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

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Project End Date: December 31, 2018 (Phase I)

Overall Objectives

- Develop unassisted water splitting devices based on III-V materials, creating pathways to improve performance in terms of efficiency, durability, and cost.
- Develop translatable, thin-film catalyst and protection layers for the hydrogen evolution reaction (HER) and/or oxygen evolution reaction (OER) onto III-V materials (Task 1), including samples provided by the National Renewable Energy Laboratory (NREL) III-V fabrication Energy Materials Network (EMN) node.
- Develop methods to fabricate a tandem InGaN/Si photoelectrochemical (PEC) water splitting device (Task 2).
- Integrate HER and/or OER catalysts with InGaN/Si system and tandem III-V structures.
- Study degradation mechanisms of PEC devices by developing an *in operando* electrochemical flow cell to inform strategies to improve catalysts and protection layers.
- Test highly active and durable unassisted water splitting devices in an on-sun setup for

extended periods of time and study effects such as light and temperature fluctuations.

- The end of project goal is demonstration of unassisted device with >20% average solar-to-hydrogen (STH) efficiency and successful on-sun testing of unassisted water splitting devices for >2 weeks.

Fiscal Year (FY) 2018 Objectives

- Demonstrate a PEC photoelectrode that achieves >10 mA/cm² under 1-sun illumination for longer than 100 h while utilizing a non-precious-metal HER catalyst.
- Demonstrate >100 h stability of OER catalysts with III-V-based PEC devices.
- Demonstrate InGaN growth by metal organic chemical vapor deposition (MOCVD) on Si (111) substrates.
- Demonstrate high-quality undoped InGaN and p-doped InGaN by MOCVD.
- Demonstrate repeatable Si p-n junctions suitable for InGaN/Si tandem devices.
- Demonstrate effectiveness of the *in operando* microscopy and spectroscopy flow cell measurement technique on a benchmark photoelectrode system such as previously developed MoS₂/III-V photocathodes.
- Fabricate an unassisted PEC water splitting device with a non-precious-metal HER catalyst that achieves STH efficiencies >5% under 1 sun to create a pathway for >20% STH.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Materials Efficiency—Bulk and Interface

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Materials Durability—Bulk and Interface
- Integrated Device Configurations
- Auxiliary Materials—For Catalysis and Durability
- Synthesis and Manufacturing—Technique Development.
- Demonstrated for the first time InGaN growth on Si (111) by MOCVD, providing a lower-cost route to fabrication of high-performance tandem absorber layers.

Technical Targets

This project is conducting research into catalyst and protection layer development in photoelectrochemical devices as well as development of InGaN/Si tandem absorbers in addition to fundamental studies of degradation in photoelectrochemical systems. Insights gained from these studies will be applied toward the design and fabrication of hydrogen production devices that meet the following DOE hydrogen production targets for photoelectrochemical water splitting systems with solar concentration:

- Photoelectrochemical hydrogen cost: \$5.70/kg (2020); \$2.10/kg (ultimate)
- Capital costs (concentrator and PEC receiver): \$124/m² (2020); \$63/m² (ultimate)
- Annual electrode cost per metric tons per day (TPD) hydrogen: \$225K/yr-TPD H₂ (2020); \$14K/yr-TPD H₂ (ultimate)
- STH energy conversion ratio: 20% (2020); 25% (ultimate)
- 1-sun hydrogen production rate 1.6e-6 kg/s per m² (2020); 2.0e-6 kg/s per m² (ultimate).

FY 2018 Accomplishments

- Demonstrated 100-hour stability for a PEC photoelectrode with >10 mA/cm² under 1 sun.
- Fabricated an unassisted PEC water splitting device with a non-precious-metal HER catalyst that achieves 1-sun STH efficiency >5%, providing a viable pathway for achieving 20% STH efficiency through improved integration of the materials and interfaces.
- Under ~1.3 suns, an MoS₂-protected GaInAsP/GaAs IMM device maintained a >10% STH for the first 2 hours, operating for an additional 10 hours while decreasing to ~60% of light-limited photocurrent before failure.

