Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplemental Information for
Stablization of Si Microwire Arrays for Solar-Driven H_2O Oxidation to O_2(g) in 1.0 M KOH(aq) using Conformal Coatings of Amorphous TiO_2

Methods

Chemicals

All chemicals were used as received unless noted otherwise. Water was filtered using a MilliPore system and had a resistivity > 18 MΩ-cm.

Si Microwire Fabrication

Phosphorous-doped ($N_D = 3 \times 10^{17}$ cm^{-3}) Si microwire arrays were grown via a Cu-catalyzed vapor-liquid-solid (VLS) process on As-doped n$^+$-Si <111> wafers (<0.005 Ω-cm, Addison)[6,25,2]. The n$^+$-Si <111> growth wafers were received as 3" wafers with a 500 nm thick thermal oxide (SiO_2) and were photolithographically patterned to form an array of 3 µm diameter holes filled with Cu in a 7 µm x 7 µm square lattice. The photolithography process began with the application of a positive photoresist layer (Shipley S1813) to the SiO_2 surface. Next, the photoresist was exposed to UV illumination through a mask that contained the growth pattern (3 µm diameter holes in a 7 µm x 7 µm square lattice), and the exposed and cured photoresist was removed with a developer (Microposit MF-319). This process left 3 µm diameter holes in the photoresist through which the underlying SiO_2 was etched with buffered HF(aq) (BHF) (Transene Inc.), to reveal the underlying Si. 500nm of high-purity Cu (EPSI 6N) was then thermally evaporated onto the sample. Through a lift-off process, all of the Cu, except for that in the 3 µm diameter holes, was removed. This entire process produced 3" growth wafers that were diced to fit into the tube furnace.

Growth of Si microwire arrays was performed in a chemical-vapor deposition (CVD) tube furnace at atmospheric pressure using $SiCl_4$ (Strem, 99.9999+%) at 25 sccm flow rate, H_2 (Matheson, research grade) at 500 sccm flow rate, and PH_3 (Matheson, 100ppm in H_2) at 0.3 sccm flow rate for 9 min. Following growth, the samples were cooled to ~ 200 °C under a 500 sccm flow of He.

Microwire Array Processing

Microwire arrays were cleaned using a 6:1:1 (by volume) H_2O:HCl(fuming, aqueous):H_2O_2(30% in H_2O) metal etch (RCA 2) for 20 min at 60 °C. The samples were then subjected sequentially to a 15 s BHF etch, a H_2O rinse, a 10 min organic (piranha) etch in 3:1 H_2SO_4(99.6%, aqueous):H_2O_2(30% in H_2O) at room temperature, and a H_2O rinse. Following a 30 s etch in 10% BHF and H_2O rinse, a 150 nm thick SiO_2 layer was grown via dry thermal oxidation in a tube furnace for 2.5 h at 1050 °C under an O_2 atmosphere. A 15 μm thick PDMS layer was deposited at the base of the wires by spin coating a solution, consisting of 1.1 g of polydimethylsiloxane (PDMS, Sylgard 185, Dow Corning) and 0.1 g of PDMS curing agent dissolved in 5 mL of toluene, onto the sample at 3000 rpm for 30 s, followed by a 30 min cure in a vacuum oven at 150 °C. These PDMS-infilled arrays were submerged in BHF for 3 min, to remove the SiO_2 on the exposed microwire surfaces. The PDMS was removed by a 30 min soak in 3:1 N-methyl-2-pyrrolidone(NMP):tetrabutylammonium fluoride(TBAF, aq 75 wt%), followed by a 30 s H_2O rinse. The samples were then dried under a stream of N_2(g) and residual organics were removed by a 10 min piranha etch.

p^+ Emitter Formation

A boron-doped p^+-Si radial emitter was formed on the processed n-Si microwire arrays by exposure of the samples in a CVD furnace to a 20:400 sccm flow of BCl_3 (Matheson, 0.25% in H_2):H_2(Matheson, research grade) at 950 °C for 30 min, immediately following a 30 s etch in 10% BHF. The samples were then rinsed with H_2O and dried under a stream of N_2(g).

