Photoelectrochemical Hydrogen Evolution Using Si Microwire Arrays

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Supporting Information

ABSTRACT: Arrays of B-doped p-Si microwires, diffusion-doped with P to form a radial n⁺ emitter and subsequently coated with a 1.5-nm-thick discontinuous film of evaporated Pt, were used as photocathodes for H₂ evolution from water. These electrodes yielded thermodynamically based energyconversion efficiencies >5% under 1 sun solar simulation, despite absorbing less than 50% of the above-band-gap incident photons. Analogous p-Si wire-array electrodes yielded efficiencies <0.2%, largely limited by the low photovoltage generated at the p-Si/H₂O junction.

One approach to achieving efficient solar-driven water splitting is to utilize dual light absorbers, with one absorber acting as a photocathode and the other as a photoanode. Such tandem designs, in principle, allow the use of relatively small-bandgap (i.e., 1.1–1.7 eV) light absorbers that are well-matched to the solar spectrum while simultaneously providing the necessary overall photovoltage (>1.23 V) required under standard conditions to produce H₂ and O₂ from H₂O. The use of a tandem structure also relaxes the stability requirements of the light absorbers, facilitating the use of photocathodes that are stable under cathodic (but not necessarily anodic) conditions, in combination with photoanodes that are stable under anodic (but not necessarily cathodic) conditions.

Si is an attractive candidate for a tandem-system photocathode, because Si is earth-abundant, is relatively cathodically stable, has a suitable band gap, and in principle can produce a significant portion of the total photovoltage needed for water splitting. Si wire arrays have attracted attention for solar-energy-conversion applications, because the use of wire arrays allows orthogonalization of light absorption and charge-carrier collection, facilitating the use of readily grown, relatively low diffusion-length material while still offering the potential for high energy-conversion efficiencies.

We report herein the use of p-Si and n⁺ p-Si wire-array photocathodes for the production of H₂ from water. The Si wires were grown by a templated vapor–liquid–solid growth process, using an earth-abundant metal catalyst, Cu, and a readily available Si precursor, SiCl₄, in an atmospheric-pressure chemical vapor deposition system. The lithographic template used in this work produced wires that were ~2.8 μm in diameter and were arranged on a square lattice with a center-to-center pitch of 7 μm.

Growth was performed for ~30 min at 1000 °C to produce wires 40–60 μm in length. The wires were doped p-type during growth with BCl₃ to produce carrier concentrations of ~10⁻¹⁷ cm⁻³, as determined by four-point probe measurements on individual wires. Scanning photocurrent measurements demonstrated that these wires had minority-carrier diffusion lengths of ~30 μm.

Some wire arrays were subsequently processed to introduce an n⁺-doped emitter shell, producing a radial n⁺ p junction in each wire. The performance of the wire-array electrodes was compared to that of similarly processed planar (100)-oriented single-crystalline Czochralski-grown p-Si electrodes (0.7 Ω cm resistivity). Figure 1a,b compares the current density–potential (J–E) behavior of planar and wire-array p-Si electrodes in aqueous pH 2.
The photocathode efficiency of the Pt/p-Si devices (planar and wires) was strongly dependent on the platinization procedure and also decayed with time. The reported data are the initial performance of the best p-Si samples obtained by the Pt deposition procedure outlined in the SI. The n+p-Si samples, in contrast, showed stable and reproducible performance, with the average Pt/n+p-Si performance far superior to the best Pt/p-Si samples.

Table 1. Electrode Parameters for Platinized Si Hydrogen-Evolving Photocathodes (100 mW cm⁻² ELH illumination)

<table>
<thead>
<tr>
<th>type</th>
<th>E(V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>ff</th>
<th>η (%)</th>
<th>n</th>
<th>samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/p-Si planar</td>
<td>0.30</td>
<td>23</td>
<td>0.3</td>
<td>2.1</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>Pt/p-Si wires</td>
<td>0.16</td>
<td>7.5</td>
<td>0.18</td>
<td>0.21</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>Pt/n-p-Si wires</td>
<td>0.56 ± 0.01</td>
<td>28 ± 1</td>
<td>0.60 ± 0.02</td>
<td>9.6 ± 0.9</td>
<td>1.8 ± 0.1</td>
<td>5</td>
</tr>
<tr>
<td>Pt/n-p-Si wires</td>
<td>0.54 ± 0.01</td>
<td>15 ± 2</td>
<td>0.71 ± 0.02</td>
<td>5.8 ± 0.5</td>
<td>1.10 ± 0.04</td>
<td>8</td>
</tr>
</tbody>
</table>

where \( i_{\text{max}} \) is the current (mA) at maximum power, \( E_{\text{max}} \) is the electrode potential at maximum power (V vs SCE), \( E(H^+/H_2) \) is the Nernst potential for H₂ evolution (V vs SCE in the electrolyte), \( P_\text{in} \) is the incident optical power density (mW cm⁻²), and \( A \) is the electrode area (cm²). The efficiency of the photocathode is thus referenced to a hypothetical, ideally nonpolarizable cathode that would operate with no overpotential losses at \( E(H^+/H_2) \). The three-electrode photoelectrochemical performance data, therefore, do not include losses that might be present at the counter electrode in a two-electrode tandem or voltage-assisted photoelectrolysis system.

