Overview

Timeline and Budget

• Project start date: 10/1/14
• Project end date: 9/30/17
• Total project budget: $3M
  o Total recipient share: $0
  o Total federal share: $3M
  o Total DOE funds spent*: $0.5M**

* As of 3/31/15
** Includes UNLV, LLNL, LANL, UH support

Barriers

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

Partners

• Interactions/collaborations
  o University of Nevada Las Vegas
  o Lawrence Livermore National Lab
  o University of Hawaii
  o Los Alamos National Laboratory
  o Stanford University
  o Colorado School of Mines
  o University of Colorado-Boulder
  o University of Louisville
  o University of Oregon
  o Denmark Technical University
Relevance

Objectives

- Long-Term: Develop highly-efficient, durable material that can operate under 10-15x (or higher) solar concentration and generate renewable hydrogen for <$2/kg from photoelectrochemical (PEC) water splitting

- Current year:
  - Push boundaries on achievable semiconductor photoelectrochemical solar-to-hydrogen (STH) efficiencies
  - Continue development of stabilizing surface modifications viable at high current densities

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2011 Status</th>
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<tr>
<td>Photoelectrochemical Hydrogen Cost \textsuperscript{b}</td>
<td>$/kg</td>
<td>NA</td>
<td>17.30</td>
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<td>2.10</td>
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<tr>
<td>Capital cost of Concentrator &amp; PEC Receiver (non-installed, no electrode) \textsuperscript{c}</td>
<td>$/m\textsuperscript{2}</td>
<td>NA</td>
<td>200</td>
<td>124</td>
<td>63</td>
</tr>
<tr>
<td>Annual Electrode Cost per TPD H\textsubscript{2} \textsuperscript{d}</td>
<td>$/yr-TPDH\textsubscript{2}</td>
<td>NA</td>
<td>2.0M</td>
<td>255K</td>
<td>14K</td>
</tr>
<tr>
<td>Solar to Hydrogen (STH) Energy Conversion Ratio \textsuperscript{e,f}</td>
<td>%</td>
<td>4 to 12%</td>
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<td>25</td>
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<tr>
<td>1-Sun Hydrogen Production Rate \textsuperscript{g}</td>
<td>kg/s per m\textsuperscript{2}</td>
<td>3.3E-7</td>
<td>1.2E-6</td>
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Relevance

DOE EERE Multi-Year Research, Development, and Demonstration Plan

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Technoeconomic analysis for a type 4 (10x concentrator) PEC reactor

Project Guiding Principles

- Primary focus is on efficiency, the largest lever to reduce H₂ costs according to technoeconomic analysis
- Scalability is primary selection criterion, more important than earth abundance
- Absorber cost and durability (lifetime) issues can be addressed through engineering

Approach

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

EERE: Applied R&D to develop cost-effective large-scale systems
NSF: Use-inspired basic research (theory, synthesis, characterization)
Emphasis on collaboration across disciplines and institutions

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

Maximize efficiency first then focus on durability via surface modifications, investigate lower-cost synthesis once material has been identified.

- **Tandem absorbers**
  - Task 1: Demonstrating attainable efficiencies
    - III-Vs by MOCVD (NREL)
  - Task 2: higher-risk, lower-cost approaches
    - In$_x$Ga$_{1-x}$N tandems (LANL)
    - III-V-N on Si tandems (NREL)
    - Coupled photoanode-photocathode systems (Hawaii, NREL)

- **Surface modifications – spectroscopy (UNLV) and modeling (LLNL)**
  - Ion-implantation & flash sputtering (NREL)
  - Thin coatings by atomic layer deposition (NREL, CU)
  - Molybdenum disulfide coatings (Stanford)

- **Benchmarking, prototyping, & demonstration**
  - Photoreactor design and outdoor device testing (NREL, JCAP-Solar Fuel Hub)
Approach: High Efficiency via Tandems


- Exceeding 20% solar-to-hydrogen (STH) feasible
- Reactors with low water penetration for 25% STH
- GaInP₂/GaAs (1.8 eV, 1.4 eV) not optimal

- Traditional MOCVD requires lattice matching from substrate through all epitaxial layers to maintain high material quality
- Metamorphic growth removes “vertical-only” constraint by incorporating a transparent, step-graded layer to allow non-lattice matched absorbers
- Inverted Metamorphic Multijunction (IMM) growth: top junction grown first, device layers removed from substrate, could potentially be re-used
Understanding and remedying semiconductor photocorrosion at PEC interfaces is a complex task that has benefitted significantly from a collaborative approach which teams experts with unique capabilities and resources.

