Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Project ID | p161

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

PI: Thomas Jaramillo[1], co-PI: James Harris[2]

[1] **Dept. of Chemical Engineering, Stanford University**

[2] **Dept. of Electrical Engineering, Stanford University**

April 30th, 2019

2019 DOE Hydrogen and Fuel Cells Annual Merit Review

Overview

Timeline

Project Start Date: 10/1/2017

Project End Date: 09/30/2020

% Complete: 34%

Barriers

Stabilization of unstable III-V surfaces in acid

Fabrication scheme for high-quality InGaN growth on Si

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

DOE Targets:

Cost of hydrogen production	$2.00/kg
Solar to hydrogen efficiency	20%
Electrode Lifetime	2 years

Budget

Budget Period 1 Funding*	**$222,556**
Budget Period 1 Funding*	**$494,523**

** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Partners

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

Harris Group
Semiconductor expertise, particularly in novel synthesis, processing, and fabrication techniques (InGaN growth)

NREL
III-V fabrication (epitaxial growth) expertise, on-sun testing expertise, unassisted water splitting device expertise

LBNL
In Situ Photoelectrochemical Raman spectroscopy

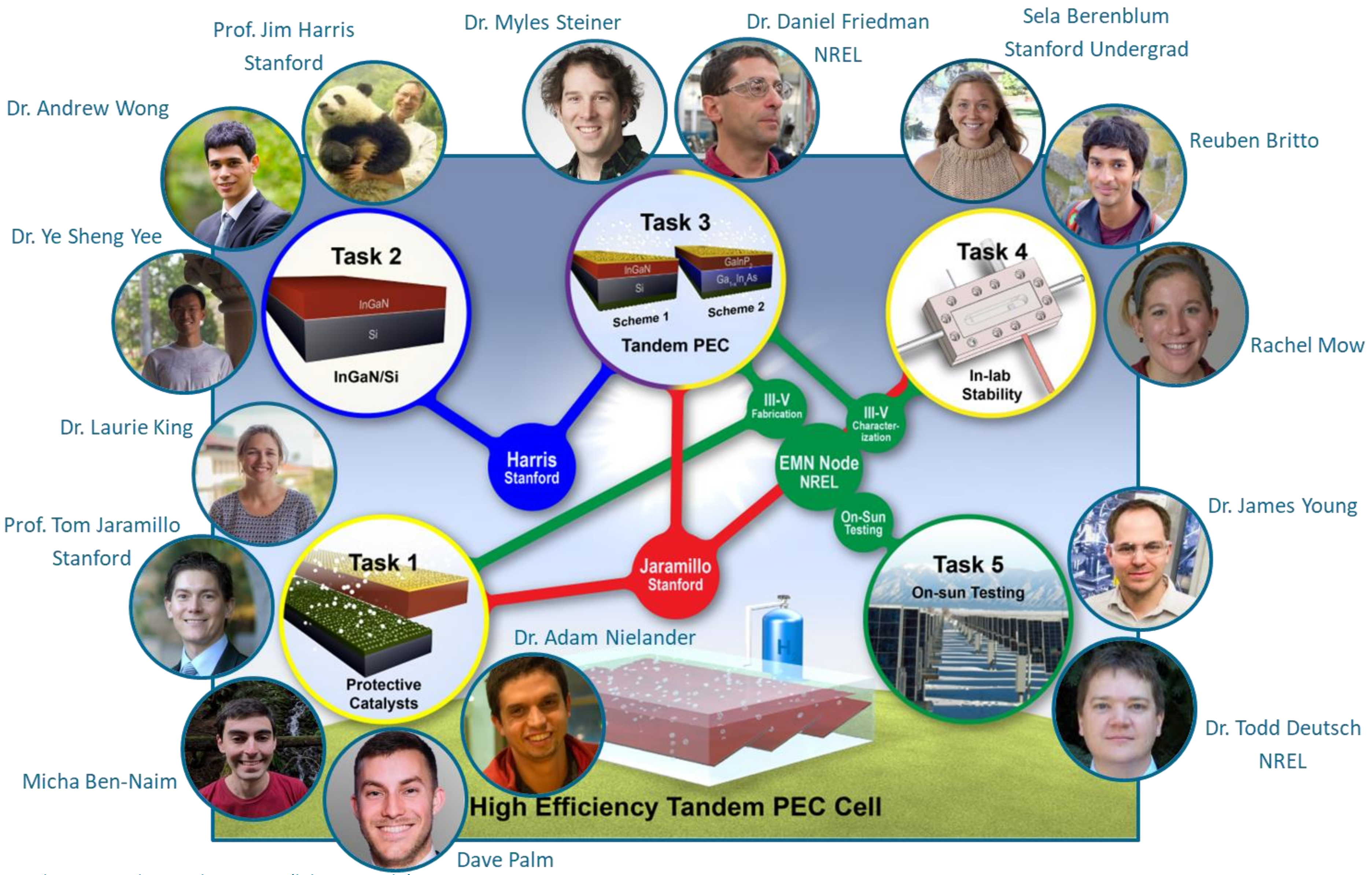
Relevance

Objective: 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/m^2 by incorporating earth-abundant protective catalysts and novel epitaxial growth schemes.

Performance Metric[1]	Units	DOE 2020 Target	DOE Ultimate Target
Hydrogen Cost	$/kg	4.00	2.00
Solar to Hydrogen (STH) efficiency	%	20	25
PEC Electrode Cost	$/m^2	200	100
Annual Electrode Cost	$/metric tons H_2 per day	510,000	135,000
Electrode Lifetime	years	2	10

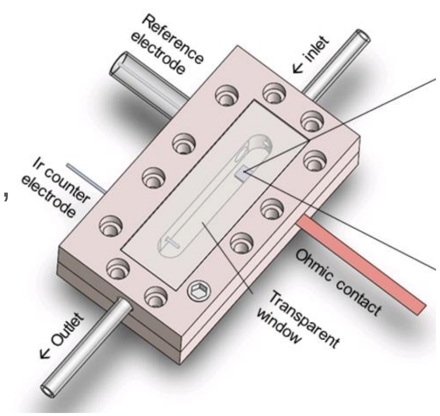
1). Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, 3.1: Hydrogen Production. https://www.energy.gov/sites/prod/files/2015/06/f23/fcto_myrdd_production.pdf

The Team


Prof. Jim Harris
Stanford
Dr. Myles Steiner
Dr. Daniel Friedman
NREL
Sela Berenblum
Stanford Undergrad
Dr. Andrew Wong
Reuben Britto
Dr. Ye Sheng Yee
Task 2
InGaN
Si
InGaN/Si
Task 3
InGaN
Si
Scheme 1
Scheme 2
Tandem PEC
Task 4
In-lab
Stability
Rachel Mow
Dr. Laurie King
III-V
Fabrication
III-V
Character-
ization
Harris
Stanford
EMN Node
NREL
On-Sun
Testing
Dr. James Young
Prof. Tom Jaramillo
Stanford
Task 1
Protective
Catalysts
Jaramillo
Stanford
Task 5
On-sun Testing
Dr. Adam Nielander
Dr. Todd Deutsch
NREL
Micha Ben-Naim
High Efficiency Tandem PEC Cell
Dave Palm

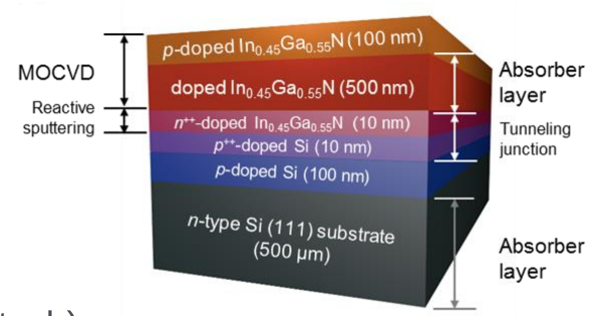
Relevance- Barriers and Innovation

- **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 monocrystalline 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

Scheme 1
III/V-III/V

a. Upright Tandem

GaInP
GaAs

- Robust fabrication
- Prior success protecting in acid

b. IMM/High Efficiency Tandem

GaInP
GaInAs

- Higher efficiency
- Novel semiconductor fabrication

- Most direct pathway to high efficiency devices

Scheme 2
III/V-Si

InGaN
Si

- New fabrication approaches
- Pathway to cheaper fabrication
- Prior success growing LEDs

End of Project Goal #1

On-sun testing of unassisted water splitting devices for ≥ 2 weeks.

