

## II.G.2 Semiconductor Materials for Photoelectrolysis

John Turner (Primary Contact), Todd Deutsch,  
Heli Wang, Adam Welch, Yanfa Yan, Wanjian Yin,  
Su-Huai Wei, Mowafak Al-Jassim

National Renewable Energy Laboratory (NREL)  
1617 Cole Blvd.  
Golden, CO 80401  
Phone: (303) 275-4270  
E-mail: John.Turner@nrel.gov

### DOE Manager

HQ: Eric Miller  
Phone: (202) 287-5829  
E-mail: Eric.Miller@hq.doe.gov

### Subcontractors:

- Stanford University, Palo Alto, CA
- University of Nevada, Las Vegas, Las Vegas, NV

Project Start Date: 2005

Project End Date: Project continuation and  
direction determined annually by DOE

### FY 2011 Accomplishments

- Improved the world-record water splitting efficiency of GaInP<sub>2</sub>/GaAs tandem cells by using a more active RuO<sub>2</sub> counter electrode. Confirmed a maximum solar-to-hydrogen efficiency of 16.3% under real solar (outdoor) conditions, a significant improvement over the 12.4% previous record and greatly exceeding the MYP 2013 10% technical target.
- Identified potential surface nitride passivation of GaInP<sub>2</sub> by nitrogen ion bombardment and electrochemical routes. Nitrided surfaces exhibited less corrosion than untreated samples.
- Validated stability of low-cost amorphous Si/SiC hybrid photoelectrodes synthesized by our corporate partner MVSys, Inc. The electrode was still able to generate photocurrent after 500 hours of testing at an applied current density of -1 mA/cm<sup>2</sup>, and is half way to the MYP 2013 technical target of 1,000 hours of durability.
- Synthesized CuO, Cu<sub>2</sub>O, and Ti alloyed Cu-Ti oxides with various structures and band gaps by reactive radio frequency (RF) magnetron sputtering. PEC characterizations of the Ti-Cu mixed oxide revealed improved performance and greater stability than Cu oxides alone.
- Characterized corrosion resistant p-In<sub>x</sub>Ga<sub>1-x</sub>N alloys synthesized by our collaborator at Los Alamos National Laboratory.



### Fiscal Year (FY) 2011 Objectives

Identify, synthesize, and characterize new semiconductor materials that have the capability of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device, either as a single absorber or as part of a high-efficiency multi-junction device.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cells Technologies Program Multi-Year Research, Development and Demonstration Plan (MYP):

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration

### 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 2013 technical targets from the MYP PEC hydrogen production goals are as follows:

- Bandgap of 2.3 eV
- 10% conversion efficiency
- 1,000-hour lifetime

### Introduction

Photoelectrochemistry combines a light harvesting system and a water splitting system into a single monolithic device. A semiconductor immersed in aqueous solution comprises the light-harvesting system. The catalyzed surface of the semiconductor is one part of the water splitting system, and the other part is another electrode in a separate compartment. The key is to find a semiconductor system that can efficiently and sustainably collect solar energy and direct it towards the water splitting reaction.

The goal of this work is to develop a semiconductor material set or device configuration that (i) splits water into hydrogen and oxygen spontaneously upon illumination, (ii) has a solar-to-hydrogen efficiency of at least 5% with a clear pathway to a 10% water splitting system, (iii) exhibits the possibility of 10 years stability under solar conditions, and (iv) can be adapted to volume-manufacturing techniques.

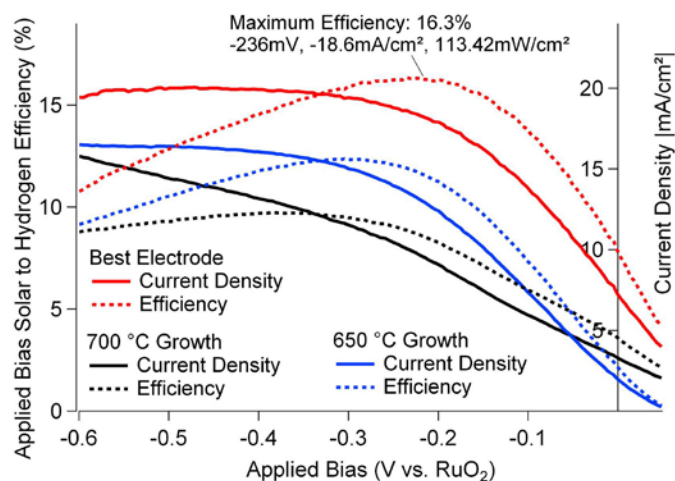
## Approach

Our approach has two thrusts, i) the study of current material sets used in commercial solar cells as well as related materials, and ii) the discovery of new semiconducting materials using advanced theoretical calculations to identify promising candidates, closely coupled with synthesis and state-of-the-art characterization. A major component of (i) focuses on III-V semiconductor materials that meet the efficiency target and engineering the surface to meet the durability target. Area (ii) has focused on chalcogenide and Cu-, W-, Ti-, and Bi-based multinary oxides.

