

## II.F.2 Semiconductor Materials for Photoelectrolysis

John Turner (Primary Contact), Todd Deutsch, Heli Wang, Adam Welch, Mowafak Al-Jassim, Houwen Tang

National Renewable Energy Laboratory  
15013 Denver West Parkway  
Golden, CO 80401  
Phone: (303) 275-4270  
Email: John.Turner@nrel.gov

DOE Manager  
HQ: Eric Miller  
Phone: (202) 287-5829  
Email: Eric.Miller@ee.doe.gov

### Subcontractors:

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

Project Start Date: 2005

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

the Multi-Year Research, Development and Demonstration Plan PEC hydrogen production goals are as follows:

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

### FY 2012 Accomplishments

- Demonstrated significantly enhanced photocurrent densities, 5 mA/cm<sup>2</sup> under bias, on n-InGaN provided by our Los Alamos National Laboratory (LANL) synthesis partner. This material has the potential to be the first non-tandem semiconductor to use visible light to split water with high efficiency (barrier Y).
- Identified a surface nitrogen ion implantation technique that completely passivated corrosion (barrier Z) on p-GaInP<sub>2</sub> surfaces that were tested at -10 mA/cm<sup>2</sup>, a current density equivalent to 12.3% solar-to-hydrogen (STH) efficiency (barrier Y), for several hours in sulfuric acid.
- Observed that co-doping hematite with both titanium and magnesium led to higher photocurrents than titanium doping alone. This experimental result validated theoretical findings that charge compensation from co-doping of durable oxide materials (barrier Z) should yield materials with more favorable electronic properties (barrier Y) than those using a single dopant.
- Surface validation study, in collaboration with UNLV and Lawrence Livermore National Laboratory (LLNL), made progress in establishing baseline spectra of as-grown p-GaInP<sub>2</sub> surface. UNLV analyzed air-excluded sample provided by NREL and used the baseline results to compare against samples that have been subjected to corrosion testing (barrier Z).

### Fiscal Year (FY) 2012 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 (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials efficiency
- (Z) Materials durability
- (AB) Bulk materials synthesis
- (AC) Device configuration Technical Targets

### Technical Targets

This project is a materials discovery investigation to identify a single semiconductor material that meets the technical targets for efficiency and stability. This project made progress towards the stability target and achieved over 100 hours of corrosion-free operation on a material that exceeds the efficiency target. The 2013 technical targets from



### 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 STH efficiency of at least 5% with a clear pathway to a 10% water splitting system, (iii) exhibits the possibility of 10-year stability under solar conditions and (iv) can be adapted to volume-manufacturing techniques.

## Approach

Our approach has two tracks, 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

### III-V Nitride Materials

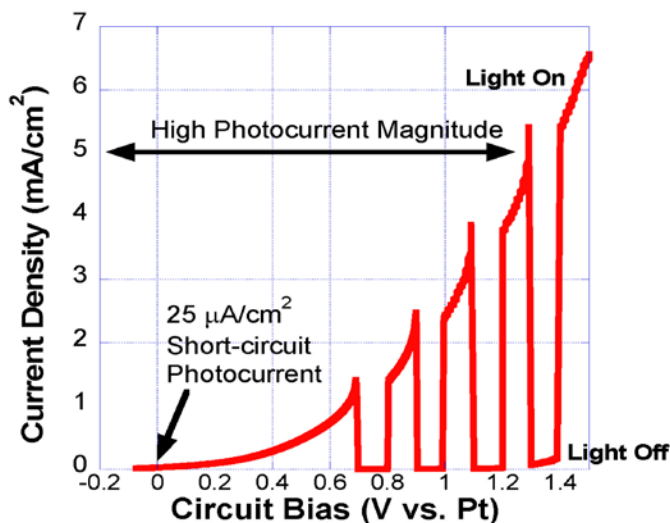
$\text{In}_x\text{Ga}_{1-x}\text{N}$  is a promising alloy that has recently seen advances in synthesis techniques that achieve high-quality thin films over the entire alloy range. High solar conversion efficiencies should be possible with these epilayer single-crystal semiconductors and previous work on III-nitrides has shown that it is a remarkably stable material set [1]. A unique feature of this material system is the broad range of band gaps achievable, that spans between that of InN (0.7 eV) and GaN (3.4 eV).

