Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

For the manuscript entitled:

Strategies for Controlling Si Nanowire Formation during Au-assisted Electroless Etching

*Dae Ho Lee, Yongkwan Kim, Gregory S. Doerk, Ian Laboriante, Roya Maboudian**

Supporting Figures

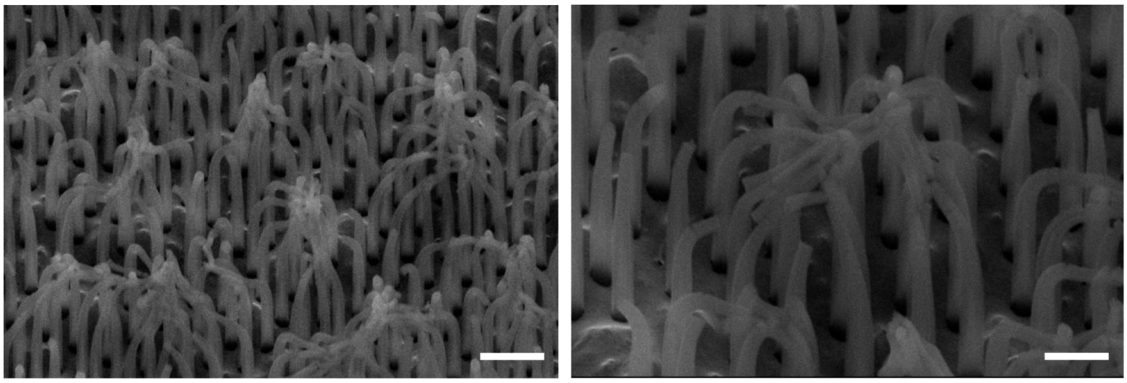

Fig. S1 Low (a) and high (b) magnification SEM images of SiNWs prepared in an etch solution with proportions $HF/H_2O_2/H_2O$ = 1.5/0.5/8.0 for 30 min. and dried with supercritical CO_2. (45° tilt view, (a) scale bar = 2 μm, (b) scale bar = 1 μm). It is evident from this figure that SiNW clumping is not from any capillary effect.

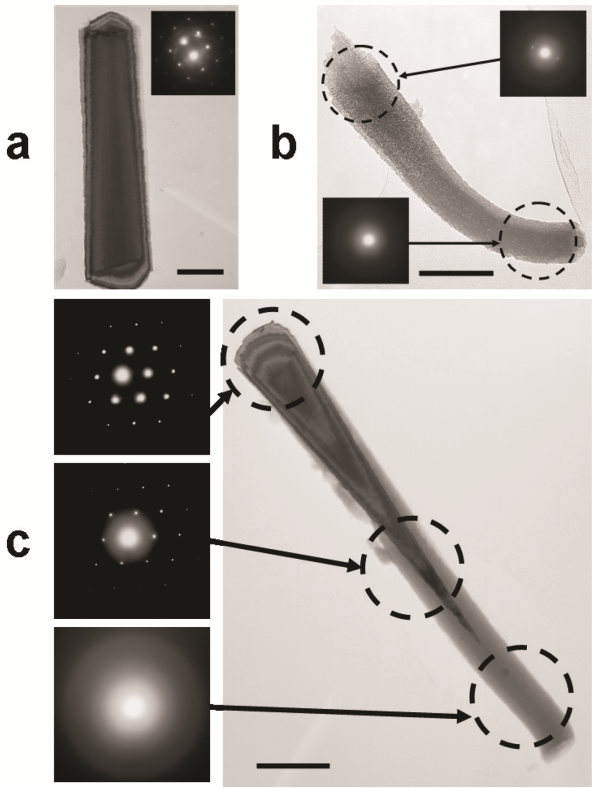

Fig. S2 TEM images of as-made SiNWs. (a) Straight SiNW (scale bar = 300 nm). Inset: Selected area diffraction (SAD) pattern from the center of this wire. (b) Hooked SiNW with SAD patterns (insets) taken from regions marked by dashed circles (scale bar = 300 nm). (c) Hooked SiNW with SAD

patterns (left) taken from regions marked by dashed circles (scale bar = 500 nm). The tapered shape of the high contrast single crystal region and the change in diffraction patterns from crystalline to amorphous from base to tip are indicative of a structural transformation towards a porous structure during the etching process.

Supplementary Discussion on the TEM result

To obtain a clearer understanding of the microstructural changes that take place during the etching process, transmission electron microscopy (TEM) images of straight SiNWs (Fig. 1a) and hooked SiNWs (Fig. 1b) are collected. Fig. S2a shows a TEM image of a straight SiNW viewed along a <001> zone axis with a corresponding selected area diffraction (SAD) pattern (inset). While this pattern is taken from the center of the wire, no changes are apparent in the SAD patterns taken from the top and bottom of the wire. The lines apparent in the diffraction pattern are Kikuchi lines, which are a consequence of the large thickness of the single crystal volume from which the pattern is obtained.[s1] The single crystal regions of the SiNW are clearly visible due to their much greater diffraction contrast when viewed along a primary zone axis as is the case here, making a minimal tapering of the crystalline region from base to tip naturally apparent. On the other hand, Fig. S2b shows a TEM image of the bent portion of a SiNW etched at a low HF/H_2O_2 ratio of 1.5/0.5. In the straight basal region, the SAD pattern is mostly a diffuse ring, although the presence of a few weak diffraction spots is indicative of some persistent crystallinity in this region. These spots are completely absent from the bent tip. The impact of etching conditions is most clear in Fig. S2c, which shows a TEM image of a SiNW just beginning to hook at the tip viewed along a <011> zone axis, with SAD patterns obtained at three points along the SiNW axis. High diffraction contrast marks the sharp single-crystal conical structure that is consistent with the oxidation and etching results shown in Fig. 2 as discussed in the main text. Furthermore, while the basal SAD pattern is representative of a predominantly single-crystal region as expected, the SAD pattern from the middle portion of the wire is characterized by a weaker spot pattern and a more diffuse zero order diffraction spot, and the SAD pattern from the top of the wire is an extremely diffuse ring pattern showing no evidence of crystalline character.

References and Notes

S1. D. B. Willliams, B. C. Carter, in *Transmission Electron Microscopy*, Springer, New York, 1996, p. 291.