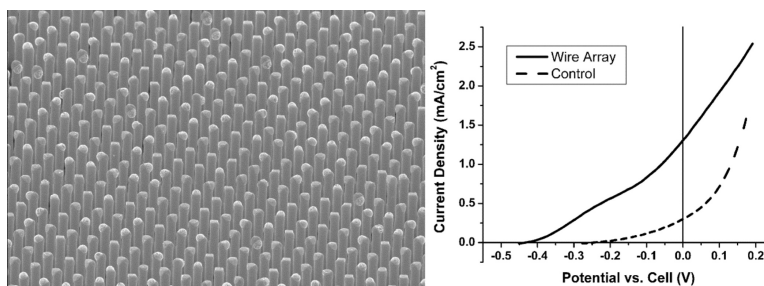Communication

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High Aspect Ratio Silicon Wire Array Photoelectrochemical Cells

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A key constraint in photon absorbers for solar energy conversion is that the material must be sufficiently thick to absorb most of the solar photons with energies above the material's band gap, yet sufficiently pure to have a high minority carrier diffusion length for effective collection of the photogenerated charge carriers. This constraint imposes a cost floor on the absorber material by dictating the minimum required purity of the absorber phase. The situation is especially severe for indirect band gap absorbers, such as Si which requires over 100 μm of thickness to absorb 90% of the energy in sunlight above the 1.12 eV band gap of Si.[1,2]

One approach to circumventing this constraint is to orthogonalize the directions of light absorption and charge-carrier collection.[2] One attractive realization of such an approach involves high aspect ratio cylindrical absorbers, such as nanowires. A preferred implementation would involve the use of wires that are sufficiently long to absorb most of the incident light, but which have sufficiently small diameters to facilitate efficient radial collection of carriers, even for relatively impure absorber materials. To fabricate such a solar cell, methods are required to prepare large area arrays of vertically aligned nanowires, to make electrical junctions to such wire arrays, and to make electrical contacts to the backsides of these devices. These challenges have been investigated by various means, including chemical vapor deposition (CVD) growth of wire arrays,[3,4] etching of flat substrates to produce wire arrays,[5,6] and conductive-polymer electrical junctions with wires.[7,8] Nanowires have also been used to facilitate collection of majority carriers in ZnO-based dye-sensitized solar cells.[9] We report herein the demonstration of all of these steps for absorbers that consist of arrays of high aspect ratio, CVD-grown, crystalline Si wires. Silicon is used in most current solar cells, and the fabrication of devices from Si is technologically well-developed, so methods for using less pure Si in solar energy conversion devices are of significant interest.

Arrays of Si wires were grown using the vapor−liquid−solid (VLS) growth method, with Au as the VLS catalyst.[10−12] A 285 nm thick SiO$_2$ buffer layer was first thermally grown on the substrate, which was a degenerately doped n-type Si(111) wafer. Oxide deposition was followed by application of a resist layer. A pattern of holes in the resist and oxide was then formed using photolithography and subsequent etching through the oxide. The Au catalyst was then thermally evaporated onto the substrate and excess Au removed during resist lift-off. VLS growth was then performed at 1050 °C using SiCl$_4$ diluted in H$_2$, producing 10−30 μm long Si wires having the desired radii and pitch. Following growth, the remaining Au catalyst was removed from the wires.[13] As shown in Figure 1, the resulting Si wires were nearly completely oriented normal to the substrate and were highly regular, in both diameter and pitch, over a large ($\sim$2 mm^2) area.[11]

Although gold is a deep-level trap in silicon, the wires grown in this study are nevertheless expected to allow effective carrier collection. Because the solubility limit of Au in Si at 1050 °C is
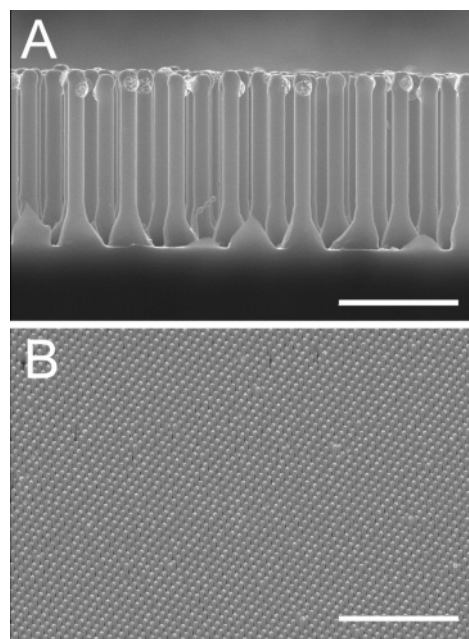

Figure 1. Scanning electron microscopy images of silicon wire arrays: (A) cross section, scale bar = 15 μm; (B) 45° view, scale bar = 85.7 μm.

$\sim$10^{16} cm^{-3}, the trap cross-section of Au is expected to produce carrier lifetimes of 2 ns.[1,14] This short lifetime would greatly restrict carrier collection in planar Si absorbers but, nevertheless, is adequate to provide carrier collection for distances of at least 1 μm.[1] A theoretical treatment has shows that optimal efficiencies are expected when the wires have a diameter comparable to the minority carrier diffusion length.[2] Smaller diameters produce increased surface area and thus increase surface and junction recombination with little concomitant improvements in carrier collection. Hence, micron-diameter Si wires were grown and used in the array junction measurements.

