Si Microwire-Array Solar Cells -- Supporting Information

Ag Back Reflector:

Figure S1 provides scanning electron microscope (SEM) images that document the fabrication of a Ag back reflector. Following two 500 nm Ag evaporations Ag uniformly coated the substrate and the wire sidewalls (Fig. S1A). PDMS was then deposited and continuously coated the Ag-coated substrate (Fig. S1A,B). (Because the SEM images shown are from the edge of a wire array, the PDMS is thinner than in the center of the wire array and there exists a small area at the immediate wafer edge where no PDMS coating exists.) A Ag etch was then used to remove any Ag that was not protected by the PDMS film at the base of the wire array (Fig. S1B). After PRS cell fabrication, the PDMS-protected Ag back reflector was revealed by cell cross-sectioning (Fig. S1C).

Separately, the textured nature of the mounting wax, which results from the presence of the Al_2O_3 scattering particles, was visible above the protective PDMS layer (Fig. S1C).

a-SiN$_x$:H Layer:

Figure S2 is an SEM image of a wire array after selective removal of the *a*-SiN$_x$:H layer from the wire tips. The bright tip is the c-Si wire, while the darker base is the *a*-SiN$_x$:H-coated c-Si wire. The difference in the extent of the exposed tip relates to variations in the wire height and variations in the height of the mounting wax etch barrier (removed prior to imaging.)

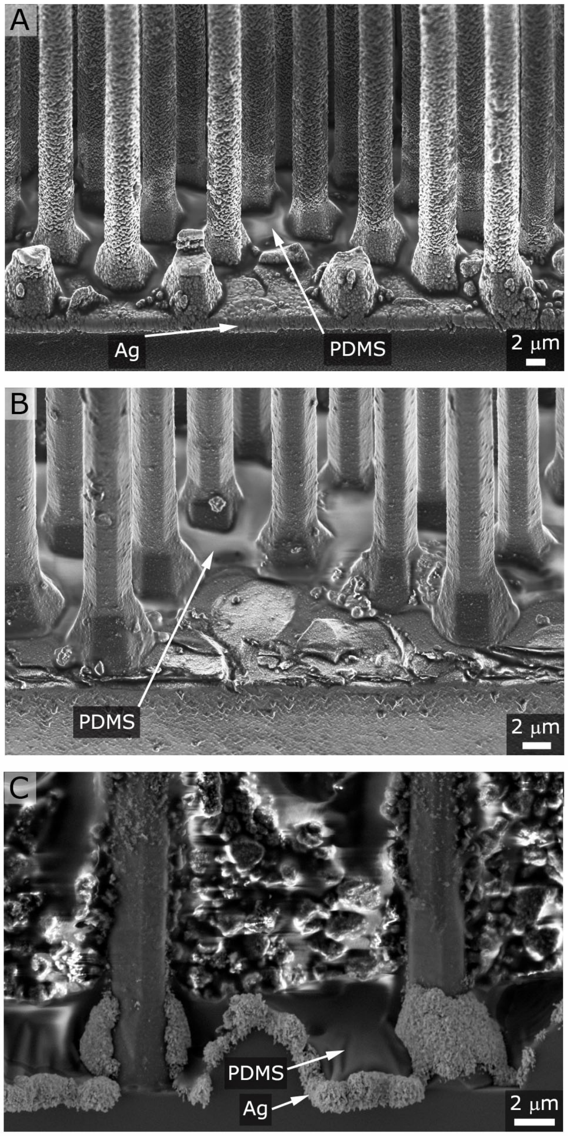

Figure S1. Tilted scanning electron microscope (SEM) images illustrating the fabrication of a Ag back reflector. A) SEM image post Ag and protective polydimethylsiloxane (PDMS) deposition. B) SEM image of the wire array from A) after a Ag-etch. C) Cross-sectional SEM image of a PRS microwire solar cell.