TiO_2 Deposition

TiO_2 was deposited by atomic-layer deposition (ALD) on np$^+$-Si microwires at 150 °C using tetrakis(dimethylamino)titanium (TDMAT) as the Ti source heated to 75 °C and H_2O as the O source. 2000 cycles were performed with pulse and purge times of 0.1 s and 15 s for the TDMAT, respectively and 0.015 s and 15 s for the H_2O respectively, with the H_2O pulse beginning each new cycle. Prior to ALD deposition, the samples were etched for 15 s in 10% HF(aq), cleaned using a RCA SC-2 procedure, and dried with N_2(g). In the RCA SC-2 procedure, the samples were immersed in a 5:1:1 (by volume) solution of H_2O, concentrated hydrochloric acid (11.1 M), and hydrogen peroxide (conc.~ 1 M) for 10 min at 75 °C.

$NiCrO_x$ Deposition

$NiCrO_x$ was deposited on np$^+$-Si/TiO_2 microwire arrays by reactive RF magnetron sputtering (AJA) with separate Ni and Cr targets at 150 W and 90 W, respectively. The deposition chamber was at a pressure of 5 mTorr, fed by 20 sccm N_2(g) and 1 sccm of O_2(g). The deposition time was 20 min, which resulted in a thickness of ~ 40 nm planar equivalent.

Electrode Fabrication

Electrodes were fabricated from diced pieces of each processed microwire growth array. To make ohmic contact to the samples, In-Ga (99.99%, Alfa-Aesar) eutectic was scratched into the back-side of the growth wafer with a diamond-tipped scribe. Exposed In-Ga (Si electrodes) was affixed to a coiled Cu-Sn wire with Ag paint (SPI 05001-AB). The active area was defined with epoxy (Loctite Hysol 9460) and the entire electrode was sealed with epoxy to the bottom of a glass tube (6mm O.D.). The electrode orientation, down- or side-facing, was determined by the orientation of the coiled wire that protruded from the glass tube. Geometric areas were measured by scanning the active area, and using software (ImageJ) to calculate the area.

Photoelectrochemical Measurements in Aqueous Solutions

Bottom-facing electrodes were used in both 1 M KOH and aqueous ferri-/ferrocyanide solutions. Four np$^+$-Si/TiO$_2$/NiCrO$_x$ and two n-Si/TiO$_2$/NiCrO$_x$ microwire array electrodes were made and tested, with the reported results being representative of all electrodes in each specified class. Three-electrode cyclic voltammetry (CV) measurements were conducted using a Biologic (SP-200) potentiostat in conjunction with a borosilicate single-compartment cell that had a flat-bottom glass window. A mercurous/mercury oxide (Hg/HgO, 1.0 M KOH filling solution) (CH Instruments) reference electrode and a fritted carbon counterelectrode were used for measurements in 1 M KOH, whereas a Luggin-capillary Pt reference electrode placed as close to the working electrode surface as possible and a Pt mesh counterelectrode were used for measurements in ferri-/ferrocyanide solutions. The ferri-/ferrocyanide data were plotted versus the solution potential at the reference electrode, while the potential axis for the 1 M KOH data was shifted to the reversible hydrogen electrode (RHE) scale based on the value provided by CH Instruments, 0.14 V vs RHE. For these experiments, illumination was provided by a Xe lamp (Oriel 67005, Newport Corporation) with an AM1.5G filter (Newport Instruments 81094) that was calibrated to 1 Sun by a calibrated Si photodiode. A mirror (10Q20BB.HR broadband dielectric mirror, Newport Corporation) was used to direct the horizontally projected illumination from the lamp in the vertical direction, to produce normal incidence light for the bottom-facing electrodes. Calibration was performed such that the highest light intensity anywhere in the cell was at the cited light intensity, and the position of the photodiode at this light intensity was marked to assure sample positioning was at the same point. Varying illumination intensities were achieved through the use of neutral density filters (ND 0.3) (Newport FSQ-OD30). This approach allowed determination of the diode quality factor by a linear line fit to a plot of the open-circuit potential vs. ln(J_{ph}).