## Results

The GaInP<sub>2</sub>/GaAs tandem cell has held the world-record efficiency (12.4%) for unbiased PEC water splitting for several years [1]. This benchmark for efficiency was established using platinum as a counter electrode anode material. We were able to improve upon this efficiency by using a counter electrode that is more active for oxygen evolution. Ruthenium dioxide (RuO<sub>2</sub>) has a lower overpotential than platinum for the water oxidation reaction at the current densities relevant to PEC water splitting. The reduction in overpotential results in enhanced efficiencies. We electrodeposited RuO<sub>2</sub> from RuCl<sub>3</sub> solution on to a platinum electrode and gathered solar-to-hydrogen efficiency data under real-solar conditions at NREL's Solar Radiation Research Laboratory. Using a portable potentiostat in a two-terminal configuration we measured the current and applied circuit bias between the GaInP<sub>2</sub>/GaAs working electrode and RuO<sub>2</sub> counter electrode. The current was due to water reduction (to hydrogen) at the photocathode and oxidation (to oxygen) at the counter electrode. The efficiency was calculated from the photocurrent density, circuit bias, and corresponding real-time measurement of solar irradiance. Two wafers were synthesized by metal organic chemical vapor deposition at different growth temperatures and each was subdivided into about twelve electrodes. The averaged two-electrode photocurrent-voltage measurements were used to calculate ensemble efficiencies for each wafer (Figure 1). The champion electrode, from the wafer that was grown at a lower temperature, had a peak solar-to-hydrogen efficiency of 16.3%. This efficiency greatly exceeds the MYP 2013 technical target of 10% and demonstrates very high solar-to-hydrogen efficiencies are possible through PEC conversion.

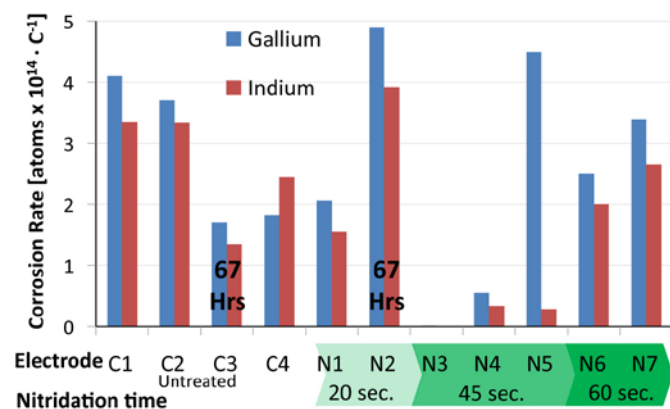
Although the GaInP<sub>2</sub> system is capable of high-efficiency conversion, it is prone to corrosion under operating conditions and does not meet the MYP technical target for durability (1,000 hours). We have previously observed that incorporating nitride into III-V semiconductor epilayers can provide enhanced stability [2] to water splitting photocathodes. However, this nitride incorporation through the bulk of the light absorber causes a reduction in conversion efficiency [3]. We hypothesize that surface nitridation might protect the interface with the electrolyte while not compromising the material's



**FIGURE 1.** Two-electrode outdoor photocurrent-voltage testing of p-GaInP<sub>2</sub>/GaAs tandem cells coupled with a RuO<sub>2</sub> counter electrode. Dashed lines are calculated efficiencies as a function of circuit bias. Data presented are the average of twelve electrodes from each wafer and the champion electrode plotted independently. The champion electrode was from the wafer grown at a lower temperature. The electrolyte used for testing was 3M H<sub>2</sub>SO<sub>4</sub> with the fluorosurfactant Zonyl FSN-100.

