Semiconductor Materials for Photoelectrolysis

2013 U.S. DOE Hydrogen & Fuel Cells Program Review

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Project ID: PD035

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline

• Project start date: 2004
• Project end date: 9/2013*
• Percent complete: 90%

Budget

• Total project funding
  o DOE share: $9.8M
• Funding received in FY12: $1100k**
• Planned funding for FY13: $720k

Barriers

• Barriers addressed
  o AE. Materials Efficiency – Bulk and interface
  o AF. Materials Durability – Bulk and interface
  o AG. Integrated Device Configurations
  o AI. Auxiliary Materials

Partners

• Interactions/collaborations
  o Lawrence Livermore National Lab
  o University of Nevada Las Vegas (UNLV)
  o Los Alamos National Laboratory
  o Colorado School of Mines
  o University of Colorado
  o University of Louisville
  o University of Hawaii
  o Stanford University (SU)
  o University of Texas-Arlington (UTA)
  o Program production solicitation – MVSystems, Inc.

* Project continuation and direction determined annually by DOE
** Includes UNLV, SU and UTA support
Relevance

Old technical targets vs. new technical targets

### 2007

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2003 Status</th>
<th>2006 Status</th>
<th>2013 Target</th>
<th>2018 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Usable semiconductor bandgap</td>
<td>eV</td>
<td>2.8</td>
<td>2.8</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Chemical conversion process efficiency (EC)</td>
<td>%</td>
<td>4</td>
<td>4</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Plant solar-to-hydrogen efficiency (STH)</td>
<td>%</td>
<td>not available</td>
<td>not available</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Plant durability</td>
<td>hr</td>
<td>not available</td>
<td>not available</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

### 2012

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2011 Status</th>
<th>2015 Target</th>
<th>2020 Target</th>
<th>Ultimate Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoelectrochemical Hydrogen Cost</td>
<td>$/kg</td>
<td>NA</td>
<td>17.30</td>
<td>5.70</td>
<td>2.10</td>
</tr>
<tr>
<td>Capital cost of Concentrator &amp; PEC Receiver (non-installed, no electrode)</td>
<td>$/m²</td>
<td>NA</td>
<td>200</td>
<td>124</td>
<td>63</td>
</tr>
<tr>
<td>Annual Electrode Cost per TPD H₂</td>
<td>$/yr-TPDH₂</td>
<td>NA</td>
<td>2.0M</td>
<td>255K</td>
<td>14K</td>
</tr>
<tr>
<td>Solar to Hydrogen (STH) Energy Conversion Ratio</td>
<td>%</td>
<td>4 to 12%</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>1-Sun Hydrogen Production Rate</td>
<td>kg/s per m²</td>
<td>3.3E-7</td>
<td>1.2E-6</td>
<td>1.6E-6</td>
<td>2.0E-6</td>
</tr>
</tbody>
</table>

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf
Relevance

• The objective of this work is to develop low band gap semiconductor material devices that can split water into hydrogen and oxygen spontaneously upon illumination with a minimum of 10% efficiency.

• The main focus this past year has been to work with state-of-the-art III-V materials that meet DOE’s near-term efficiency targets and optimize surface treatments that promote durability.

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<tr>
<td>Photoelectrochemical Hydrogen Cost (^b)</td>
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</tr>
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<td>3.3E-7</td>
<td>1.2E-6</td>
<td>1.6E-6</td>
<td>2.0E-6</td>
</tr>
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</table>
Approach

The US DOE PEC Working Group approach towards efficient and durable solar H₂ production

NREL-led Project Focus:
- Extend durability of highly efficient materials
- Ensure efficiencies are maintained and not compromised by durability treatments
- Investigate new materials that can achieve ultra-high future efficiency goals
Approach: Engineering Known Materials