INTRODUCTION

The overall goal of this project is to develop unassisted water splitting devices based on III-V materials, creating pathways to improve efficiency, durability, and cost toward DOE targets for hydrogen production via photoelectrochemistry. One major objective is to develop systems that can achieve >20% STH efficiency. Another objective is to develop high-efficiency systems that can operate on-sun for at least 2 weeks by understanding and mitigating degradation mechanisms. This research will provide new approaches to tandem photoelectrode design and fabrication that can lead to cost reduction to <\$200/m². We propose two distinct schemes. Scheme 1 aims to develop high-efficiency tandem III-V photoabsorbers (e.g., GaInP₂/GaInAs) with Scheme 2 targeting cost reduction while maintaining high efficiency by growing InGaN on crystalline Si. Both schemes will be coupled with thin-film, semi-transparent catalytic/protection layers containing reduced or zero precious metal content that can enhance durability with low cost.

APPROACH

To date, the PEC water splitting devices with the highest STH efficiencies (~10%–19%) use tandem III-V structures, generally consisting of a GaInP₂ (~1.8 eV) top absorber paired with either a GaInAs (~1.2 eV) or GaAs (1.4 eV) bottom absorber. However, these devices exhibit instability in acidic electrolyte. To mitigate this, our approach is to develop thin-film, semi-transparent catalytic/protection layers with suitable interface energetics. Our work utilizes earth-abundant transition metal sulfides and transition metal phosphides that are highly active and acid-stable. To complement this, we are also developing solution processable Ir-containing OER catalysts. While the tandem III-V/III-V approach in Scheme 1 allows for high efficiency, current methods of fabrication are costly. In parallel, we are pursuing tandem InGaN/Si absorber devices (Scheme 2) that offer potential for reduced cost by eliminating the III-V growth substrate. Collaboration with Dr. Friedman's EMN node enables the fabrication of III-V tandem absorbers with tuned bandgaps to optimize current matching in the device. Moreover, continued collaboration with EMN nodes on PEC characterization, corrosion analysis, and on-sun testing will provide the key insights needed to continue developing PEC technology.

RESULTS

We demonstrated that a thin coating of molybdenum disulfide, a non-precious-metal HER catalyst, can impart both long-term stability as well as high catalytic activity to a pn⁺-GaInP₂ photocathode. After 110 hours of testing, the MoS₂-protected device showed no loss of photocurrent density with respect to the initial photocurrent value (Figure 1), which was a main deliverable of Phase 1. The MoS₂ film was deposited by an initial ~3 nm Mo sputter followed by a sulfidation in an H₂S atmosphere. Furthermore, the Ir OER catalyst remained active and intact during these stability tests. Publication #1 noted below describes related work involving 100-h stability of a similar fabricated photocathode that provides photocurrent densities >10 mA/cm².

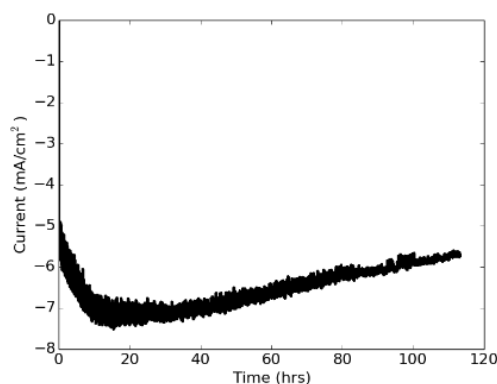


Figure 1. Electrochemical chronoamperometric characterization of pn⁺-GaInP₂/MoS₂ photocathodes in 0.5 M sulfuric acid at a constant potential of +0.1 V versus normal hydrogen electrode

We translated the MoS₂ protection scheme to inverted metamorphic multijunction (IMM) unassisted water splitting devices. These devices consist of a large bandgap III-V (e.g., GaInP₂) and small bandgap III-V (e.g.,

GaAs) grown inverted in order to minimize defect propagation in the top absorber. A compositionally graded buffer layer is also used to allow non-lattice matched III-V absorbers, such as GaInAs and GaInP₂, to be paired in order to take advantage of better bandgap matching. Under ~1.3 suns, an MoS₂-protected GaInAsP/GaAs IMM device maintained >10% STH for the first 2 hours, operating for an additional 10 hours while decreasing to about 60% of its light-limited photocurrent before failure. This is a significant improvement over the control sample, a sibling IMM sample prepared with the champion NREL PtRu catalyst that catastrophically failed within only 3 hours of testing (Figure 2). Preliminary investigation of the surfaces indicate that micron-sized defects and pinholes are present before electrochemical testing of these devices and are most likely due to the complex IMM fabrication process. We believe our MoS₂-protected IMM devices fail earlier than the III-V systems fabricated using more conventional processes (non-IMM, see Figure 1) because our protection layers are not designed to handle the larger defects that emerge from IMM fabrication. During Phase 2, we will work with the NREL fabrication node to address this issue. This will enable on-sun testing for weeks, which is a primary deliverable of Phase 2.