End of Project Goal #2

Demonstration of an unassisted water splitting device with ≥ 20% STH efficiency.

Approach: Milestones ahead

Milestone	Project Milestones	Completion Date	Percent Complete	Progress Notes
2.0	**Task 2: Tandem InGaN/Si fabrication**			
2.4	Demonstrate working tandem InGaN/Si solar cell device	5/31/19	30%	Achieved by MOCVD
2.5	Demonstrate a tandem InGaN/Si solar cell with power conversion efficiencies of > 10%	12/31/19	10%	Achieved by MOCVD
3.0	**Task 3: III-V fabrication and PEC device development for tandem III-V and InGaN/Si**			
3.2	Demonstrate InGaN/Si tandem absorbers that produce hydrogen during light-driven, unassisted water splitting	9/30/19	0%	
3.3	3.3.1: Demonstrate InGaN/Si as a photoelectrode for unassisted water splitting with >1% STH 3.3.2: Design and implement improved dual III-V tandem absorbers which achieve STH efficiency >15%	3/31/20	0% 50%	achieved 10% STH
3.4	3.4.1: Demonstrate unassisted water splitting device with >20% STH efficiency that maintains at least 10% STH efficiency for >100 h. 3.4.2: Demonstrate unassisted water splitting using InGaN/Si with >2% initial STH that continues to produce hydrogen after >100 hrs of continuous illumination	9/30/20	0% 0%	
4.0	**Task 4: In-Lab Stability Studies**			
4.2	Utilize the flow cell for analyzing the degradation mechanisms of the III-V based tandem PEC devices.	9/30/20	25%	flow cell and Raman
5.0	**Task 5: On-sun testing**			
5.1	5.1.1: Finalize the outdoor PEC cell setup, design and protocols to enable on-sun data collection for >24 hours 5.1.12: Collect >10 mL of hydrogen from an unassisted water splitting device in an on-sun testing in one day	12/31/19	0%	
5.2	Demonstrate photoelectrode that generates hydrogen under diurnal conditions on-sun for greater than or equal to 2 weeks	9/30/20	0%	
End of Project Goal	**On-sun testing of Scheme 1 and 2 unassisted water splitting devices for longer than 2 weeks. Demonstration of an unassisted water splitting device with an average greater than 20% STH efficiency.**	**9/30/20**	**0%**	

Approach: Leveraging of the EMN Resource Nodes

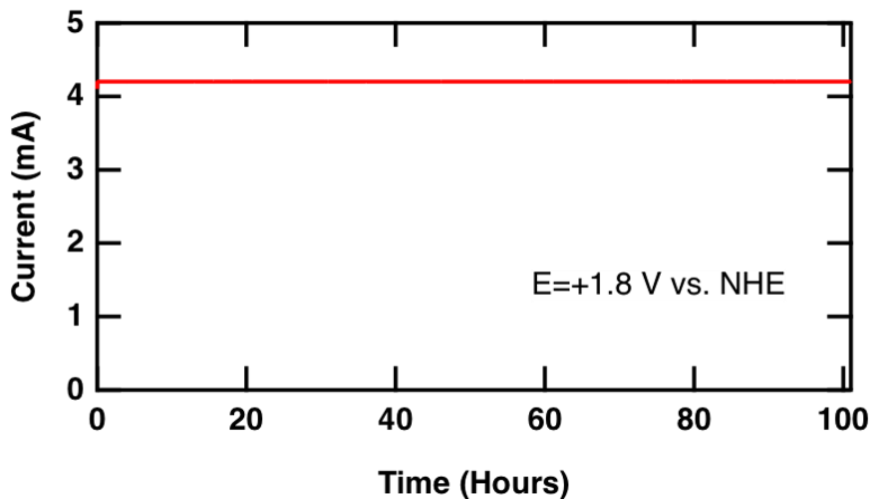
▸ NREL: Characterization of Semiconductor Bulk and Interfacial Properties, ***Todd Deutsch*** ▸ NREL: Corrosion Analysis of Materials, ***Judith Vidal, Todd Deutsch, James Young*** – Pre- and post- characterization and failure analysis of photocathodes and unassisted water splitting devices	Worked with to analyze our photoelectrodes before and after testing to determine failure mechanisms and strategies for improvement.
▸ NREL: III-V Semiconductor Epi-structure and Device Design and Fabrication, ***Daniel Friedman*** – Design and fabrication of III-V materials and systems	Worked with to fabricate high-quality absorbers compatible with our catalytic protection layers.
▸ NREL: On-Sun Solar-to-Hydrogen Benchmarking, ***Todd Deutsch*** – Testing station for collection of on-sun data for unassisted water splitting devices	Worked with to design our electrodes to be compatible with NREL's on-sun testing setup.

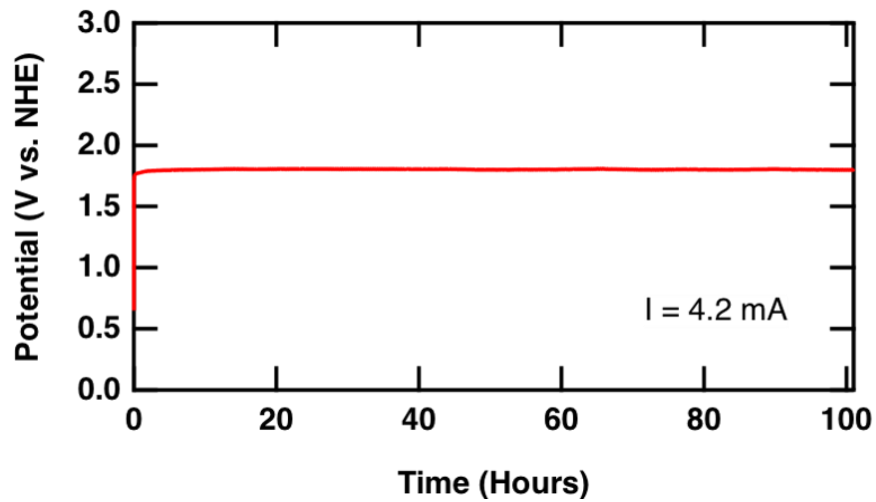
Accomplishments: Phase 1 Milestones

Milestone	Project Milestones	Completion Date	Percent Complete	Progress Notes
1.0	**Task 1: Translatable, thin-film catalyst and protection layer development**			
1.1	Demonstrate >100 h stability for a III-V photocathode which utilizes a non-precious metal HER catalyst	3/31/18	100%	Achieved 110 hr
1.2	Demonstrate >100 h stability of OER catalysts in conjunction with a III-V based PEC device	9/30/18	100%	Achieved >100 hr
2.0	**Task 2: Tandem InGaN/Si fabrication**			
2.1	Demonstrate high-crystalline-quality n++- $In_{0.45}Ga_{0.55}N$ growth on Si (111) substrates by sputter deposition, with n-type doping > 10^{20} cm^{-3} and root-mean-square surface roughness < 0.5 nm.	12/31/17	100%	Achieved by MOCVD
2.2	Demonstrate high-quality undoped $In_{0.45}Ga_{0.55}N$ and p-doped $In_{0.45}Ga_{0.55}N$ by MOCVD, grown on n++-doped $In_{0.45}Ga_{0.55}N$ sputter-deposited template layers, with properties similar to those measured for the sputter deposited films (see milestone 2.1)	6/30/18	100%	Achieved by MOCVD
2.3	Demonstrate repeatable Si p-n junctions with the desired hole concentrations and doping profiles.	9/30/18	100%	Achieved by epitaxy and MOCVD
4.0	**Task 4: In-Lab Stability Studies**			
4.1	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.	12/31/2018	85%	Achieved with flow cell and Raman
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.**	**12/31/2018**	**100%**	**#1: Achieved** **#2: Achieved**