- **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**
    - Show where we are in parameter space wrt. amounts of N & PtRu

- **Ogitsu group at LLNL**
  - Develop theoretical tool chest for modeling PEC systems
  - Simulate x-ray spectra to correlate UNLV experimental results with surface/near surface compositions
  - Model III-V surfaces to uncover the key mechanisms of surface corrosion
Innovative materials discovery and development for faster product development. Key elements include:

- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

Surface Validation: Photocorrosion of III-V materials with Heske (UNLV), Ogitsu (LLNL)

**Correlate Spectroscopy with Theory on Nitrided p-GaInP₂**

**System: Establish Base for Predictive Capabilities**

- Based on observation that nitridation led to stabilized GaInP₂ surface: Model the local nitrogen environment to understand measured spectra
- Theoretical N₂⁺ implanted GaInP₂ nitrogen K-edge XES spectrum by LLNL constructed from various types of nitrogen impurity states as well as the experimental XES measured by UNLV group at LBNL synchrotron

**MGI Elements Incorporated: theory, modeling, experimental**

- Encourage and enable integrated R&D
- Enable creation of accurate, reliable simulations
- Support creation of accessible materials data repository (sharepoint)
- Provide opportunities for integrated research experiences
Approach: Pathways to III-V Semiconductor Cost Reductions

- **Optical concentration**
  - 10x-100x uses less absorber

- **Re-use substrate**
  NREL report PR-6A00-60126
  - Epitaxial lift-off
  - Multilayer epitaxial assemblies
  - Spalling
  - Laser lift-off

- **Alternative substrate**
  NREL report PR-6A00-60126
  - III-V on Si
  - Metal foil
    - Close-space vapor transport
    - Ion beam assisted deposition

- **Alternative precursors**
  - Close-spaced vapor transport
  - Hydride vapor phase epitaxy

This is a very active area of research that includes commercial cell manufacturers and funding support from ARPA-E.
Inverted growth – light-facing wider bandgap grown first

- Top junction lattice-matched to substrate
- Device transferred to handle material and substrate removed
  - Potential substrate re-use
  - Reflective back contact
Progress: IMM Devices for Increased Utilization of Solar Spectrum – On the Path to Higher Efficiency

Increasing bandgap-limited current
- Absorber junctions in series: voltages add, current limited by lower value (current matching)
- Lowered bottom junction increases total photon flux but lowers voltage

Integrated IPCE

Increased device current
Buried junction to improve voltage
Anti-reflection to smash world-record
Progress: Met 400-hour Milestone – 468 Hours of Durability with N$_2^+$/PtRu

Fouling of the electrode was minimized by changing the electrolyte every weekday.

- p-GaAs with N$_2^+$ ion bombardment and PtRu sputtering
- Operated at 15mA/cm$^2$ in 3M H$_2$SO$_4$ with 1mM Triton X-100
- Some fouling still occurred
- Cleaning in methanol and nitric acid restored light-limited photocurrent to original value
- Photocurrent onset potential was degraded
  - Catalyst deactivation?
  - Catalysts loss?

Over 150 hrs durability with MoS$_2$

Jaramillo (Stanford) poster PD119
Progress: Mapping Pt & Ru Distribution from \( \text{N}_2^+ / \text{PtRu} \) Surface Modification

- Simultaneously treated GaAs substrate and GaInP\(_2\) epilayers
- Digested entire GaAs wafer, portions of GaInP\(_2\) in aqua regia and Pt, Ru determined by ICP-MS
- Reported in thickness (nm) of compact film
- Results:
  - Nitridation step significant source of PtRu
  - Fairly uniform spatial distribution
  - Full treatment on GaAs much greater than sum of parts

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( p^+)-GaAs Subs. Ru (nm)</th>
<th>p-GaInP(_2) Epi. Ru (nm)</th>
<th>( p^+)-GaAs Subs. Pt (nm)</th>
<th>p-GaInP(_2) Epi. Pt (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitridation</td>
<td>0.22 ±0.02</td>
<td>0.25 ±0.07</td>
<td>0.18 ±0.02</td>
<td>0.19 ±0.06</td>
</tr>
<tr>
<td>Sputtering</td>
<td>0.28 ±0.04</td>
<td>0.17 ±0.01</td>
<td>0.19 ±0.02</td>
<td>0.13 ±0.01</td>
</tr>
<tr>
<td>Full</td>
<td>1.59 ±0.21</td>
<td>0.44 ±0.07</td>
<td>1.65 ±0.2</td>
<td>0.33 ±0.05</td>
</tr>
</tbody>
</table>
Progress: Work with Surface Validation Partner (UNLV) to Understand PtRu Loading Now vs. Then

- Original “magic” sample: (Old ion gun, no sputtering)
- First repetition of protection: (Old ion gun, PtRu sputtering)
- New “standard” treatment: (New ion gun, PtRu sputtering)