Recent n-InGaN semiconductors exhibited significantly enhanced photocurrent densities as compared to previous InGaN materials. The samples were grown by our collaborator, Todd Williamson, at LANL by energetic neutral atom beam lithography and epitaxy on sapphire and silicon substrates. Under a moderate bias, the water oxidation photocurrent magnitudes were up to  $5 \text{ mA/cm}^2$  (Figure 1).

Durability of n-InGaN grown on silicon substrates was evaluated by looking for a decline in photocurrent under a constant applied bias. In 0.5M sulfuric acid, the electrodes were biased at 1.3 V vs. Ag/AgCl and after an hour the photocurrent declined to 10% of its original value. The durability of this material is lower than anticipated for a nitride semiconductor, but the electrode viability can likely be extended through the application of a surface catalyst or by varying the electrolyte composition.

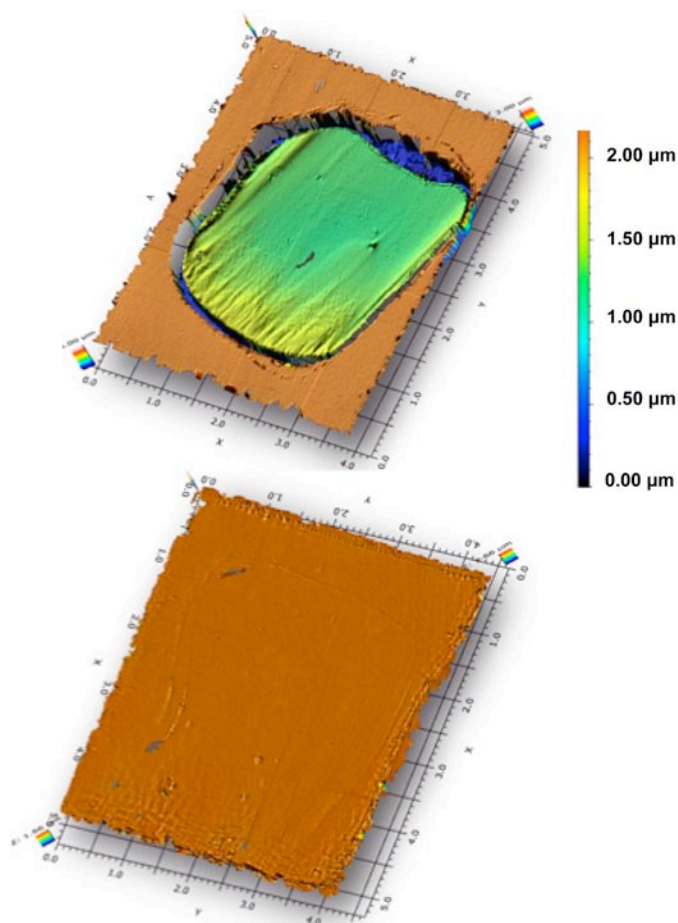
### Protection Strategies for High-Efficiency III-V Materials

A tandem semiconductor configuration consisting of a photovoltaic p/n-GaAs bottom cell and a PEC p-GaInP<sub>2</sub> top cell has demonstrated (unbiased) solar-to-hydrogen conversion



**FIGURE 1.** Two-electrode chopped-light photocurrent density vs. circuit bias for n-InGaN on sapphire in 0.5M  $\text{H}_2\text{SO}_4$ . The light source was a 250-Watt tungsten lamp calibrated to AM1.5G using a 2.0 eV reference cell. The photocurrent density of  $5 \text{ mA/cm}^2$  at 1.2 V applied bias (vs. a Pt counter electrode) is about 50% of the theoretical maximum for this 2.2 eV band gap material. Though this material exhibited a photocurrent at zero bias, indicating spontaneous photoelectrolysis at true short-circuit, the magnitude was low.

