Protective Catalyst Systems on III-V and Si-based Semiconductors for Efficient, Durable Photoelectrochemical Water Splitting Devices

Thomas F. Jaramillo
Stanford University
June 13th, 2018

Project ID #PD161

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Project Overview

Project Partners
PI: Thomas F. Jaramillo, Stanford University
Co-PI: James S. Harris, Stanford University
Partner Organizations:
- National Renewable Energy Laboratory (NREL)
- PEC Working Group

Project Vision
To develop unassisted water splitting devices that can achieve > 20% solar-to-hydrogen (STH) efficiency, operate on-sun for at least 2 weeks, and provide a path toward electrodes that cost $200/m² using earth-abundant protective catalysts and novel epitaxial growth schemes.

Project Impact
Develop protective catalysts to stabilize III-V’s in acid for weeks of on-sun unassisted water-splitting and introduce a new tandem III-V/Si system that has the potential to dramatically reduce cost.

* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)
**Approach – Summary**

**Project Motivation**
Previous collaborative work with NREL and the Harris group showcased the ability to protect III-V surfaces and fabricate high STH devices. These results give us a path towards high efficiency and stable III-V/III-V and III-V/Si PEC devices.

**Proposed Targets**

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-to-hydrogen (STH)</td>
<td>16.7% - GaInP/GaInAs</td>
<td>&gt;20%</td>
</tr>
<tr>
<td>Stability (III-V)</td>
<td>~80 hrs – GaInP/GaAs</td>
<td>2 weeks on-sun</td>
</tr>
<tr>
<td>Si/III-V Tandem</td>
<td>Si-InGaN microwire synthesis</td>
<td>High quality InGaN epitaxial growth on Si</td>
</tr>
</tbody>
</table>

**Barriers**

**Stabilization of III-V surfaces in acid**

*Solution*: Fabricate conformal MoS\(_2\) & other non-precious protective catalysts that are stable and active for H\(_2\) evolution in acid.

**Fabrication scheme for high-quality InGaN growth on Si**

*Solution*: Design and synthesize graded buffer layers and MOCVD recipe development for high quality InGaN growth on Si substrates.

**Collection of on-sun data at the weeks time-scale**

*Solution*: By stabilizing unassisted water splitting devices for 100’s of hours of continuous illumination, we can test them outside for weeks.

**Partnerships**

**Jaramillo Group**
Electrochemistry, catalysis, protective layer expertise (characterization, catalysis deposition)

**Harris Group**
Semiconductor expertise, especially in novel fabrication techniques (InGaN growth)

**NREL**
III-V fabrication (epitaxial growth) expertise, on-sun testing expertise, photoelectrochemistry and corrosion expertise
**Approach – Project Motivation**

**Collaborating with NREL:**
Stabilizing GaInP photocathodes with MoS₂ protective catalysts

**Stabilizing Silicon:**
Stabilizing Si photocathodes for months with MoS₂ protective catalysts
Laurie A. King, et. al. ACS Appl. Mater. Interfaces, 2017, 9 (42), pp 36792–36798

**Previous Jaramillo and Harris group collaboration:**
> 30% STH with a GaInP/GaAs/GaInNAs triple junction PV paired with Pt and Ir electrolyzers

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**Cost-effective production of H₂ by solar water-splitting requires devices that are:**
- high efficiency,
- durable,
- and low cost.


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**Techno-economics of H₂ production by PEC (10% STH)**


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**Modeling device structure for optimal STH efficiencies**
## Approach – Two device architectures

<table>
<thead>
<tr>
<th>Scheme 1</th>
<th>Scheme 2</th>
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</thead>
<tbody>
<tr>
<td><strong>III/V-III/V</strong></td>
<td><strong>III/V-Si</strong></td>
</tr>
<tr>
<td>GaInP</td>
<td>InGaN</td>
</tr>
<tr>
<td>GaInAs</td>
<td>Si</td>
</tr>
</tbody>
</table>

**Scheme 1**
- High efficiency
- Robust design
- Prior success protecting in acid

**Scheme 2**
- Novel
- Pathway to cheaper fab
- Prior success growing LEDs

Scheme 1 is the most direct pathway to high efficiency devices. The PV industry is actively working to lower costs.

Scheme 2 involves InGaN materials that have already been scaled-up for LED manufacturing, representing an intrinsically lower-cost approach.