Accomplishments for Task 1: Protective Catalysts

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
1.2	Demonstrate >100 h stability of OER catalysts in conjunction with a III-V based PEC device	9/30/18	100%	Achieved >100 hr	50%



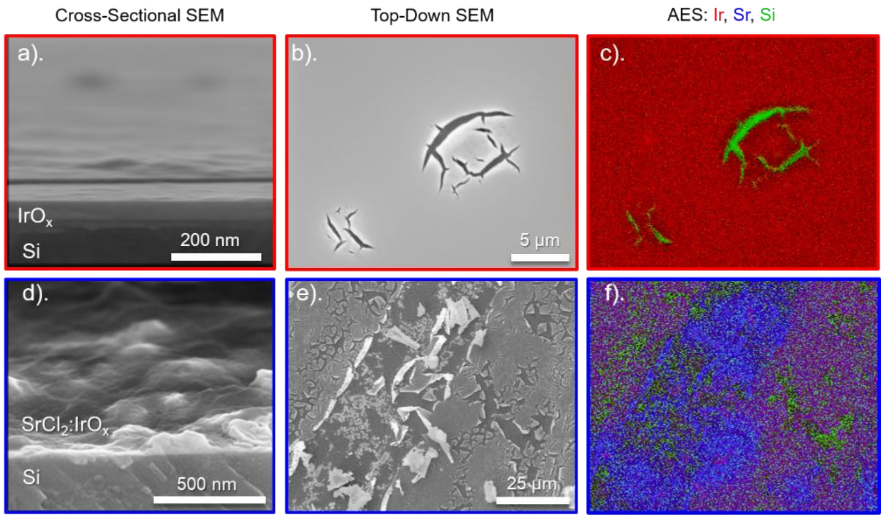


Chronopotentiometry of an Ir catalyst with an applied current of 4.2 mA in 0.5 M H_2SO_4. Left: Current vs time. Right: Potential vs Time.

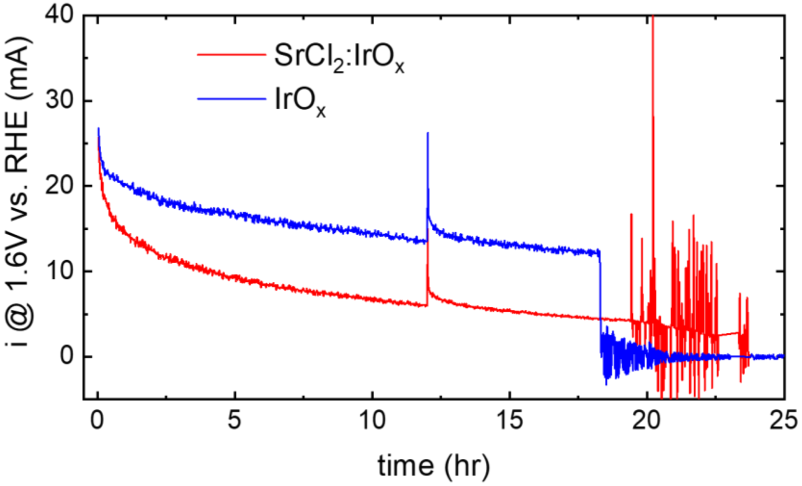
- We demonstrated stable OER catalysis with time scales commensurate with PEC measurements.

Accomplishments for Task 1: Protective Catalysts

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
1.2	Demonstrate >100 h stability of OER catalysts in conjunction with a III-V based PEC device	9/30/18	100%	Achieved >100 hr	50%



Structure and Morphology of IrO_x (a-c) and $SrCl_2$:IrO_x (d-f) Catalysts.

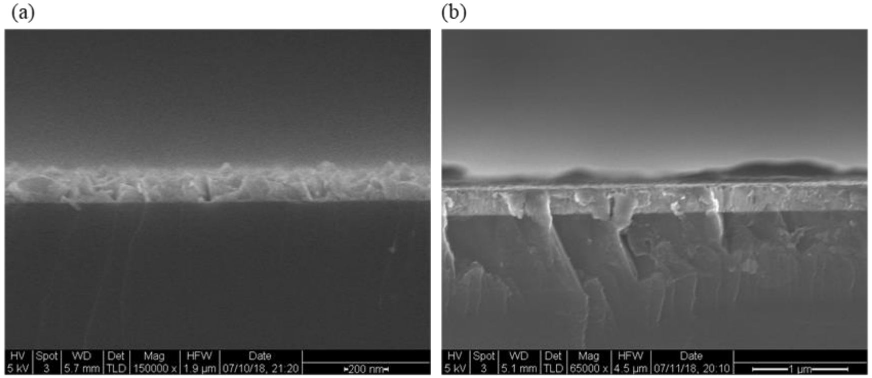


Anode chronopotentiometry for electrodes with geometric areas of 3.3 cm^2

- The thin-film catalysts we have developed using straightforward wet chemical processes can potentially be used either as counter electrode material or as a protective catalyst layer for photoanodes.

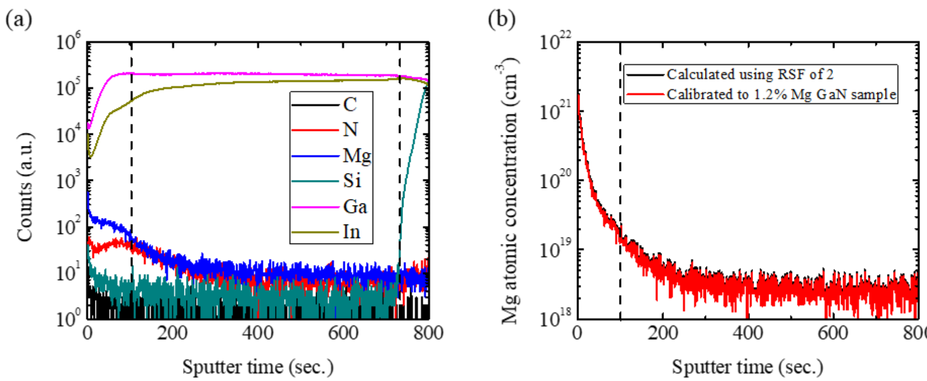
Accomplishments for Task 2: InGaN/Si Fabrication

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
2.2	Demonstrate high-quality undoped $In_{0.45}Ga_{0.55}N$ and p-doped $In_{0.45}Ga_{0.55}N$ by MOCVD, grown on n++-doped $In_{0.45}Ga_{0.55}N$ sputter-deposited template layers, with properties similar to those measured for the sputter deposited films (see milestone 2.1)	6/30/18	100%	Achieved by MOCVD	50%



(a) Mg-doped InGaN film grown at 750° C on Si

(b) InGaN solar cell device stack grown using a 2-step process with undoped InGaN grown at 550° C, followed by Mg-doped InGaN grown at 750° C. Particles above film in (b) are likely excess Mg-containing materials, which are removed via HCl etch.



