Supporting information for:

Electrical Characteristics and Chemical Stability of Non-Oxidized, Methyl-Terminated Silicon Nanowires

Hossam Haick[†], Patrick T. Hurley[*], Allon I. Hochbaum[‡], Peidong Yang[*,‡,§], and Nathan S. Lewis[*,†]

Division of Chemistry and Chemical Engineering, California Institute of Technology, MC 127 72, 1200 E. California Blvd., Pasadena, CA 91125, Department of Chemistry, University of California, Berkeley, California 94720, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(I) Modification of Silicon nanowires (Si NWs)

Hydrogen-terminated Si NWs (H-Si NWs) were prepared by etching away the amorphous SiO_2 coating by exposing the Si NWs to buffered-HF for 60 s and then $NH_4F_{(aq)}$ for 30 s.

Methyl-terminated Si NWs (CH_3-Si NWs) were prepared by immersing H-terminated Si NWs into a saturated solution of PCl_5 in C_6H_5Cl that contained a few grains of $C_6H_5OOC_6H_5$ to act as a radical initiator. The reaction solution was heated to 90-100 °C for 5 min. Samples were then removed from the reaction solution and rinsed in tetrahydrofuran (THF) followed by a rinse in CH_3OH and were then dried under a stream of $N_2(g)$. Samples were occasionally also rinsed in 1,1,1-trichloroethane (TCE) before drying under $N_2(g)$. The chlorine-terminated Si NWs were alkylated by immersion in 0.2-0.5 M CH_3MgCl, in either diethyl ether or THF (Aldrich). The reaction was performed for 5-10 min at 70-80 °C. Excess THF was added to all reaction solutions for solvent replacement. At the end of the reaction time, samples were removed from the reaction solution and were then rinsed in THF, CH_3OH, and occasionally TCE. Samples were then dried under a stream of $N_2(g)$, and immersed in isopropanol solvent.

(II) Transmission Electron Microscopy (TEM) of the Studied Si NWs

Transmission electron microscopy (TEM) was performed using a Philips EM 430 (300 KV) with 2.3 Å point-to-point resolution. The samples of Si NWs were prepared by evaporating a drop of a dilute iso-propanol solution of the Si NWs onto an amorphous carbon-coated Cu TEM grid. TEM images of the Si NWs were obtained 15-60 min after synthesis/preparation.

Figures 1S (a) and (b) show the general morphology of the SiO_2-Si NWs used in this study. It can be seen from the images that the samples consist almost entirely of a smooth core and uniform sheath, with dimensions that changed from sample-to-sample. TEM images of several samples showed that the core diameter of SiO_2-Si NWs ranged between 57 and 67 nm, with average value of 62 nm, and that the SiO_2 sheath thickness ranged between 6 and 12 nm, with average value of 9 nm. Energy dispersive spectroscopy (EDS) on a sheath of single SiO_2-Si NWs showed a high concentration of oxygen, a finding that is attributed a layer of SiO_2. The length of the Si NWs (not shown) was found to be between 4 and 11 μm, with an average value of 7 μm.

Figure 1S. TEM micrograph of (a) central segment of SiO_2-Si NW, (b) edge segment of SiO_2-Si NW, (c) H-Si NW, and (d) CH_3-Si NW. TEM micrographs of several SiNWs from each type and from different batches were collected to obtain statistics on the diameter distribution of the various SiNWs.

TEM images of freshly-prepared H-Si NWs (Figure 1S (c)) showed similar diameters to that of SiO_2-Si NW cores, but with undetectable amounts of oxide. The outer surface of the H-Si NWs was almost uniform and had a low-concentration of defects. For CH_3-Si NWs, the TEM images (cf. Figure 1S (d)) showed similar features to that of H-Si NWs, with only one difference: the outer surface of CH_3-Si NWs was less smooth.

* Division of Chemistry and Chemical Engineering, Caltech.
‡ Department of Chemistry, University of California – Berkeley.
† Materials Science Division, LBNL, Berkeley.

(III) Electrical Measurements

Devices were fabricated by integrating an individual Si NW with four Al electrodes (each with 5.0±0.1 μm in length and 400±20 nm in width) that were mutually separated by 800±50 nm, on top of a 300 nm thermally oxidized degenerately doped p-Si (0.001 Ω cm^{-1}) substrate, using e-beam lithography and lift-off techniques. For characterizing Si NWs using probe station, each of such four electrodes was integrated with Al pad (2 mm × 2 mm). The mutual separation between the pads was 3 mm.

To assess the electrical characteristics of the various Si NWs, voltage-dependent back-gate measurements were performed. In these measurements, voltages between -5 and +5 V, in steps of 1 V, were applied to the degeneratively doped silicon substrate. For each gate voltage, the current-voltage (*I-V*) characteristics were measured between the inner two Al electrodes, i.e., between the drain (*d*) and source (*s*), contacted by a micromanipulator (Karl Suss), at a bias range between -1.5 and +1.5 V, in steps of 10 mV, under ambient conditions. To probe for possible hysteresis in the electrical properties of Si NWs, the *I-V* scans were carried out in a "sweep" manner. More specifically, the *I-V* measurements were carried out starting from -1.5 V upward to +1.5 V (designated as a forward scan), in steps of 10 mV, and, successively, from +1.5 V downward to -1.5 V (designated as a backward scan), in steps of 10 mV. For all *I-V* measurements, a 16-bit digital acquisition board (DAQ) (National Instruments) was used for the voltage source. Currents were measured using an EG&G Brookdeal preamplifier model 5006, and the output voltage of the preamplifier was measured using either an analog-to-digital input on the BNC 2090 board or with a Keithley 230 programmable voltage source.