A predominant factor that limited the energy-conversion efficiency of both the planar and wire-array p-Si photocathodes was the relatively low \( V_{oc} \) of the p-Si/H₂O electrolyte. The observed \( V_{oc} \) values are consistent with prior studies of p-Si/H₂O interfaces, which indicate that the potential of the Si valence-band edge is not sufficiently positive with respect to \( E(H^+/H_2) \) to produce a high photovoltage (Figure 2a). The Pt/p-Si photocathodes also exhibited relatively low fill factors at all light intensities, consistent with the presence of a thin oxide barrier at the Pt–Si interface, formed during Pt deposition, that impeded interfacial charge transport. Likewise, \( J-E \) data collected in the dark for similarly platinized p-Si electrodes showed a large series resistance compared to the Pt disk electrode. In contrast, p-Si (and p-Si) electrodes with discontinuous 1-nm-thick electron-beam-evaporated Pt films exhibited dark hydrogen-evolution activity similar to that of the polished Pt disk electrode, indicating the presence of an ohmic contact between p-Si and Pt in the absence of an interfacial oxide.

To overcome these drawbacks, a buried metallurgical n+p junction was introduced into the Si wires. Figure 2 shows how the buried junction decouples the band bending and photovoltage characteristics of the electrode from the energetics of the semiconductor/liquid contact. The general scheme for the fabrication of such n+p radial junctions is presented in Figure 3. For comparison, an n emitter was also diffused into p-Si wafers to yield planar n+p junctions (see SI).

To provide an electrocatalyst for H₂ evolution, Pt was deposited onto the planar and wire-array n+p electrodes via electron-beam evaporation. For the planar electrodes, \( ~1 \text{nm} \) of Pt was deposited, which coalesced into sub-micrometer Pt particulate islands (Figure 4c). Evaporated Pt was used because it yielded electrodes with much higher fill factors than those subjected to electropolished Pt deposition, consistent with the \( J-E \) data measured for evaporated Pt on n-Si electrodes (Figure 4a). The wire arrays were first partially filled with wax (Figure 4d inset), and a planar-equivalent thickness of 1.5 nm of
Pt was evaporated onto the top portion of the wires. The wax infiltration prevented the evaporated Pt, which formed an ohmic contact to both the n− shell and the p-type wire core, from causing shunts at defective/broken wires near the bottom of the wire array. The conductive n− shell transported collected electrons vertically to the catalyst-coated tips of the wires.

Figure 4 compares the J−E behavior of typical planar and wire-array Pt/n− p-Si electrodes. Average photoelectrode parameters are given in Table 1. The high Voc is consistent with the presence of a buried metallurgical p−n junction with low dark/recombination current. The high fill factor is consistent with the high electrocatalytic performance of the thin Pt film in acidic aqueous electrolytes and with a low-resistance contact between the n−Si and the Pt. Increasing the incident light intensity such that Jsc > 30 mA cm−2 marginally decreased the ff of the wire-array electrodes to 0.68 ± 0.02, suggesting that the amount of Pt added to the exposed wire tips would be sufficient to sustain, with minimal overpotential, the current densities associated with a wire-array device that absorbed all of the incoming light at 1 sun Air Mass 1.5 illumination conditions.

Integrating-sphere optical measurements have revealed that the optical absorption is minimized when Si wire arrays are oriented at normal incidence relative to a direct-beam illumination source.20 As shown in Figure 5a, the short-circuit photocurrent density of the Pt/n− p-Si wire arrays increased when the electrode was tilted relative to the incident beam direction until θ ∼ 35°, at which point the improved absorption was offset by the decreased photon flux that struck the electrode at higher angles of incidence.