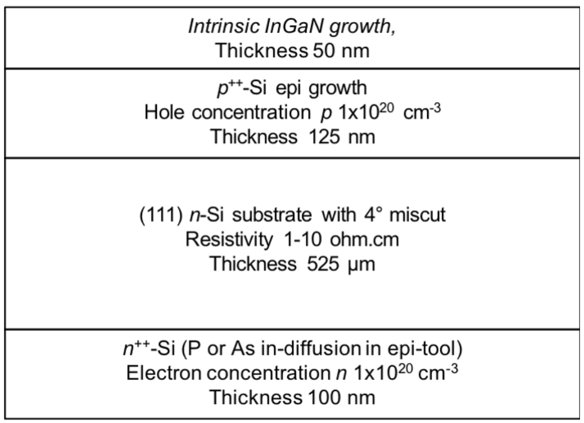
(a) Raw data for secondary ion mass spectrometry (SIMS) depth profile for InGaN solar cell device stack

(b) calculated Mg atomic concentrations from the SIMS depth profile in (a).

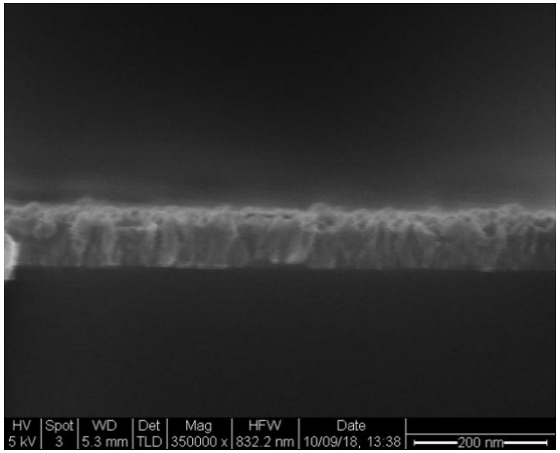
- We have been able to fabricate high quality InGaN structures on Si with sufficient Mg doping needed for p-type behavior.
- Work is in progress to achieve rectifying behavior.

Accomplishments for Task 2: InGaN/Si Fabrication

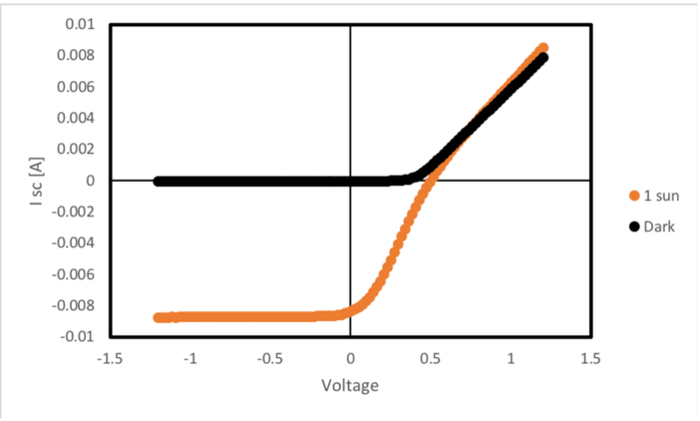
Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
2.3	Demonstrate repeatable Si p-n junctions with the desired hole concentrations and doping profiles.	9/30/18	100%	Achieved by epitaxy and MOCVD	90%



Si p-n junction device structure with InGaN incorporated



Cross sectional SEM of InGaN on pn-Si PV

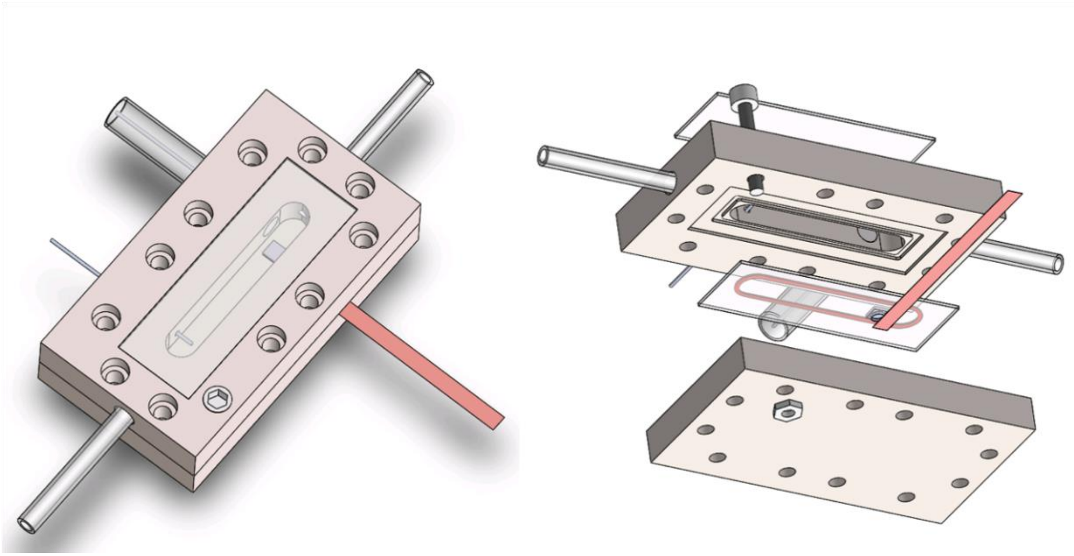


IV characteristics Si p-n junction with an intrinsic InGaN layer on top. V_{oc} = 0.5 V, J_{sc} = 14.7 mA/cm^2, P_{max} = 1.28 mW, FF = 0.31 Efficiency = 2.2%.

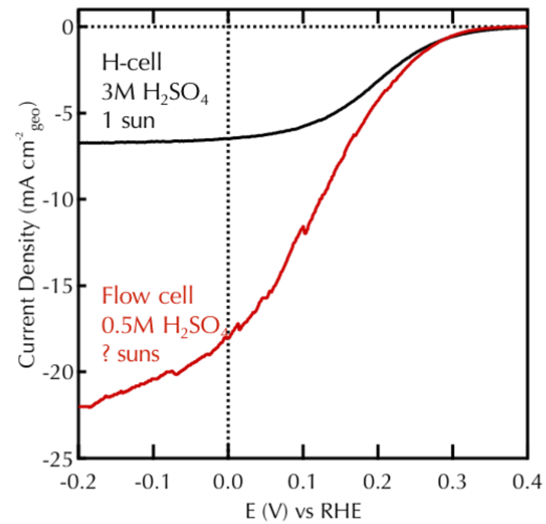
- We have successfully fabricated a working Si/InGaN device that is compatible with future InGaN fabrication developments. This reflects a high quality Si/InGaN interface.
- In this device the intrinsic InGaN layer is unlikely to be contributing photogenerated charge carriers. Future work on p-InGaN growth will allow for higher performance devices.

