Supporting Online Material for


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Materials and Methods
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Growth of p-Si Microwire Arrays: Si microwires arrays were grown as described by Kayes et al. The substrates were boron-doped p+ -Si (111) wafers, having a resistivity, ρ < 0.001 Ω cm, that were coated with 300 nm of thermal oxide (Silicon Quest International). Arrays of 3-μm-diameter circular holes, on a square lattice with a 7 μm pitch, were defined in the oxide by photolithographic exposure of a mask on a photosresist layer (Microchem S1813) followed by a buffered HF(aq) etch. The holes were then filled with 300 nm of copper (ESPI metals, 6N) via thermal evaporation onto the patterned photoresist, followed by a subsequent liftoff.

Patterned substrates approximately 1.5 × 1.5 cm in dimension were then annealed in a tube furnace for 20 min at 1000 °C under H2 flowing at a rate of 500 sccm. Wire growth was performed by the introduction of SiCl4 (Strem, 99.99+%), BCl3 (Matheson, 0.25% in H2), and H2 (Matheson, research grade) at flow rates of 10, 1.0, and 500 sccm, respectively, for 20-30 min. Following growth, the tube was purged with N2(g) at 200 sccm and was allowed cool to ~650 °C over the course of ~30 min. This relatively slow cooling step improved the photoelectrochemical performance of the resulting wire arrays.

Characterization of Microwire Arrays. The resistivity of selected wires was measured by standard single-wire 4-point probe methods, using contacts made from sputtered Al having 1% Si (see supplementary reference 2 for details on methodology). Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4100 microscope operating at 30 keV.

Device Fabrication. Si wire arrays (as-grown on the template wafer) were cleaved into square ~ 0.5 cm × 0.5 cm pieces. Contacts to the wire-array chip were made by rubbing Ga-In
eutectic on the back side of the chip, followed by attachment of a coiled tin-copper wire using conductive silver paint. The wire arrays were then sealed face down at the end of glass tubing through which the wire had previously been fed using Hysol 1C epoxy. Black nail polish was used to define the active area of the wire-array device (~0.1 cm²). Prior to photoelectrochemical measurements, the p-Si wire arrays were etched as follows: 10 s 10 % aq. HF, 30 min 30 wt. % aq. FeCl₃, 10 s 10 % aq. HF, 1 min 20 wt. % aq. KOH, and 10 s 10 % aq. HF. After each step, the wires were rinsed thoroughly with 18.3 MΩ cm resistivity H₂O, and dried under a stream of N₂(g). This sequence of etching removed the copper catalyst, the outer ~50 nm of Si, and the native oxide, without significantly etching the patterned thermal oxide that surrounded the bases of the wires, as was confirmed using SEM imaging.

**Photoelectrochemical Measurements.** A custom, flat-bottomed, Ar-purged, glass cell was fitted with the face-down wire-array electrode, a calibrated Si photodiode (UDT UV-005) held at the same vertical position as the wire-array electrode, a large carbon cloth electrode, a small carbon cloth reference electrode (poised at the solution potential), a standard calomel reference electrode (SCE), a Pt-mesh counter electrode separated from the main cell compartment by a medium porosity glass frit, and a stir bar (see Fig. 2 of the main text). The cell was filled with ~ 50 mL of electrolyte that contained 0.5 M K₂SO₄ and 0.050 M methyl viologen dichloride (MV²⁺, Aldrich, 98%), and was buffered at pH = 2.9 using 0.1 M potassium hydrogen phthalate and sulfuric acid. Prior to photoelectrochemical measurements, the Nernst potential of the solution was driven to -0.6 V vs. SCE using the large carbon cloth electrode as a working electrode and the frit-separated Pt mesh as a counter electrode. The electrolyte turned deep blue, due to the formation of the MV⁺ radical cation at a concentration of ~ 3 mM. Oxygen, which reacts with MV⁺, was excluded by purging the cell with H₂O-saturated Ar. The stir bar was situated directly next to the Si wire sample, and was rotated at the maximum speed possible without causing excessive vortexing of the electrolyte solution. Stirring was accomplished by an external bar magnet attached to an electric motor (NWSL 12270-9) that was controlled by a DC power supply (Rail Power 1370). Efficient stirring was critical to minimize mass-transport effects.

Current-potential data for the Si wire-array and planar Si photocathodes were collected as a function of illumination intensity in a three-electrode configuration using a Princeton Applied
Research (PAR) Model 273 potentiostat. The working electrode was the p-Si wire-array sample, the large carbon cloth was the counter electrode, and the reference electrode was the small carbon cloth that was poised at the solution potential (-0.6 V vs. SCE) and placed near the working electrode. A 1-W, 808-nm diode laser (Thor Labs L808P1WJ) was used as the illumination source to minimize the optical absorption by the solution. Photoelectrochemical data are compared at an incident 808-nm light intensity of 60 mW cm$^{-2}$, because the maximum short-circuit current density obtainable (39 mA cm$^{-2}$) under such conditions is similar to the maximum short-circuit current density obtainable for Si under 100 mW cm$^{-2}$ of air mass 1.5 (AM 1.5) solar illumination (43 mA cm$^{-2}$).

