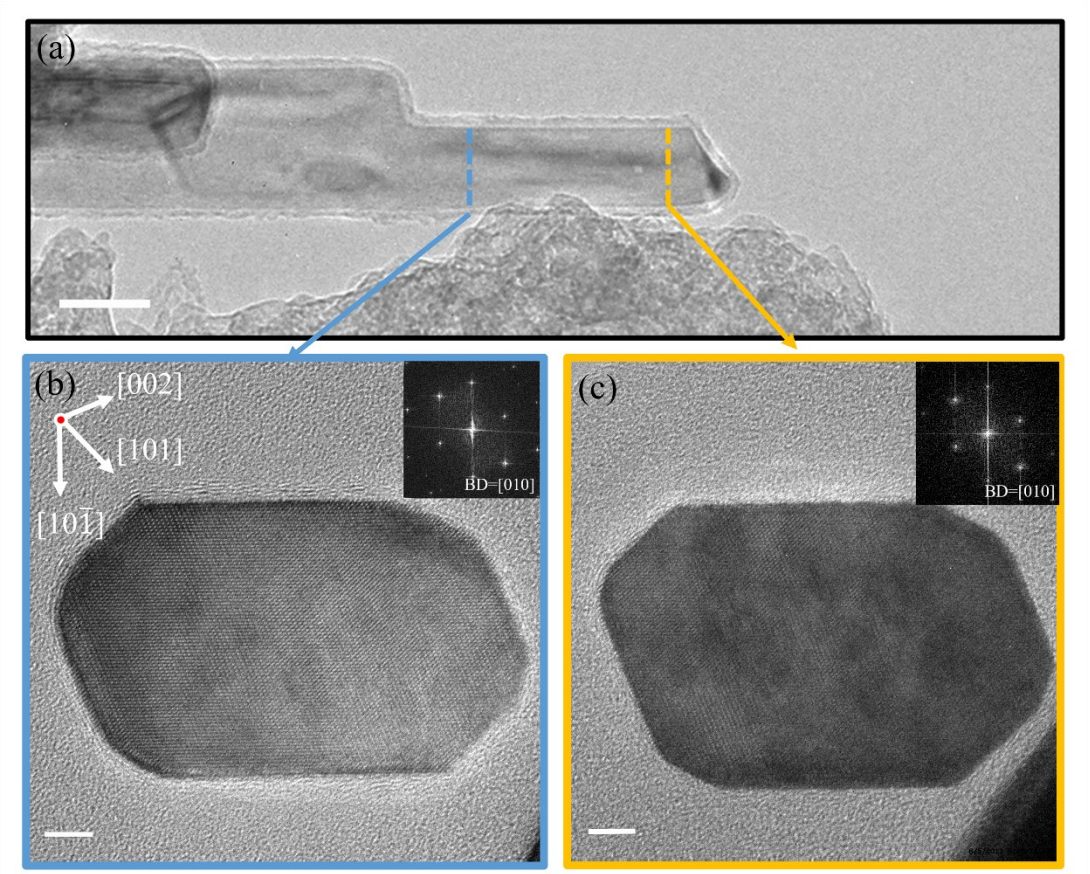

Fig. S1 Cross-sectional specimens obtained from various axial positions of a TiO_2 NW. (a) Side-view TEM image of a TiO_2 NW (scale bar, 20nm). (b-c) High-resolution TEM images showing cross-sections of the same TiO_2 NW in (a) at its middle (b) and front end (c), respectively (scale bar, 2 nm).

