
II.D.1 High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production

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Subcontractors:

- University of Nevada, Las Vegas, Las Vegas, NV (XGB-2-11673-01)
- University of Hawaii, Honolulu, HI (XGJ-5-52227-01)

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Project End Date: September 30, 2017

Overall Objectives

- Develop a semiconductor-based, solar-driven, water-splitting photoelectrochemical (PEC) device with greater than 20% solar-to-hydrogen (STH) efficiency and several thousand hours of stability under normal operating conditions.
- Incorporate components that can be fabricated cost-effectively and are straightforward to scale up such that a plant scaled to 50,000 kg H₂ per day can achieve an estimated production cost of \$1–\$2/kg hydrogen using only sunlight and water as feedstocks.
- Demonstrate a prototype photoreactor that produces 3 L of standard hydrogen within an 8-hour period under moderate solar concentration (~10x).

Fiscal Year (FY) 2017 Objectives

- Push boundaries on achievable semiconductor PEC STH efficiencies.
- Benchmark STH efficiencies for multijunction (tandem) PEC devices.
- Continue to develop stabilizing surface modifications that are viable at high current densities.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (AE) Materials efficiency – bulk and interface
- (AF) Materials durability – bulk and interface
- (AG) Integrated device configurations
- (AI) Auxiliary materials

Technical Targets

This project is a materials discovery investigation to identify a single semiconductor material that meets the technical targets for efficiency and stability. The 2015 technical targets from the PEC hydrogen production goals in Table 3.1.8.A of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan are the following.

- 15% STH conversion efficiency
- 900-hour replacement lifetime (half a year at 20% capacity factor)
- \$300/m² PEC electrode cost

FY 2017 Accomplishments

- We tested a new III-V alloy, GaInAsP, as a candidate for the 1.7-eV bandgap top cell in a higher-efficiency tandem device, and discovered it has good intrinsic stability and photoconversion efficiency. We sent a series of GaInAsP samples to the Heske group, our surface validation team collaborators at the University of Nevada, Las Vegas to get a better understanding of the surface stabilization mechanism.
- We achieved very good durability results with the Jaramillo group at Stanford University on buried-junction pn-GaInP₂ capped with MoS₂. We measured 100 h with little degradation and plan to extend the testing.
- We designed a capillary mass-spectrometer-based faradaic yield system and measured trace signals of H₂ and O₂ from GaAs water-splitting microcells from Jongseung Yoon's laboratory at the University of Southern California, testing the limit of quantitative detection for this custom instrument.

- We synthesized and tested epitaxial capping layers that could potentially offer more stability and less parasitic optical absorption than the standard GaInP₂ cap because of an engineered wider bandgap.
- We modeled antireflective texturing of III-V surfaces with Professor Yoon at the University of Southern California and identified structures that should have reflection below 5% across the relevant wavelengths. The model was validated experimentally.
- We commenced testing of our photoreactor on a two-axis solar tracker.



INTRODUCTION

Photoelectrolysis cells combine a light-harvesting system and a water-splitting system into a single, monolithic device. The catalyzed surface of a semiconductor is the light-harvesting component, as well as one part of the water-splitting system, with the balance consisting of a spatially separated counter electrode. Discovering a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water-splitting reaction could provide renewable and economically competitive fuel for the hydrogen economy.

The goal of this work is to develop a semiconductor material set or device configuration that:

- Splits water into hydrogen and oxygen spontaneously upon illumination without an external bias.
- Has a solar-to-hydrogen efficiency of at least 15%, with a clear pathway to exceed 20%.
- Can ultimately be synthesized via high-volume manufacturing techniques with a final hydrogen production cost below \$2/kg.

APPROACH

All proven zero-bias PEC devices with STH over 1% rely on two series-connected semiconductor junctions (tandem cell) to increase the majority-carrier potential at the counter electrode [1–4], providing sufficient potential difference (photovoltage) for water splitting. Tandem devices also overcome the band-alignment challenge common to PEC materials.

For maximum efficiency, the subcell currents in series-connected devices must be equal, creating the requirement of current matching. The maximum theoretical current generated by a semiconductor can be calculated by assuming unity quantum yield for every above-bandgap photon in the solar spectrum. Using the accepted lower heating-value efficiency equation [5], 20% STH corresponds to a short-

circuit current density of 16.26 mA/cm² under air mass 1.5 global (1-sun). The largest bottom-cell bandgap that can be used and still achieve 20% STH is 1.41 eV. However, quantum yields are never 100% and semiconductors are not true step-function devices. Therefore, to realistically achieve STH values in excess of 20%, we must use lower top-cell and bottom-cell bandgap combinations, which guides our selection of candidate semiconductors.