Control samples consisted of Czochralski-grown (111)-oriented single crystalline p-Si wafers ($\rho = 0.7 \, \Omega \, \text{cm}$), and a wire-array sample in which the wires had been physically removed from the substrate. These samples were prepared and etched using a nominally identical procedure to that described for the wire-array samples.

The current-potential data for both the wire-array and planar-control samples were recorded as a function of light intensity (Fig. 3). In both cases, $\Phi_{\text{ext}}$ measured at short circuit decreased with increasing light intensity, with the wire-array devices affected more than the planar ones. This observation suggested that mass-transport of the MV$^{2+}$/MV$^+$ couple was affecting the measured current-potential behavior at higher light intensities. This effect was not due to depletion of MV$^{2+}$ near the p-Si surface, because use of higher MV$^{2+}$ concentrations (i.e., 0.1 M) did not improve $\Phi_{\text{ext}}$. We believe that the large concentrations of MV$^+$ radical cation generated at the p-Si surface (compared to the bulk solution of ~3 mM) absorb a larger fraction of the incoming light if not effectively removed via convection, hence lowering the photocurrent and $\Phi_{\text{ext}}$. This is consistent with the measured absorption spectra of the aqueous MV$^{2+}$/MV$^+$ electrolyte, which shows significant absorption at 808 nm despite this wavelength being an overall minimum in the absorption of this redox system in visible/near-IR spectral region. This issue is particular to the aqueous MV$^{2+}$ system and could be largely alleviated by utilizing less-absorbing redox couples, for example, cobaltocenium/cobaltocene in CH$_3$CN. Furthermore, a transparent conducting glass counter electrode would replace the carbon electrodes in thin-layer cell design that was engineered to produce high efficiencies under AM 1.5 illumination conditions.
In certain cases the photocurrent density ($J_{sc}$) was also measured in the absence of the MV$^+$ radical cation using solar simulation from a tungsten-halogen lamp with an ELH-type bulb. This configuration allows for testing in an optically transparent solution, and hence measurement of accurate values for $J_{sc}$ under solar illumination. Under these conditions the cell does not operate as a regenerative photovoltaic, because the potentiostat drives oxygen evolution at the Pt counter (as opposed to MV$^+$ oxidation). Therefore it is not possible to extract photoelectrochemical parameters besides $J_{sc}$ (i.e. the $V_{oc}$ and fill factor) under these conditions.

**Overpotential Corrections.** When the current density driven across an electrode-electrolyte interface is a significant fraction of the mass-transport-limited anodic or cathodic current densities for that same system ($J_{l,a}$ and $J_{l,c}$, respectively), a significant voltage drop, or concentration overpotential ($\eta_{conc}$), exists across the electrode-electrolyte interface.$^3$ This loss mechanism is inherent to photoelectrochemical cells and would not be present, for instance, in a solid-state cell composed of the same semiconductor material. In addition, a voltage loss is present due the uncompensated resistance ($R$) of the electrolyte solution, given by $I*R$. To estimate the inherent performance of the p-Si wire-array and of the planar-control samples, these losses were corrected at each point of the $J$-$E$ curve using the following equations:

$$\eta_{conc} = \frac{RT}{nF} \left\{ \ln \left( \frac{J_{l,a}}{-J_{l,c}} \right) - \ln \left( \frac{J_{l,a} - J}{J - J_{l,c}} \right) \right\} \quad (1)$$

$$E_{corr} = E - \eta_{conc} - I \cdot R \quad (2)$$

The values of $J_{l,a}$ and $J_{l,c}$ were estimated from the limiting current measured for the specific electrode of interest in forward bias and from measurements made on a similarly-sized glassy carbon electrode in the same cell configuration, respectively. The uncompensated resistance, $\sim 20 \, \Omega$, was extracted from the inverse slope of the $J$-$E$ curve collected using the glassy carbon working electrode, after correction for the concentration overpotential using Eqn. (1).
Angle-resolved Photocurrent Measurements. p-Si wire-array, planar p-Si ($\rho = 0.7 \ \Omega \ \text{cm}, \ (111)-oriented$), and planar p$^+$/Si ($\rho = 0.001 \ \Omega \ \text{cm}, \ (111)-oriented$) photoelectrodes, with areas of $\sim 0.25 \ \text{cm}^2$ were prepared as described above, except that the electrode faces were mounted perpendicular to the glass rod. The samples were attached on a manual rotation stage and submersed in a flat-sided electrochemical cell that was filled with the same electrolyte as described above, except that 0.010 M MV$^{2+}$ was used. The samples were illuminated with a 633 nm He-Ne laser (power = 2.6 $\mu$W) whose spot size ($\sim 1 \ \text{mm}^2$) was much smaller than the sample area. The backscattered diffraction pattern from the wire-array sample, or the specular reflection from the planar samples, was used to align the photoelectrode normal to the incoming radiation, to within $\sim 1^\circ$. The samples were biased at -0.45 V vs. SCE, and a lock-in amplifier (Stanford Research Systems Model 830) was used to measure the chopped ($\sim 3 \ \text{Hz}$) photocurrent as a function of the angle of incidence. These measurements were conducted in the absence of the reduced form of methyl viologen to avoid issues associated with the oxygen sensitivity, and solution absorbance, of the MV$^+$ radical cation.

Supplementary References