high-efficiency bulk absorption properties. We achieved promising preliminary results from surface nitridation of GaInP<sub>2</sub> by two distinct routes; electrochemical and ion bombardment. The semiconductor surface appeared to be protected when (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was used as the electrolyte for a 24-hour durability analysis. Afterwards, X-ray photoelectron spectroscopy (XPS) detected ammonia (NH<sub>3</sub>) on the surface. Depth profiles, made by alternating sputtering with XPS analysis, found the control (unprotected) sample was gallium deficient and indium rich while the sample tested in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> had a composition identical to as-grown material. Bombarding GaInP<sub>2</sub> surfaces with low-energy N<sub>2</sub><sup>+</sup> ions also appeared to provide some protection from corrosion. We performed ion surface treatments for 20, 45, and 60 seconds and all prevented a decline in photocurrent after operation for 24-hours in pH 0 sulfuric acid where untreated samples had a notable loss in performance. We also analyzed the durability solutions for trace levels of semiconductor components by inductively coupled plasma mass spectrometry (ICP-MS). In two of the three electrodes tested, the 45-second treatment was effective in reducing the amount of corrosion detected by ICP-MS (Figure 2). We are continuing to investigate surface nitridation as a potential route to achieve both the efficiency and durability targets in the MYP.

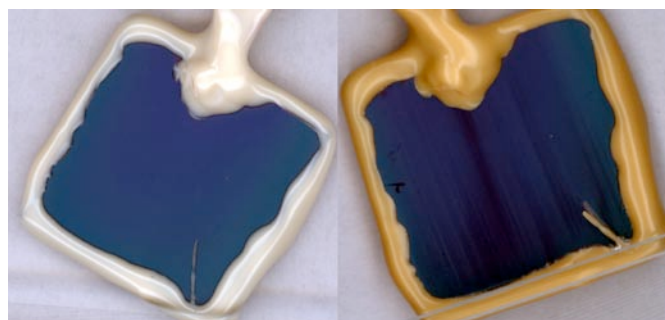
We continued to work with our private industry collaborator, MVSystems, Inc. to develop a potentially low-cost, high-volume water splitting material system with good durability. These amorphous (a-Si/SiC) semiconductors are synthesized by plasma enhanced chemical vapor deposition on transparent conductive substrates. The p-SiC is the capping layer and forms a PEC contact with the electrolyte.



**FIGURE 2.** ICP-MS detected gallium and indium from control and ion bombardment nitrided p-GaInP<sub>2</sub> electrode corrosion solutions. The durability testing consisted of galvanostatic testing at -10 mA/cm<sup>2</sup> in 0.5M H<sub>2</sub>SO<sub>4</sub> under AM1.5G illumination for 24 hours (except in the two noted durations of 67 hours). The analytes were detected in parts per million (mass) units and converted to atoms/Coulomb to normalize for variation in electrode surface area, charge passed, and solution volume.

It has a wider band gap and better stability than amorphous Si. There are two amorphous p-i-n buried photovoltaic (PV) junctions that provide the necessary potential difference needed for water electrolysis. The PV/PEC layers, known together as a hybrid photoelectrode, are stacked vertically in an integrated monolithic device. This device configuration is able to split water at 1.6% efficiency without an external bias. Recently, we were able to demonstrate this system is capable of extended durability. In one test we applied -1 mA/cm<sup>2</sup> in pH 2 buffer under AM1.5G (from a tungsten lamp) for 310 hours and the surface appeared almost completely unaltered by the testing, except for some streaking likely caused by hydrogen bubble evolution (Figure 3). The electrode did suffer a moderate (~30%) reduction in photocurrent magnitude after 310 hours of testing, but there was no dark current under high reverse bias, a common feature of damaged electrodes. We also performed a 500-hour test on a different electrode under the same conditions described above. After 500-hours of durability analysis, three-electrode current-potential curves exhibited both a decreased magnitude of photocurrent and dark current onset at a low potential. The electrode surface also appeared degraded afterwards. Even though the durability electrodes suffered a performance loss, the results demonstrate that the 2013 MYP technical target of 1,000-hours of operation could be achieved with this material. However, the testing conditions are relatively mild, compared to what a real-world electrode might see under operation. The goal for this material is 5% solar-to-hydrogen efficiency, which correlates to -4 mA/cm<sup>2</sup>, a current density four times higher than these electrodes were subjected to.

We also synthesized and characterized several oxide and chalcopyrite semiconductors that theoretical calculations had identified as good candidates for photoelectrolysis. We



**FIGURE 3.** Photographs of an a-Si/a-SiC hybrid photoelectrode before (left) and after (right) 310 hours of durability testing showing a relatively unaltered surface. The semiconductor is about 4 cm<sup>2</sup> and encased in insulating epoxy.

synthesized CuO, Cu<sub>2</sub>O, and Ti alloyed Cu-Ti and found that the band gaps of CuO and Cu<sub>2</sub>O could be engineered by incorporating Ti. We found that Ti incorporation improved the film quality and as a result, Ti incorporated CuO films exhibited much lower dark current than the pure CuO, indicating enhanced stability. Despite band gaps in the visible portion of the electromagnetic spectrum, the overall magnitude of photocurrent for these films is well below what is necessary to be considered viable for solar photoconversion.

