

## Supporting Information

### Appendix A: Metallic Catalyst Removal Procedure

The Si microwires were grown on (111)-oriented Si substrates by a chemical-vapor-deposition, vapor–liquid–solid (VLS) growth process.<sup>13,20,48</sup> For most samples, the Cu VLS catalyst was removed from the top and sidewalls of the microwires by chemical etching. After growth a slow cool down procedure was performed, diffusing the metallic catalyst from the Si. The etch procedure for removing the catalyst and for etching off the SiO<sub>2</sub> that resulted from the catalyst removal was:

- 10 s, 10% aq. HF
- RCA2 etch: 20 min, DI water:HCl:H<sub>2</sub>O<sub>2</sub> (7:1:1, v/v/v)
- 10 s, 10% aq. HF
- RCA2 etch: 20 min, DI water:HCl:H<sub>2</sub>O<sub>2</sub> (7:1:1, v/v/v)
- 10 s, 10% aq. HF
- 1 min, 30 wt.% aq. KOH
- 10 s, 10% aq. HF

After each step, the microwires were rinsed thoroughly with DI water and were dried under a stream of N<sub>2</sub>(g). An RCA2 etch was used to remove the metallic catalyst. The KOH(aq.) removed Cu impurities at the Si surface. The diluted HF(aq.) was used to remove the native oxide as well as any oxides that formed during the catalyst removal process.

## **Appendix B: Microwire Methylation Procedure**

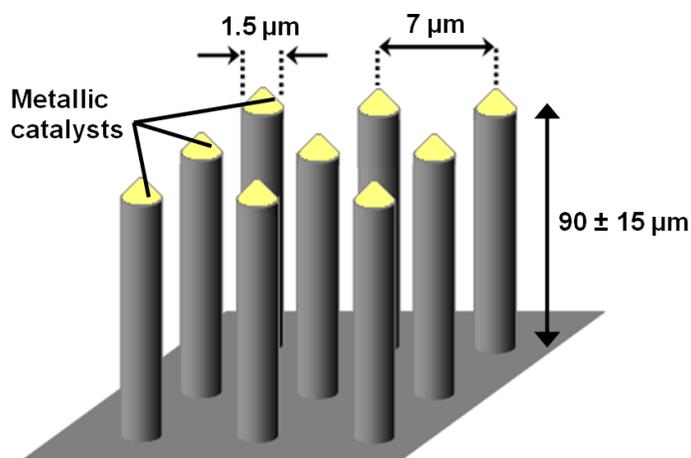
Following the methylation procedure that has been reported for planar Si,<sup>27</sup> the microwires were first etched in 10% aq. HF to remove the native oxide. Samples were then placed into a N<sub>2</sub>(g)-purged flushbox. Using a saturated solution of PCl<sub>5</sub> in chlorobenzene, the microwires were chlorinated at 90 °C for 45 min. The microwires were then rinsed and placed in a 1.0 M methyl Grignard (CH<sub>3</sub>MgBr) solution for between 1 h and 1 day at 60 °C.

## **Appendix C: Preparation of Conducting Polymer Films**

PEDOT:PSS was purchased from Clevios as an aqueous solution. To prepare 12 wt.% PEDOT:PSS:Nafion, 1250 mL of Nafion solution (from Sigma-Aldrich, 10 wt.% dispersion in water) and 750 mL PEDOT:PSS were mixed for 2-5 min on a vortex mixer. The solution was then spin coated on the target substrate at 2000 rpm for 20 s. The films were allowed to dry for 6–8 h and then annealed for 1 h at 100–150 °C.

