Supporting Information

Light trapping in silicon nanowire solar cells

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Methods

Synthesis of silica spheres

10 mL concentrated ammonium hydroxide, 7 mL water and 31 mL ethanol were added to a round bottom flask and stirred at 800 RPM. 3 mL tetraethylorthosilicate (TEOS) were injected and the reaction proceeded for 8 hours at room temperature giving 400 nm diameter beads. A secondary injection consisting of 3 mL TEOS and 0.5 mL water increased the size of the beads to 530 nm without creating more nucleates. After 4 hours, the beads were centrifuged and washed four times with water before being suspended in 7.5 mL of water. This solution was used for dipcoating.

Silicon wafer preparation for dipcoating

Silicon wafers were n-type and consisted of a low resistivity substrate with a thin, high resistivity epixtaxial layer. The 20 and 8 μm absorbing layer wafers had bulk wafers with resistivities of 0.01 and 0.001 Ω•cm, respectively with 5 and 7.5 μm epitaxial layers with resistivites of 10 and 0.8 Ω•cm, respectively. The total absorbing layer thicknesses were estimated by adding the minority carrier diffusion lengths in the highly-doped bulk wafers of 15 μm and 0.5 μm taken from literature to the lightly-doped epitaxial layer thicknesses. The thickness ratio was consistent with photocurrent measurements on planar control solar cells fabricated in parallel. The wafers were

sonicated for several minutes in acetone and isopropanol, cleaned with oxygen plasma for 5 minutes, boiled in piranha (concentrated H_2SO_4:30% H_2O_2 1:3) for at least 2 hours, rinsed with water and blown dry with nitrogen. This treatment ensured a clean and hydrophilic surface and was important to achieve uniform, large-area close-packed monolayer films of silica beads.

Dipcoating

The dipcoating assembly contained a syringe pump connected to a thick wire terminating in a clip for the silicon wafer, a glass cuvette 50 mm long with a 2 mm wide channel to hold the silica bead suspension and a plastic box enclosing the assembly to prevent air currents from disturbing the assembly process. The dipcoating was conducted on an air table to reduce vibrational perturbations and the pull speed was adjusted to form uniform monolayers of beads.

Deep reactive ion etching

Silicon nanowires were formed using the silica bead layer as a mask for deep reactive ion etching using a Surface Technologies Systems Advanced Silicon Etch tool. Alternating etching (SF_6) and sidewall passivation (C_4F_8) steps using a 13.56 MHz plasma with a pulsed 380 kHz chuck bias signal allow for highly directional etching. An 8 minute etch led to 5 μm long nanowires while a 4 minute etch gave 2 μm long nanowires. The silica bead mask was removed by immersing the substrate in 10:1 H_2O:HF solution for 5 minutes.

Junction formation

The p-n junction was formed by boron diffusion using 0.1% BCl_3 in 10% H_2/Ar gas at 900 ^oC for 8 minutes. Diffusion calculations using these conditions give an expected junction depth of approximately 160 nm.

Contact formation

The back contact was made by evaporating 100 nm Ti followed by 50 nm Au immediately after a 15 s dip in 10:1 NH_4F:HF solution. The top contact was made using photolithography followed by a 30 s mild O_2 plasma and 15 s 10:1 NH_4F:HF dip and 800 nm Al followed by 200 nm Pd sputtered to form a top electrode finger pattern. The contacts were not annealed to avoid thermal mismatch-induced stress and cracking or peeling. The large-area solar cells were cut into 5 mm x 6 mm devices using an automatic wafer dicing saw.

Photovoltaic measurements

The solar cells were tested in a Janis probe station both in the dark and under simulated sunlight at 300 +/- 2 K. The solar simulator consisted of a 150 W Xe lamp, focusing optics and an AM1.5G filter from Newport. The power was tested with four different optical meters (thermopile detector type) and the average was used to set the intensity to 100 mW/cm^2. Current-voltage scans were collected at 300 mV/s. 5-10 different solar cells were tested for each combination of absorbing layer thickness and nanowire length and the reported values are the average and standard deviation of that data.

Thin silicon window formation

Double-sided polished silicon on insulator (SOI) wafers with a 7.5 μm device layer, a 500 nm buried oxide and a 525 μm handle layer were coated with about 250 nm of low-stress silicon nitride using a commercial low-pressure chemical vapor deposition system. Windows on the back-side were formed with photolithography and the silicon nitride was etched using a CF_4 plasma. The photoresist mask was removed in acetone and the silicon was etched in a 30% aqueous KOH solution at 90 ^{o}C for approximately 2.5 hours to reach the buried oxide. The end point was determined when the windows stopped bubbling. The silicon nitride mask was removed in concentrated (50%) HF. Further processing followed the procedures used on standard wafers.

Optical measurements

Transmission measurements were made with a Shimadzu NIR-UV double beam spectrometer. Equivalent apertures on both the sample and blank were used to ensure that only the window structure was in the beam path. The transmission was calibrated before each measurement and always read 100% +/-1% when there was no sample in the beam path.