Accomplishments for Task 4: In-Lab Stability Studies

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
4.1	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.	12/31/2018	85%	Achieved with flow cell and Raman	85%



Schematic of flow cell for operando optical and Raman microscopy



Linear sweep voltammogram of an MoS_2 protected GaInP photocathode tested in the flow cell and a typical electrochemical H-cell

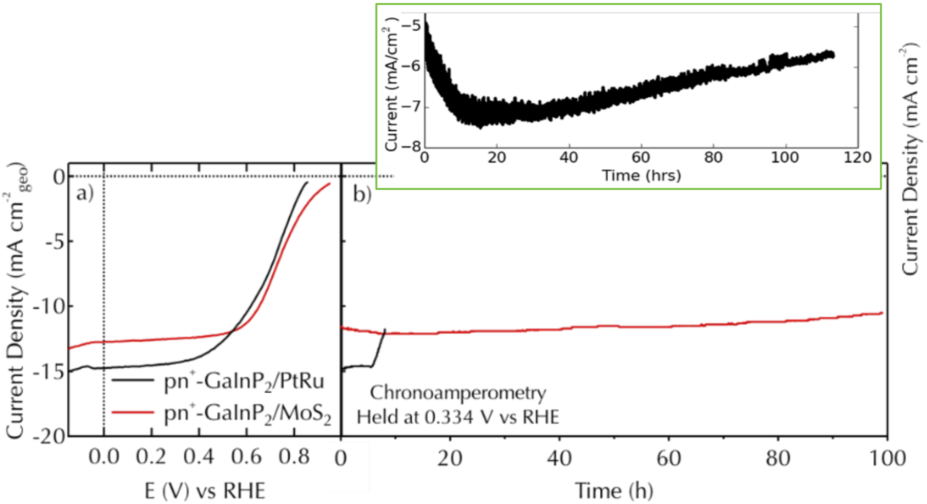
- We have developed a functional flow cell capable of electrochemical measurements designed for *operando* microscopy and spectroscopy.

Nodes Utilized:
Corrosion Analysis of Materials
On-Sun Solar to Hydrogen Benchmarking

Accomplishments for Go/No-Go

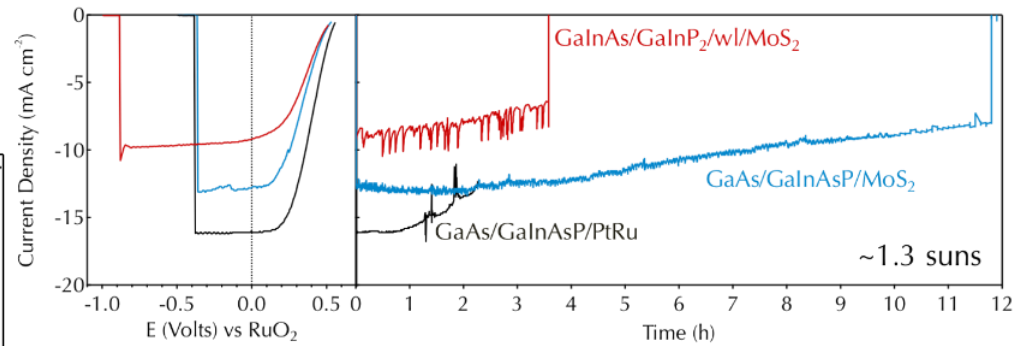
Milestone #	Project Milestones	Task Completion Date		Progress Notes	Progress Increase FY18-FY19
		Original Planned	Percent Complete		
1.1	Demonstrate >100 h stability for a III-V photocathode which utilizes a non-precious metal HER catalyst	3/31/18	100%	Achieved 110 hr	10%
Go/No-Go	**The following two 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.	**12/31/2018**	**100%**	**#1: Achieved** **#2: Achieved**	10%

Go/No-Go #1 met with pn^+-$GaInP/MoS_2$ photocathodes.



Performance of the pn^+-$GaInP_2/PtRu$ and pn^+-$GaInP_2/MoS_2$ photo-cathodes in 3 M sulfuric acid. a) LSV collected prior to stability testing b) CA measurement taken at a constant potential of 0.334 V vs RHE.

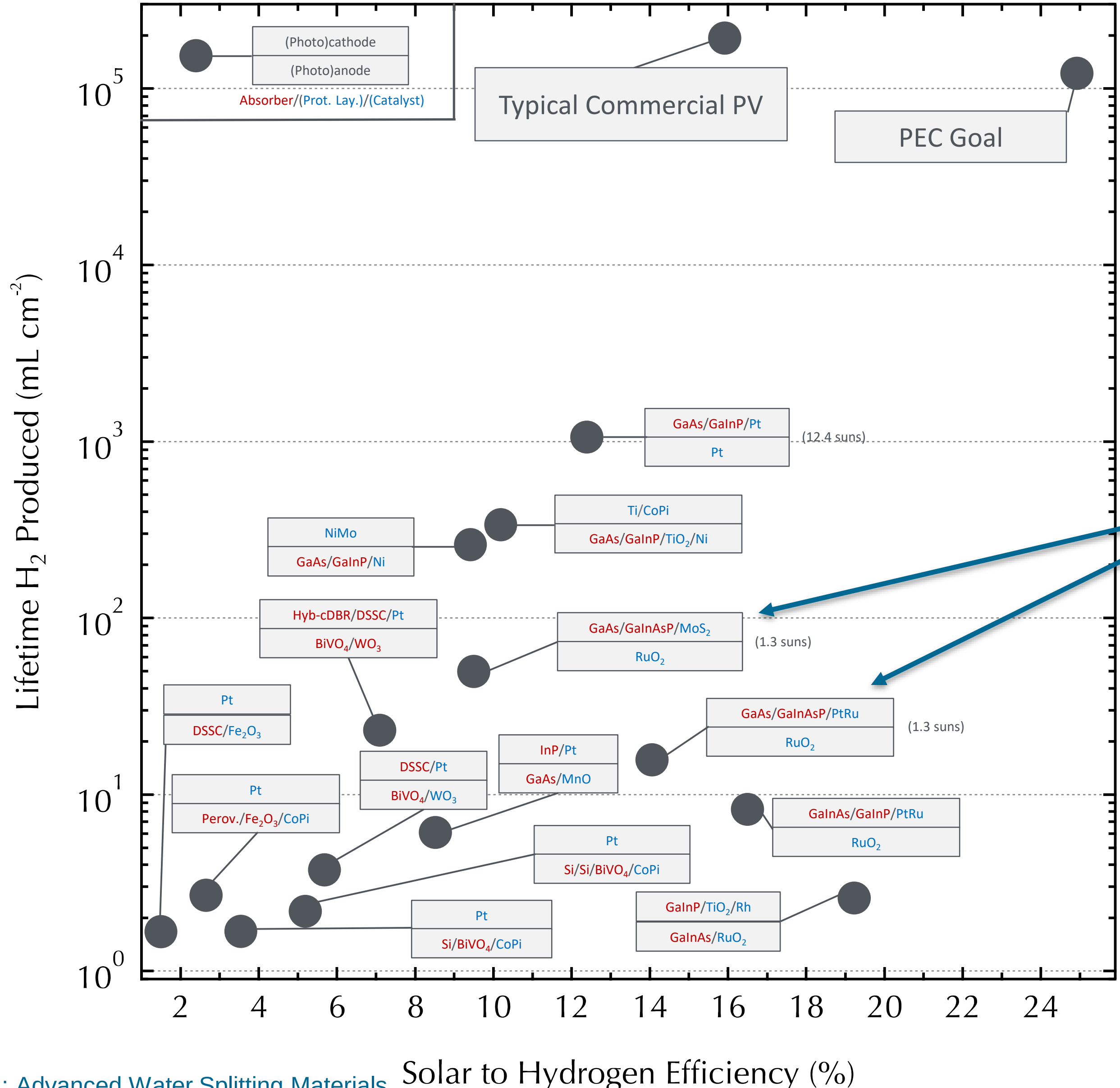
Go/No-Go #2 met with $GaAs/GaInAsP/MoS_2$ unassisted water splitting tandems.



Electrochemical characterization of $GaInAs/GaInP_2$/wl(window layer)/MoS_2, $GaAs/GaInAsP/MoS_2$, and $GaAs/GaInAsP/PtRu$ unassisted water splitting devices in 0.5 M sulfuric acid.

