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

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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.

- Demonstrate an unassisted device with >20% average solar to hydrogen (STH) and successful on-sun testing of unassisted water splitting devices for >2 weeks.

Fiscal Year (FY) 2019 Objectives

- Demonstrate a working tandem InGaN/Si solar cell device
- Demonstrate InGaN/Si tandem absorbers that produce hydrogen during light-driven, unassisted water splitting.
- Develop improved tandem III-V absorbers with improved efficiency and durability
- Develop unassisted water-splitting devices that maintain at least 10% STH for >100 h
- Demonstrate the effectiveness of the in operando microscopy and spectroscopy flow cell measurement technique on a benchmark photoelectrode system.

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
- Materials Durability–Bulk and Interface
- Integrated Device Configurations
- Auxiliary Materials–For Catalysis and Durability
- Synthesis and Manufacturing–Technique Development.

Technical Targets

This project is conducting research into catalyst and protection layer development in PEC devices as well as development of InGaN/Si tandem absorbers in addition to fundamental studies of degradation in photoelectrochemical systems.

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

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 & PEC Receiver): \$124/m² (2020); \$63/m² (ultimate)
- Annual Electrode Cost per TPD H₂: \$225K/yr-TPDH₂ (2020); \$14K/yr-TPDH₂ (ultimate)
- Solar to Hydrogen (STH) Energy Conversion Ratio: 20% (2020); 25% (ultimate)
- One-Sun Hydrogen Production Rate 1.6e-6 kg/s per m² (2020); 2.0e-6 kg/s per m² (ultimate).

FY 2019 Accomplishments

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 electrolytes. 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 the 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, Photophysical Characterization, and On-Sun Testing will provide the key insights needed to continue developing PEC technology.

- Demonstrated rectifying and photovoltaic behavior of InGaN/Si and NiO/n-InGaN, respectively.
- Utilized low-cost metal oxides to demonstrate photoanode behavior of NiO/InGaN with 0.8 mA/cm² of photocurrent.
- Developed new III-V device architectures with an AlInP window layer and GaInP₂ capping layer to improve efficiency and durability.
- Demonstrated a MoS₂-protected GaInP₂/GaInAs inverted metamorphic multijunction (IMM) tandem with >12% STH efficiency.
- Progressed toward in situ Raman spectroscopy to monitor degradation.
- Demonstrated direct nucleation and growth of InGaN on Si by metal organic chemical vapor deposition (MOCVD) followed by growth of Mg-doped InGaN toward the growth of an InGaN p-n junction.

RESULTS

Previously, we have demonstrated Mg p-type doping in MOCVD-grown InGaN, and we demonstrated the growth of p-type doped InGaN on top of intrinsic InGaN on Si (111). However, we previously were unable to observe rectification for the p-n InGaN junction. One likely cause of this is the influence of defect and grain boundary states that can cause charge compensation in the p-type doped InGaN layer. In order to increase the grain size of the intrinsic and doped InGaN layers to mitigate this potential effect, we introduced a several nm interlayer of $\text{In}_{0.10}\text{Al}_{0.90}\text{N}$ on top of the Si (111) to improve lattice matching between the Si and InGaN, which could increase grain size and reduce the effect of charge compensation. Our initial attempt did not yield any notable difference in the morphology, and we still do not observe rectification in the p-n InGaN junction (Figures 3 and 4). However, we plan to tune the growth of the InAlN interlayer to achieve better control of the morphology that can allow us to achieve rectification between p-doped InGaN and n-type intrinsic InGaN.

Previous literature demonstrates the potential for pairing NiO with n-GaN and n-InN to form rectifying p-n junctions. Based on those observations, we deposited a 30 nm NiO layer and 3 nm Au top contact via e-beam evaporation before the deposition of our metal contact layers. After fabrication of a device as shown schematically in Figure 1a, we can observe rectifying behavior that appears to be characteristic of the presence of a type-II junction, as shown in Figure 1b. In addition, we were able to observe a photoresponse, with a photocurrent density of 0.21 mA/cm^2 . It is likely that a significant number of photons are being absorbed or reflected by the Au film, which may exhibit poor conformality to the surface of InGaN grown by MOCVD. While the overall efficiency (0.01%) is quite low, we believe that optimization of the device structure and improvements to the quality of the Au film are highly likely to lead to an improvement in photocurrent and device efficiency.