Photoelectrochemical Characterization in Non-Aqueous Solvents

Bottom-facing electrodes that contained n-p$^+$-Si microwire arrays were etched for 10 s in BHF immediately prior to introducing the samples into a glove box.

Solutions for photoelectrochemical measurements consisted of CH_3CN (anhydrous, 99.8%, Sigma Aldrich) dried through Al_2O_3 sieves in a solvent column system and stored over 3Å dry molecular sieves, 1M $LiClO_4$ (battery grade, 99.99%, Sigma Aldrich), and 25 mM bis(cyclopentadienyl) iron(II) (ferrocene, $FeCp_2^0$, Sigma Aldrich) and 3 mM bis(cyclopentadienyl) iron(III) tetrafluoroborate (ferrocenium, $FeCp_2^+\cdot BF_4^-$, Sigma Aldrich). Ferrocene was purified by vacuum sublimation at room temperature, and ferrocenium was recrystallized prior to use. An ELH-type W–halogen lamp with a dichroic rear reflector was used for illumination, and was set to produce the same current density on a calibrated Si photodiode as was obtained from 100 mW cm^{-2} of 1 Sun AM1.5 G illumination. Three-electrode photoelectrochemical data were obtained in a single-compartment cell by use of a Biologic potentiostat (SP-200), with a Pt counter electrode and a Pt quasi-reference electrode at scan rates of 20 mV-s^{-1}.

Spectral Response

Spectral response measurements were obtained to determine the external quantum efficiency (Φ_{ext}) as a function of wavelength. Monochromatic light with a bandwidth of 10 nm was produced using an Oriel monochromator and an Oriel Xe lamp. The beam was chopped at 20 Hz and was focused to a spot size that under-filled the sample. A mirror (10Q20BB.HR broadband dielectric mirror, Newport Corporation) was used to direct the horizontal beam vertically for the bottom-facing electrodes. The electrodes were tested in the same photoelectrochemcial cell as described above for the 1 M KOH measurements . Each electrode was held potentiostatically at 1.63 V vs RHE with a Biologic potentiostat (SP200) that was connected to a lock-in amplifier (SRS 830). A second lock-in amplifier was connected to a second photodiode that continuously monitored the light intensity provided by a quartz beam-split portion of the incident beam. Calibration of the light incident on the electrodes was performed using a bottom-facing calibrated photodiode (Newport FDS100-CAL) that was placed in the same location as the electrodes.

Oxygen-Evolution Faradaic Efficiency

The Faradaic efficiency for oxygen evolution of a single np$^+$-Si/TiO_2/$NiCrO_x$ microwire array electrode was measured in the same cell as for the 1 M KOH measurements described above. Both the oxygen concentration and the charge passed were simultaneously monitored over a 40 min photoelectrochemical measurement, After a 10-min waiting period at open circuit, the microwire electrode was held potentiostatically at 1.63 V vs RHE with a Biologic potentiostat (SP200) for 30 min, and the oxygen concentration in solution was measured over the entire 40 min period with an Ocean Optics fluorescent probe (NeoFox HIOXY). Illumination was provided by a Xe lamp (Oriel 67005, Newport Corporation) with a AM 1.5G filter and was calibrated to 1-Sun intensity with a Si photodiode. Prior to measurement, the solution (approximately 48 mL in volume) was purged with $N_2(g)$ for ~ 20 min to obtain a near oxygen-free environment

The10-min measurement at open circuit without oxygen production provided a measurement of the oxygen leak rate of the cell. These leak rates were interpolated during the 40 min photoelectrochemical measurement and were subtracted from the overall oxygen detection to yield an oxygen evolution rate for the electrode itself. The corrected oxygen concentration data were then converted to micrograms of O_2, using the amount of O_2 dissolved in water at room temperature under 1 atm (7700 $\mu g \cdot L^{-1}$), the solution volumne (~48 mL), and the concentration of O_2 in air under 1 atm at 25°C (20.9%). 100% Faradaic efficiency was assumed as 4 electrons are used to generate 1 O_2 molecule, i.e. 0.33 mA h of charge passed to generate 100 μg of O_2. All the data were processed using a Matlab script.

