Next-Generation Si Microwire Array Devices for Unassisted Photoelectrosynthesis

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California Institute of Technology
May 15, 2013

Project ID #
PD099

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Overview

Project Timeline

- Start date: November, 2011
- End date: June, 2013
- Percent complete: 75%

Budget

- Total project funding
  - DOE share: $150,000
  - Contractor share: $0
- Funding by year
  - FY12: $75k
  - FY13: $50k (projected)

Barriers Addressed

- Photoelectrochemical Hydrogen Production – Photoelectrode System
- Materials Durability – Bulk and Interface
- Integrated Device Configurations

Partners / Collaborators

- University of Manitoba (Freund, Oliver, Thomson Groups): evaluation of single microwire–polymer junctions
- Technical University of Denmark (Chorkendorff Group): amorphous-MoS\textsubscript{x} electrocatalyst synthesis
- École Polytechnique Fédérale de Lausanne (Ballif Group): amorphous-Si:H semiconductor deposition
**Objective:** Fabricate a scalable Si microwire array-based device for sunlight to clean H$_2$ fuel production, through hydrohalic acid splitting

<table>
<thead>
<tr>
<th>DOE Barriers and Targets</th>
<th>Project Goal</th>
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</table>
| Photoelectrochemical Hydrogen Production – Photoelectrode System | • Fabricate polymer-embedded arrays of n-type and p-type crystalline Si microwires  
  • Demonstrate stable sunlight-driven hydrohalic acid splitting  
  • Identify stable and efficient non-noble-metal electrocatalysts |
| AF) Materials Durability – Bulk and Interface | • Stabilize Si from oxidation while passing anodic current in aqueous HI and HBr electrolytes |
| AG) Integrated Device Configurations | • Fabricate an organic photovoltaic that contains ionically conductive materials  
  • Fabricate a tandem Si microwire array with an integrated amorphous-Si light absorber  
  • Demonstrate sunlight-driven H$_2$ evolution through HBr splitting with a tandem device |
## Approaches / Milestones

### Status & Description of Milestones

<table>
<thead>
<tr>
<th>A) 100% Complete</th>
<th>B) 75% Complete</th>
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<tbody>
<tr>
<td>Stable n-type Si microwire array electrodes decorated with Pt electrocatalysts for sustained sunlight-driven iodide oxidation in HI((aq)) with &gt; 3% sunlight-to-electrical energy conversion efficiency and &gt; 80% stability of the short-circuit photocurrent density, (j_{sc}) (200 hr operation)</td>
<td>Peeled, flexible, radial buried-homojunction pn(^+)-doped Si microwire array devices decorated with Pt electrocatalysts and partially embedded in Nafion(^\circledR) for stable HI((aq)) splitting with &gt; 3% sunlight-to-hydrogen energy conversion efficiency</td>
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### Results

<table>
<thead>
<tr>
<th>Substeps achieved:</th>
<th>Substeps achieved:</th>
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<tbody>
<tr>
<td>Optimal CVD–VLS growth procedure for n-type Si microwire arrays, including:</td>
<td>Pt electrocatalyst deposition on the backsides of peeled, polymer-embedded Si microwire arrays by electron-beam evaporation</td>
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<tr>
<td>• Post-growth microwire processing and etching</td>
<td>• Methylation of the backsides of peeled, polymer-embedded Si microwire arrays for protection</td>
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<tr>
<td>• Surface methylation of microwires for protection</td>
<td>• Fabrication of a measurement system, including:</td>
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<td>• Potentiostatic electrochemical deposition of Pt</td>
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<td></td>
<td>• A means of forced convection (inductive stirring)</td>
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<td>• An imaging system (borescope)</td>
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<td>• In situ reaction product detection capabilities to 1% (j_{sc}) (mass spectrometry and visible spectroscopy)</td>
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**Remaining barrier:** Devices leak through macroscopic pinholes in the Nafion\(^\circledR\) membrane, preventing useful efficiency measurements
## Approaches / Milestones