Enhancing durability of GaInP₂/GaAs tandem system through material engineering

• **High efficiency**
  - Only demonstrated system that exceeds unbiased 10% solar-to-hydrogen target
    - 12.4% with Pt-black counter electrode,
      >16% with RuO₂ CE at moderate bias
  - Metal organic chemical vapor deposition (MOCVD) synthesis
    - Synthesis by NREL’s III-V team

• **Focus: optimize stability treatment**
  - Ideal system for observing and modeling corrosion
  - Can tolerate efficiency losses due to protective treatment and still meet 10% target

• **III-V cost barriers are falling due to innovative synthesis routes**

New technical targets for efficiency require new (III-V) materials
Approach: Surface Validation Team

Partner with specialists that have unique expertise and resources

Detailed spectroscopic measurements to observe and understand the chemistry of the surface and near-surface of III-V (GaInP$_2$)

- **Heske group at UNLV**
  - XPS, XAS, XES, IPES, UPS, AFM
    - Some measurements at Advanced Light Source (ALS)
  - Snapshots of surface pre-, intermediate, post-exposure
  - Identify common features of and conditions that lead to corrosion
  - **Characterize stabilized surfaces**

**Goals**—Use combination of surface spectroscopy and theory to...

1. Study PEC corrosion in III-V’s, the simplest (model) system to uncover corrosion initiation sequence and develop remediation strategy
2. Identify chemical character and mechanism of successful protective treatments
3. Apply lessons learned to other systems capable of high efficiency solar water splitting
Partner with specialists with unique expertise and resources

Theoretical modeling of the electronic structure of III-V (GaInP₂)

- **Partner with Ogitsu group at LLNL**
  - Calculate XAS and XES spectra to correlate experimental result with surface/near surface compositions
  - Ab initio molecular dynamics simulations
  - Model surfaces for mechanistic understanding of hydrogen evolution and corrosion

Goals—Use combination of surface spectroscopy and theory to...

1. Study PEC corrosion in III-V’s, the simplest (model) system to uncover corrosion initiation sequence and develop remediation strategy
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## Approach – Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Due Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Submit all materials for the 18 documents to publisher for inclusion of PEC standard methods book.</td>
<td>01/13</td>
<td>Completed</td>
</tr>
<tr>
<td>Complete feasibility study of synthesizing CuBiW$_2$O$_8$, an ideal band gap oxide (estimated around 2.2 eV) that theory has predicted to have low electron and hole effective masses, and report results.</td>
<td>04/13</td>
<td>Completed</td>
</tr>
<tr>
<td>Using epilayer p-GaInP$_2$, determine optimal conditions to achieve reproducible protection of the semiconductor surface to provide long-term (&gt;100 hours) durability of high-efficiency III-V photoelectrodes at conditions greater than 10mA/cm$^2$.</td>
<td>05/13</td>
<td>Completed</td>
</tr>
<tr>
<td>Complete short-circuit lifetime measurements of GaInP$_2$/GaAs tandem cells that have had the best available nitrogen ion implanted surface passivation treatments identified in milestone 3.4.2 and determine the durability benchmarked against the 1000 hour operational lifetime at ≥10% efficiency target.</td>
<td>07/13</td>
<td>60%</td>
</tr>
<tr>
<td>Evaluate stability of dilute bismide semiconductor material in a PEC environment compare to near-term goal of 100 hours at 10mA/cm$^2$ and make go/no-go decision on further studies.</td>
<td>07/13</td>
<td>60%</td>
</tr>
<tr>
<td>Evaluate III-V material efficiency and durability using photoreactors with intrinsic solar concentration (≤10x) under on-sun conditions and report on material</td>
<td>09/13</td>
<td>40%</td>
</tr>
</tbody>
</table>

To date, all program milestones have either been met or are on-track for on-time completion.
Technical Accomplishments – UNLV Spectroscopic Characterization

Collaboration with UNLV instrumental in identifying/optimizing nitrogen ion (N$_2^+$) treatment

- **Identify conditions that led to successful nitride treatment**
  - After initial success, we were unable to reproduce the protective treatment
  - Breakthrough provided by UNLV allowed us to repeat stability treatment
  - XPS Survey showed enabling component of working treatment (unintentional metal contamination)