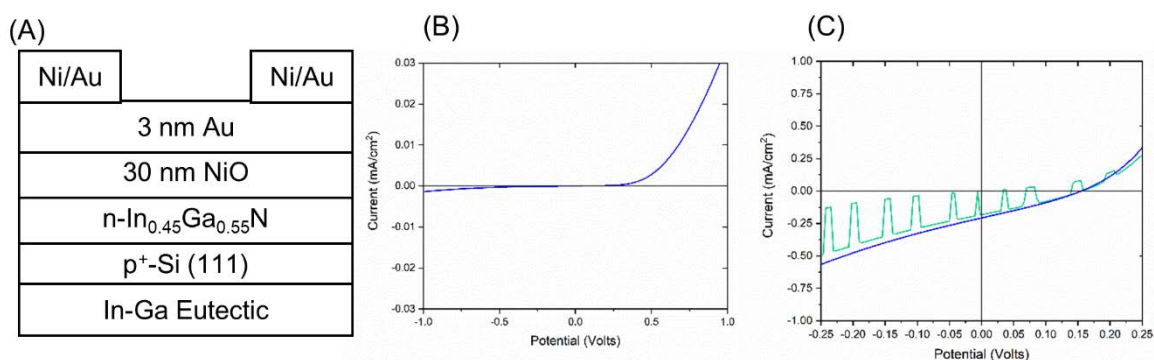


Figure 1: (A) Device schematic of InGaN with a 30nm NiO layer deposited by E-beam. (B) Current-Voltage characteristic of the device showing rectifying behavior. (C) Current-voltage behavior under illumination (blue) and in chopped light/dark (green)

We then tested the NiO-coated InGaN for photoanode performance without an Au top contact (Schematic in Figure 2A). This architecture utilizes p-type NiO both to extract charges from n-type $\text{In}_{0.13}\text{Ga}_{0.87}\text{N}$, but it also to act as a semi-transparent OER catalyst. Although this sample contained an Mg-doped layer, we believe it will have predominantly n-type character based on our previous reports. On the other hand, as previously reported, we have consistently observed diode behavior from growing p-type NiO on n-type InGaN.

An image of the finished InGaN photoanode device is shown in Figure 2b. In a 0.1 M KOH electrolyte, we observe a clear modulation of the open-circuit voltage in the presence of light in the dark that strongly suggests that this electrode is photoactive (Figure 2c). Under UV-enhanced light with a total photon flux equivalent to 1.99 suns, we observe the onset of the OER reaction as positive potential is applied, as demonstrated in Figure 2d. Comparison to the dark curve (Figure 2e) demonstrates a minimal extent to which the dark catalysis is contributing to the current. Furthermore, the chopped curve shown in Figure 2f demonstrates the on/off characteristics of the InGaN photoanode in light and dark. Future efforts will focus on attempting to optimize the performance of the InGaN photoanode top cell to facilitate a successful Si/InGaN tandem cell that will minimize issues caused by the current mismatch.