At a given gate voltage, V_g, the total resistance of Si NW-based device, $[R_{sd}]_{V_g}$, measured by two-probe methods, includes: the resistance of the Si NW core, R_{wire}, and the contact resistance (R_c) between the Si NW and the Al electrodes at the source, R_{cs}, and at the drain, R_{cd}. Assuming $R_{cs} = R_{cd} = R_c$, the following relation is obtained:

$$[R_{sd}]_{V_g} = R_{wire} + 2R_c \qquad (1)$$

To determine the contact resistance between the Si NW and Al electrodes, four-point probe transport measurements were carried out, at bias range between -1.5 and +1.5 V, in steps of 10 mV, with the two inner electrodes serving as voltage probes and the two outer electrodes serving as current probes. The resistance of the central Si NW (core) segment, R_{wire}, was calculated by dividing the voltage by the current. The two inner electrodes were also used to measure the current vs voltage relationship (two-point probe measurements), which provided the total resistances of the central segment of Si NW and the Al-Si NW contacts. The relation between the resistance measured by two-probe ($R_{2\text{-}probe}$), four-probe ($R_{4\text{-}probe}$), and Al-Si NW contact resistance (R_c) is given by:

$$R_{2\text{-}probe} = R_{4\text{-}probe} + 2R_c = R_{wire} + 2R_c \qquad (2)$$

At a given gate voltage, the relationship between the extrinsic conductance, g_{ex}, measured in the gate-dependent measurements, and the intrinsic conductance, g_{in}, determined by the four-probe measurements, is:

$$g_{ex} = \frac{g_{in}}{1 + g_{in}R_c + 2R_c / R_{wire}} \qquad (3)$$

In voltage-dependent back-gate measurements, g_{in} is defined as:

$$g_{in} = \frac{\partial I_d}{\partial V_g} = \mu_h C_g V_{sd} / L^2 \qquad (4)$$

where I_d is the measured current in the drain, taking into account the contact resistance between Si NW and Al, V_g is the gate voltage, μ_h is the hole mobility, L is the channel length (800 ± 50 nm in our devices), V_{sd} is the voltage applied between the source and drain, and C_g is the device capacitance, given by:

$$\frac{C_g}{L} = \frac{2\pi\varepsilon\varepsilon_o}{ln(2h/r)} \qquad (5)$$

where, r is the (external) radius of the Si NW (r = 71±8 nm for SiO_2-Si NWs, and r = 62 ± 5 nm for H-Si NW and CH_3-Si NW), h is the thickness of the oxide layer of the gate (300 ± 5 nm in our devices), ε is the permittivity of the SiO_2 layer of the substrate (= 3.7), and ε_o is the vacuum permittivity (= 8.85148×10^{14} F cm^{-2})

The electrical measurements for the various devices were performed as a function of exposure time to air after 1 h, 2 h, 3 h, 1 day (= 24 h), 1 week (=168 h), 2 weeks (= 336 h), and 4 weeks (=672 h). At each point of time, two- and four point probe, and voltage-dependent back-gate measurements were performed.

(IV) Two- and Four-Point Probe Measurements

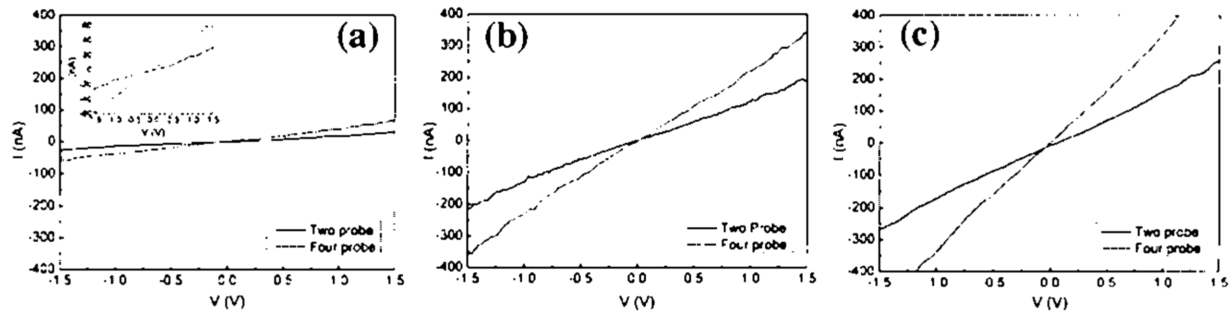

Figure 2S. Current-voltage (I-V) characteristics measured by two- and four-probes at forward scan, at bias regions between -1.5 V and +1.5 V, for (a) SiO_2-Si NWs, (b) H-Si NWs, and (c) CH_3-Si NWs. The y-scales of the various three graphs are identical. *Inset of SiO_2-Si NW graph:* magnification of the main plot between -60 nA and +60 nA.