We also synthesized BiVO<sub>4</sub> thin films by co-evaporation of Bi<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> and evaluated their PEC performance. We observed that a Bi:V ratio of roughly 1:1 leads to n-type conductivity behavior and very low dark current. When the Bi:V ratio was increased to 1.1:1 the result was a compensated film. A compensated semiconductor exhibits both n-type and p-type behavior, depending on the bias. It is known that cation vacancies can form easily in BiVO<sub>4</sub> and the act as acceptors. It is possible that under certain vapor pressures, Bi or V vacancies may form and lead to p-type conductivity. This effect might be exploited for developing a solid-state, oxide p/n homojunction photovoltaic cell.

Ternary I-III-VI<sub>2</sub> chalcopyrite materials have drawn great interest in recent years due to their potential application for solar cells. In general, I-III-VI<sub>2</sub> chalcopyrite materials have a variety of direct band gaps and have excellent optical absorption coefficients, good carrier transport properties, and stability. We synthesized and characterized chalcopyrite CuAlTe<sub>2</sub> thin films by both co-evaporation and sequential deposition methods. Several films were synthesized that had ideal band gaps for photoelectrolysis, in the range of 1.64 - 2.25 eV. Energy dispersive X-ray spectroscopy detected oxygen in all CuAlTe<sub>2</sub> samples. The oxygen contamination during the evaporation seems to deteriorate the film quality and lead to serious carrier recombination resulting in poor photoconversion efficiencies. In addition to low photocurrents, the CuAlTe<sub>2</sub> films were unstable during PEC characterizations and are, therefore, not viable for photoelectrolysis using these synthesis conditions.



Pure nitride semiconductors (instead of mixed group V) are also an area of interest as they have high stability and potentially high efficiency. We characterized p-doped  $\text{In}_x\text{Ga}_{1-x}\text{N}$  synthesized by our collaborator at Los Alamos National Laboratory. The p-doping allows the semiconductor to operate as a photocathode, a generally more stable operating configuration that pushes highly corrosive, oxidizing holes towards the bulk of the material and away from the interface. The photocurrents achieved by these materials were very low due to growth on an insulating sapphire substrate. We are currently characterizing a set of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  that was synthesized on conductive substrates and are evaluating the stability under current densities in the  $10 \text{ mA/cm}^2$  range, a magnitude equivalent to what a deployed device would see.

## Conclusions

- p-GaInP<sub>2</sub>/GaAs is capable of over 16% solar-to-hydrogen conversion efficiency and could meet the MYP efficiency and durability technical targets with an appropriate corrosion mitigation treatment, even if the treatment results in a loss of efficiency.
- Surface nitridation of GaInP<sub>2</sub> has demonstrated the ability to offer protection to the semiconductor surface after 24-hours of simulated operational conditions.
- Thin film a-Si-based carbides have the potential to be inexpensive water splitting electrodes and have demonstrated good durability over several hundred hours of low current density water splitting.
- The Cu-Ti alloyed oxides that we synthesized have variable band gaps, but have poor photoconversion properties and inadequate stability.

## Future Direction

- We plan to continue to investigate stabilization of the GaInP<sub>2</sub> interface through nitridation. We will work in collaboration with theory and advanced characterization groups to identify the corrosion mechanism and develop a passivation strategy.
- Because of their stability, we plan to investigate other III-V nitride semiconductor configurations and evaluate efficiencies.
- We plan to continue to work with MVSsystems, Inc. on improving efficiency and stability of a-Si/a-SiC hybrid photoelectrodes through targeted surface modification techniques.
- We plan to synthesize and photoelectrochemically characterize new oxide and chalcopyrite semiconductors and evaluate their potential for water splitting photoelectrodes.