- **UNLV partners aid in optimizing nitride treatment conditions**
  - Nitride difficult to detect in dilute amounts by conventional techniques (low-Z element)
  - Significant time between original treatment and its repetition, ion-gun was abused
  - UNLV XES analysis at Advanced Light Source gives us feedback we need to tune our new ion source to achieve the level of nitride incorporation in original “champion” sample

- Synchrotron data collection by Michael Weir
- Analysis by Michael Weir, Lothar Weinhardt, Kyle George, Clemens Heske
- Co-inventors on provisional patent application
Technical Accomplishments – Reproduce Protective Treatment on GaInP₂

Trace amounts of Ga and In in corrosion solutions indicate a protected surface

Photoelectrode durability conditions
- 3M H₂SO₄ with fluorosurfactant
- AM1.5 G simulated light
- -10mA/cm² (12.3% STH equivalent) constant current applied
- 24 hours
- Tandem electrode conditions slightly different (constant V)

Feedback and analysis from UNLV identified enabling component of treatment (applied via sputtering) and allowed us to reproduce protective effect

Durability Electrolyte Analysis by ICP-MS

Untreated
Two separate (identical) treatments
Treated tandem
Control (untreated p-GaInP₂ epilayer) etched significantly (~1 μm)

- Constant current (-10mA/cm²) for 24 hours in 3M H₂SO₄

Tandem electrode (p-GaInP₂ on p/n-GaAs) had no detectable etching after 24 hours at about twice the current density

- Constant voltage (-1V vs Pt CE)
- Average ~ -18.5mA/cm²
  - Equivalent flux of 23% efficiency
- Important step toward future devices
  - 25% STH under 10X light concentration ~200mA/cm²

Progress in optimizing nitrogen ion (N₂⁺) treatment: promising results at very high currents

Technical Accomplishments - Tandem Surface Protection
Technical Accomplishments—PEC Performance Maintained

In addition to preventing physical degradation the nitrogen ion ($\text{N}_2^+$) treatment maintains PEC performance of $\text{p-GaInP}_2$ after 24 hours of durability testing at -10 mA/cm$^2$ in 3M H$_2$SO$_4$.

Treated and untreated samples have equivalent light-limited photocurrent magnitudes (no loss of efficiency).

Dark current, reduced photocurrent and shift in onset potential are indicative of corrosion.

3M H$_2$SO$_4$
AM1.5G
GaInP$_2$ ref cell

Black: pre-durability
Red: post-durability
Technical Accomplishments – New III-V materials

Tandem materials with lower band gaps needed to meet 25% STH target – Optimal combination for stacked system is 1.6eV/0.9eV

- **Continued work to optimize In$_x$Ga$_{1-x}$N material system**
  - Continuously variable band gap between 3.4 eV (GaN) and 0.7 eV (InN)
  - Samples synthesized by molecular beam epitaxy at LANL by Todd Williamson
  - Poster PD097

- **Dilute Bismides (GaAs$_{1-x}$Bi$_x$)**
  - Incorporating bismuth in to GaAs during growth lowers the $E_g$ from 1.42 eV without significant loss in electron and hole mobility
  - Samples synthesized by molecular beam epitaxy at NREL by Aaron Ptak

- **Tandem absorber considerations**
  - Band gap – $E_g$ (eV)
    - Lower band gap utilizes greater portion of solar spectrum and can achieve higher photocurrents
    - GaInP$_2$/GaAs is 1.8eV/1.4eV
  - Lattice constant – $a$ (Å)
  - Charge carrier mobilities – $\mu$ (cm$^2$/V-s)
Technical Accomplishments – Photoreactor for On-sun Testing

Photoreactor design, fabrication, and testing

Developed photoreactor for outdoor testing to evaluate durability and efficiency under real-world conditions