An additional variable that can be used to match the currents is the thickness of the top cell; a thinner cell will allow more photons through to the bottom cell. This gives us some additional flexibility in the bandgaps that may be used. The lower limit of useable bandgaps is ~0.8 eV [6], dictated by the short penetration depth of lower-energy photons through water.

We will focus on III-V semiconductors, which exhibit the highest conversion efficiencies among all photoabsorber materials, and design tandem junctions to maximize the spectrally split device current, while achieving sufficient voltage to drive the maximum current through the device. We plan to initially focus on devices grown by conventional III-V metal-organic vapor-phase epitaxy to demonstrate maximum possible efficiencies. We will then port successful device structures to emerging synthesis techniques—such as spalling, epitaxial lift-off, or hydride vapor-phase epitaxy—that have the potential to meet low-cost absorber targets. We plan to improve the stability of III-V semiconductor water-splitting electrodes by a variety of surface-protecting modifications that include nitridation/sputtering, atomic layer deposition of oxides/nitrides, and thin coatings of MoS₂.

RESULTS

Solar-to-Hydrogen Efficiency Benchmarking

During the course of benchmarking over 16% STH efficiency on our inverted metamorphic multijunction (IMM) cells [7], we identified and documented two more potential sources of measurement error that were not included in our *Energy & Environmental Science* manuscript [8] that detailed ways of improving STH measurement accuracy. One systematic error we discovered is a consequence of applying light from a diverging illumination source through the multiple interfaces of an electrochemical cell. The different indices of refraction between air/glass/electrolyte cause a concentration error that can increase the light intensity on the sample by 10%, relative to the calibrated value, under commonly used experimental conditions. We recommended using a highly collimated source (i.e., sunlight with a collimating tube) to mitigate this source of error. We also made a recommendation against setting light intensity from a solar simulator with the reference diode *inside* the electrochemical cell, either with air or electrolyte inside the cell. In the case of an air-filled cell, reflection at the glass/

electrolyte interface is significantly lower than at a glass/air interface, resulting in a light intensity on the PEC sample that is about 5% greater than the calibrated value. Immersing the reference cell in electrolyte during light-intensity calibration can eliminate the reflection error at the inner electrochemical cell interface, whereas the infrared absorption of water attenuates light on a typically used Si reference cell, leading to an overcompensated simulator intensity.

To report STH water-splitting efficiency, the fraction of current going to hydrogen and oxygen generation (Faradaic efficiency) must be known. We designed and built a new Faradaic efficiency measurement system based on product gas detection by a capillary mass spectrometer. Using a mass spectrometer has several advantages over the more commonly used gas chromatograph in detecting product gases, including the following: greater sensitivity, continuous measurement, and ability to provide qualitative as well as quantitative information. We demonstrated the capability of this system by measuring the Faradaic efficiency of solar water splitting on GaAs microcells synthesized by our collaborator. We were able to quantitatively determine oxygen and hydrogen generated on 0.0025-cm^2 microcells at only $50\ \mu\text{A}$ of current. The corresponding concentrations of oxygen and hydrogen under the measurement conditions were 200 ppm and 400 ppm, respectively. Confirming a near-unity Faradaic yield, we were able to use collimated sunlight to benchmark 13.1% STH efficiency from these GaAs microcells [9].

For longer-term performance assessment under more realistic conditions, i.e., those that include temporal intermittency from clouds and diurnal cycles, we designed and fabricated a photoreactor for testing on a two-axis solar tracker. The photoreactor (Figure 1) can be fitted with a Fresnel lens for measurements at low optical concentrations ($\sim 10\times$), and it is equipped with quantitative gas-collection capabilities, can accommodate a variety of sample dimensions, and has Nafion[®] membrane separators to prevent mixing of hydrogen and oxygen.