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Approach - Barriers and Innovation

**Barrier: Stabilization of III-V surfaces in acid**
- **Innovation:** Use MoS$_2$ and other non-precious protective catalysts that are stable in acid, conductive, and active for HER. Developing an understanding of fundamental degradation mechanisms through *in situ* studies and leverage those insights into better protective catalysts
  - **Task 1:** Translatable, thin-film catalyst and protection layer development
  - **Task 3:** III-V fabrication and PEC device development for tandem III-V and InGaN/Si
  - **Task 4:** In-situ stability studies
- **EMN Nodes:** i) Characterization of Semiconductor Bulk and Interfacial Properties (Todd Deutsch), ii) Corrosion Analysis of Materials (Todd Deutsch), and iii) III-V Semiconductor Epi-structure and Device Design and Fabrication (Daniel Friedman)

**Barrier: Fabrication scheme for high-quality InGaN growth on Si**
- **Innovation:** First demonstration of direct nucleation and growth of high-crystalline-quality InGaN on Si by MOCVD in this field
  - **Task 2:** Tandem InGaN/Si fabrication

**Barrier: Collecting on-sun data at the weeks time-scale**
- **Innovation:** By stabilizing III-V unassisted water splitting devices for 100’s of hours, we can test them outside for weeks
  - **Task 5:** On-sun testing at NREL
- **EMN Nodes:** On-Sun Solar-to-Hydrogen Benchmarking (Todd Deutsch)
## Approach – Budget Period 1 Scope of Work

<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Project Milestones</th>
<th>Type</th>
<th>Task Completion Date (Project Quarter)</th>
<th>Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Demonstrate &gt;100 h stability for a III-V photocathode which utilizes a non-precious metal HER catalyst</td>
<td>Milestone</td>
<td>3/31/18</td>
<td>&gt;90% Achieved 100 hr</td>
</tr>
<tr>
<td>1.2</td>
<td>Demonstrate &gt;100 h stability of OER catalysts in conjunction with a III-V based PEC device</td>
<td>Milestone</td>
<td>9/30/18</td>
<td>In progress</td>
</tr>
<tr>
<td>2.1</td>
<td>Demonstrate high-crystalline-quality n++- In$<em>{0.45}$Ga$</em>{0.55}$N growth on Si (111) substrates by sputter deposition, with n-type doping &gt; $10^{20}$ cm$^{-3}$ and root-mean-square surface roughness &lt; 0.5 nm.</td>
<td>Milestone</td>
<td>12/31/17</td>
<td>100% Achieved by MOCVD</td>
</tr>
<tr>
<td>2.2</td>
<td>Demonstrate high-quality undoped In$<em>{0.45}$Ga$</em>{0.55}$N and p-doped In$<em>{0.45}$Ga$</em>{0.55}$N by MOCVD, grown on n++-doped In$<em>{0.45}$Ga$</em>{0.55}$N sputter-deposited template layers, with properties similar to those measured for the sputter deposited films (see milestone 2.1)</td>
<td>Milestone</td>
<td>6/30/18</td>
<td>In Progress</td>
</tr>
<tr>
<td>2.3</td>
<td>Demonstrate repeatable Si p-n junctions with the desired hole concentrations and doping profiles.</td>
<td>Milestone</td>
<td>9/30/18</td>
<td>10% In Progress</td>
</tr>
<tr>
<td>4.1</td>
<td>Demonstrate effectiveness of the operando microscopy and spectroscopy flow cell measurement technique on a benchmark photoelectrode system such as previously developed MoS$_2$/III-V photocathodes.</td>
<td>Milestone</td>
<td>12/31/2018</td>
<td>50% In Progress</td>
</tr>
</tbody>
</table>
| Go/No-Go    | **The following two criteria will be met:**  
1) Demonstrate a PEC photoelectrode that achieves >10 mA/cm$^2$ under 1 sun illumination for longer than 100 h.  
2) Fabricate an unassisted PEC water splitting device with a non-precious metal HER catalyst that achieves STH efficiencies > 5% under 1 sun illumination to provide a viable pathway for achieving 20% STH efficiency through integration strategies of the materials and interfaces under investigation. | Go/No-Go | 12/31/2018                            | >90% #1 Achieved 100 hr #2 Achieved |
Relevance & Impact