- Made from PMMA for optimal chemical resistance and optical transparency
- Mounted on a solar tracker at NREL’s Solar Radiation Research Laboratory
- Real-time solar spectral and intensity data used to evaluate solar-to-hydrogen efficiency

Gases collected by inverted pipettes
Pressures equalized by leveling funnel

[Image of photoreactor and setup]

[Diagram of photoreactor dimensions]
Standardization of PEC result reporting

• Motivated by inaccurate efficiency reporting throughout PEC literature
• Material that didn’t make it into abbreviated Journal of Materials Research (JMR) review paper turned into a Springer short book
• Photoelectrochemical Water Splitting – Standards, Experimental Methods, and Protocols
• Editors:
  o Zhebo Chen – Stanford
  o Huyen Dinh – NREL
  o Eric Miller – DOE

Original JMR paper cited over 100 times

http://www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html
NREL and UNLV collaborate with the Quantum Simulations (Ogitsu) group at Lawrence Livermore National Lab to help interpret and complement experiments. One highlight is the use of calculated N K-edge x-ray emission spectra of various nitride incorporation environments in GaInP₂ to deconvolute UNLV measured spectra of N₂⁺ treated GaInP₂ materials.

See next talk PD058 for details of theory work at LLNL.
Collaborations

Partners (extensive collaboration with all)

- University of Nevada Las Vegas
  - As-grown, nitride treated, and PEC tested GaInP₂ samples sent to Heske group for X-ray spectroscopic characterization both at UNLV and the Advance Light Source to identify corrosion intermediates and products and uncover chemistry of protected surfaces
  - Key partner in surface validation project

- Lawrence Livermore National Laboratory
  - Ogitsu group uses molecular dynamic simulations and theoretical calculations coupled with observations from UNLV analysis to elucidate corrosion mechanism
  - Key partner in surface validation project (PD058)

- University of Hawaii
  - CuGaSe₂, and RuO₂ from Hawaii for Pt catalyst studies; WO₃ from Hawaii for dual photoelectrode testing; cooperative PEC characterization; sample exchange and validation (PD053)

- Stanford University
  - Jaramillo group- subcontract on high surface area transparent conductive oxides and quantum confined nanostructured transition metal dichalcogenides (PD033)
  - Key partner in PEC standardization efforts

- University of Texas-Arlington
  - Professor Muhammad Huda for PEC materials theory and modeling (PD052)

- MVSystems, Inc. (Industry)
  - Program production solicitation
  - We provide efficiency and durability characterization of a-SiC:H obtained from our collaborator (PD053)
Collaborations

Partners (extensive collaboration with all)

- Los Alamos National Laboratory
  - Todd Williamson synthesizes InGaN samples (PD097)

- Colorado School of Mines
  - Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange

- University of Colorado-Boulder
  - Host two NSF-graduate research fellow associates

- University of Louisville
  - Sunkara group - ALD of TiO$_2$ on GaInP$_2$
  - Several graduate students visited to learn PEC characterization techniques

- University of Oregon
  - Boettcher group - Joint InGaN PEC characterizations
Proposed Future Work

• Work with surface validation team
  o Optimize nitrogen ion treatment and understand protective mechanism through spectroscopic observations and theoretical modeling by our surface validation team partners

• Expand nitrogen ion implantation treatment
  o Once optimized, apply to GaInP$_2$/GaAs tandem surfaces and test at short-circuit until failure and compare against 1000-hour near-term goal (key milestone)
  o Apply anti-corrosion treatment to other III-V surfaces and determine if protection translates to other material sets

• Investigate emerging III-V alloys
  o Variable band gap In$_x$Ga$_{1-x}$N and GaAs$_{1-x}$Bi$_x$ systems
  o Develop tandem configurations that will provide potential difference necessary for photoelectrolysis while maximizing current in order to meet future DOE efficiency targets

• Photoreactor testing under on-sun conditions
  o Evaluate efficiency and durability of III-V materials in photoreactors mounted on solar trackers that use intrinsic (~10x) concentration
  o Response to diurnal and intermittent (clouds) light cycling