Durability Testing

IMM cells have advantages over upright tandems when in pursuit of higher STH efficiencies. However, the stability of the IMM cells is significantly lower than we previously observed with upright tandem water-splitting PEC cells. Corrosion on upright cells tends to be characterized by a more uniform etching from the surface toward the substrate. Degradation of IMM cells initiates locally—apparently centered around native defects in the material—leading to blistering and delamination from the Si handle, and ultimately resulting in catastrophic failure (Figure 2). It is possible that these native defects are also present in the upright cells, but their tendency to lead to catastrophic failure is tempered by the $700\text{-}\mu\text{m}$ -thick GaAs substrate. The IMM form factor of a very thin ($\sim 5\ \mu\text{m}$) absorber layer in direct

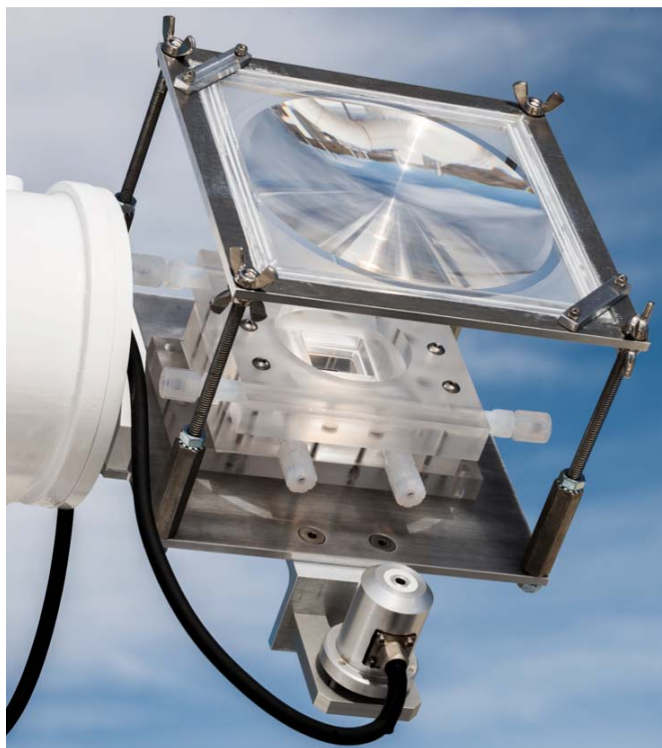


Photo credit: NREL-Dennis Schroeder

FIGURE 1. Photograph of our photoreactor mounted on a two-axis solar tracker for on-sun testing.

contact with a gold hole-collecting back contact appears to be a less stable configuration than the upright cells that have GaAs substrate between the absorber layer and gold back contact. Similar single-crystal epitaxial III-V semiconductors are flexible when removed from their substrates—a property often highlighted as advantageous for solid-state photovoltaics—and would be expected to be susceptible to delamination should adhesion with its rigid handle become compromised. It is unclear whether the GaAs substrate provides a chemical buffer, slowing etching progression of acidic electrolyte to the gold back contact, or is merely additional mechanical support for a flimsy absorber layer.

We have attempted to passivate the IMM surfaces with epitaxial capping layers (GaInAsP and GaInAsN), which, based on experience, should have greater stability than GaInP₂. However, the mechanical instability of the IMM cells prevents us from evaluating their chemical stability. An example of this can be seen in Figure 3, where the GaInAsN-capped IMM structure exhibits good stability under electrochemical durability testing, but physical observation of the surface (Figure 3 inset) reveals a surface that is already deteriorating in discrete locations. Initial attempts have been unsuccessful to map native defects with optical microscopy and locally passivate them.