This project advances towards <$2/kg hydrogen by:


Leveraging EMN Resource Nodes:

• NREL EMN Node: Characterization of Semiconductor Bulk and Interfacial Properties, Todd Deutsch
  – Characterization of fundamental semiconductor properties and growth defects before and after testing

• NREL EMN Node: Corrosion Analysis of Materials, Todd Deutsch
  – Pre- and post- failure analysis and improved understanding of catalyst corrosion and interfaces

• NREL EMN Node: III-V Semiconductor Epi-structure and Device Design and Fabrication, Daniel Friedman
  – Fabrication of III-V materials and systems and improved understanding of growth defects

• NREL EMN Node: On-Sun Solar-to-Hydrogen Benchmarking, Todd Deutsch
  – Testing station for collection of on-sun data for unassisted water splitting devices

This project is heavily engaged with the EMN nodes, which are absolutely necessary for the success of this project; the HydroGEN Consortium R&D model is working extremely well. Furthermore, we expect that our node utilization is helping to improve node capabilities by generating expertise such as improved understanding of catalyst corrosion and interface energetics in the PEC node as well as improved understanding of growth defects in the III-V fabrication node. We expect that the on-sun solar-to-hydrogen benchmarking node will also be of greater benefit to the community as we gain knowledge on testing our devices when the time comes.
## Accomplishments: Go/No-Go Milestones

<table>
<thead>
<tr>
<th>Go/No-Go Milestones</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
</table>
| #1 Demonstrate a PEC photoelectrode that achieves >10 mA/cm² under 1 sun illumination for longer than 100 h.  
**Significance:** *Clear demonstration of ability to stabilize III-V surfaces for time lengths that enable on-sun testing, a future goal of the project.* | 12/31/2018 | Achieved 100 hr |
| #2 Fabricate an unassisted PEC water splitting device with a non-precious metal HER catalyst that achieves STH efficiencies > 5% under 1 sun illumination to provide a viable pathway for achieving 20% STH efficiency through integration strategies of the materials and interfaces under investigation.  
**Significance:** *Clear demonstration of an operable unassisted water splitting device that contains no precious metal HER catalyst. This device can then be stabilized and used for on-sun testing as well be the starting point for the creation of a >20% STH efficient device.* | 12/31/2018 | Achieved |
Accomplishments for Task 1: Protective Catalysts

Single-crystal pn\textsuperscript+-GaInP\textsubscript{2}

Grown with organometallic vapor-phase epitaxy on a degenerately p-doped GaAs (100) substrate

Sputter and sulfidize 3nm of Mo

Deposited with a DC magnetron sputterer and sulfidized in 90% H\textsubscript{2}/10% H\textsubscript{2}S gas at 150 C for 2 hours

Flash sputter PtRu

Sample passed under sputter head for <1 s to create 2-5 nm PtRu particles with ~30% surface coverage

Samples tested in a compression cell with 3 M H\textsubscript{2}SO\textsubscript{4}

Conformal MoS\textsubscript{2} films were achieved on GaInP, and were compared to the champion PtRu nanoparticulate coatings prepared at NREL.
Accomplishments for Task 1: Protective Catalysts

MoS$_2$ vs PtRu on pn$^+$ GaInP Photocathodes

The MoS$_2$ functioned as a catalyst with an earlier onset potential than a platinum-modified pn$^+$ GaInP$_2$ photocathode.

GaAs substrate exposed indicating corrosion of GaInP$_2$

Chronoamperometry
Held at 0.295 V vs RHE

MoS$_2$ was used to protect pn$^+$ GaInP$_2$ for >100 hrs in 3M sulfuric acid.

<table>
<thead>
<tr>
<th>Task 1 Milestones</th>
<th>Completion Date</th>
<th>Status</th>
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<tbody>
<tr>
<td>1.1 Demonstrate &gt;100 h stability for a III-V photocathode which utilizes a non-precious metal HER catalyst</td>
<td>3/31/2018</td>
<td>Achieved 100 hr</td>
</tr>
<tr>
<td>1.2 Demonstrate &gt;100 h stability of OER catalysts in conjunction with a III-V based PEC device</td>
<td>9/30/2018</td>
<td>In Progress</td>
</tr>
</tbody>
</table>

The MoS$_2$ protective catalyst coating achieved superior stability compared to champion PtRu nanoparticle coatings from NREL, without sacrificing activity/efficiency.