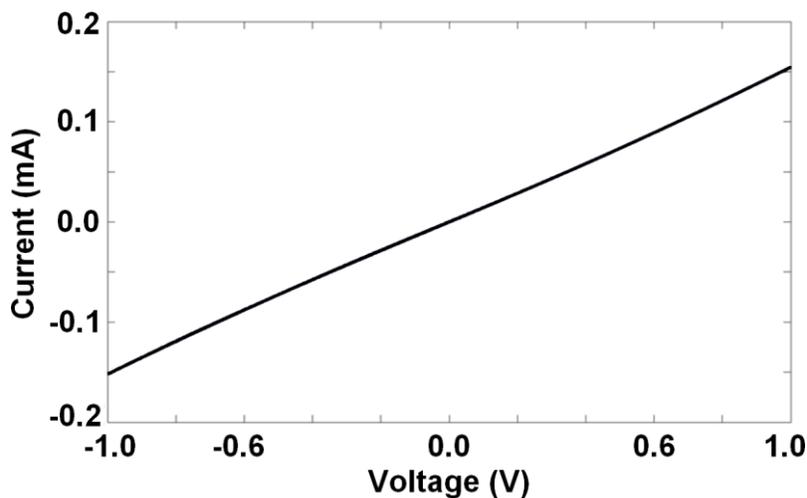
## **Appendix D: Formation of Microwire / Polymer Junctions**

After removal of the metallic catalyst (Figure D.1) and native oxide (appendix A), a corner of the Si substrate was scraped using a razor blade, to remove a small portion of the microwires which were then suspended in isopropanol or acetonitrile. Single-microwire measurements were performed by deposition of this solution (~10 µL) onto an insulating substrate (e.g. glass). Direct contacts to the individual microwires were formed by use of tungsten probes in a probe station.



**Figure D.1:** Schematic diagram of a microwire array. The average diameter of the microwires is  $1.5 \mu\text{m}$  and the array pitch size is approximately  $7 \mu\text{m}$ . The length of the microwires is  $90 \pm 15 \mu\text{m}$ . The VLS grown catalyst metallic caps are shown in yellow.

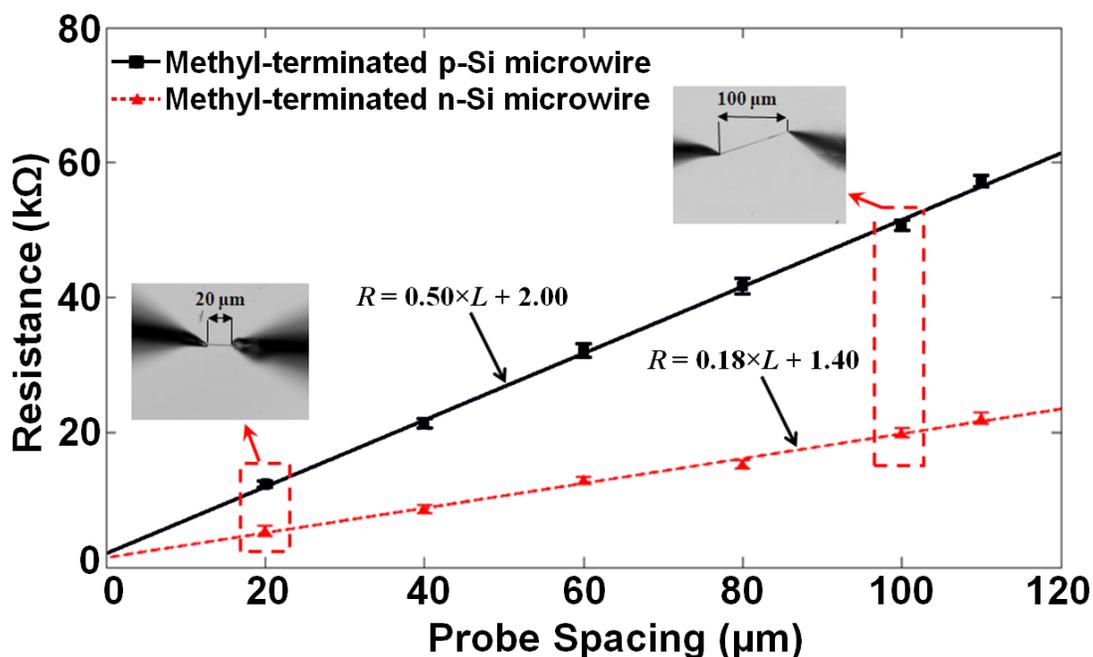
The W probes were etched using KOH(aq.), to remove tungsten native oxide and to improve the quality of the contacts. An ohmic contact to the conductive polymer was formed by sputtering Au directly on the polymer. The  $I$ - $V$  profile for the Au contacts to the conducting polymer is shown in Figure D.2.