## FY 2011 Publications/Presentations

### Publications

1. W.-J. Yin, H.W. Tang, S.-H. Wei, J. Turner, M.M. Al-Jassim, Yanfa Yan, "Band structure engineering of semiconductors for enhanced PEC water splitting" *Phys. Rev. B* **82**, 045106 (2010).
2. W.-J. Yin, S.-H. Wei, M.M. Al-Jassim, J. Turner, and Yanfa Yan, "Doping properties of monoclinic BiVO<sub>4</sub> studied by the first-principle density-functional theory" *Phys. Rev. B* **83**, 155102 (2010).
3. L. Chen, S. Shet, H.W. Tang, H.L. Wang, T. Deutsch, Yanfa Yan, J. Turner, M. Al-Jassim, "Electrochemical deposition of copper oxide nanowires for photoelectrochemical applications" *J. Mater. Chem.* **20**, 6962 (2010).
4. L. Chen, S. Shet, H. Tang, K.-S. Ahn, H. Wang, Yanfa Yan, J. Turner, and M. Al-Jassim, "Amorphous copper tungsten oxide with tunable band gaps" *J. Appl. Phys.* **108**, 043502 (2010).
5. S. Shet, K.-S. Ahn, H. Wang, R. Nuggehalli, Y. Yan, J. Turner, and M. Al-Jassim, "Effect of substrate temperature on the photoelectrochemical responses of Ga and N co-doped ZnO films" *J. Mater. Sci.* **45**, 5218-5222 (2010).
6. M. Huda, A. Walsh, Yanfa Yan, S.-H. Wei, and M.M. Al-Jassim, "Electronic, structural, and magnetic effects of 3d transition metals in hematite," *J. Appl. Phys.* **107**, 123712 (2010).
7. W.-J. Yin, S. Chen, J.-H. Yang, X.-G. Gong, Yanfa Yan, S.-H. Wei, "Effective band gap narrowing of anatase TiO<sub>2</sub> by strain along a soft crystal direction" *Appl. Phys. Lett.* **96**, 221901 (2010).
8. Heli Wang and John A. Turner, "Characterization of hematite thin films for photoelectrochemical water splitting in a dual photoelectrode device" *J. Electrochem. Soc.* **157**, F173 (2010).

### Presentations

1. "Photoelectrochemical Production of Hydrogen: Issues and Possibilities", SPIE – Solar Hydrogen and Nanotechnology V, San Diego, CA, August 5, 2010. J. Turner, *Invited*.
2. "Material issues for photoelectrochemical water splitting", ORCAS 2010, International Conference on Energy Conversion, University of Washington, Friday Harbor, WA, September 22, 2010. J. Turner, *Invited*.
3. "Material Issues for Photoelectrochemical Water Splitting", Lawrence Livermore National Lab Colloquium, Livermore, CA, September 30, 2010. J. Turner, *Invited*.
4. "Semiconducting Materials for Photoelectrochemical Water Splitting", at the Solar Fuels: Catalysis and Photoconversion meeting, University of North Carolina at Chapel Hill, January 13, 2011. J. Turner, *Invited*.
5. "Materials Issues for Photoelectrochemical Water Splitting", at the official opening of the Solar Fuels Laboratory, Nanyang Technological University, Singapore, February 8, 2011. J. Turner, *Invited*.

6. “Semiconducting Materials for Photoelectrochemical Water Splitting”, Third Annual Workshop on Electrochemistry at the Center for Electrochemistry at the University of Texas at Austin, February 20, 2011. J. Turner, *Invited*.
7. “Impact of oxygen evolution catalysts on the efficiency of photoelectrochemical water splitting”, session: Chemical Carbon Mitigation: A Physiochemical Approach, American Chemical Society Meeting, March 30, 2011, Jeff Lou presenting, *Invited*.
8. “Semiconductor Photoelectrodes for Direct Water Splitting” Pacifichem 2010 Congress, Honolulu, HI. December 15–20, 2010. T. Deutsch, *Contributed*.
9. “Bandgap engineering of metal oxides for PEC water splitting” SPIE’s Solar Hydrogen and Nanotechnology V, San Diego, CA, August 1–5, 2010. Y. Yan, *Invited*.
10. “The durability of p-GaInP<sub>2</sub> for photoelectrochemical water splitting” SPIE’s Solar Hydrogen and Nanotechnology V, San Diego, CA, August 1–5, 2010. H. Wang, *Invited*.
11. “Durability of p-GaInP<sub>2</sub> for photoelectrochemical water splitting” Pacifichem 2010 Congress, Honolulu, HI. December 15–20, 2010. H. Wang, *Contributed*.

12. “Direct Water Splitting Using Visible Light” GE Global Research Solar Fuels Symposium, Niskayuna, New York. November 1, 2010. T. Deutsch, *Invited*.

13. “Passivation of III-V Photoelectrochemical Water Splitting Electrodes via Surface Nitridation” Gordon Research Conference, Renewable Energy: Solar Fuels, Ventura, California. January 16–21, 2011. T. Deutsch, *Poster*.

## References

1. O. Khaselev and J.A. Turner, *Science* **280**, 425 (1998).
2. T.G. Deutsch, K.A. Koval, J.A. Turner, *J. Phys. Chem. B* **110**, 25297 (2006).
3. T.G. Deutsch, J. Head, J.A. Turner, *J. Electrochem. Soc.* **155**(9), B903 (2008).