• Monitor breakthrough advances in III-V synthesis
  o Develop economic models (with NREL analysts) to determine if cutting-edge techniques such as epitaxial lift off can provide high volume III-V fabrication at the cost reductions necessary to achieve economical PEC hydrogen production (Alta Devices, Microlink Devices)
Project Summary

Relevance: Spearheading research in high-efficiency materials in order to meet DOE metrics and objectives for solar-hydrogen generation

Approach: Focus on high-efficiency III-V crystalline semiconductor systems, an NREL core competency: investigation of new materials and configurations as well as stabilization of GaInP$_2$ surface

Technical Accomplishments: Reproduced protective treatment for GaInP$_2$ surfaces and are optimizing it with assistance from UNLV; progress in understanding nitride incorporation and its role in mitigating corrosion through spectroscopy and theory partnership; characterized new III-V material GaAs$_{1-x}$Bi$_x$ with a potential for higher photocurrents; constructed a prototype photoreactor for mounting on a solar tracker and evaluating PEC devices under natural sunlight; Springer brief PEC standards publication

Collaborations: Several ongoing, active collaborations with synthesis, modeling, and characterization groups

Proposed Future Work: Optimize nitrogen ion implantation treatment with surface validation partners; apply anti-corrosion treatment to other III-V’s and tandem system – test to failure at short-circuit and compare against 1000-hr benchmark; investigate emerging III-V materials with potential for higher efficiencies; photoreactor for III-V efficiency and stability evaluation under concentrated on-sun conditions; III-V economics at scale
Acknowledgements

- Henning Döscher – NREL
- Heli Wang – NREL
- Clay Macomber – NREL
- Huyen Dinh – NREL
- Erin Brahm – (intern) Sawanee (UG)
- Andrew Pinkard – (intern) CalState San Marcos (UG)
- Adolfredo Alvarez – (intern) Stanford (UG)
- Adam Welch – NREL/Colorado School of Mines (GS)
- Aaron Ptak – NREL
- Arrelaine Dameron – NREL
- All of our amazing collaborators noted throughout this presentation
Technical Back-Up Slides
Logistical issues with surfactant

Surfactant is necessary to facilitate bubble evolution but makes quantitative analysis of electrolysis products nontrivial.

Semiconductor degradation is much more rapid under bubble evolution in electrolyte without surfactant.
Technical Back-Up

- IPCE of treated electrode pre- and post-durability corroborate higher photocurrents after durability testing
- One possible explanation—hydrogen evolution could be passivating surface damage caused by ion implantation leading to improved IPCE at higher energies.

IPCE conditions:
3M H$_2$SO$_4$ with fluorosurfactant
-0.75V vs. Ag/AgCl
300W Xe lamp with 335nm long-pass filter
Light chopped at 0.2 Hz
Technical Back-Up

- Surface nitridation conditions

  - 3 cm Ion Tech gridded source.
  - Angle: 55 degrees
  - Distance: 8 inches.
  - Pressure: 7.0 E-4 torr (Nitrogen)
  - Filament current (Source) 3.21A
  - Discharge current 0.22A
  - Discharge voltage 55V
  - Beam current 12mA
  - Beam voltage 550V
  - Accelerator current 2mA
  - Accelerator voltage 100V
  - Neutralizer current 10mA
  - Filament current (neutralizer) 2.94V

Samples treated for 30 seconds
Technical Back-Up

Spectral mismatch simulating AM1.5G using laboratory light sources

- **Sun**: 5800K blackbody radiator
  - Absorption bands due to atmospheric constituents
- **Tungsten**: 3200K blackbody
- **Xe**: 6000K-with emission lines

Scaled fluxes for comparison

Multijunction absorber device STH efficiencies measured under simulated light sources need to be validated under actual solar conditions
Pretty good match of outdoor spectrum with reference spectrum
Variation due to altitude, aerosol optical depth