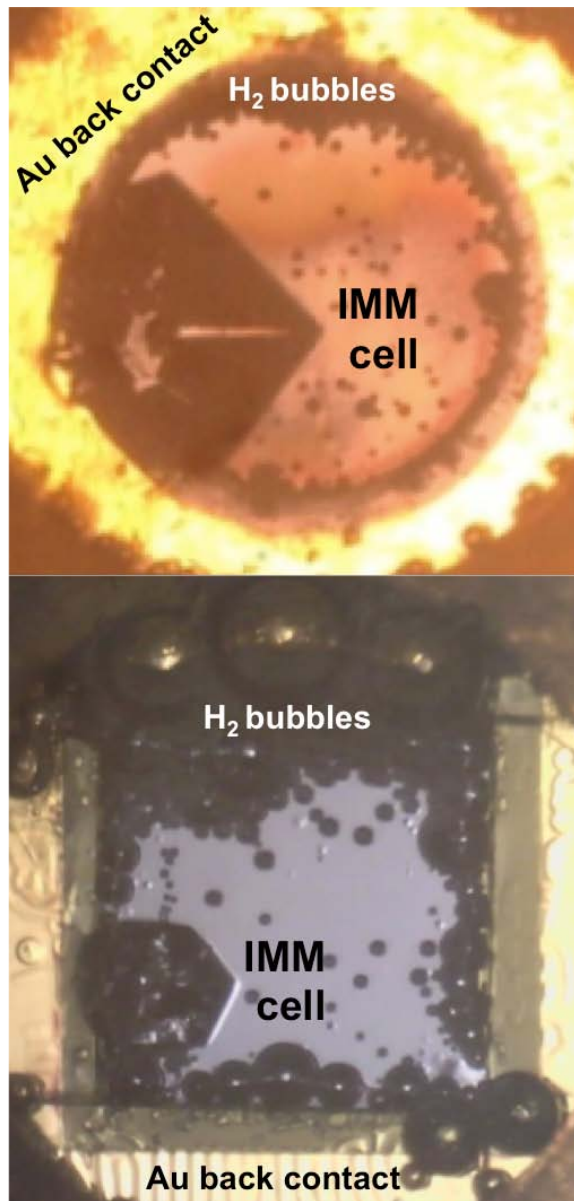


FIGURE 2. Photographs of two different IMM cell failures during durability testing in 0.5 M sulfuric acid. We tried IMM cells with circular mesas (top) as well as square mesas (bottom), but most exhibited failure mechanisms similar to these. The separation of the semiconductor layer from the silicon handle can be seen to the left of the “IMM cell” label in each image. The width of the IMM cell is about 4 mm in both photos.

CONCLUSIONS AND UPCOMING ACTIVITIES

- We have established robust protocols for accurately benchmarking solar-to-hydrogen efficiency that have their foundations in the methodology used to certify the efficiency of multijunction solid-state solar photovoltaic cells.

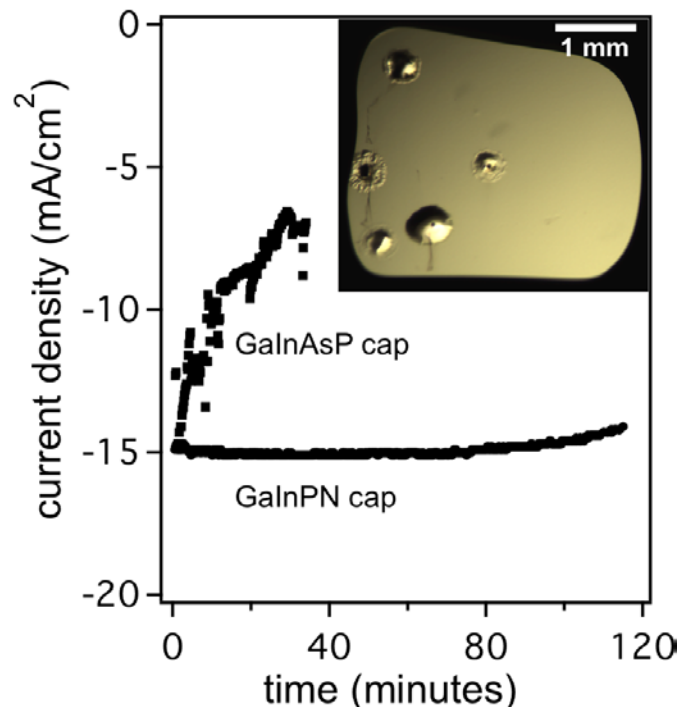


FIGURE 3. Current density vs. time plots for two IMM cells with different protective capping layers. These electrodes were tested at short circuit (0 V vs. a RuOx counter electrode) in 0.5 M sulfuric acid. A flat line indicates stability. Although the current for the GalnP-capped electrode implies resistance to corrosion, the left side of the photograph in the inset shows that this electrode had several defects that led to blistering of the IMM layer.

- IMM cells are a good platform for meeting the STH efficiency targets established in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, but they are more susceptible to corrosion than upright tandems.
- Upcoming activities will focus on surface modifications that increase STH efficiency by reducing reflection at the semiconductor/electrolyte interface. We will also focus on durability by potentially developing upright metamorphic cells.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

- 2017 DOE Hydrogen and Fuel Cells Program R&D Award (Young, Steiner, Deutsch)
- (Pending) Devices and methods for photoelectrochemical water splitting. Application No. 15/078,206