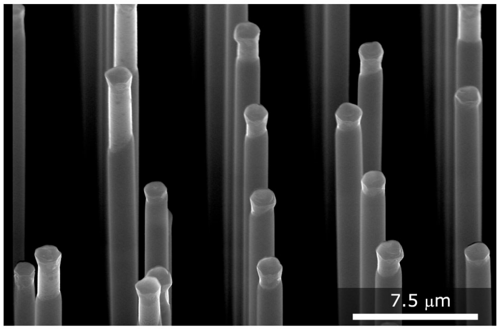

Figure S2. SEM image of a wire array after selective removal of a-SiN$_x$:H from the wire tips. The mounting wax, which was used as an etch barrier, has been removed from the wire array for clarity.

Cell Area:

Scanning photocurrent microscopy (SPCM) images (90 μm x 90 μm) (Fig. S3A) were overlaid to produce a photocurrent map of the cell perimeter (Fig. S3B), which was then analyzed to calculate the cell area (Fig. S3C).

Area analysis was performed using the 'thresholding' feature in Image J. Thresholding was done in such a way that all of the wires within the cell perimeter (defined by the photoactive wires) were selected. The indent on the left side of the cell resulted from contact shadowing and an appropriate correction to the cell area was made. A small photocurrent signal was present outside of the cell perimeter (Fig. S3A) and is presumed to arise from light that was scattered/reflected into the active area. Though this additional collection area was accounted for during the thresholding process, no correction should have been necessary given that an equivalent amount of light would have also been scattered/reflected out of the cell.

As discussed in the text the dark spots (Fig. S3A,B) indicate wires that are not electrically contacted by the indium tin oxide (ITO). Comparing Fig. S3B with Fig. 4C, the fraction of electrically inactive wires was higher near the cell perimeter (2-20%), which is not unexpected given the decreased ITO thickness at the device edge.

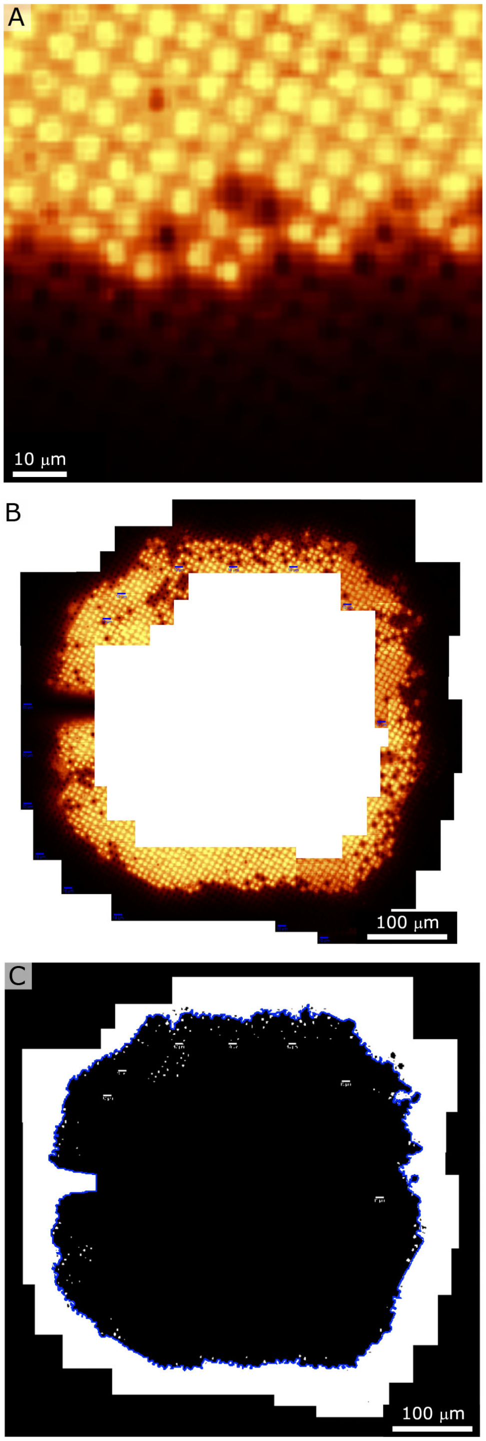

Figure S3. Measuring PRS C4R5's active area. A) 90 μm x 90 μm scanning photocurrent microscopy (SPCM) image along the cell perimeter. B) Twenty-six SPCM images over-laid to map out the cell perimeter. C) Image of B) after thresholding. The blue line is the cell perimeter from which the cell area was calculated.