efficiencies well over the Multi-Year Research, Development and Demonstration Plan STH efficiency target of 10% but is prone to corrosion [2]. III-V nitride semiconductors, however, have exhibited excellent durability in a PEC environment in the past [3]. Thus surface nitridation of p-GaInP<sub>2</sub> was investigated as a means of reducing corrosion in the aqueous electrolyte. Thin films of p-GaInP<sub>2</sub> grown by metal organic chemical vapor deposition on a p-GaAs substrate were nitrided by implantation with low-energy  $\text{N}_2^+$  ions at room temperature. Control and nitrided samples were tested for durability by applying a constant current of  $-10 \text{ mA/cm}^2$ , a current density equivalent to 12.3% STH efficiency, in 3M  $\text{H}_2\text{SO}_4$  for long durations under Air Mass 1.5 Global (solar spectrum, AM1.5G) illumination. After the durability tests the electrodes were disassembled and optical profilometry was used to measure the volume of material lost from the surface due to corrosion during operation. One electrode survived 115 hours with no detectable degradation (Figure 2). Several of the nitrided samples entirely resisted corrosion over 24 hours of testing, where similarly tested untreated samples experienced around  $1 \mu\text{m}$  of material loss from their surfaces (Figure 3). The respective electrolytes were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to determine concentrations of indium and gallium in solution to quantify semiconductor corrosion. The ICP-MS results correlated well with the optical profilometry data, with only trace quantities of analyte detected in the nitride-treated durability electrolytes. The nitrogen ion implantation led to only a modest reduction in photoconversion efficiency. Surface nitridation by ion bombardment could hence be an

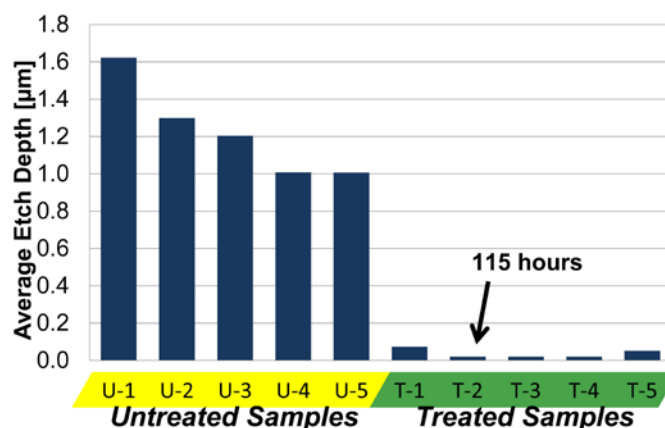


**FIGURE 2.** Optical profilometry of p-GaInP<sub>2</sub> electrode surfaces after durability analysis in sulfuric acid. The image on the top is of a sample that had no surface passivation treatment and experienced etching of about 1 μm of material from the surface in the area not masked by epoxy (i.e. exposed to the electrolyte). The nitride treated sample on the bottom exhibited no detectable damage after passing -10 mA/cm<sup>2</sup> of photocurrent for 115 hours, the equivalent to 12.3% STH conversion.

effective passivation treatment to ensure durability for a highly efficient PEC material, ultimately yielding a viable device capable of converting sunlight and water to a benign solar fuel.

### NREL Synthesis of Metal Oxide Alloy Thin Films

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) is an n-type semiconducting material that exhibits several potential advantages for PEC hydrogen production. It has an ideal band gap (2.0-2.2 eV), is composed of abundant, non-toxic elements, and can be synthesized via low-cost routes. However, the intrinsic poor conductivity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has hindered its PEC performance. Previous studies have shown that the incorporation of Ti can enhance the PEC performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Ti incorporation in hematite is limited by solubility, where too high a concentration can lead to TiO<sub>2</sub> crystallites that compromise the material's



**FIGURE 3.** Optical profilometer determined etch depths for p-GaInP<sub>2</sub> electrode surfaces subjected to continuous operation of -10 mA/cm<sup>2</sup> under AM1.5 G illumination for 24 hours (or longer where noted). The untreated electrodes had a significant fraction of their overall 2 μm thickness removed while the nitrided electrodes exhibited little or no loss of material.

electronic properties. By co-incorporating Mg with Ti, charge compensation can be achieved that allows an increase in the solubility of Mg and Ti. It also provides a mechanism to tune the carrier density while simultaneously reducing the density of charge defects. Our previous work has shown that charge-compensated donor-acceptor co-alloying is an effective approach to improve the electronic properties of a host material [4].