Reuben J. Britto, James L. Young, Ye Yang, Myles Steiner, David LaFehr, Daniel Friedman, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. Submitted.

HydroGEN: Advanced Water Splitting Materials
Accomplishments for Task 1: Protective Catalysts

This demonstrates that a non-precious, protective catalyst layers based on MoS$_2$ may be suitable for efficient and stable unassisted water splitting devices.

Reuben J. Britto, James L. Young, Ye Yang, Myles Steiner, David LaFehr, Daniel Friedman, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. Submitted.
HydroGEN: Advanced Water Splitting Materials

Accomplishments for Task 2: Tandem InGaN/Si

- $\text{In}_x\text{Ga}_{1-x}\text{N}$ Indium compositions up to 39% achievable by MOCVD without phase separation.
- Six-fold rotational symmetry evidenced by InGaN (101) peak indicates strong in-plane texturing.
- RMS roughness from X-ray reflectivity $\sim$ 5nm.

High-quality films of InGaN have been successfully grown using MOCVD.
Accomplishments for Task 2: Tandem InGaN/Si

- Hall effect data:
  - $\text{In}_{0.16}\text{Ga}_{0.84}\text{N}$: background electron density $n \sim 2.5 \times 10^{17} \text{ cm}^{-3}$.
  - $\text{In}_{0.55}\text{Ga}_{0.45}\text{N}$: background electron density $n \sim 1.8 \times 10^{20} \text{ cm}^{-3}$.

<table>
<thead>
<tr>
<th>Task 2 Milestones</th>
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</tr>
</thead>
<tbody>
<tr>
<td>2.1 \text{Demonstrate high-crystalline-quality} n^{++}\text{-doped In}<em>{0.45}\text{Ga}</em>{0.55}\text{N growth on Si (111) substrates by sputter deposition, with n-type doping &gt; 10^{20} \text{ cm}^{-3} and root-mean-square surface roughness &lt; 0.5 nm}</td>
<td>\text{Achieved by MOCVD}</td>
</tr>
<tr>
<td>2.2 \text{Demonstrate high-quality undoped In}<em>{0.45}\text{Ga}</em>{0.55}\text{N and p-doped In}<em>{0.45}\text{Ga}</em>{0.55}\text{N by MOCVD, grown on n^{++}-doped In}<em>{0.45}\text{Ga}</em>{0.55}\text{N sputter-deposited template layers}</td>
<td>\text{In progress}</td>
</tr>
</tbody>
</table>

Smooth, highly conformal, crack-free, polycrystalline In$_x$Ga$_{1-x}$N films grown on Si (111).
Accomplishments for Task 3: Unassisted Water Splitting

Unassisted water splitting for ~12 hours and STH > 5% with a III-V/III-V inverted metamorphic multijunction (IMM) PEC device using MoS$_2$ as a protective catalyst coating.

<table>
<thead>
<tr>
<th>Task 3 Milestone (Same as Go/No-Go #2)</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabricate an unassisted PEC water splitting device with a non-precious metal HER catalyst that achieves STH efficiencies &gt; 5% under 1 sun illumination to provide a viable pathway for achieving 20% STH efficiency through integration strategies of the materials and interfaces under investigation.</td>
<td>12/31/2018</td>
<td>Achieved</td>
</tr>
</tbody>
</table>


Reuben J. Britto, James L. Young, Rachel Mow, Myles Steiner, Daniel J. Friedman, Todd G. Deutsch, and Thomas F. Jaramillo. In Prep.

HydroGEN: Advanced Water Splitting Materials
## Accomplishments for Task 4: In-Situ Stability Studies

### Task 4 Milestone

<table>
<thead>
<tr>
<th></th>
<th>Task 4 Milestone</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Demonstrate effectiveness of the in-situ microscopy and spectroscopy flow cell measurement technique on a benchmark photoelectrode system such as previously developed MoS$_2$/ III-V photocathodes.</td>
<td>12/31/2018</td>
<td>In Progress</td>
</tr>
</tbody>
</table>

**Successful initial development of *in-situ* microscopy flow cell for photoelectrochemical (PEC) studies.**

Reuben J. Britto, Sela Berenblum, Laurie A. King, James L. Young, Todd G. Deutsch, and Thomas F. Jaramillo. *In Prep.*
Collaboration: Effectiveness

