Supporting Information

High Aspect Ratio Silicon Wire Array Photoelectrochemical Cells

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Fabrication of Wire Array Samples and Controls

Degenerately doped N-type Si(111) wafers (0.004 ohm-cm) were thermally oxided to produce a 285 nm oxide film. These wafers were then coated with S1813 photoresist (Microchem), exposed to the pattern (square array of 3 μm holes, 7 μm center to center), and developed in MF319 (Microchem). The wafers were then etched for 4 min in buffered-HF improved (Transene) (CAUTION: *fluoride-containing solutions such as 11 M (40% by weight) NH_4F, buffered HF, and 27 M (48% by weight) HF pose a serious contact hazard. Hydrofluoric acid is highly toxic and corrosive and may cause serious burns which may not be immediately painful or visible. Fluoride ions readily penetrate the skin and can cause destruction of deep tissue and bone)*, followed by thermal evaporation of 500 nm gold and lift-off of the photoresist, to leave the catalyst islands separated by an oxide buffer. The samples were then brought into a tube furnace at 1050 °C and annealed in H_2 for 20 min at a flow rate of 1000 sccm. The wires were subsequently grown for 20 min in a mixture of H_2 (1000 sccm) and $SiCl_4$ (20 sccm). Control samples consisted of oxidized wafers that contained patterned openings in the oxide, but no gold was deposited, and wires were not grown on such samples.

Photoelectrochemical Measurements

Following growth, the wire array samples were etched for 10 s in 10% HF(aq) to remove the native oxide. The samples were then soaked for 10 min in TFA solution (Transene), which contains I^-/I_3^-, to etch away the gold particles. SEM images confirmed removal of the bulk of the Au catalyst particle, although a hollow shell of material appeared to remain (See Figure 1A). The wire array samples were subsequently dipped in 1 M HCl(aq) and rinsed with H_2O. The samples were then etched for 10 s in 10% HF(aq) to remove native oxide, rinsed with H_2O, and dried under a stream of N_2. Ga/In was immediately rubbed onto the back of the sample, and the samples were attached to a wire coil using silver paint. The samples were then sealed inside a glass tube, leaving ~ 2 mm^2 of exposed front surface area, using 20-3004 LV epoxy (Epoxies, Etc.) to coat the front face and sealing the rest of the sample with Hysol 1C epoxy (Loctite). Control samples were prepared similarly.

The photoelectrochemical measurements were performed in a solution consisting of 200 mM of dimethylferrocene (Me_2Fc), 0.5 mM of Me_2FcBF_4, and 1 M of $LiClO_4$ in methanol. Methanol was clearly observed to wet the wire array surfaces during both processing and photoelectrochemical measurements. The working electrode was either a wire array sample or a control sample. The counter electrode was a Pt mesh, and the reference electrode was a Pt wire enclosed in a Luggin capillary that contained the same solution as the main cell. All cell components were assembled under an inert atmosphere and were sealed before being placed under positive pressure of Ar. During measurements, the cell was illuminated using a 300 W ELH-type projector bulb. The light intensity was calibrated using a Si photodiode to produce a photocurrent equivalent to that obtained under 100 mW cm^{-2} of AM1.5 illumination at the working electrode

surface. The solution was stirred vigorously during measurement, and a stream of air was used to keep the cell temperature constant under illumination.

Photoelectrochemical measurements were conducted using a Solartron 1287 potentiostat and the CoreWare software. To measure the open-circuit voltage in the light, the open-circuit potential was first allowed to equilibrate in the dark (always to within 10 mV of 0 V). The light was then switched on and the sample was allowed to equilibrate in the light. The reported V_{oc} is the difference between the potential in the dark and the potential in the light. *J-V* data were then recorded in the light at a scan rate of 10 mV s^{-1}. The short-circuit photocurrent densities were recorded as the current density measured at a bias of 0 V vs the Nernstian potential of the cell. The electrode area used to calculate the current density was measured using a flatbed scanner. Averages shown are for six wire array samples and four control samples, with the indicated error equal to the standard error of the mean.