Transmission electron microscopy (TEM) characterization of the wires indicated that they were single crystalline and grew in the <111> direction, as expected from the orientation of the substrate wafer (Figure S1). Four-point probe measurements and field-effect measurements on individual nanowires indicated that the as-grown wires were n-type, with resistivities of 0.32 ohm·cm, corresponding to dopant densities of 2.5 × 10^{16} cm^{-3} (Figure S2).

The junction properties of such Si wire arrays were probed using a liquid electrolyte. The liquid electrolyte provided a convenient, conformal method of contacting the Si wires and allowed measurements of the performance of the wires without requiring a diffused metallurgical junction to the Si wires in the array. In particular, the 1,1′-dimethylferrocene (Me$_2$Fc)$^{+/0}$ redox system in CH$_3$OH has been shown to yield excellent junctions with n-type Si, providing bulk diffusion−recombination-limited photovoltages in excess of

Table 1. Photocurrent and Photovoltage of Wire Array Cells

	V_{oc} (mV)	J_{sc} (mA/cm^2)
wire array	389 ± 18	1.43 ± 0.14
control	232 ± 8	0.28 ± 0.01
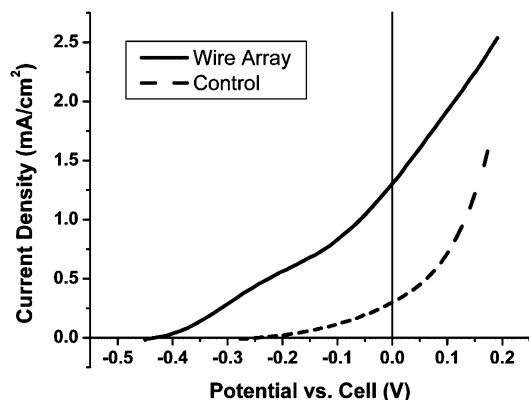
Figure 2. Current density versus voltage behavior for a Si wire array (solid) and control samples (dashed). The electrode potential was measured versus a Pt reference poised at the Nernstian potential of the 0.2 M Me_2Fc/0.5 mM Me_2Fc^+/1.0 M $LiClO_4$−CH_3OH cell.

670 mV under 100 mW cm^{-2} of AirMass (AM) 1.5 conditions.[15−19] Such junctions also form an in situ inversion layer in the n-Si, in essence forming an in situ p$^+$ emitter layer, while also producing a highly passivated surface.[20] Hence these liquid junctions are well-suited as systems for providing initial probes of the solar device conversion properties of arrays of n-type Si wires. This expectation has been verified by measurements of photoelectrodes made from n-type macroporous Si, which have shown that high photovoltages can be obtained even with significant increases in surface area of the junction relative to the geometric projected area of the substrate, through use of the $Me_2Fc^{+/0}$−CH_3OH liquid contact.[21]

Table 1 summarizes the average values for the open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of the Si wire array photoelectrodes. To generate control samples, an oxidized substrate wafer was patterned with holes, but no catalyst was deposited into the openings, and wires were not grown on the samples. The V_{oc} in the wire array samples was relatively large (350−400 mV) given the high surface area per unit projected area. This value of V_{oc} reflects the relatively low surface recombination velocity of the Si/$Me_2Fc^{+/0}$−CH_3OH interface and good bulk properties of the Si wires, without which much lower V_{oc} values would be observed. The short-circuit photocurrent densities of the wire array samples were relatively low, 1−2 mA cm^{-2}. However, the wires were only 20 μm in length, so the expected J_{sc} of 43 mA cm^{-2} that could be attained for complete absorption and collection of all solar photons with energies above the 1.12 eV band gap of Si is reduced to 34 mA cm^{-2} for a 20 μm thickness of Si absorber.[1,2] In addition, the array of 2 μm diameter wires on a 7 μm pitch only fills 6.5% of the projected surface plane, thereby producing an expected maximum J_{sc} of 2.2 mA cm^{-2}, in agreement with the observed J_{sc}.

Representative current density versus voltage curves are shown in Figure 2. The fill factor was relatively low and presumably reflects either a shunt or residual recombination at the junction that could potentially be reduced through improved surface passivation methods. The observed photoactivity was not dominated by the substrate because the degenerately doped substrate produced only a low photovoltage and nearly no photocurrent. In addition, the wide bases of the wires suggest that relatively little, if any, direct contact was formed between any remaining oxide-free substrate and the liquid electrolyte. Thus, it is likely that all of the observed photocurrent and photovoltage are due to the wires rather than the substrate.

In summary, high fidelity, vertically aligned arrays of high aspect ratio silicon wires have been fabricated over relatively large areas, and their energy conversion properties have been measured in a photoelectrochemical cell. Although the wires were grown with Au as the catalyst, the wire array samples showed significantly higher photocurrents and photovoltages than the control samples. Hence, as described herein, a nearly photoinactive substrate has been rendered photoactive by the scalable, relatively low-cost, VLS growth of arrays of Si wires.

Supporting Information Available: Experimental details for wire array fabrication, photoelectrochemical measurements, TEM data showing crystal composition, and four-point probe measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA074897C