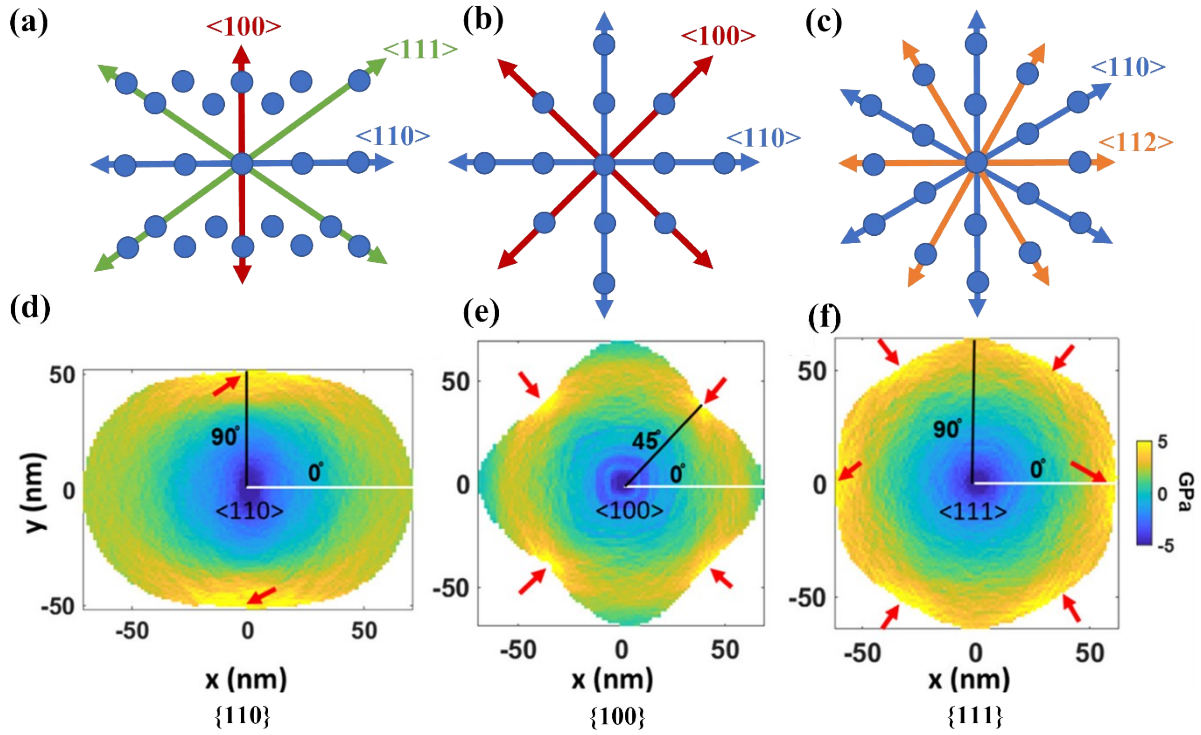

Fig. S2 Crystallographic symmetry and anisotropic lithiation of Si with different axial orientations. (a-c) Schematics of the atomic distributions on the {110}, {100}, and {111} crystal planes of Si. (d-f) Morphology and hoop-stress distribution in the lithiated Si nanopillars with axial orientations of <110>, <100>, and <111>. Reproduced with permission from ref. [1], Copyright 2021, American Chemical Society.

Fig. S2 compares the lithiation behavior in Si NWs with <110>, <100>, and <111> orientations. As shown in Fig. S2, the <110>-oriented Si NW exhibits <110>, <100>, and <111> directions on its cross-sectional plane, with <110> and <100> being perpendicular to each other. Due to the low symmetry of the lithiation direction distribution and the significantly faster lithiation rate along the <110> direction compared to the <100> and <111> directions, the cross-sectional shape of the <110>-oriented NW becomes elliptical, displaying pronounced anisotropic lithiation, with the radial expansion at 0° being markedly greater than that at 90°. In contrast, for the <100>-oriented Si NW, <100> and <110> are the main lithiation directions on the cross-sectional plane, and these directions are more symmetrically distributed. As a result, the anisotropic lithiation observed in the <100>-oriented NW is less significant than in the <110> oriented NW, with smaller differences in lithiation rates among directions. For the <111>-oriented Si NW, the primary in-plane lithiation directions are <112> and <110>. They form a sixfold symmetric pattern on the cross-sectional plane. This high symmetry leads to the weakest anisotropic lithiation. Overall, these simulation results further validate our observation that

higher in-plane symmetry can suppress anisotropic lithiation, promoting more uniform lithiation across the NWs.

However, we acknowledge that our previous conclusion may have been too strong. Lithiation uniformity depends not only on the degree of crystallographic symmetry but also on which specific low-index directions act as the main lithiation pathways and on the relative differences in lithiation rates among them. Therefore, the in-plane lithiation direction distribution needs to be coupled with the differences in lithiation rates along these directions to control the occurrence of anisotropic lithiation.

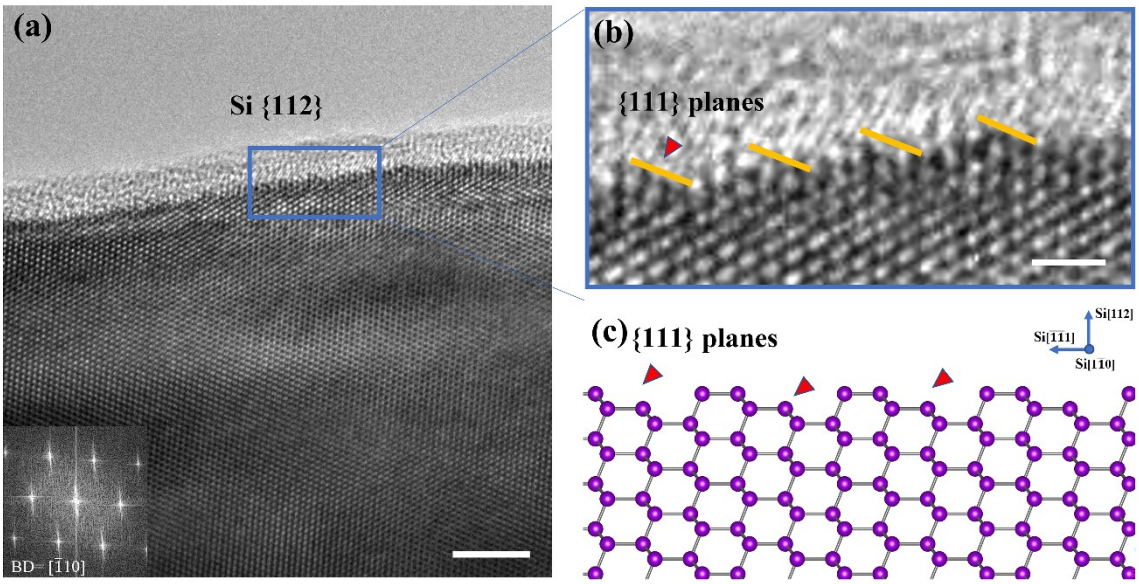

Fig. S3 Atomic-resolution characterization of the Si {112} surface. (a) High-resolution TEM image showing the {112} surface of the Si NW. Inset shows the corresponding fast Fourier transform pattern (scale bar, 5nm). (b) Magnified image of the marked region in (a), showing the exposed {111} lattice planes (scale bar, 1nm); (c) Atomic structure of the Si {112} surface.

Reference

[1] F. Shuang and K. E. Aifantis, *ACS Appl. Mater. Interfaces*, 2021, **13**, 21310–21319.