Figure 5b shows the typical spectral response for the planar and wire-array Pt/n− p-Si electrodes. The planar electrode showed a peak external quantum yield, Φext of ∼0.65, consistent with reflection losses at the Si−water interface and weak absorption by the thin Pt film. The large decrease in Φext for λ < 400 nm can be attributed to poor charge-carrier collection in the n+ emitter, which could be improved by optimization of the doping parameters.21 The spectral response for the wire-array electrode, with Φext peaking near 500 nm, is consistent with the published optical absorption of the wire arrays.20 When the wire arrays were tilted relative to the incident beam, the peak Φext value increased to 0.76, demonstrating that the internal quantum efficiency (Φint) for charge collection in this radial Pt/n− p-Si architecture is ≥0.76. Convolution of the spectral response in Figure 5b with the American Society for Testing and Materials Air Mass 1.5 global spectrum (ASTM AM1.5G) predicts a Jsc at θ ∼ 35° of 13.4 mA cm−2. The photocurrents measured under ELH illumination were typically ∼15% larger than the photocurrent predicted from the ASTM AM1.5G spectrum. This difference is due to the mismatch between the ASTM AM1.5G and ELH-lamp spectra and is amplified by the peaked shape of the wire-array spectral response compared with that of planar Si electrodes (Figure 5b).14,22 Subsequent measurement of the wire-array electrodes under 100 mW cm−2 of Oriel Xe solar simulation with an AM1.5G filter set (which has a somewhat better match to the ASTM AM1.5G spectra, see SI) yielded Jsc = 13 ± 1 mA cm−2, and therefore produced photo-electrode efficiencies of ∼5%.

The H2-evolving Pt/n− p-Si wire-array electrodes were relatively stable under cathodic conditions. After >22 h of continuous operation under 1 sun illumination, with the electrode poised potentiostatically near the maximum power point (0.4 V vs RHE), the ff of a Pt/n− p-Si wire array electrode decreased slightly, from 0.67 to 0.62. Etching the electrode for 5 s in 10% aqueous HF restored the ff to 0.65, indicating the possible formation of a thin surface oxide due to incomplete cathodic protection. Additional efforts to protect the Si surface from oxidation should improve the durability of this system, as has been shown for Si microsphere photocathodes producing H2 in aqueous HBr.23

The data presented herein demonstrate that high photovoltages, fill factors, and Φint values are achievable through the use...
of radial-junction photocathodes fabricated from Si grown via a vapor–liquid–solid mechanism. The thermodynamic efficiencies of the Pt/n-p-Si wire-array photocathodes reported here of 5–6% are higher than those measured for thin-film CuGaSe₂ (<1%, due to low photovoltages), p-Si wafer photocathodes (2–3%) studied herein and previously, and planar p-WSe₂ single crystals (6–7%), but only for low-level monochromatic illumination. However, the Si wire-array performance is below that reported for Rh-modified single-crystal InP (~13%) as well as for planar Pt/n-p-Si samples studied herein and previously (~10%). These planar Si electrodes could themselves be substantially improved through optimization of doping, antireflective surface texture, and catalyst placement. The wire arrays, however, provide several potential advantages. They allow the use of lower-purity Si with shorter minority-carrier diffusion lengths, in conjunction with the ability to transfer the partially embedded wire arrays into a flexible polymer-based electrode form factor. Compared to a planar device, the wire arrays also afford an increased surface area for electrolyt catalyst attachment, which may be important when utilizing non-precious metal electrocatalysts with lower per-atom activities.

By increasing the light absorption in the Si wire-array electrodes, it should be possible to double the energy-conversion efficiencies to values that approach those achieved for optimized single-crystal photocathodes (i.e., >10%). Structures that incorporate optical light-trapping features, including an Ag back reflector and Al₂O₃ scattering particles, have been shown to increase the absorption in Si wire arrays. Preliminary measurements on electrodes with these features added yielded Jₛₑ = 24.5 mA cm⁻² under ELH-type solar simulation (see SI). However, the processing steps associated with the introduction of the light-trapping features degraded the ff (0.55) and Voc (0.49 V), so the efficiency improved only marginally (η = 6.6%).

Efforts are underway to enhance light absorption while maintaining and/or improving the demonstrated photocathode properties, to replace Pt with non-precious-metal hydrogen-evolution catalysts, and to integrate these Si wire-array photocathodes with efficient photoanodes such that the direct, efficient photoelectrolysis of water, without wires or external biasing, can be achieved.

ASSOCIATED CONTENT

Supporting Information. Detailed procedures for growth, processing, and testing of the planar and wire-array Si electrodes; analysis of the wire-array electrodes with light trapping features; spectral irradiance curves for the light sources used. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(16) Such an ideal electrode, of course, does not exist. This method of calculating electrode efficiency thus includes losses associated with both concentration and kinetic overpotentials, as well as series resistance, and hence underestimates the actual photoelectrode performance relative to a real dark cathode for H₂ production in this same electrolyte.