- **EMN Collaboration**
  - Weekly meetings between Stanford (Reuben Britto) and NREL (James Young, Rachel Mow, Myles Steiner, Todd Deutsch) in the form of videochats
  - Weekly exchange of samples fabricated at NREL and further processed at Stanford
  - Parallel photoelectrochemical testing and characterization of samples at Stanford and NREL to ensure accuracy and accelerate research progress

- **Positive interactions with the broader HydroGEN community**
  - Kickoff meeting in November at NREL provided an opportunity to engage with the community, learn about the plethora of available tools, and hit the ground running
  - Event planned at ECS in Seattle to engage the HydroGEN community
  - Much of the HydroGEN community has been engaged and will continue to be engaged at PEC working group meetings

- **Incorporating project data onto the HydroGEN data hub**
  - Using the H2awsm tools shown at the kickoff meeting in November, we plan to upload our data for the greater community
  - We plan to upload the data present in our compilation of photocathode stability figure as well as our chronoamperometry and linear sweep voltammetry data
  - We expect that this will help accelerate the stability benchmarking effort

Collaboration with the EMN nodes and the broader HydroGEN community have been excellent, contributing greatly to the success of the project thus far.
Proposed Future Work

Currently, work is on track to proceed on schedule and on budget for Period 1. The following work is proposed for Period 2: Jan 1, 2019 – Sep 30, 2020, Budget $500k, contingent on the project’s continuation past budget Period 1.

- **Development of Si/InGaN Junction by MOCVD for Unassisted Water Splitting Devices:**
  - Fabrication of photovoltaics, and optimization of electronic properties
  - Implement protection scheme and catalyst
  - Demonstrate unassisted water splitting

- **Develop Strategies to Boost performance of Tandem Photoabsorber Systems, Towards 20% STH**
  - Boost stability and catalysis on tandem photoabsorber systems by optimizing electrolyte and deposition techniques: thickness, temperature, and composition to minimize pinholes and increase film durability
  - Perform On-sun Measurements at NREL, targeting device operation > 2 weeks

- **Probe corrosive failure mechanisms via development of a flow cell for operando microscopy and spectroscopy**
  - Harness insights towards creation of more stable and active electrodes

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Project Summary

Task 1 – Protective Catalysts
• MoS₂ protected pn⁺ GaInP₂ for ~100 hrs in 3M sulfuric acid.

Task 2 – High Quality InGaN on Si
• Direct nucleation of high-crystalline-quality InₓGa₁₋ₓN on Si (111) substrates using MOCVD

Task 3 – Stable Unassisted Water Splitting
• Greater than 5% STH unassisted water splitting for ~12 hours with a III-V/III-V PEC device using MoS₂ in lieu of any precious metal HER catalysts

Task 4 – In-situ Stability Studies
• Successful *in-situ* linear sweep voltammogram (LSV) data collected on a GaInP photocathode
Technical Back-Up Slides
Thin MoS$_2$ layers show promise as a protection scheme for III-V materials
A: n+/p GaInP$_2$ on deg. doped GaAs (photocathode)
- experimenting with different protection strategies (ALD deposition, in-situ characterization)

B: pn$^+$ GaInP$_2$ on pn GaAs (upright tandem)
- for ~10% STH unassisted water splitting for >100 hrs and for outdoor on-sun testing

C: Inverted equivalent of B
- for identifying issues caused by the inversion process on the path toward protecting true IMMs

D: True IMM GaInAsP/GaInP$_2$ or future variants
- for achieving >20% STH, and for outdoor on-sun testing
GaN on Si tandem solar cell
Efficiency ~ 0.1%


InGaN on Al₂O₃ solar cell
Efficiency ~ 2.3%


InGaN on Al₂O₃ MQW PEC
HBr hydrogen evolution efficiency 1.5%


InGaN/Si core/shell nanowires
Water splitting efficiency 0%

Growth of InGaN over the entire composition range at 450°C

In\textsubscript{0.73}Ga\textsubscript{0.27}N

Growth of In\textsubscript{0.4}Ga\textsubscript{0.6}N at 450°C

(a)


Growth of In\textsubscript{0.15}Ga\textsubscript{0.85}N at 550°C

No report of direct MOCVD growth of InGaN on Si to date.