**August and November, 2012: 9- and 12-Month Reports**

<table>
<thead>
<tr>
<th>Status &amp; Description of Milestones</th>
<th>Results</th>
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</thead>
</table>
| **C) 90% Complete;** Radial, buried-homojunction np⁺-doped Si microwire array electrodes with > 3% sunlight-to-electrical energy conversion efficiency in (non-)aqueous electrolyte  
(Prerequisite: Milestone A) | **Substep achieved:** Optimal boron emitter doping conditions from BN source wafers of 7 min at 950 °C  
Remaining barrier: A 2.2% efficiency was observed in non-aqueous electrolyte, but a > 3% efficiency was attained for aqueous iodide photo-oxidation |
| **D) 50% Complete;** Peeled, flexible, radial buried-homojunction n(p⁺)-doped Si microwire array devices decorated with Pt electrocatalysts and partially embedded in Nafion® for stable HI(aq) splitting with > 3% sunlight-to-hydrogen energy conversion efficiency  
(Prerequisites: Milestones B, C) | **Substep achieved:** In situ growth of an n⁺-doped region at the bottom of the microwires to form a low-resistance tunnel junction between the backsides of n-type Si microwires and Pt  
Remaining barrier: Low-resistance contacts were not present after a required high-temperature oxidation step which gettered the dopants |
<p>| <strong>E) No Go; 10% Complete;</strong> Innovation Project: Ionically conductive organic photovoltaic with $V_{ion\text{-drop}} &lt; 10$ mV (at 10 mA/cm²), $V_{oc} &gt; 600$ mV, and $j_{sc} &gt; 10$ mA/cm² | Remaining barrier: Efficient organic photovoltaics were fabricated by drop casting, but their water and air instability occluded measurements when Nafion® was introduced or when in contact with aqueous electrolyte |</p>
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<tr>
<th>Status &amp; Description of Milestones</th>
<th>Results</th>
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</thead>
<tbody>
<tr>
<td><strong>F) 50% Complete</strong>: Stable p-type Si microwire array electrodes for sustained bromide oxidation in HBr(aq) in the dark with &gt; 80% current stability (200 hr operation)</td>
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<tr>
<td><strong>Substep achieved</strong>: PEDOT:PSS on surface-functionalized planar Si was stable for halide oxidation</td>
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<td><strong>Remaining barrier</strong>: Atomic layer deposition of TiO$_x$, AlO$_x$, or MnO$_x$ on Si partially stabilized the Si but also significantly attenuated current flow</td>
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<tr>
<td><strong>G) Go; 50% Complete</strong>: Peeled, flexible, stable, tandem amorphous-Si on crystalline Si microwire array devices with Pt and partially embedded in Nafion® for stable HBr(aq) splitting with &gt; 8% sunlight-to-hydrogen energy conversion efficiency</td>
<td></td>
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<tr>
<td><strong>Substep achieved</strong>: Amorphous Si was deposited by PECVD on pn$^+$-doped Si microwire arrays, which exhibited $V_{oc-max} \approx 960$ mV in non-aqueous electrolyte, and $V_{oc-max} \approx 780$ mV for aqueous H$_2$ evolution</td>
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<td><strong>Remaining barrier</strong>: There is room for improvement because planar devices exhibited $V_{oc-max} \approx 1.2$–1.3 V</td>
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<td><strong>H) 50% Complete</strong>: Peeled, flexible, stable, tandem p-Si</td>
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<td><strong>Substep achieved</strong>: A &gt; 90% transparent electrically and ionically conductive membrane was fabricated</td>
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<td><strong>Remaining barrier</strong>: The optimal membrane formulation, containing Ag nanowires, PEDOT:PSS, and Nafion®, is not yet determined</td>
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### Approaches / Milestones