Samples were synthesized by radio frequency reactive co-sputtering of Fe<sub>2</sub>O<sub>3</sub>, Ti, and MgO targets to deposit Fe<sub>2</sub>O<sub>3</sub>, (Fe<sub>0.87</sub>Ti<sub>0.10</sub>Mg<sub>0.03</sub>)<sub>2</sub>O<sub>3</sub>, (Fe<sub>0.84</sub>Ti<sub>0.09</sub>Mg<sub>0.07/2</sub>)<sub>2</sub>O<sub>3</sub>, (Fe<sub>0.79</sub>Ti<sub>0.09</sub>Mg<sub>0.12/2</sub>)<sub>2</sub>O<sub>3</sub> on F-doped tin oxide coated glass substrates. We compared the PEC properties in neutral solutions and while the co-incorporated films did exhibit up to a tenfold increase in photocurrent magnitude at the same potential, all of the films had poor photoconversion properties. Under 5 sun illumination from a tungsten lamp, the photocurrent densities at +0.8 V vs. Ag/AgCl ranged from 5 μA/cm<sup>2</sup> for pure hematite to 50 μA/cm<sup>2</sup> for (Fe<sub>0.84</sub>Ti<sub>0.09</sub>Mg<sub>0.07/2</sub>)<sub>2</sub>O<sub>3</sub>. For a viable PEC water splitting system, the photocurrent density should be about 10 mA/cm<sup>2</sup> under one sun. While the results serve as an experimental confirmation of charge-compensating co-alloying in a novel host material, the method of synthesis and alloying missed the mark. Typical hematite samples are reported in literature to be capable of generating a few mA/cm<sup>2</sup> under bias at 1 sun. Improving the performance of status quo hematite by co-doping would be a remarkable result. However, as synthesized, none of the films were viable to serve as photoelectrodes.

### Advanced Materials Characterization and Support

Through a “surface validation study” framework, we collaborate with UNLV and LLNL, experts in surface spectroscopy and theoretical modeling, respectively. The



goals of this study are to i) study the PEC corrosion in III-V materials, an ideal system for elucidating the corrosion pathway and developing a remediation strategy, ii) identify the chemical character and mechanism of successful protective treatments, iii) apply lessons learned to other inexpensive systems that are more difficult to model and observe.

Semiconductor samples that are exposed to air or electrolyte will react and leave a modified surface that prevents unambiguous correlation with experimental effects and surface chemistry. UNLV (C. Heske, M. Weir, K. George, L. Weinhardt) used a suite of spectroscopic techniques to establish a benchmark electronic character of as-grown p-GaInP<sub>2</sub> sample surfaces. UNLV performed ion-stimulated desorption in order to gently clean air-exposed GaInP<sub>2</sub> surfaces and also analyzed non-air-exposed samples that were provided by NREL. Understanding the baseline spectra will allow UNLV to prepare surfaces that have had air and electrolyte exposure, a required condition for PEC testing, and deconvolute chemical changes due to corrosion from those due to environmental interaction during handling and transit. UNLV also analyzed nitrogen ion implanted GaInP<sub>2</sub> by X-ray emission spectroscopy (XES) at the Advanced Light Source at Lawrence Berkeley National Laboratory synchrotron and detected nitride bonds that are likely responsible for the resistance to corrosion.

The Quantum Simulations group at LLNL (T. Ogitsu, B. Wood, W.-I. Choi), used theoretical calculations to help interpret and complement X-ray absorption spectroscopy experiments on bulk GaP, InP, and GaInP<sub>2</sub> performed by UNLV. There was very good agreement between the theoretically derived and experimentally observed XES under standard conditions which validated the complex model. The next steps are to push the complexity of the models to match the non-standard surfaces and conditions encountered in these real PEC systems. These models should provide insight into experimental spectroscopic observations of corroded GaInP<sub>2</sub> surfaces.

## Conclusions

- InGaN is capable of high photon conversion efficiency yielding improved photocurrent densities but the stability must be addressed for it to be a possible candidate for economical PEC water splitting.
- Nitrogen ion implantation of p-GaInP<sub>2</sub> has demonstrated the ability to stop corrosion of the semiconductor surface for 115 hours of simulated 12% STH operational conditions. This result demonstrates significant progress towards the near-term technical targets for efficiency (10%) and durability (1,000 hours) for this material.
- Leveraging the expertise of our collaborators in the surface validation study has led to progress in understanding the chemical state of as-grown and corroded III-V surfaces.