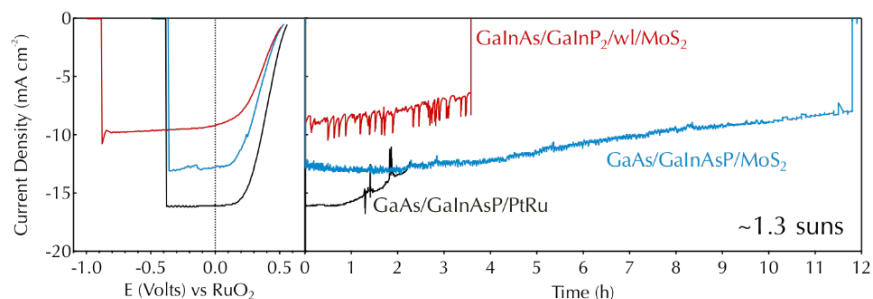


Figure 2. PEC characterization of GaInAs/GaInP₂/wl(window layer)/MoS₂, GaAs/GaInAsP/MoS₂, and GaAs/GaInAsP/PtRu unassisted water splitting devices in 0.5 M sulfuric acid

In terms of finding a suitable OER catalysis for PEC systems, we tested an Ir wire for >100 hours in 0.5 M H₂SO₄ with an applied current of 4.2 mA, since that is the approximate anode current when 20 mA/cm² is passing through a photocathode with an area of ~0.2 cm². We also are investigating the properties of our new solution-processed strontium iridium oxide (SrIrO_x) thin-film OER catalyst, which is compatible with planar photoanodes. Iridium oxide (IrO_x) and strontium iridium oxide (SrIrO_x) films were synthesized on p⁺ silicon substrates via spin coating to use as OER catalysts. Stability of 3.3 cm² anodes was measured by performing chronoamperometry at 1.6 V versus reversible hydrogen electrode for 24 hours. Initially, the IrO_x anode showed better stability performance than SrIrO_x. Stability is likely limited by the initial defects and heterogeneity in the films as well as by film delamination from the silicon substrate, which occurred at 19.5 and 18 hours, respectively. Current efforts are aimed at improving film adhesion by employing sticking layers and testing other substrates.

Toward the development of tandem InGaN/Si devices, we utilized MOCVD for nucleation and growth of InGaN films of good crystalline quality for the first time. Figure 3a is an X-ray diffraction symmetric (2theta-omega) scan of our InGaN films with various indium compositions. From the (002) diffraction peaks on this figure, it is evident that the MOCVD-grown InGaN films have excellent out-of-plane orientation. For the In_{0.55}Ga_{0.45}N film, we see the appearance of a secondary diffraction peak corresponding to that of InN, indicating that some degree of phase separation has occurred at such high indium compositions. Figure 3b is an X-ray diffraction phi scan of the (101) peak of InGaN, showing clear six-fold in-plane rotational symmetry, characteristic of good in-plane orientation for hexagonal wurtzite crystal structures. The InGaN films have smooth, densely packed film morphologies suitable as photovoltaic absorbers.

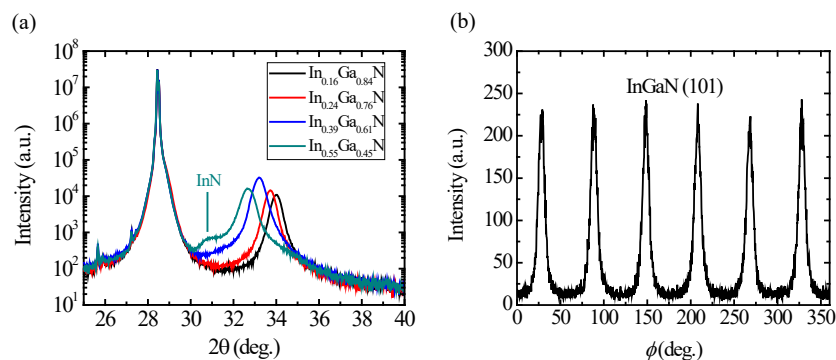


Figure 3. (a) X-ray diffraction symmetric (2theta-omega) scans of the (002) reflection for MOCVD-grown InGaN films with varying indium compositions, and (b) X-ray diffraction phi scans of the InGaN (101) reflection for a typical MOCVD-grown InGaN film

We conducted Hall effect measurements of our MOCVD-grown InGaN films. For the $\text{In}_{0.16}\text{Ga}_{0.84}\text{N}$ film, the background electron density is around $2.5 \times 10^{17} \text{ cm}^{-3}$, rendering it suitable as a photovoltaic absorber with a relatively wide depletion region width of $\sim 90 \text{ nm}$. For the $\text{In}_{0.55}\text{Ga}_{0.45}\text{N}$ film, the background electron density increases to $1.8 \times 10^{20} \text{ cm}^{-3}$, which is typical of InGaN films with high indium content but is unsuitable for photovoltaic applications.