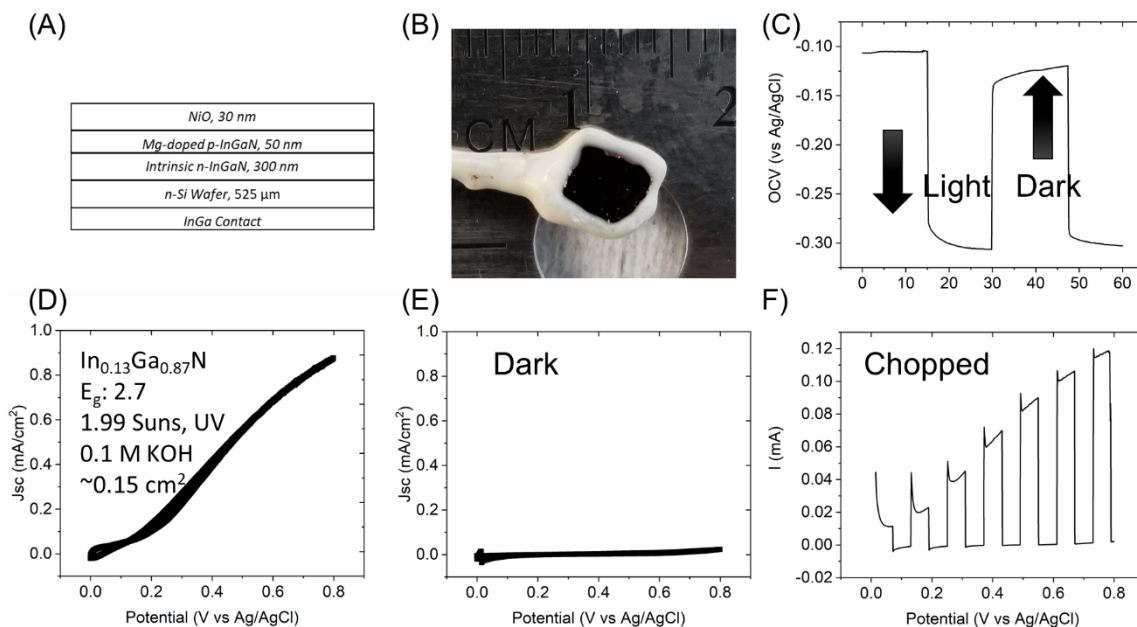


Figure 2: (A) Device stack with NiO hole extraction layer/catalyst. (B) Image of an electrode in epoxy. (C) Open circuit potential under illumination and in the dark. (D-F) Current-Voltage (JV) Characteristics under illumination (D), in the dark (E), and chopped (F).

Toward the development of III-V PEC devices with improved stability and durability, we investigated new device architectures. Recent work at NREL has shown the effectiveness of an AlInP window layer at passivating the surface, which reduces surface recombination, thereby increasing current. However, AlInP is unstable in acidic electrolytes; thus, a GaInP₂ capping layer is added to protect the underlying window layer. The current-voltage (JV) characteristics under illumination and incident photon-to-current efficiency (IPCE) are shown, with the pnwc device producing the earliest photocurrent onset and highest saturation photocurrent (Figure 3a). Post-test XPS shows that in the pnw structure, there was total dissolution of the AlInP window layer and MoS₂ catalyst coating, leaving a GaInP₂ surface (Figure 3). This indicates that the JV measurements for the pnw sample are more accurately bare GaInP₂. As only the pnwc sample retains the window layer, the boost in photocurrent likely comes from the presence of the surface-passivating window layer. Thus, the pnwc structure will be adopted for future studies, including upright and IMM tandem photocathodes

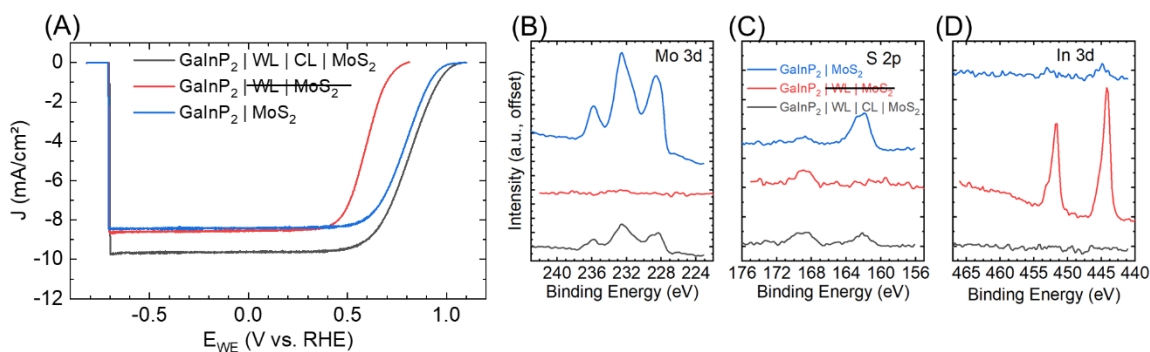


Figure 3: (A) Linear sweep voltammograms of different GaInP₂ photocathode structures. (B-D) post-test XPS of Mo 3d (B), S 2p (C), and In 3d (D) for each of the three photocathodes. The MoS₂/WL/GaInP₂ architecture had all MoS₂, and AlInP window layer dissolves, exposing the GaInP₂ absorber.

Using this top cell architecture with a window and capping layer, we grew an IMM tandem device protected with MoS₂: MoS₂/WL/CL/GaInP₂/GaInAs. The tandem device was tested for PEC hydrogen production under

1 sun illumination, and with 0 V applied bias, there was 11 mA/cm² of photocurrent density, corresponding to an STH efficiency of 12.8% (Figure 4).

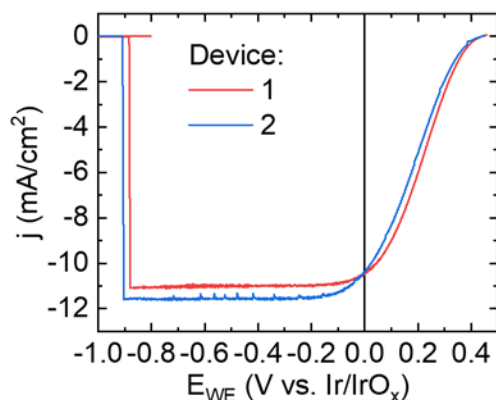


Figure 4: LSV under 1 sun illumination of IMM tandem MoS₂/GaInP₂/GaInAs.