Table S1. V_{oc} and *FF* (All Devices)

As-Grown:	V_{oc} **(mV)**	***FF* (%)**
C4R2	401	59.3
C4R3	209	44.9
C4R4	452	61.4
C4R5	257	42.2
C4R6	478	59.1
C3R2	419	43
C3R3	339	52
C3R4	474	66.2
C3R5	453	65.8
C3R6	485	68.4
C2R3	482	69.4
C2R4	492	70.1
C2R5	484	71.6
C2R6	429	59.1
C1R6	463	54.4

Scatterer:	V_{oc} **(mV)**	***FF* (%)**
C1R1	477	61.7
C2R1	429	54.8
C3R1	387	53.5
C4R1	475	61.4
C1R2	498	67.5
C2R2	503	68.6
C3R2	481	54.3
C4R2	475	65.1
C1R3	497	64.9
C2R3	486	60.4
C3R3	505	68.8
C2R4	499	68

PRS:	V_{oc} **(mV)**	***FF* (%)**
C2R1	491	59.3
C3R1	487	61.2
C4R1	488	59.7
C5R1	485	61.9
C2R2	497	61
C3R2	493	60.8
C4R2	495	61.1
C5R2	489	60
C2R3	499	63.3
C3R3	497	63
C4R3	495	62.9
C5R3	493	61.5
C2R4	504	62.6
C3R4	494	64.5
C4R4	502	62.5
C5R4	501	61.5
C2R5	503	66.1
C3R5	500	67.2
C4R5	498	65.4
C5R5	497	62.6
C2R6	502	63.4
C3R6	499	63.3
C4R6	489	61
C5R6	485	64.3

V_{oc} and *FF*:

As seen in Table S1 above, the V_{oc} and *FF* were remarkably consistent for the PRS solar cells. The V_{oc} and *FF* were also consistent between the best Scatterer and As-Grown solar cells, however some cells with lower V_{oc} and *FF* were observed. For the As-Grown solar cells, obvious fabrication defects (cracking of the mounting wax prior to ITO deposition) may have resulted in the larger variation in cell performance. Between cells with similar performance (within each respective cell type), we attribute much of the variation in *FF* to the observed variations in the probe tip to ITO contact resistance.

Indium Tin Oxide:

Figure S4 plots the transmission as a function of wavelength for a glass coverslip with and without a 150 nm-thick indium tin oxide (ITO) layer. Transmission through the ITO was found to be > 80% for wavelengths > 500 nm, and at least 65% for wavelengths between 400 and 500 nm.

Strong oscillations in transmission were observed as a result of Fabry-Pérot interference. Thus, a 5 nm running average was used to smooth the oscillations in transmission for wavelengths > 700 nm. As can be seen by comparing the smoothed data below, the oscillations were inherent to the thin nature of the glass coverslip.

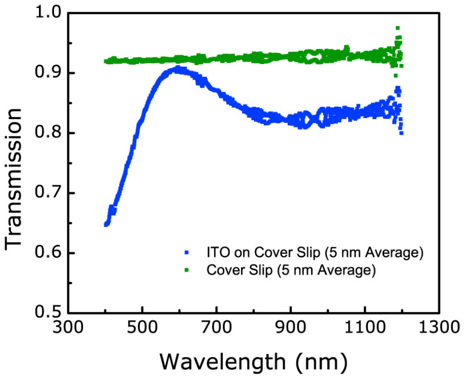

Fig. S4. Transmission as a function of wavelength for a glass coverslip with and without a 150 nm-thick indium tin oxide coating. A 5 nm running average was applied to smooth the oscillations in transmission at wavelengths greater than 700 nm.