Nodes Utilized:
Characterization of Semiconductor Bulk and Interfacial Properties
III-V Semiconductor Epi-structure and Device Design and Fabrication
Corrosion Analysis of Materials, On-Sun Solar to Hydrogen Benchmarking

Accomplishments and Progress: Unassisted water-splitting systems



Typical Commercial PV: 16% avg. eff. over 25 yr, CF: 16%, lifetime energy in equiv. H_2

PEC Goal: 25% STH over 10 yrs, CF: 16%

This project

All data from 2 electrode spontaneous water splitting stability tests

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

Comment	Response
"Several of the project milestones contain qualitative statements or components. For example, Milestone 1.1 states, "Demonstrate >100 h stability," but "stability" is not defined as less than some absolute or less than some relative change from the starting point."	We have made Phase 2 milestones more specific to define what stability and performance metrics must be met. For instance, milestone 3.4.1 states: "Demonstrate unassisted water splitting device with >20% STH efficiency that maintains at least 10% STH efficiency for >100h."
"This project seeks to use a (roughly) seven-layer device to effect the desired water-splitting reaction. It benefits from the use of established solar-cell manufacturing technologies. However, the complexity of the construct will ultimately limit the amount of cost reduction."	While the III-V/III-V device stack does have several layers, this project provides a pathway for lower cost. For instance, InGaN grown by MOCVD offers large cost savings over the usual MBE growth, and the use of Si as the substrate is a substantial cost-reducing element. In addition, we leverage technologies that have already been scaled up in the photovoltaic and LED industries, while our catalysts are earth-abundant and do not contribute significant cost.
"Significant advances are required to achieve the project's goal of 20% STH efficiency, and a clear pathway to this was not presented. Also, parasitic absorption losses in the MoS_2 may need to be investigated in further detail to avoid light losses in this layer."	20% STH efficiency is indeed an ambitious goal, we believe that can be achieved with IMM tandems which allow for more ideal band gap combinations. The InGaN/Si platform also offers a route to high efficiencies, though that system requires more R&D to achieve similar performance to that of established III-V/III-V tandems. As we optimize MoS_2 coatings onto these systems, we will focus more attention on improving parasitic light absorption.
"The work exploring corrosion mechanisms of failure is poorly articulated and should receive intense scrutiny. The mechanism of failure is likely a compounded action of chemical and physical phenomena that may not be easily de-convoluted."	Indeed understanding mechanisms of corrosion is a monumental challenge in many areas, including PEC. For this reason in Phase 2 of this project we will be employing operando spectroscopy and microscopy measurements at the LBNL EMN node to study degradation mechanisms in greater detail.
"This project needs a strong chemist if the transition metal chemistry is to be fully leveraged. Also, discussion with the PI indicated that an engineer could probably add value in devising how this technology could operate in the field."	We will leverage chemistry expertise across the project team and EMN node network. The planned 2-week on-sun experiments will inform field operation.
"The approach is strong, with high levels of collaboration and coordination with EMN nodes." "This project has a very competent chemical engineer as the principal investigator (PI). All project participants are well accomplished as individuals and in teams. The idea of using a transition metal to simultaneously protect the surface and to affect the desired chemical reaction stands to open a rich fertile field of catalysis."	

Collaboration and Coordination: EMN Nodes

Phase 1

- NREL: Characterization of Semiconductor Bulk and Interfacial Properties
  - ***Todd Deutsch***
- NREL: Corrosion Analysis of Materials,
  - ***Judith Vidal, Todd Deutsch***
- NREL: III-V Semiconductor Epi-structure and Device Design and Fabrication
  - ***Daniel Friedman***
- NREL: On-Sun Solar-to-Hydrogen Benchmarking
  - ***Todd Deutsch***

Any proposed future work is subject to change based on funding levels

Phase 2

- NREL: Characterization of Semiconductor Bulk and Interfacial Properties
  - ***Todd Deutsch***
- NREL: Corrosion Analysis of Materials,
  - ***Judith Vidal, Todd Deutsch***
- NREL: III-V Semiconductor Epi-structure and Device Design and Fabrication
  - ***Daniel Friedman***
- NREL: On-Sun Solar-to-Hydrogen Benchmarking
  - ***Todd Deutsch***
- LBNL: Photophysical Characterization of Photoelectrochemical Materials and Assemblies
  - ***Jason Cooper***

Collaboration and Coordination: EMN and beyond

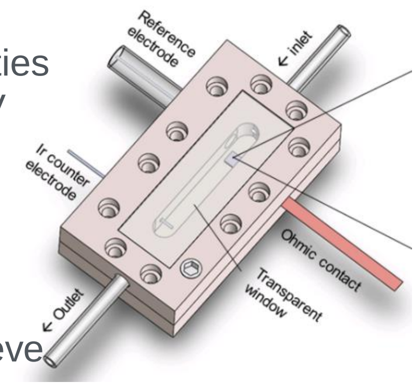
- **EMN Collaboration**
  - Weekly meetings between Stanford (Reuben Britto) and NREL (James Young, Rachel Mow, Myles Steiner, Todd Deutsch) in the form of videochats
  - Weekly exchange of samples fabricated at NREL and further processed at Stanford
  - Parallel photoelectrochemical testing and characterization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

- **Positive interactions with the broad HydroGEN community**
  - Kickoff meeting in November 2017 at NREL provided an opportunity to engage with the community, learn about the plethora of available tools, methods, and expertise.
  - PEC community meeting at ECS in Seattle in May 2018 to discuss HydroGEN, benchmarking, and related activities.
  - HydroGEN EMN Advanced Water Splitting Technology Pathways Benchmarking & Protocols Workshop, Tempe, AZ in October 2018.
  - Presentation to Hydrogen Production Tech Team (HPTT) in February 2019.

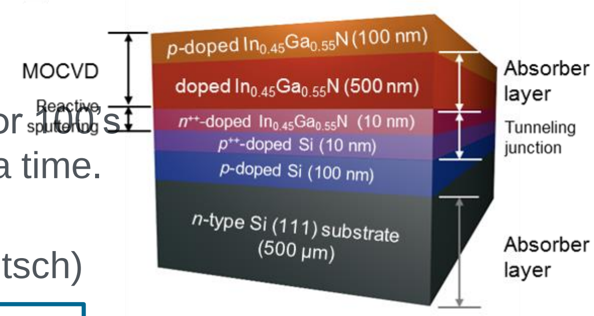
- **Incorporating project data onto the HydroGEN data hub**
  - We learned how to use the H2awsm tools at the kickoff meeting to upload our data for the broader community.
  - All of our photocathode stability data and linear sweep voltammetry data will be uploaded.
  - We hope this will help accelerate the stability benchmarking effort.

Remaining Challenges and Barriers

- **Barrier: Mechanistic understanding to stabilize 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 fab 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), and iv) Photophysical Characterization of Photoelectrochemical Materials and Assemblies



- **Barrier: Fabrication scheme for high-quality InGaN growth on Si**
  - **Innovation:** We will continue to modify InGaN on Si growth conditions to achieve p doping to form a homojunction and yield rectifying behavior.
    - **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 hours, we will develop procedures for outdoor testing for weeks at a time.
    - **Task 5:** On-sun testing at NREL
  - **EMN Nodes:** On-Sun Solar-to-Hydrogen Benchmarking (Todd Deutsch)



Any proposed future work is subject to change based on funding levels

Proposed Future Work

Scheme 1
III/V-III/V

a. Upright Tandem

GaInP
GaAs

- Robust fabrication
- Prior success protecting in acid

b. IMM/High Efficiency Tandem

GaInP
GaInAs

- Higher efficiency
- Novel semiconductor fabrication

- Most direct pathway to high efficiency devices

Scheme 2
III/V-Si

InGaN
Si

- New fabrication approaches
- Pathway to cheaper fabrication
- Prior success growing LEDs

End of Project Goal #1

On-sun testing of unassisted water splitting devices for ≥ 2 weeks.