To develop the growth of p-type InGaN through MOCVD, we added Cp_2Mg as the Mg precursor for p-type doping. We developed a two-step process first with growth at 550°C for the undoped InGaN absorber layer to achieve uniform wetting of the substrate, followed by growth of the Mg-doped InGaN layer at 750°C . Following MOCVD growth of the device stack, secondary ion mass spectroscopy analysis confirmed Mg incorporation. We observe Mg concentrations above 10^{19} cm^{-3} in the Mg-doped InGaN layer, which closely matches the Mg atomic concentrations of p-GaN reported in literature. The same InGaN device stack was further processed into solar cell devices. We observe no current rectification when sweeping between -1 V and 1 V . This lack of rectification could be because of the presence of compensating defects like nitrogen vacancies V_{N}^+ , which have lower formation energies when higher amounts of Mg doping is introduced. We are now investigating the root cause of the compensating defects, and experiments to demonstrate p-type InGaN are underway.

As a first step toward a tandem InGaN/Si device, a 125-nm-thick $\text{p}^{++}\text{-Si}$ layer ($1 \times 10^{20} \text{ cm}^{-3}$) was epitaxially grown on a (111) n-Si substrate. A 50-nm *intrinsic* InGaN layer was also grown by MOCVD on top of the Si p^{++} layer, although we have not yet fully developed p-InGaN growth on Si. The intrinsic InGaN is unlikely to be contributing photogenerated carriers, but we incorporated it in the growth process to demonstrate that we can fabricate a full tandem device once p-InGaN growth is developed. The photovoltaic device showed rectifying behavior characteristic of a p-n junction. Current-voltage data was taken in the dark and under 1 sun (not shown) with an unoptimized efficiency of 2.2%.

To demonstrate an *in operando* flow cell for photoelectrodes, we designed, machined, and tested a flow cell for use as an *in operando* microscopy and spectroscopy tool for our PEC devices. The flow cell operates with a thin quartz window $< 1 \text{ cm}$ above the sample allowing the surface to be within the working distance of a Raman or optical microscope. This flow cell contains slots for reference and counter electrodes. During validation, the current-voltage curve of a MoS_2 -protected p-GaInP photocathode matched the onset of a sibling sample tested in a typical H-cell indicating the viability of this cell for electrochemical characterization.

Furthermore, we successfully acquired *ex situ* Raman spectroscopic data of the MoS_2 protective catalyst deposited on a Si photoabsorber. The next step is to take Raman spectra of the samples *in situ*. This requires immersion of the objective lens of a Raman spectrometer in order to achieve this and we have established a dialogue with Jason Cooper of Lawrence Berkeley National Laboratory to develop that capability. This

motivates the possible inclusion of the “Photophysical Characterization of Photoelectrochemical Materials and Assemblies” node at Lawrence Berkeley National Laboratory during Phase 2 of work.

CONCLUSIONS AND UPCOMING ACTIVITIES

In summary, we demonstrated 100-hour stability for high-performance PEC photoelectrodes with >10 mA/cm² under 1 sun, and we fabricated an unassisted PEC water splitting device with a non-precious-metal HER catalyst with STH efficiencies $>5\%$ under 1 sun. This strategy provides a viable pathway for $>20\%$ STH efficiency through improved integration of materials and interfaces. Under ~ 1.3 suns, an MoS₂-protected GaInAsP/GaAs IMM device achieved $>10\%$ STH for 2 hours. In pursuit of low-cost, high-performance tandem PEC absorber layers, we also demonstrated the first InGaN growth on Si (111) by MOCVD.