**Figure D.2:** Two-electrode measurements of the current-voltage response between two 32 nm thick Au pads and intervening conducting polymer films coated on a glass substrate.

## Appendix E: Use of the Resistance vs. Tungsten Probe Spacing to Estimate the Doping Concentration of Methyl-Terminated Si Microwires

Figure E.1 depicts the resistance vs. probe separation data obtained for methyl-terminated p-type and n-type Si microwires. Each data point is the average of seven independent measurements in which the probe was completely disconnected from the microwire before the contact for the next measurement was made. The resistance per unit length was constant for all of the measurements, having values of  $0.50 \text{ k}\Omega\cdot\mu\text{m}^{-1}$  for the p-type and  $0.18 \text{ k}\Omega\cdot\mu\text{m}^{-1}$  for the n-type Si microwires. The contact resistance was calculated by performing a linear fit to the resistance versus probe separation data, in conjunction with the evaluation of the intercept of the plot (Figure E.1).



**Figure E.1:** Contact resistance measurements for methyl-terminated ( $\text{CH}_3$ -terminated) p- and n-type Si microwires with  $\sim 1.5 \mu\text{m}$  diameter. Seven independent measurements were performed for each selected point across the length of the microwire. These measurements were repeated with other microwires of different doping type, different doping concentration, and originating from different fabrication batches. Observation of the expected trends confirmed the validity of the measurement.

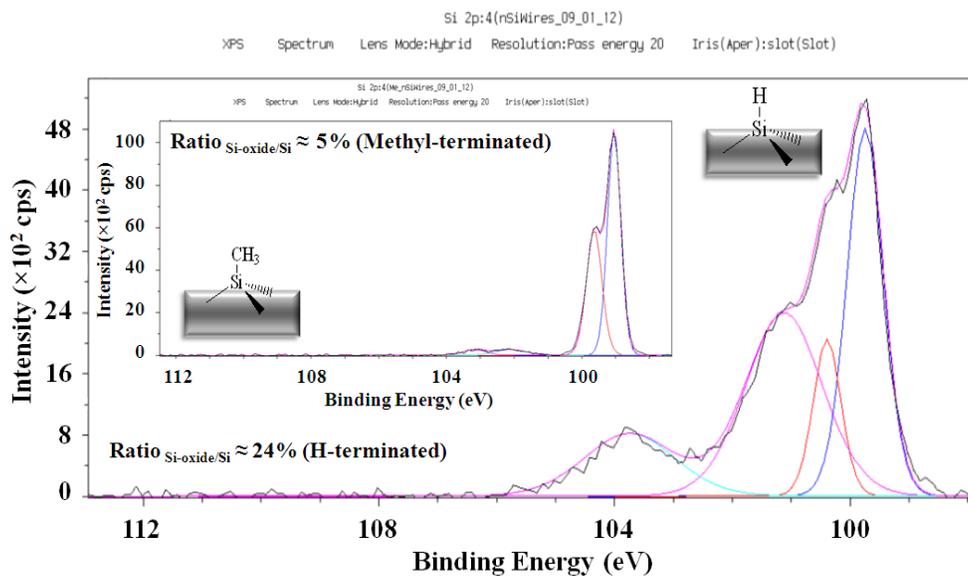
The calculated contact resistance values (i.e. y intercepts) were reasonably similar for both doping types of Si microwires. Although the data analysis confirmed that the contact resistance was a negligible contribution to the total measured resistance, the contact resistance was still subtracted prior to calculating the resistivity of the microwires and, in turn, prior to estimation of the doping concentration of the microwires. The range of microwire doping concentrations was calculated to be  $10^{17}$ – $10^{18}$  cm<sup>-3</sup>, and no detectable variation in the resistance measurements was observed between different regions of the microwires or between different microwires, suggesting that the p- and n-type doping concentration was uniform over the length scales considered<sup>14,47</sup>.