Single Wire Measurements

The as-grown wires were removed from the growth substrate by sonication in isopropanol, and were then spin-coated onto a degenerately doped (n-type) silicon wafer that was covered with 100 nm of Si_3N_4. The substrate was then coated with lift-off resist (LOR3A, Microchem), followed by photoresist (S1813, Microchem). The electrodes were aligned to the wire samples using a Suss MA-6 mask aligner. Following pattern development, the wire samples were etched for 20 s in buffered HF(aq) to remove the native oxide, and 300 nm of Al, followed by 800 nm Ag, was then thermally evaporated onto the sample. The contacts were subsequently annealed at 250 °C for 30 min in

forming gas (90% N_2, 10% H_2). An example device is shown in the inset of Figure S2. Ohmic behavior was observed for the annealed Al contacts, and the resistivity was calculated based on the probe spacing and wire diameter (as determined by SEM). To determine the carrier type, the conductivity of the sample was measured at various back gate bias potentials between -60 V and 60 V. The samples were found to be n-type, based on the increase in conductivity with increasing gate bias.

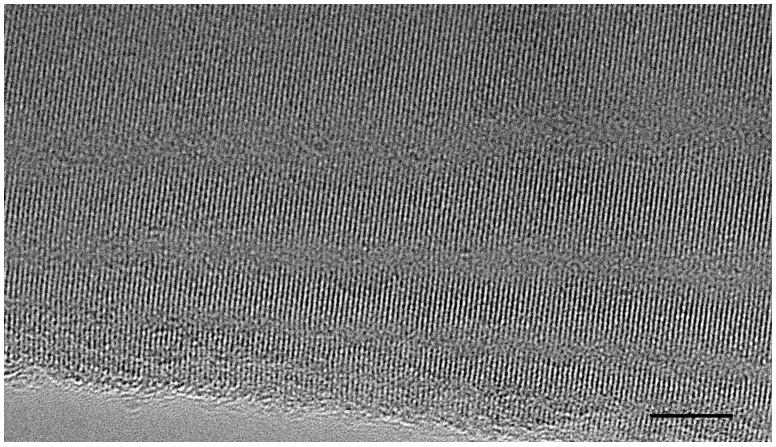

Figure S1 – TEM image of a Au-catalyzed, $SiCl_4$-grown, nanowire. The scale bar is 5 nm. The vertical lines are lattice fringes; the horizontal bands are due to the curved surface of the wire causing interference fringes. No crystal defects were observed by TEM in the wires. A lattice spacing of 0.307 ± 0.004 nm is inferred from these images. This lattice spacing, combined with the fact that the wires grew as single crystals normal to a Si(111) wafer, is consistent with the growth being in the <111> direction (the Si (111) lattice parameter is ~0.314 nm).

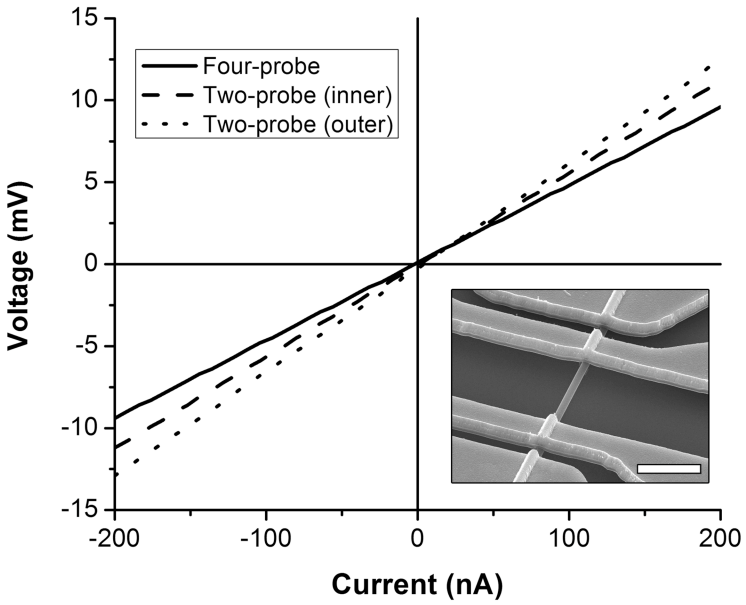

Figure S2 - Typical *I-V* measurement for an individually contacted wire using the four-point probe technique. The wire resistance was 50 kΩ for this sample, corresponding to a doping level of 2.9×10^{16} cm^{-3}, assuming the same carrier mobility as in bulk Si. Inset: a SEM image of a four-point probe measurement device, viewed at 45°. The scale bar is 6 μm.