Work in Phase 2 will focus on the development of working InGaN/Si tandem devices as well as on-sun testing of unassisted water splitting devices for longer than 2 weeks. We will also pursue unassisted water splitting devices with $>20\%$ average STH efficiency. Our collaborations with the EMN nodes have been fruitful for creating and understanding high-quality PEC systems. We believe that continued work with PEC characterization, corrosion analysis, on-sun testing, and III-V fabrication EMN nodes will be invaluable for the success of this project in Phase 2.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. R.J. Britto, J.L. Young, Y. Yang, M.A. Steiner, D.T. LaFehr, M. Beard, T.G. Deutsch, T.F. Jaramillo, “Interfacial Engineering of Gallium Indium Phosphide Photoelectrodes for Hydrogen Evolution with Precious Metal and Non-Precious Metal Based Catalysts,” *Submitted*.
2. J.A. Gauthier, L.A. King, F. Tucker Stults, R.A. Flores, J. Kibsgaard, Y.N. Regmi, K. Chan, T.F. Jaramillo, “Transition Metal Arsenide Catalysts for the Hydrogen Evolution Reaction,” *Submitted*.
3. T.F. Jaramillo, “New Catalysts and New Routes for the Sustainable Production of Fuels and Chemicals,” Invited Presentation at Uppsala University, Department of Chemistry, Uppsala, Sweden, December 2018.
4. T.F. Jaramillo, “Developing Catalysts and Processes for the Sustainable Production of Fuels and Chemicals,” Invited Presentation at Massachusetts Institute of Technology, Department of Chemistry, Inorganic Chemistry Seminar, Cambridge, MA, December 2018.
5. T.F. Jaramillo, “Integrating non-Precious Metal H₂ Evolution Catalysts into Water Electrolyzers and Photoelectrochemical Water Splitting Devices,” Presentation at Annual Meeting of the American Institute of Chemical Engineers (AIChE), Pittsburgh, PA, October 2018.
6. T.F. Jaramillo, “Electrocatalyst Development for the Production and Consumption of Chemical Fuels,” Invited Presentation at the Bosch Energy Research Network (BERN) Symposium 2018, Sunnyvale, CA, September 2018.
7. T.F. Jaramillo, “Design and Development of Catalytic Interfaces for Electrochemical and Photoelectrochemical Processes,” Invited Presentation at the 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2018.
8. T.F. Jaramillo, “The Past, Present, and Future of Photoanodes for Photoelectrochemical (PEC) Water-Splitting,” Invited Presentation at the Center for Chemical Innovation (CCI) Solar Fuels Capstone Meeting, Ventura, CA, July 2018.
9. T.F. Jaramillo, “Catalyzing Electrochemical Processes for Sustainable Energy,” Invited Presentation at the Gordon Research Conference (GRC): Catalysis, Accelerating Catalytic Solutions to Global Grand Challenges, Colby-Sawyer College, New London, New Hampshire, June 2018.
10. T.F. Jaramillo, “Protective Catalyst Systems on III-V and Si-based Semiconductors for Efficient, Durable Photoelectrochemical Water Splitting Devices,” Invited Poster Presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, D.C., June 2018.

11. T.F. Jaramillo, “Design and Development of Catalyst Materials for the Production of Fuels and Chemicals in a Sustainable Manner,” Invited Presentation at the 4th International Conference on Electrochemistry, Rome, Italy, June 2018.
12. T.F. Jaramillo, “Towards Unassisted Water-Splitting Systems: Development of Catalysts, Semiconductors, and Interfaces,” Invited Presentation at the 233rd Electrochemical Society Meeting, Seattle, WA, May 2018.
13. T.F. Jaramillo, “Catalyst Development for Sustainable Processes Involving Electrochemical Transformations,” Invited Presentation at the École Polytechnique Fédérale de Lausanne (EPFL) Winter School: Challenges and Opportunities in Energy Research, Crans-Montana, Valais, Switzerland, March 2018.
14. T.F. Jaramillo, “Developing New Materials and Processes for the Sustainable Production of Fuels and Chemicals,” Invited Presentation at the University of Texas–El Paso, Department of Chemistry, El Paso, TX, February 2018.
15. T.F. Jaramillo, “Protective Catalyst Systems on III-V and Si-Based Semiconductors for Efficient, Durable Photoelectrochemical Water Splitting Devices,” Invited Presentation at the Hydrogen Production Tech Team (HPTT) Meeting, WebEx, February 2018.
16. T.F. Jaramillo, “Carbon-free Production of H₂, NH₃, and Carbon-based Fuels and Chemicals,” Invited Presentation at The Future of Renewable Transportation, Stanford Energy 3.0 Workshop, Stanford University, Stanford, CA, February 2018.
17. T.F. Jaramillo, “Electrocatalyst Design and Development for Key Reactions in Solar Fuels,” Invited Presentation at the Renewable Energy: Solar Fuels Gordon Research Conference, Ventura, CA, January 2018.