Enhancement Factor (EF) calculations

1. EF from J_{sc} measurements:

The J_{sc} for solar cell 1 is given by:

$$J_{sc_1} = A_1 \cdot I_o \cdot IQE_1 \cdot q \qquad (1)$$

where A_1 is the fraction of incident light that is absorbed, I_o is the flux of incident photons per unit area, IQE_1 is the internal quantum efficiency (defined as the #electrons out/#photons absorbed) and q is the elemental charge. If we have two solar cells, 1 and 2, with the same nanowire length, diameter and spacing but with different silicon absorbing layer thicknesses, then I_o, IQE_1 and q will be the same. Therefore, if we divide J_{sc1} by J_{sc2} we get:

$$\frac{J_{sc_1}}{J_{sc_2}} = \frac{A_1}{A_2} \tag{2}$$

which demonstrates that if the charge separation and extraction efficiencies are the same, then the photocurrents are only determined by the absorption. The absorption is given by:

$$A_1 = 1 - R_1 - T_1 \tag{3}$$

where R_1 is the reflectance and T_1 is the total transmission. The total transmission is equal to the product of the three transmission components:

$$T_1 = (1 - R_1) \cdot T_{bulk_1} \cdot T_{LT_1} \tag{4}$$

where T_{bulk} is the transmission from the nanowire and bulk silicon substrate assuming standard absorption and T_{LT} is the reduced transmission due to light trapping. Substituting (3) and (4) into (2) gives:

$$\frac{J_{sc_1}}{J_{sc_2}} = \frac{(1 - R_1) \cdot (1 - T_{bulk_1} \cdot T_{LT_1})}{(1 - R_2) \cdot (1 - T_{bulk_2} \cdot T_{LT_2})} \tag{5}$$

Since the two solar cells have the same nanowire length, diameter and spacing, they should have the same reflectance and light trapping properties. With these assumptions the reflectance falls out of the expression and we can solve equation (5) for T_{LT} to give:

$$T_{LT} = \frac{J_{sc_1} - J_{sc_2}}{J_{sc_1} \cdot T_{bulk_2} - J_{sc_2} \cdot T_{bulk_1}} \tag{6}$$

T_{bulk} can be calculated with:

$$T_{bulk} = \frac{\int_{300nm}^{1100nm} e^{-\alpha(\lambda) \cdot t_{Si}} \cdot I_o(\lambda) d\lambda}{\int_{300nm}^{1100nm} I_o(\lambda) d\lambda} \tag{7}$$

where $\alpha(\lambda)$ is the absorption coefficient of silicon, $I_o(\lambda)$ is the photon flux from the AM1.5G spectrum and t_{si} is the thickness of the silicon. In order to account for the loss in absorption from the volume of silicon removed by the etching process, T_{bulk1} and T_{bulk2} have two components and are given by:

$$T_{bulk_1} = f_{NW} \cdot T_{bulk} + (1 - f_{NW}) \cdot T_{bulk-NW} \quad (8)$$

where f_{NW} is the fractional area covered by nanowires (not etched) and $T_{bulk\text{-}NW}$ is the transmission calculated for the thickness of the silicon absorbing layer in the etched areas. The effective path length for light in the silicon nanowire arrays is found by solving equation (9) for t_{LT}:

$$T_{bulk_1} \cdot T_{LT} = \frac{\int_{300nm}^{1100nm} e^{-\alpha(\lambda) \cdot t_{LT}} \cdot I_o(\lambda) d\lambda}{\int_{300nm}^{1100nm} I_o(\lambda) d\lambda} \quad (9)$$

The path length enhancement factor (EF) then is given by:

$$EF = \frac{t_{LT}}{t_{Si}} \quad (10)$$

Since there is some variation in the J_{sc} measurements, the upper bound for the EF was taken by setting J_{sc1} to the average plus the standard deviation and J_{sc2} to the average minus the standard deviation, while the lower bound used the opposite combination of averages and standard deviations.

2. EF from transmission measurements:

Figure 4 shows the transmission as a function of wavelength for thin silicon windows before and after etching. The total fraction of photons transmitted between 300 nm and 1100 nm (T_{tot}) was calculated with:

$$T_{tot} = \frac{\int_{300nm}^{1100nm} T(\lambda) \cdot I_o(\lambda) d\lambda}{\int_{300nm}^{1100nm} I_o(\lambda) d\lambda} \quad (11)$$

where $T(\lambda)$ is the measured transmission. Using T_{tot} and a reflectance of 15% for the untapered nanowire arrays (reported by Zhu et al) along with equations (4), (9) and (10) give EF values for the different nanowire arrays. Since there is some uncertainty about the amount of reduced transmission that leads to scattering versus absorption, we multiply the EF extracted from transmission measurements by a percentage that gives good agreement with the EF from the J_{sc} measurements (95% and 85% for the upper and lower bounds gives good agreement). From the data it is also apparent that the coupling percentage is related to the roughness factor; we find good agreement when we use a logarithmic relation.

Planar Transmission – Optical Model:

The transmission for a thin, double-polished, planar silicon slab can be modeled as a dielectric with two reflective surfaces (air-silicon front surface and silicon-air back

surface). This structure is called an etalon and has strong interference patterns determined by:

$$T_{etalon}(\lambda) = \frac{1}{1 + F \cdot \sin^2\left(\frac{\varphi}{2}\right)} \tag{12}$$

where F is the Finesse coefficient:

$$F = \frac{4 \cdot R}{(1-R)^2} \tag{13}$$

and $\varphi(\lambda)$ is the phase lag:

$$\varphi(\lambda) = \frac{4 \cdot \pi \cdot n \cdot t_{Si}}{\lambda} \tag{14}$$

and the reflectance is given by the Fresnel equation:

$$R = \left(\frac{n_{Si} - n_{air}}{n_{Si} + n_{air}}\right)^2 \tag{15}$$

This intensity modulation is averaged over 8 nm (slit width during measurement) and then multiplied by the transmission for the silicon slab considering a single-pass absorption:

$$T_{Si}(\lambda) = e^{-\alpha(\lambda) \cdot t_{Si}} \tag{16}$$

to give the final transmission curve.