To further improve the activity and stability of our photocathodes, improvements to the protection scheme are necessary. To this aim, we aim to utilize atomic layer deposition (ALD) to improve uniformity and reduce defects of the MoS₂ and other transition metal dichalcogenide (TMD) coatings. We submitted a user proposal to the Molecular Foundry at Lawrence Berkeley National Laboratory (LBNL), which was accepted. The Foundry has expertise in depositing controlled, ultra-thin MoS₂ films by depositing MoO_x by ALD followed by a tube furnace H₂/H₂S anneal.

Utilizing *in situ* Raman spectroscopy will allow us to better characterize degradation mechanisms of our photoelectrodes and design protective schemes with improved stability. Thus we are leveraging the Photophysical Characterization of Photoelectrochemical Materials and Assemblies node at LBNL, utilizing the Raman microscope that can be immersed in acidic electrolytes by using a Teflon film protection barrier. Our ex-situ experiments will be used as a starting point for our in-situ work.

CONCLUSIONS AND UPCOMING ACTIVITIES

In summary, we demonstrated the photovoltaic behavior of MOCVD InGaN with a NiO hole extraction layer. In addition, wide bandgap In_{0.13}Ga_{0.87}N with a NiO catalyst/hole extraction layer was shown to act as a photoanode with 0.8 mA/cm² of photocurrent. This strategy provides a pathway towards reduced absorber fabrication costs. For GaInP₂ photocathodes, a window layer and capping layer were shown to improve photocurrent as well as photovoltage by reducing surface recombination and stabilizing the window layer, respectively. Using this architecture for the top GaInP₂ cell, an IMM tandem yielded 12.8% STH.

Work in the 3rd and final year will focus on the development of improved InGaN/Si tandem devices as well as on-sun testing of unassisted water splitting devices for longer than 2 weeks. Our efforts towards ALD protection layers should allow for improved device longevity. 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, Photophysical Characterization, On-Sun Testing, and III-V Fabrication EMN nodes will be invaluable for the success of this project in phase 2.

FY 2019 PUBLICATIONS/PRESENTATIONS

Publications

1. R.J. Britto, J.L. Young, Y. Yang, M.A. Steiner, D.T. LaFehr, D.J. Friedman, 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. *J. Mater. Chem. A* **2019**, 7, 16821-16832.

2. Joseph A. Gauthier, Laurie A. King, Faith Tucker Stults, Raul A. Flores, Jakob Kibsgaard, Yagya N. Regmi, Karen Chan, Thomas F. Jaramillo. Transition Metal Arsenide Catalysts for the Hydrogen Evolution Reaction. *J. Phys. Chem. C* **2019**, 123 (39), 24007-24012

Presentations

3. T.F. Jaramillo, “Integrating Non-Precious Metal H₂ Evolution Catalysts into Water Electrolyzers and Photoelectrochemical Water-Splitting Devices” 2018 AIChE Annual Meeting in Pittsburgh, PA, October 2018.
4. 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 2019.
5. T.F. Jaramillo, “Development of Catalytic Coatings for H₂-Producing Photocathodes in Solar Water-Splitting”, Materials Research Society 2019 Spring Meeting & Exhibit, Phoenix, AZ, April 2019.
6. T.F. Jaramillo, “Protective Catalyst Systems on III-V and Si-based Semiconductors for Efficient, Durable Photoelectrochemical Water Splitting Devices,” Invited Oral Presentation at the U.S. DOE Hydrogen and Fuel Cells Program Annual Merit Review, Office of Renewable Energy and Energy Efficiency (EERE), Washington, D.C., May 2019.
7. T.F. Jaramillo, “Materials Discovery and Development for the Sustainable Production of Fuels and Chemicals,” 236th Meeting of The Electrochemical Society (ECS), Atlanta, GA, October 2019.
8. T.F. Jaramillo, “Designing new catalysts and processes for the sustainable production of fuels and chemicals,” Chemical Sciences Roundtable, Advances, Challenges, and Long-Term Opportunities of Electrochemistry: Addressing Societal Needs, National Academies of Sciences, Engineering, and Medicine, Washington, D.C., November 2019.