- X-ray photoelectron spectroscopy (XPS) by Monika Blum at UNLV reveals significantly (order of magnitude) greater noble metal loading on newer samples
- “Magic” samples had more N (by XES) and less PtRu than current parameter space
- Can’t achieve low PtRu and high N with current set-up
- Future: new non-air-exposed samples to UNLV to evaluate N loading & distribution

Approximate % of treated GaInP₂ samples with desired durability:
- New “standard” treatment: 30%
- New “standard” treatment: 30%
- First repetition of protection: 90%
- Original “magic” sample: 90%

Not where we want to be in terms of N and PtRu loading for max durability.
Progress: Reactor Design

- Initial design had optical concentration from curved front window and large pathlength through electrolyte.
- Electrolyte absorbs large fraction of usable infrared photons.
- New design for lab characterization and demonstration that reduces electrolyte pathlength from 2 cm to 4 mm.
Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

- “It is unclear what impact lifetime has on cost projections. A tornado plot would help”
  - Response: We have included a tornado plot for a type 4 (concentrator) PEC reactor that shows the impact of lifetime on hydrogen cost projections on slide 4.

- “The singular weakness of this project is the disconnect with the fabrication team for III-V material. It appears the material is produced with a foundry-type relationship. It would be better served if the material fabrication was a more integral part of the project, with shared ownership in the success.”
  - Response: We have significantly strengthened our interaction with the III-V group in several ways. We wrote in dedicated, direct funding for synthesis in the FOA proposal, we share a postdoc (Henning Döscher) that has expertise in PEC and III-V synthesis that designs and submits run recipes with our input, and we have regular meetings with the III-V group. The enhanced confederation has already borne fruit: the co-inventors on our provisional patent application on IMM III-Vs for photoelectrolysis is a combination of PEC and III-V group members.
Collaborations

• Partners (extensive collaboration with all)
  o University of Nevada Las Vegas
    – Partner in surface validation project
  o Lawrence Livermore National Laboratory
    – Partner in surface validation project
  o University of Hawaii (PD116)
    – Gaillard group – Partner on dual photoelectrode approach; sample exchange and validation
  o Los Alamos National Laboratory
    – Mark Hoffbauer – InGaN samples
  o Stanford University (PD119)
    – Jaramillo group – Key partner in MoS$_2$ for stabilization efforts
  o Technische Universität Ilmenau, (Germany)
    - Henning Döscher, Marie Curie fellow, is a member of our PEC group and NREL’s III-V group
  o Technical University of Denmark
    – Ib Chorkendorf – DTU hosts one of our students, sample exchange
  o Colorado School of Mines
    – Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange
  o University of Colorado-Boulder
    – Two NSF-graduate research fellow associates under Steve George and Art Nozik are part of our group
  o University of Louisville
    – Sunkara group – novel III-Vs (GaAs$_x$Sb$_{1-x}$)
    – Joint characterizations/publication
  o University of Oregon
    – Boettcher group – Student exchange, joint III-V-N PEC characterizations
  o Helmholtz-Zentrum, Berlin (Germany)
    - Roel Van de Krol – We host student studying transparent OER catalysts
Remaining Challenges and Barriers

• **Efficiency:**
  - Push solar-to-hydrogen efficiency from 12% to beyond 20% for meeting ultimate DOE targets

• **Durability:**
  - Extend our 0.2 year durability to 2 years in the short-term and 10 years long-term
  - More realistic real-world durability assessments
  - Identification and control of non-obvious but stability-relevant process parameters

• **Semiconductor costs:**
  - Reduce synthesis costs by factor of 10 compared to current cost of small-batch III-V materials

• **System testing:**
  - Identify promising photoreactor designs and components
    - Window/body material, sealant/epoxy, membrane, counter electrode
Future Work—Towards *Economical* Hydrogen

In order to achieve the EERE plant-gate, untaxed cost targets of $1-2/kg H₂ (1kg H₂ = 1gge) requires a PEC system that has 25% solar-to-hydrogen (STH) efficiency, a semiconductor cost around $150/m², and 10 years of stability.

- **Efficiency**
  - Demonstrate >15% STH efficiency at short circuit for at least 1 hour (milestone)
  - Push efficiency by testing lower bandgap configurations that sacrifice voltage to achieve higher currents (efficiencies)

- **Durability**
  - Demonstrate 875 hours of durability at current density equivalent to 15% STH under 1 sun using three surface passivation approaches; work with surface validation team to understand mechanism of protection

- **Semiconductor Cost**
  - Simulate photoreactor performance with higher concentration using multi-physics modeling to evaluate what levels are practically achievable
  - Request samples for PEC characterization from others developing innovative III-V synthesis routes being developed by other DOE programs (SunShot, arpa-e)
    - Epitaxial lift-off, spalling, HVPE, CSVT

- **Photoreactor Prototyping**
  - Design and build photoreactors with low optical concentration and low electrolyte penetration depth for on-sun measurements on a solar tracker.
# 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:
- Developed IMM III-V devices capable of accessing highest possible STH efficiencies, continued optimization of surface treatment conditions and PtRu quantification; GaAs durability – 468 hours of stability @ 15 mA/cm$^2$ (improvement on previous 315 hours @ 15 mA/cm$^2$); began collaborative effort with Stanford on MoS$_2$ protection of III-Vs; modeled absorption of sunlight by water and influence on attainable STH efficiencies – published manuscript and designed new cells based on results; along with UNLV made progress in understanding history of PtRu on GaInP$_2$.