## **Appendix F: Comparative XPS Analysis of H-Terminated and CH<sub>3</sub>-Terminated Microwires vs. Time**

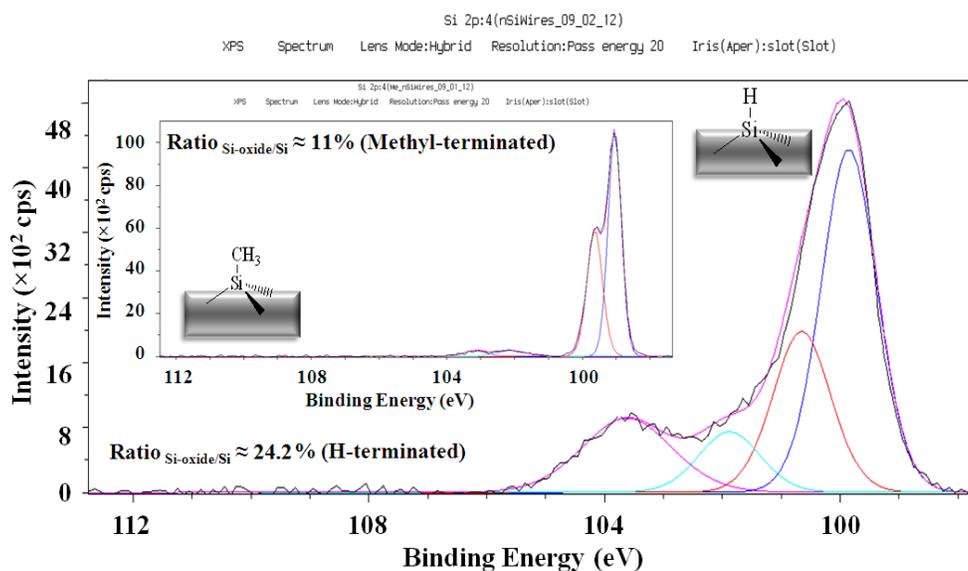
Figure F.1 shows the initial XPS analysis results on H-terminated and CH<sub>3</sub>-terminated n-Si microwire samples. To collect these data, a large amount of microwires (760 μg) were scraped from the growth substrate and placed onto a Au-coated substrate. H-terminated Si microwires were freshly etched and then mounted in the XPS chamber (day 1). Methyl-terminated microwires were also collected from a recently methylated batch of Si microwires. Both samples were kept under lab conditions for 1 month, and then subjected to the XPS analysis again. The relative amount of oxidized Si was determined from the ratio of the area fitted to the ~103 eV (oxidized Si) and the ~99 eV (neutral Si) peaks. Although the H-terminated wires were etched before the measurements, the time interval between the etch and mounting the samples into the XPS chamber was long enough for the native oxide to form. The oxide ratio for the case of H-terminated microwires remained roughly constant over the course of a month indicating the presence of this saturated native oxide layer. The unchanged ratio for H-terminated samples

(~24%) following a one-month period contrasts greatly with the changed ratio recorded for the methyl-terminated samples (from ~5% initially to ~11% after one month). This clearly indicated that methylation improved oxidative stability.

The oxide observed for methyl-terminated Si samples was attributed to imperfect surface methylation and/or to oxide formation at the backside of the microwires, where the wires had been mechanically removed from the growth substrate.



(a)



(b)

**Figure F.1:** XPS analyses for H-terminated and CH<sub>3</sub>-terminated n-Si microwire samples in the Si 2p region; (a) at day 1 and (b) after one month. A higher rate of oxide growth was observed for H-terminated samples compared to CH<sub>3</sub>-terminated samples. The oxide observed on methyl-terminated samples was attributed to the backside of the microwires, where the samples had been removed from the growth substrate.