#### November, 2013: 24-Month Report

<table>
<thead>
<tr>
<th>Status &amp; Description of Milestones</th>
<th>Results</th>
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<tr>
<td><strong>K) 50% Complete</strong>; Mo/W(S,Se)$_2$ nanometer-sized electrocatalysts for efficient halide oxidation and H$_2$ evolution in the dark with &lt; 150 mV overpotential at 10 mA/cm$^2$</td>
<td><strong>Substep achieved:</strong> PEDOT:PSS on surface-functionalized planar Si was stable and somewhat catalytic for halide oxidation. <strong>Remaining barrier:</strong> Amorphous MoS$_x$ on Si met this goal for H$_2$ evolution but MoS$_x$ is not stable during sustained halide oxidation</td>
</tr>
<tr>
<td><strong>L) 25% Complete</strong>; Peeled, flexible, stable, tandem p-Si</td>
<td></td>
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<tr>
<td><strong>I, J, M)</strong> Removed these milestones, because my program timeline will be curtailed when I begin my independent faculty career this fall</td>
<td>N/A</td>
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(Prerequisites: Milestones B, C, D, F, K)
Accomplishments / Progress

- Four major steps in the CVD–VLS growth fabrication process of n-type Si microwire arrays, with optional radial n⁺-type emitters

- Electrically active dopant density in individual n-type Si microwires before and after processing calculated from four-point-probe resistance measurements

- Dopant densities of ~1 x 10¹⁷ cm⁻³ resulted in the most efficient devices

- 6-month

Fabrication protocol for n-type Si microwire arrays
Accomplishments / Progress

Efficient n-type Si microwires were realized

- Three-electrode $j-E$ measurements in Me$_2$Fc$^{+/0}$–LiClO$_4$–CH$_3$OH demonstrate a state-of-the-art corrected $\eta = 3.4\%$
- Electrode is an n-type Si microwire array after thermal oxidation processing

- Three-electrode spectral response measurements of the same electrode type in the same electrolyte demonstrate external quantum yields similar to those previously measured for p-type Si microwire arrays
Efficient and stable n-type Si microwires photo-oxidize iodide

- Three-electrode \( j-E \) measurements in fuming aqueous HI demonstrate a state-of-the-art uncorrected \( \eta = 3.6\% \)
- Electrode is an n-type Si microwire array after thermal oxidation, surface methylation (scheme), and Pt catalyst deposition
- Stability was > 80 \% of \( j_{sc-initial} \) over 200 hours continued operation while continuously illuminated
Accomplishments / Progress

- Three-electrode \( j-E \) measurements in \( \text{Me}_2\text{Fc}^{+0}/\text{LiClO}_4-\text{CH}_3\text{OH} \) demonstrate a corrected \( \eta = 2.2\% \)

- Electrode is an undoped Si microwire array grown on an \( n^+ \)-Si substrate after thermal oxidation and \( p^+ \) radial emitter doping

- Three-electrode \( j-E \) measurements in fuming aqueous HI demonstrate an uncorrected \( \eta = 3.5\% \)

- Same electrode type but with Pt catalyst deposition (instability was due to lack of surface methylation)

**Efficient (\( n^+ \))ip\(^+ \)-doped Si microwires were realized**
Accomplishments / Progress

- Two-point-probe individual n-type Si-microwire–PEDOT:PSS j–E measurements (inset) evaluating the contact resistances: one that had been annealed 10 hr on an n+(P)-Si substrate, and one that was grown as an axially doped n+n-Si microwire and then went through the thermal oxidation process.
- Three-electrode j–E measurements in fuming aqueous HI demonstrate an uncorrected $\eta = 2.6\%$.
- Electrode is an axially doped n+n-Si microwire array grown after thermal oxidation, surface methylation, and Pt catalyst deposition (inset).

$n^+n$-doped Si microwires are efficient with little shunting, but are not degenerate after the thermal oxidation step.
Accomplishments / Progress

PEDOT:ClO$_4$ stabilizes Si from oxidation and efficiently catalyzes bromide oxidation, while a-MoS$_x$ is stable during H$_2$ evolution catalysis in fuming HBr

- Three-electrode $j$–$E$ measurement in fuming aqueous HBr demonstrate very efficient and stable bromide oxidation catalysis in the dark

- Electrode is planar p-Si with mixed methyl/thienyl surface chemistry, and electropolymerized PEDOT:ClO$_4$

- Three-electrode chronoamperometry measurement in fuming aqueous HBr demonstrate very stable H$_2$ evolution catalysis in the dark

