Supporting Information

Non-Lithographic Formation of Three Dimensional Periodic Nanostructures by Germanium Nanowire Etching

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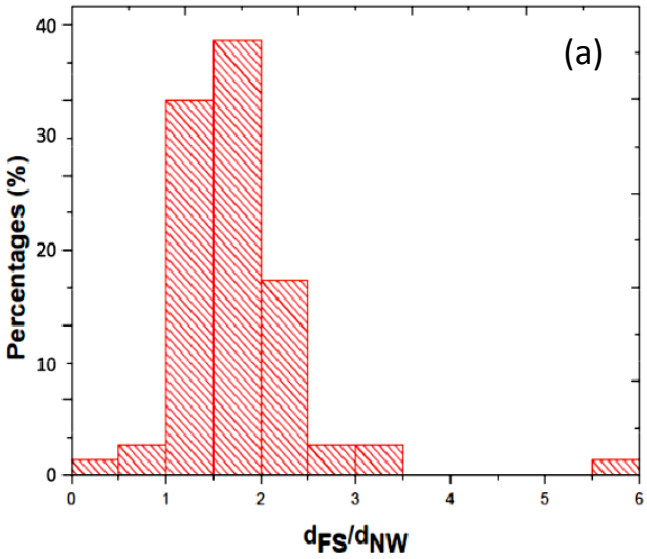
Materials and Methods

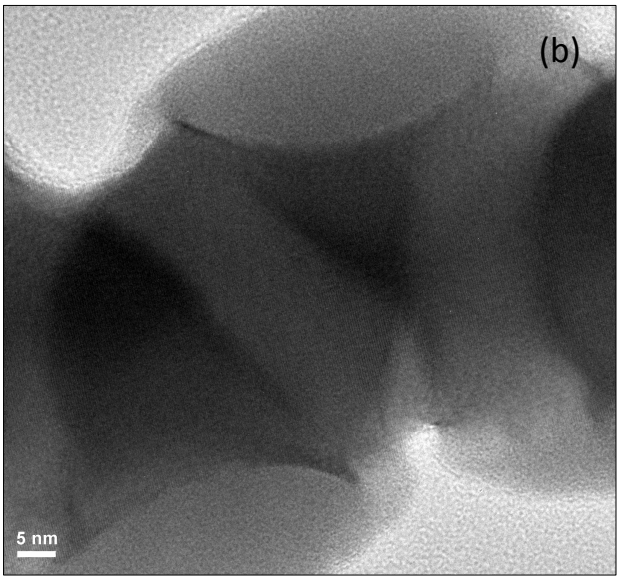
*Anodization***.** The germanium nanowires used in these experiments were grown using the vapor transport method as described previously.[1]Samples were grown on 5 × 15 mm gold-coated (100) Si wafers through a VLS approach; GeNWs were etched in a Pyrex electrolytic cell (Fig. S1). The substrate containing GeNWs was placed into the electrolyte vertically and served as anode. A 5×15 mm platinum foil as cathode was located 1 cm away from the anode in a parallel fashion. EthanolicHCl solutions (varying from 1:1 to 1:16 of 37.5% HCl:EtOH v/v) were used as the electrolyte. Anodization proceeded under a constant current or voltage. GeNWs were sonicated in acetone after etching and dispersed onto carbon-coated Cu grids for TEM characterization immediately to minimize surface oxidation of the etched nanostructures.

In selected experiments, a copper deposition step was added to the GeNW/substrate surface by applying cathodic bias to a saturated $Cu(NO_3)_2$, $CuSO_4$, or $CuCl_2$ solution before anodization; the magnitude of applied bias selected for a given experiment is identical to the magnitude of anodic bias in the subsequent HCl etching step.

Sample Characterization. Structural characterization was principally achieved by scanning electron microscopy (SEM, JEOL-6100) with an energy dispersive X-ray spectroscopy (EDX) system, high resolution transmission electron microscopy (HRTEM, JEOL-2100), and X-ray diffraction (XRD, Philips-3100). Visible photoluminescence (PL) spectroscopy was measured using a custom system with excitation via a CW Kimmon IK5452R-E HeCd laser at a wavelength of 325 nm. A variable frequency chopper was employed to provide a reference frequency. The samples were mounted inside an evacuated Janis CCS-150 cryostat having a temperature range between 8 and 325 K. The PL signal was probed by a Spex 1401 monochromator with a spectral resolution of 0.18 cm^{-1} and an RCA C31034 photomultiplier tube detector connected to a Stanford Research-830 lock-in amplifier for background noise reduction.

1. Wu, J., Coffer, J.L., Punchaipetch, P., Wallace, R.M. Adv. Mater.,**2004**,16, 1444-1448.





Supplemental Figure.(a) Relationship between periodic etched feature size (d_{FS}) and GeNW diameter; (b)HRTEM image of etched helical GeNWs; anodization conditions: 20 V, 20 s, followed by 4V, 5 min, 1:16 HCl:ethanol electrolyte. Cu passivation step: 1.3 mA/cm^2, 10 min; (c) PL of etched GeNWs, with a λ_{ex} = 325 nm at both room temperature and 8K; (d) SEM images after electrodeposition in saturated $Cu(NO_3)_2$ with 6.5 mA/cm^2 current density for 5min. (left) Si wafer edge (scale bar, 5 μm) and (right) central area (scale bar, 20 μm). Corresponding EDX spectra are given as insets.