Supporting Information for:

PROFILING PHOTOINDUCED CARRIER GENERATION IN SEMICONDUCTOR MICROWIRE ARRAYS VIA PHOTOELECTROCHEMICAL METAL DEPOSITION

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S1. Contents

This document contains a description of the experimental and computational methods utilized in this work (Sections S2 and S3) and voltammetry data (Section S4).
S2. Experimental Methods

Materials and Chemicals. HAuCl₄·3H₂O (99.999%, Sigma-Aldrich), KCl (99%, Sigma-Aldrich), buffered HF (Transene Inc), In (99.999 %, Alfa Aesar), Ga (99.999 %, Alfa Aesar), and CH₃OH (ACS grade, BDH chemicals) were used as received. H₂O with a resistivity ≥ 18.2 MΩ cm (Barnstead Nanopure System) was used throughout. Microwire arrays were constructed by etching either p-Si(100) wafer sections (1.0 – 10.0 Ω cm, B-doped, 525 ± 25 µm thick, single-side polished, Addison Engineering) or n-Si (100) wafer sections (1.0 – 10.0 Ω cm, P-doped, 525 ± 25 µm thick, single-side polished, Addison Engineering).

Fabrication of Microwire Arrays. S1813 positive photoresist was spin coated at 4000 rpm onto the top of Si wafers. The wafers were then heated on a hotplate at 115 °C for 1 min. The photoresist was then exposed using UV illumination through a square lattice mask consisting of holes with a 3 µm diameter and a 7 µm pitch. The photoresist was developed using MF-319 developer and the wafers were baked for 10 min at 115 °C. A 200 nm thick Al₂O₃ mask was then deposited onto the patterned wafer using electron-beam evaporation. PG-remover was used to liftoff the photoresist. After the liftoff, Fomblin oil was applied to the back of the wafers to act as a thermal contact material, and the wafers were loaded into the etching chamber. Wires were etched using a cryogenic inductively coupled plasma reactive ion etching process (ICP-RIE) with an Oxford DRIE 100 ICP-RIE system. Etching was performed at low capacitive coupled power of 5 W to reduce damage due to the momentum of the ions. A high inductively coupled power of 900 W was used to increase the number of ions in the plasma to achieve high rates of chemical etching. The chamber was maintained at -120 °C and a pressure of 10 mTorr during the etching process. Etching
was performed using SF₆ : O₂ ratios ranging from 70 sccm : 5.5 sccm to 70 sccm : 8 sccm for 30 min. Variation of the O₂ concentration in the plasma enabled control over the wire taper. After etching, the wafers were dipped in buffered HF to chemically remove the Al₂O₃ mask.

**Photoelectrochemical Deposition.** Si microwire arrays were cut into ~ 1 cm x 1 cm sections. Immediately before deposition, each section was rinsed with CH₃OH, followed by H₂O, and then immersed in buffered HF(aq) for ~ 60 s to remove any surficial SiOₓ from the Si. The sample was then rinsed with H₂O and dried with a stream of N₂(g). A Ga/In eutectic was scratched into the back side of each section using a carbide scribe, and the section was mounted on a ~ 2 cm x 2 cm Ti plate using Cu tape. This assembly was then sealed with a Ti backplate into a single compartment O-ring compression that confined the contact region between the solution and the Si microwire array section to a circular area of 0.1 cm². The cell was equipped with a pyrex window that enabled illumination during deposition. A three-electrode configuration was utilized with a graphite-rod counter electrode (99.999 %, Sigma-Aldrich) and a Ag/AgCl reference electrode (3 M KCl, Bioanalytical Systems). Au was deposited from an aqueous solution of 0.010 M HAuCl₄ and 0.100 M KCl. All depositions were performed using a Princeton Applied Research Model 273 potentiostat. Depositions were carried out at room temperature by biasing the illuminated microwire array potentiostatically at -1.25 V vs. Ag/AgCl until an integrated charge density of 0.10 C cm⁻² had been passed.

**Electrode Illumination.** Illumination for the photoelectrochemical depositions was provided by narrowband diode (LED) sources (Thorlabs) with respective intensity-weighted λ_avg values and
spectral bandwidths (FWHM) of 461 and 29 nm (M470L2), 516 and 30 nm (M505L3), 630 and 18 nm (M625L3), and 940 and 30 nm (M940L2), respectively. The output of each diode source was collected and collimated with an aspheric condenser lens (Ø30 mm, f = 26.5 mm). The light intensity incident on the electrode was measured by placing a calibrated Si photodiode (Thorlabs FDS10X10), in the photoelectrochemical cell with the electrolyte, at the location of the electrode, and measuring the steady-state current response of the Si photodiode. Depositions that utilized the diode with \( \lambda_{\text{avg}} = 461 \) nm as the illumination source were performed with a light intensity of 77 mW cm\(^{-2}\) at the electrode. Depositions using the diodes with \( \lambda_{\text{avg}} = 516, 630, \) and 940 nm, were performed with intensities of 64, 50, and 33 mW cm\(^{-2}\), respectively.

**Microscopy.** Scanning-electron micrographs (SEMs) were obtained with a FEI Nova NanoSEM 450 at an accelerating voltage of 5.00 kV and working distance of 5.00 mm using an Everhart-Thornley secondary electron detector.
S3. Computational Methods

**Generation Profile Simulation.** Photocarrier generation profiles in Si wire arrays under steady-state illumination with unpolarized light were simulated using three-dimensional full wave electromagnetic simulations via a finite-difference time domain (FDTD) method. Modeling was performed using the FDTD Solutions software package (Lumerical). Si microwire arrays were simulated using a single three-dimensional unit cell with periodic boundary conditions along the x and y axes to depict a 7 µm square lattice similar to the fabricated arrays, in conjunction with infinite boundary conditions rendered as perfectly matched layers (PML) along the z axis. Idealized microwire arrays corresponding to the four different fabricated shapes were constructed in the 3D simulation region by approximating the tapered microwires as truncated cones or multiple sections of truncated cones. The absorption was simulated under polarized illumination and then the CW-generation rate analysis group in the FDTD Solutions software was used to derive the generation rate per unit volume. The generation rate under unpolarized illumination was obtained by averaging the generation rate data with itself by interchanging the x- and y-axes as permitted by the square symmetry of the wire lattice.
S4. Voltammetry

Figure S1. Linear sweep voltammogram (at a scan rate of 50 mV s\(^{-1}\)) obtained with a p-Si microwire array with a ~ 3 µm wire diameter, 7 µm wire pitch, and 30 µm wire height in an aqueous solution of 0.010 M HAuCl\(_4\) and 0.100 M KCl under chopped illumination with a LED source having \(\lambda_{\text{avg}} = 461\) nm and an intensity of 77 mW cm\(^{-2}\).