- Electrode is planar p-type Si with mixed methyl/thienyl surface chemistry, and electrodeposited amorphous MoS$_x$
Accomplishments / Progress

- Three-electrode \( I–E \) measurements in fuming aqueous HCl demonstrate an uncorrected \( \eta = 1.2\% \) for \( \text{H}_2 \) evolution
- Electrode is a p-type Si microwire array after thermal oxidation, \( n^+ \) radial emitter doping, and Pt catalyst deposition (inset)

Unassisted HI splitting occurs via \( \text{H}_2 \) evolution at an illuminated \( pn^+ \)-doped Si microwire photocathode while a backside electrode oxidizes iodide to triiodide
Accomplishments / Progress

Apparatus and measurement system for free-standing hydrohalic acid splitting from peeled, polymer-embedded microwire arrays was developed

- Apparatus and conditions used to quantify I$_3^-$ and H$_2$ products in situ using visible spectroscopy and mass spectrometry
- Fiber optic excitation source, inductive stirrers, gas-tight cathode compartment, and 2 mm pathlength anode compartment
- Products generated at (current) rates > 100 µA/cm$^2$ can be detected
Accomplishments / Progress

- Three-electrode $j–E$ measurements in aqueous 0.5 M H$_2$SO$_4$ demonstrate photoelectrochemical H$_2$ evolution using amorphous MoS$_x$ catalysts

- Electrode is a p-type Si microwire array after thermal oxidation, p$^+$ radial emitter doping, and a-MoS$_x$ electrochemical deposition

- Three-electrode spectral response measurements of the same electrode in the same electrolyte demonstrating the loss in absorbance above 850 nm with subsequent a-MoS$_x$ deposition due to light absorption by the a-MoS$_x$ semiconductor catalyst

Amorphous MoS$_x$ on pn$^+$-doped Si microwires catalyzes H$_2$ evolution in acidic electrolytes
Accomplishments / Progress

• Scheme depicting arrangement of materials in tandem amorphous-Si on crystalline Si microwire arrays

• Three-electrode $j–E$ measurements in CoCp$_2$–LiClO$_4$–CH$_3$CN demonstrate a state-of-the-art uncorrected $\eta = 0.65\%$ with $V_{oc} = 960$ mV, and uncorrected $\eta = 0.43\%$ with $V_{oc} = 780$ mV in 0.5 M H$_2$SO$_4$ after Pt electrocatalyst deposition

Tandem amorphous-Si on crystalline-Si microwire arrays obtain larger photovoltages than Si microwire arrays alone
Accomplishments / Progress

- Two Si microwire arrays, each partially embedded in Nafion®, and held together with a composite membrane consisting of Nafion®, PEDOT:PSS and Ag nanowires in a 2.33 : 4.15 : 4.15 ratio (inset)

- Membrane performance parameters for the state-of-the-art membrane composition

- This composition results in a negligible 0.4 mV potential drop at 10 mA/cm² and thus can be made less electrically conductive and more transparent and adhesive

A transparent electrically and ionically conductive membrane was fabricated

Design of Experiments Optimized Component

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<thead>
<tr>
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<th>Measured</th>
<th>Calculated</th>
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<tbody>
<tr>
<td>Sheet/Longitudinal Conductance (mS/sq)</td>
<td>69 ± 20</td>
<td>N/A</td>
</tr>
<tr>
<td>Transverse, Area-Specific Conductance (S cm⁻²)</td>
<td>26.9 ± 0.2</td>
<td>22.8</td>
</tr>
<tr>
<td>Integrated Transmittance (&lt; 1100 nm; %)</td>
<td>89 ± 6</td>
<td>92</td>
</tr>
<tr>
<td>Time to Complete Delamination (min)</td>
<td>46 ± 19</td>
<td>37</td>
</tr>
</tbody>
</table>
Accomplishments / Progress

- Solid-state two-electrode $j-E$ measurements of a drop cast organic photovoltaic (scheme) to mimic a deposition condition that could be amenable to the backsides of peeled, polymer-embedded Si microwire arrays

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This project is a no-go for making this OPV ionically conductive
Collaborations