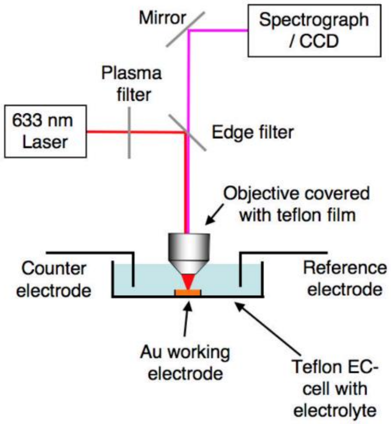
End of Project Goal #2

Demonstration of an unassisted water splitting device with ≥ 20% STH efficiency.

Any proposed future work is subject to change based on funding levels

Proposed Future Work

In Situ Testing



- Incorporating the Photophysical Characterization of Photoelectrochemical Materials and Assemblies node at LBNL for *in situ* Raman studies
- Develop testing protocols for *operando* cell

On- Sun Testing

https://h2awsm.org/capabilities/sun-photoelectrochemical-solar-hydrogen-benchmarking

- Continue working On-Sun Solar-to-Hydrogen Benchmarking node to adapt our electrodes to NREL's rooftop solar tracking PEC testing apparatus
- Improve device stability to enable testing outside for ≥ 2 weeks

End of Project Goal #1

On-sun testing of unassisted water splitting devices for ≥ 2 weeks.

End of Project Goal #2

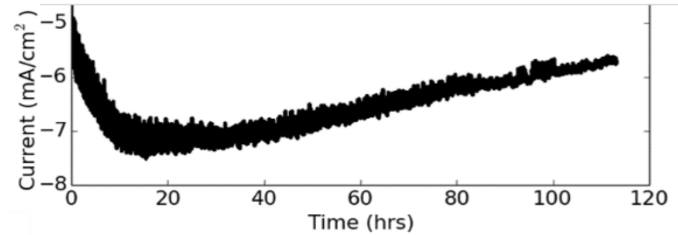
Demonstration of an unassisted water splitting device with ≥ 20% STH efficiency.

Any proposed future work is subject to change based on funding levels

Summary

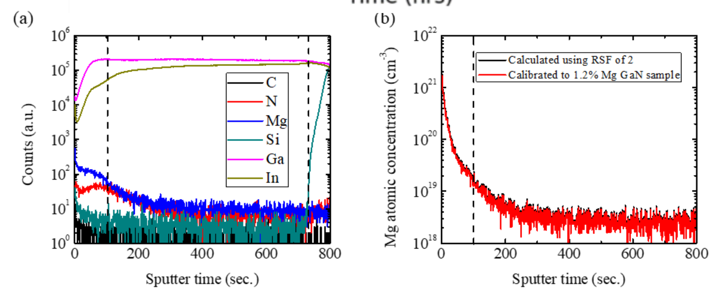
Task 1 – Protective Catalysts

- MoS_2 protected pn^+ $GaInP_2$ for 110 hrs in 0.5*M* sulfuric acid.



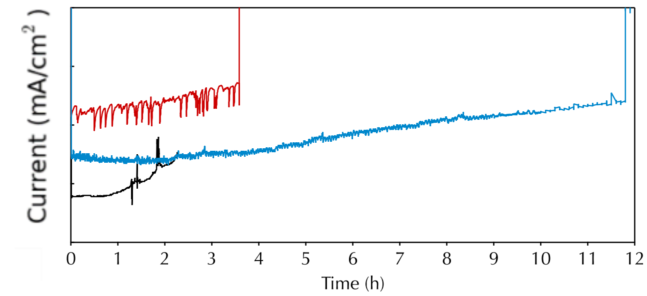
Task 2 – High Quality InGaN on Si

- Direct nucleation of high-crystalline-quality undoped and p-doped $In_xGa_{1-x}N$ on Si (111) substrates using MOCVD



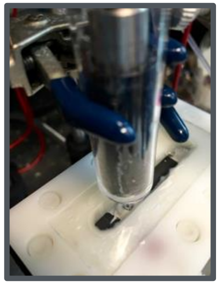
Task 3 – Stable Unassisted Water Splitting

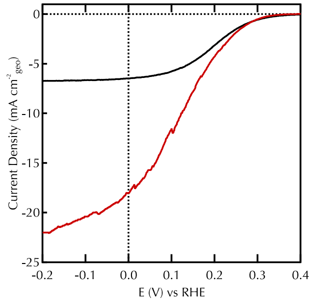
- Greater than 5% STH unassisted water splitting for ~12 hours with a III-V/III-V PEC device using MoS_2 in lieu of any precious metal HER catalysts



Task 4 – In-situ Stability Studies

- Successful in-situ LSV data collected of a GaInP photocathode

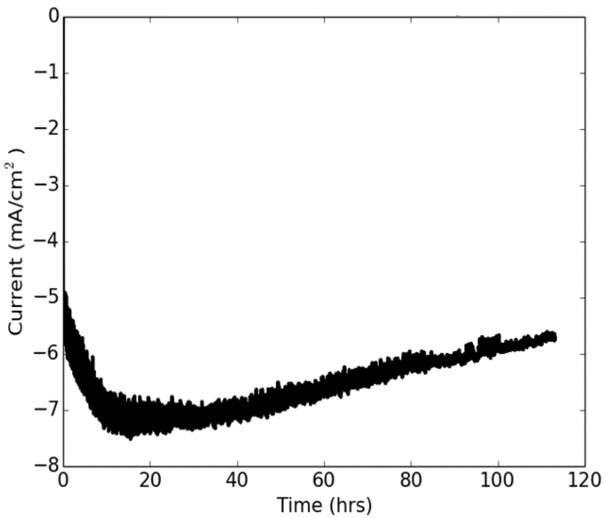




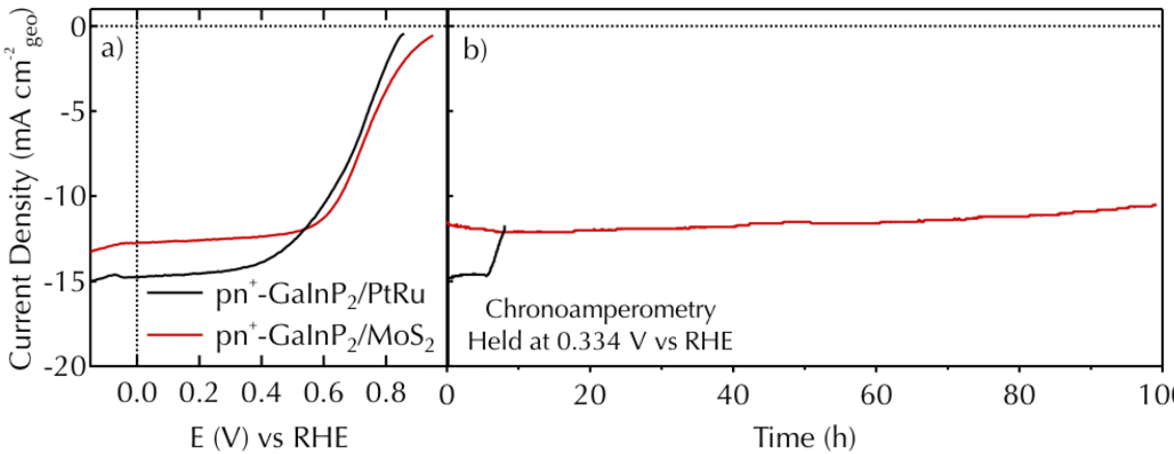
Technical Back-Up Slides

Accomplishments for Task 1: Protective Catalysis

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	FY18 Progress
		Original Planned	Percent Complete		
1.1	Demonstrate >100 h stability for a III-V photocathode which utilizes a non-precious metal HER catalyst	3/31/18	100%	Achieved 110 hr	100 hr



Electrochemical chronoamperometric characterization of pn$^+$-GaInP$_2$/MoS$_2$ photocathodes in 0.5 M sulfuric acid under 1 sun illumination. Chronoamperometry measurement taken at a constant potential of +0.1 V vs NHE.