FY 2017 PUBLICATIONS AND PRESENTATIONS

1. “Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures,” James L. Young, Myles A. Steiner, Henning Döscher, Ryan M. France, John A. Turner, and Todd G. Deutsch, *Nature Energy* **2**, 17028 (2017).
2. “Employing overlayers to improve the performance of $\text{Cu}_2\text{BaSnS}_4$ thin Film based Photoelectrochemical Water Reduction Devices,” Jie Ge, Paul J. Roland, Prakash Koirala, Weiwei Meng, James L. Young, Reese Petersen, Todd G. Deutsch, Glenn Teeter, Randy J. Ellingson, Robert W. Collins, and Yanfa Yan, *Chem. Mater.* **29**(3), 916–920 (2017).
3. “Covalent surface modification of GaAs(100) photocathodes for water splitting in highly Acidic Electrolyte,” L.E. Garner, K.X. Steirer, J.L. Young, N.C Anderson, E.M. Miller, J.S. Tinkham, T.G. Deutsch, A. Sellinger, J.A. Turner, and N.R. Neale, *ChemSusChem*. **10**, 767–773 (2017).
4. “Printed assemblies of GaAs photoelectrodes with decoupled optical and reactive interfaces for unassisted solar water splitting,” Dongseok Kang, James L. Young, Haneol Lim, Walter E. Klein, Huandong Chen, Yuzhou Xi, Boju Gai, Todd G. Deutsch, and Jongseung Yoon, *Nature Energy* **2**, 17043 (2017).
5. “Influence of support electrolytic in the electrodeposition of Cu-Ga-Se thin films,” A.M. Fernandez, J.A. Turner, B. Lara-Lara, and T.G. Deutsch, *Superlattices and Microstructures* **101**, 373–383 (2017).
6. “Inverted metamorphic multijunction semiconductors for exceptionally high photoelectrolysis efficiencies: Materials development and measurement challenges,” XXV International Materials Research Congress of the Materials Research Society, Cancun, Mexico. August 16, 2016. (Deutsch) *Invited*
7. “Inverted metamorphic multijunction III-V semiconductors for solar hydrogen production,” Materials Research Society Fall Meeting. Boston, MA. November 30, 2016. (Deutsch)
8. “Solar-to-hydrogen efficiency – Shining light on photoelectrochemical device performance,” Materials Research Society Fall Meeting. Boston, MA. November 28, 2016. (Deutsch)
9. “Inverted metamorphic multijunction semiconductors for exceptionally high photoelectrolysis efficiencies: Materials development and measurement challenges,” Pacific Rim Meeting of Electrochemical and Solid State Science (PRiME), Honolulu, HI. October 6, 2016. (Deutsch)
10. “Advanced device design for photoelectrochemical water splitting derived by a detailed balance approach,” Pacific Rim Meeting of Electrochemical and Solid State Science (PRiME), Honolulu, HI. October 6, 2016. (Döscher)
11. “High photoelectrochemical water splitting efficiencies: Materials development and measurement challenges” 253rd American Chemical Society National Meeting and Exposition, San Francisco, CA. April 5, 2017. (Turner) *Invited*
12. “Recent advances in III-V multijunction photo-electrochemical water splitting,” Materials Research Society Spring Meeting, Phoenix, AZ. April 19, 2017. (Deutsch) *Invited*
13. “Solar-to-hydrogen efficiency: Shining light on photoelectrochemical device performance,” Materials Research Society Spring Meeting, Phoenix, AZ. April 19, 2017. (Young)
14. “Photo-electrochemical hydrogen generation from inverted metamorphic multijunction III-Vs,” 13th International Conference on Concentrator Photovoltaic Systems, Ottawa, Ontario. May 3, 2017. (Deutsch)
15. “Recent advances in III-V multijunction photo-electrochemical water splitting,” 231st Meeting of the Electrochemical Society, New Orleans, LA. May 30, 2017. (Deutsch) *Invited*
16. “Solar-to-hydrogen efficiency: Shining light on photoelectrochemical device performance,” Materials Research Society Spring Meeting, Phoenix, AZ. April 19, 2017. (Young)
17. “High-efficiency tandem absorbers for economical solar hydrogen production,” DOE Hydrogen and Fuel Cells Program Annual Merit Review. Washington, DC. June 8, 2017. (Deutsch)
18. “Photo-electrochemical hydrogen generation from inverted metamorphic multijunction III-Vs,” 44th IEEE Photovoltaic Specialists Conference, Washington, DC. June 26, 2017. (Deutsch)

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9. “Printed assemblies of GaAs photoelectrodes with decoupled optical and reactive interfaces for unassisted solar water splitting,” Dongseok Kang, James L. Young, Haneol Lim, Walter E. Klein, Huandong Chen, Yuzhou Xi, Boju Gai, Todd G. Deutsch, and Jongseung Yoon, *Nature Energy* **2**, 17043 (2017).