Experimental:

Wire Array Growth. Si microwire arrays were grown as described previously.[5] The growth substrates were boron-doped p^{++}-Si (111) wafers, having a resistivity, $\rho < 0.001$ Ω·cm, that were coated with 450 nm of thermal oxide (Silicon Quest International). Arrays of 4-μm-diameter circular holes, on a square lattice with a 7 μm pitch, were defined in the oxide by photolithographic exposure and development of a photoresist layer (Microchem S1813), followed by a buffered HF(aq) (BHF) etch (Transene Inc.) The holes were then filled with 600 nm of Cu (ESPI metals, 6N) via thermal evaporation onto the patterned photoresist, followed by liftoff. Patterned substrates approximately 1.5 cm × 1.5 cm in dimension were then annealed in a tube furnace for 20 min at 1000 °C under H_2 flowing at a rate of 500 sccm. Wire growth was performed by the introduction of $SiCl_4$ (Strem, 99.9999+%), BCl_3 (Matheson, 0.25% in H_2), and H_2 (Matheson, research grade) at flow rates of 10, 1.0, and 500 sccm, respectively, for 30 min. Following growth, the tube was purged with N_2 at 200 sccm and was allowed cool to ~ 650 °C over the course of ~30 min.

p-n Junction Fabrication. Following growth the Cu catalyst was removed from the wire arrays by etching in 5% HF(aq) for 30 s, 6:1:1 by volume H_2O:H_2O_2(30% in H_2O):conc. HCl (aq.) at 75 °C for 15 min, and 20 wt % KOH (aq.) at 20 °C for 60 s. A conformal SiO_2 diffusion-barrier that was 200 nm in thickness was grown via dry thermal oxidation at 1100 °C for 2 h. The wire array samples were then coated with a solution that contained 4.4 g hexamethycyclotrisiloxane (Sigma-Aldrich), 1 g PDMS (Sylgard 184, Dow Corning), and 0.10 g of curing agent in 5 ml of dicholoromethane; spun at 1000 RPM for 30 s; and cured at 150 °C for 30 min, to produce a 10–20 μm thick PDMS layer selectively at the base of the wire array.[6] After a quick etch (~2 s) in a 1:1 mixture of 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (Sigma-Aldrich) and dimethylformamide (PDMS etch)[26] and a DI rinse, these partially infilled arrays were immersed for 5 min in BHF, to remove the exposed diffusion-barrier oxide. The PDMS was then completely removed by etching for 30 min in PDMS etch. A 10 min piranha etch (3:1 aq. conc. H_2SO_4:H_2O_2) was performed to remove residual organic contamination. After etching the wires for 5 s in 10% HF (aq), thermal P diffusion was performed using solid source CeP_5O_{14} wafers (Saint-Gobain, PH-900 PDS) at 850 °C for 10 min (As-Grown and Scatterer) or 15 min (PRS) under an N_2 ambient, to yield a radial p-n junction in the wire regions unprotected by the thermal oxide. A 30 s etch in BHF was used to remove the surface dopant glass.

Photovoltaic Device Fabrication. The *As-Grown* cell was fabricated as follows. After p-n junction fabrication, the wire array was heated to 150 °C on a hot plate, and mounting wax (Quickstick 135, South Bay Tech.) was melted into the array. Excess wax was removed from the array using a glass coverslip. The mounting wax was then etched in an O_2 plasma (400 W, 300 mTorr) until the wire tips were sufficiently exposed for electrical contacting (30-90 min). After etching with BHF for 30 s, 150 nm of indium tin oxide [0.0007 Ω·cm] was sputtered (48 W, 3 mTorr, 20:0.75 sccm Ar:10% O_2 in Ar) through a shadow mask, to serve as a transparent contact to the n-type shell of the Si microwires, thereby defining the area of the microwire solar cells. Contact to the p-type core of the Si microwires was established through the p^+-Si substrate by scribing a Ga/In eutectic onto the back side of the growth wafer.