• n-type Si microwire backside contacts
  » Prof. Michael Freund, Prof. Derek Oliver, Prof. Douglas Thomson, Dr. Iman Yahyaie, Elahe Asgari at the University of Manitoba (individual microwire evaluation)
  » Prof. Nathan Lewis, Noah Plymale at Caltech (metal contact characterization)

• Amorphous MoS$_x$ electrocatalysts on Si microwire arrays
  » Prof. Ib Chorkendorff, Dr. Brian Seger at the Technical University of Denmark (DTU) (catalyst synthesis techniques)
  » Prof. Nathan Lewis, Chris Roske at Caltech (deposition and electrode evaluation)

• Amorphous-Si:H || crystalline-Si microwire tandem arrays
  » Prof. Christophe Ballif, Dr. Corsin Battaglia, Mathieu Boccard at the École Polytechnique Fédérale de Lausanne (EPFL) (a-Si:H PECVD deposition)
  » Prof. Nathan Lewis, Amanda Shing at Caltech (electrode evaluation)

• Electrically and ionically conductive membranes
  » Prof. Nathan Lewis, Sang Hee Park, Rasmus Nørregård at Caltech (fabrication and characterization)

• Ionically conductive organic photovoltaics
  » Prof. Nathan Lewis, Marino DiFranco at Caltech (fabrication and device evaluation)
## Proposed Future Work

**FY2013 (July, 2013: 20-Month Report)**

<table>
<thead>
<tr>
<th>Description of Work</th>
<th>Plan to Meet Milestones</th>
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<tbody>
<tr>
<td><strong>B, D)</strong> Re-evaluate peeled, flexible, radial buried-homojunction Si microwire array devices with Pt electrocatalysts and partially embedded in Nafion® for stable HI(aq) splitting with &gt; 3% sunlight-to-hydrogen energy conversion efficiency</td>
<td>Continue to perfect the infilling and peeling technique for microwire arrays partially embedded in Nafion®, alter formulation of Nafion® precursor solution to assist in more uniform, pinhole-free casting of membranes</td>
</tr>
<tr>
<td><strong>H)</strong> Optimize formulation for electrically and ionically conductive membrane using Nafion®, PEDOT:PSS, and Ag nanowires</td>
<td>Define the essential parameters and evaluation techniques to quantify the membranes, and perform a design of experiments analysis to determine the optimal membrane composition</td>
</tr>
<tr>
<td><strong>F, K)</strong> Continue to evaluate PEDOT:PSS and other candidate catalysts and protective layers to catalyze bromide oxidation and protect Si from oxidation in fuming HBr, respectively</td>
<td>Investigate nitride and carbide nanoparticle materials known to be efficient and stable halide oxidation catalysts in nitrile-based electrolytes</td>
</tr>
<tr>
<td><strong>G)</strong> Continue to evaluate amorphous-Si on crystalline Si microwire array photoelectrodes for H₂ evolution</td>
<td>Alter the deposition protocol to increase the amorphous Si conformality and introduce a stable, conductive, transparent coating to attenuate a-Si oxidation</td>
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## Project Summary

A scalable Si microwire array-based device for sunlight to clean H₂ fuel production, through hydroiodic acid splitting, was demonstrated.

<table>
<thead>
<tr>
<th>DOE Barriers and Targets</th>
<th>Key Take-Home Points</th>
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| **Photoelectrochemical Hydrogen Production – Photoelectrode System** | • Peeled Nafion®-embedded arrays of n-type and p-type crystalline Si microwires were fabricated  
• Stable and efficient sunlight-driven hydroiodic acid splitting was demonstrated  
• Amorphous MoSₓ catalyzes H₂ evolution in fuming HBr and is stable |
| **AF) Materials Durability – Bulk and Interface** | • PEDOT:ClO₄ stabilizes Si from oxidation while passing anodic current in aqueous HI and HBr electrolytes |
| **AG) Integrated Device Configurations** | • An efficient tandem Si microwire array, with an integrated amorphous-Si light absorber, was fabricated  
• A transparent electrically and ionically conductive membrane for a tandem device design was fabricated |