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

## Proposed Future Work:
Push STH efficiency limits with IMM III-Vs; evaluate III-V-N/Si tandems for lower cost, higher stability alternative; examine stacked mechanical (dual electrode) tandems with Hawaii; push three surface passivation approaches (N$_2^+$/PtRu, MoS$_2$, ALD TiO$_2$) to achieve over 875 h durability; design and fabricate concentrator cells and commence regular outdoor testing.
Technology Transfer Activities

- **Non-provisional patent filed on nitridation/sputtering surface protection (May 2014)**

**Stable photoelectrode surfaces and methods**
Publication number: US 20140332374 A1

**ABSTRACT**
Disclosed herein are methods of treating a semiconductor surface by nitridation and deposition of a ruthenium alloy. Also disclosed are semiconductors treated with these methods, their incorporation into photoelectrochemical cells, and their use in photoelectrochemical water splitting.

- **Provisional patent filed on using inverted metamorphic multi-junction III-Vs to achieve maximum attainable STH efficiency**
Acknowledgements

- John Turner – NREL
- Henning Döscher – NREL
- Heli Wang – NREL
- James Young – NREL/CU-Boulder (GS)
- Skye Rios – NREL/CU-Boulder (GS)
- Clay Macomber – NREL
- Huyen Dinh – NREL
- Anna Duda – NREL
- Arrelaine Dameron – NREL
- Andrew Norman – NREL
- All of our amazing collaborators noted throughout this presentation
Technical Back-Up Slides
Cost modeling projections for high-volume production of dual junction GaInP₂/GaAs PV on GaAs substrates using epitaxial lift-off (ELO) technology for substrate re-use. To get PEC material estimates in $/m², $/W is multiplied by 350W/m² (the efficiency).

Modeling performed by Mike Woodhouse of NREL's Strategic Analysis group, with funding provided by the DOE SunShot Initiative, “A Manufacturing Cost Analysis Relevant to Single- and Dual-Junction Photovoltaic Cells Fabricated with III-Vs and III-Vs grown on Czochralski Silicon”.

Publication Number NREL/PR-6A20-60126
Cost modeling projections for high-volume production of dual junction GaAs$_{0.75}$P$_{0.25}$/Si PV on Si substrates. To get PEC material estimates in $/m^2$, $/W$ is multiplied by 370W/m$^2$ (the efficiency). Modeling performed by Mike Woodhouse of NREL’s Strategic Analysis group, with funding provided by the DOE SunShot Initiative, “A Manufacturing Cost Analysis Relevant to Single- and Dual-Junction Photovoltaic Cells Fabricated with III-Vs and III-Vs grown on Czochralski Silicon”. Publication Number NREL/PR-6A20-60126

\[ \text{$0.60/W \times 370W/m^2 = \$222/m^2$} \]
Details of Ion Implantation and PtRu Sputtering Surface Modification

- Rotating sample stage – 15 rpm
- \( \text{N}_2^+ \text{ ion implantation first} \)
  - Key parameters: Angle (55°), distance (20 cm), pressure (8x10^{-4} \text{ N}_2), beam voltage (550 V), beam current (12 mA)
  - Rotated 9 min through ion source (exposed 30 s)
- PtRu alloy sputtering second
  - Two passes through sputter plume (exposed < 0.5 s)

PtRu morphology & loading

- Scanning transmission electron microscopy
  - ~ 5 nm particles with approximately 30% surface coverage
- Inductively coupled plasma mass spectrometry
  - Several samples digested in aqua regia, diluted solutions analyzed for PtRu
  - Equivalent coverage (assuming a continuous thin film) is between 1-2 nm
    - Adds $2/m^2$ to absorber costs
    - Requires 66 g of Pt for a 1000 kg/day type 4 reactor array using ultimate DOE targets (25% STH, 15x concentration)
Simulating AM 1.5 G Solar Spectrum

- Tungsten light source
- Xenon light source
- Filters
- Beam splitter

Graph showing photon flux (A/m²/nm) vs. wavelength (nm) with AM1.5G, Xe-W Simulator, and Xe AM1.5G Filter traces.