Fabrication of the *Scatterer* cell was performed identically to that of the As-Grown cell, except that prior to infilling with wax, Al_2O_3 light-scattering particles (0.08 μm nominal-diameter, South Bay Technology) were added to the wire array. The wire-array was placed face-up in a flat-bottomed glass centrifuge tube and ~ 3 ml of an ethanolic dispersion of the particles (~0.3 mg/ml) were added. Centrifugation (~3000 RPM) for 5 min was used to drive the particles to the base of the wire-array.

Fabrication of the *PRS* cell was performed identically to that for the Scatterer cell, except that prior to the addition of the Al_2O_3 particles, an a-SiN_x:H passivating layer and a Ag back reflector were added to the cell. After p-n junction fabrication, the wire arrays were etched for 5 min in BHF, to completely remove the remaining oxide diffusion barrier. A standard clean was then performed (10 min in 5:1:1 by volume H_2O:H_2O_2(30% in H_2O): NH_4OH(15% in H_2O) at 75 °C, 30 s in BHF, 10 min in 6:1:1 by volume H_2O:H_2O_2(30% in H_2O):conc. HCl (aq.) at 75 °C, 30 s in BHF), prior to deposition of an a-SiN_x:H layer (~ 140 nm thick at the wire tip and ~ 60 nm thick at the wire base) using plasma-enhanced chemical vapor deposition, as described previously.[1] The a-SiN_x:H was then etched for 15 s in BHF, prior to the deposition of a total of 1 μm planar-equivalent of Ag via thermal evaporation (two successive 500 nm evaporations at two different specimen-tilt angles (± ~5 degrees) with sample rotation, to ensure continuous coverage of the growth substrate). The array was then infilled with ~5 μm of PDMS using a process similar to the one described above. This PDMS etch barrier allowed the Ag at the wire tips and sidewalls to be selectively removed by etching for 6.5 min in 8:1:1 methanol: NH_4OH(15% in H_2O): 30 wt.% aq. H_2O_2. A thin layer (~40 nm) of SiO_2 was then sputtered to improve the incorporation of the Al_2O_3 particles. The Al_2O_3 scattering elements, mounting wax, and ITO were then added as described above.

Characterization. Dark and light current-voltage measurements were performed on a probe station with a 4-point source-measure unit (Keithley 238). Contact to the ITO top contact was made with a micromanipulator-controlled Au-coated tungsten probe tip. Simulated solar illumination was provided by a 1000 W Xe arc lamp with air mass (AM 1.5G) filters (Oriel), calibrated to 1-sun illumination by an NREL-traceable Si reference cell (PV Measurements, Inc.). Spectral response measurements were performed in an overfilled geometry using chopped (30 Hz) illumination from a 300 W Xe arc lamp coupled to a 0.25 m monochromator (Oriel) that provided ~2 nm spectral resolution. The specimen photocurrent was normalized (by area) to that of a 3 mm-diameter calibrated photodiode, to determine the external quantum yield. The signals were measured with independent lock-in detection of the sample and calibration channels. Scanning photocurrent microscopy measurements were performed using a confocal microscope (WiTEC) in a light-beam-induced current (LBIC) configuration described previously.[9] Scanning photocurrent microscopy (SPCM) images were formed by rastering each device beneath a ~1.0 μm-diameter laser spot (λ = 650 nm) while recording the short-circuit current (0 V bias) under otherwise dark conditions. Multiple 90 μm x 90 μm SPCM images were manually stitched together and post-processed to determine the active cell area using image processing software (Image J) (see Supporting Information Fig. S3.)