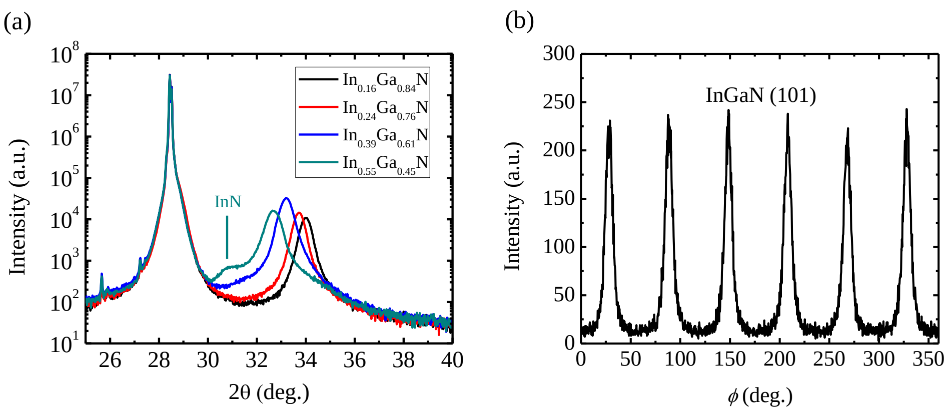
Electrochemical characterization of the pn$^+$-GaInP$_2$/PtRu and pn$^+$-GaInP$_2$/MoS$_2$ photocathodes in 3 M sulfuric acid. a) LSV collected prior to stability testing b) CA measurement taken at a constant potential of 0.334 V vs RHE.

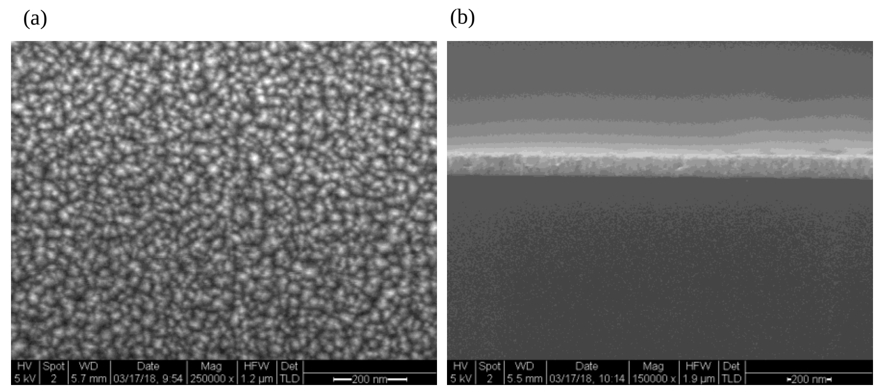
- We have demonstrated >100 hr stability.
- These results also meet the criteria of Go/No-Go #1.

Nodes Utilized:
Characterization of Semiconductor Bulk and Interfacial Properties
III-V Semiconductor Epi-structure and Device Design and Fabrication
Corrosion Analysis of Materials

Accomplishments for Task 2: InGaN/Si Fabrication

Milestone #	Project Milestones	Task Completion Date (Project Quarter)		Progress Notes	FY18 Progress
		Original Planned	Percent Complete		
2.1	Demonstrate high-crystalline-quality n++- $In_{0.45}Ga_{0.55}N$ growth on Si (111) substrates by sputter deposition, with n-type doping > 10^{20} cm^{-3} and root-mean-square surface roughness < 0.5 nm.	12/31/17	100%	Achieved by MOCVD	100%





(a) XRD symmetric (2theta-omega) scans of the (002) reflection for MOCVD-grown InGaN films with varying indium compositions

(b) XRD phi scans of the InGaN (101) reflection for a typical MOCVD-grown InGaN film.

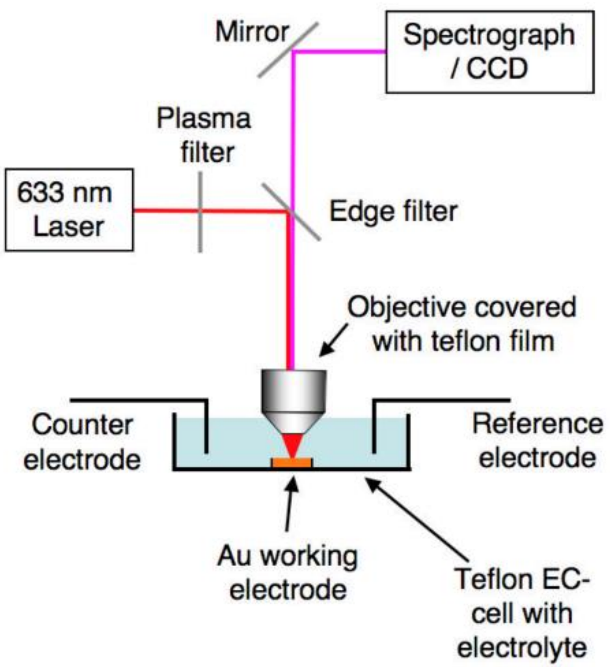
(a) Plan-view Scanning Electron Microscopy (SEM) image of $In_{0.24}Ga_{0.76}N$ film

(b) Cross-section SEM image of the same $In_{0.24}Ga_{0.76}N$ film.

- We have developed first growth of crystalline InGaN on Si by MOCVD.

Path to *in-situ* and *operando* studies on photocathodes

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)	
			Date	Month
4.2	Utilize the flow cell for analyzing the degradation mechanisms of the III-V based tandem PEC devices.	Milestone	9/30/20	M36



In-situ Raman setup

Thin-film MoS_2 grown as a catalytic protection layer is Raman-active in *ex situ*, and suitable for *in situ* and operando studies in the future

- Aiming to incorporate the Photophysical Characterization of Photoelectrochemical Materials and Assemblies node at LBNL for *in situ* Raman studies during Phase 2
- Use the *in situ* studies to determine testing protocols for *operando* testing with the flow cell

Path to Stable On-Sun Testing

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)	
			Date	Month
5.1	5.1.1: Finalize the outdoor PEC cell setup, design and protocols to enable on-sun data collection for >24 hours 5.1.12: Collect >10 mL of hydrogen from an unassisted water splitting device in an on-sun testing in one day	Milestone	12/31/19	M27
5.2	Demonstrate photoelectrode that generates hydrogen under diurnal conditions on-sun for greater than or equal to 2 weeks	Milestone	9/30/20	M36
	On-sun testing of Scheme 1 and 2 unassisted water splitting devices for longer than 2 weeks. Demonstration of an unassisted water splitting device with an average greater than 20% STH efficiency.	**End of Project Goal**	**9/30/20**	**M36**

- Continue working On-Sun Solar-to-Hydrogen Benchmarking node to adapt our electrodes to NREL's rooftop solar tracking PEC testing apparatus
- Improve device stability to 100's of hour to enable testing outside for >2 weeks

https://h2awsm.org/capabilities/sun-photoelectrochemical-solar-hydrogen-benchmarking