Imaging

All scanning-electron micrograph (SEMs) were taken on an FEI Nova NanoSEM 450.

Data

np^+-Si Microwire Array Non-aqueous PEC

Prior to coating the np^+-Si and n-Si microwires, small areas of each growth wafer were diced and made into bottom-facing electrodes for use in non-aqueous photoelectrochemical measurements with a ferrocenium/ferrocene redox couple. Figure S1 shows representative photoelectrochemical (PEC) data for these two different electrode types. The np^+-Si microwire arrays exhibited an open-circuit voltage, V_{OC} = 461 ± 31 mV and a light-limited current density, J_{ph} = 11.8 ± 2.2 mA – cm^{-2} over eight electrodes, while the n-Si microwire arrays demonstrated V_{OC} = 311 mV and J_{ph} = 8 mA cm^{-2} with only two electrodes tested.

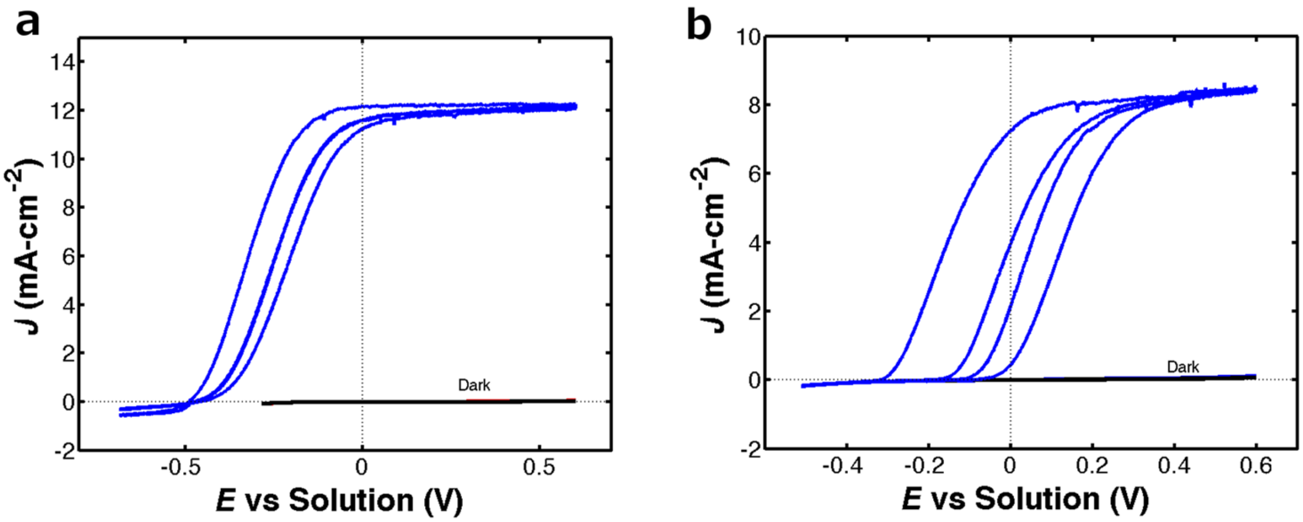

Figure S 1: Non-aqueous ferrocenium/ferrocene photoelectrochemical performance of a) np$^+$-Si and b) n-Si microwire arrays under 100 mW cm^{-2} of ELH-type W-halogen illumination.