## Future Direction

- Test nitrogen ion implanted GaInP<sub>2</sub>/GaAs tandem cells at short-circuit until failure and compare results against near-term technical targets.
- Further investigate the role of ion implantation in stabilizing PEC interface through surface validation collaboration; apply treatment to other PEC systems.
- Develop photoreactor and protocols for benchmarking efficiency and durability of PEC materials under real solar conditions.

## FY 2012 Publications

1. “Electronic and optical properties of CoX<sub>2</sub>O<sub>4</sub> (X=Al, Ga, In) alloys” C. Feng, W-J Yin, J. Nie, X. Zu, M.N. Huda, S-H Wei, M.M. Al-Jassim, J.A. Turner, and Yanfa Yan, *Appl. Phys. Lett.* **100**, 023901 (2012).
2. “Mott insulators: An early selection criterion for materials for photoelectrochemical H<sub>2</sub> production” Muhammad N. Huda, Mowafak M. Al-Jassim, and John A. Turner, *J. Renewable Sustainable Energy* **3**, 053101 (2011).
3. “Phase separation in Ga and N co-incorporated ZnO films and its effects on photo-response in photoelectrochemical water splitting” Sudhakar Shet, Kwang-Soon Ahn, Ravindra Nuggehalli, M.M. Al-Jassim, J.A. Turner, and Yanfa Yan, *Thin Solid Films*, **519**(18), 5983-5987 (2011).
4. “Doping properties of monoclinic BiVO<sub>4</sub> studied by first-principles density-functional theory” Wan-Jian Yin, Su-Huai Wei, M.M. Al-Jassim, J.A. Turner, and Yanfa Yan, *Phys. Rev. B*, **83**(15), 155102 (2011).
5. Nanoporous black silicon photocathode for H<sub>2</sub> production by photoelectrochemical water splitting” Jihun Oh, Todd G. Deutsch, Hao-Chih Yuan, Howard M. Branz, *Energy Environ. Sci.* **4**, 1690-1694 (2011).
6. “Synthesis and characterization of titanium-alloyed hematite thin films for photoelectrochemical water splitting” Houwen Tang, M.A. Matin, Heli Wang, Todd Deutsch, Mowafak Al-Jassim, John Turner, Yanfa Yan, *J. App. Phys.* **110**, 123511 (2011).
7. “Cobalt-phosphate (Co-Pi) catalyst modified Mo-doped BiVO<sub>4</sub> photoelectrodes for solar water oxidation” Satyananda Kishore Pilli, Thomas E. Furtak, Logan D. Brown, Todd G. Deutsch, John A. Turner, Andrew M. Herring, *Energy Environ. Sci.* **4**, 5028-5034 (2011).
8. “Light induced water oxidation on cobalt-phosphate (Co-Pi) catalyst modified semi-transparent, porous SiO<sub>2</sub>-BiVO<sub>4</sub> electrodes” Satyananda Kishore Pilli, Todd Deutsch, Thomas E. Furtak, John Turner, Logan D. Brown, and Andrew M. Herring. *Phys. Chem. Chem. Phys.*, Accepted Manuscript, March 06 (2012). DOI: 10.1039/C2CP40673J.

## FY 2012 Presentations

1. “Toward economical solar hydrogen production: Surface passivation of GaInP<sub>2</sub> by plasma nitridation” 242<sup>nd</sup> American

Chemical Society National Meeting, Denver, CO, August 28 – September 1. (Welch) *Contributed*

2. “Semiconducting Materials for Photoelectrochemical Water Splitting”, 242<sup>nd</sup> American Chemical Society National Meeting, Denver, August 29, 2011. (Turner) *Invited*

3. “Photoelectrochemical Water Splitting”, DOE Laboratory Energy R&D Working Group (LERDWG), September 21, 2011. (Turner) *Invited*

4. “Surface nitridation of p-GaInP<sub>2</sub> for durable photoelectrochemical water splitting” 220<sup>th</sup> ECS meeting, Oct.12, 2011. (Wang) *Invited*

5. “Hydrogen Production from Photoelectrochemical Cells: Theoretical considerations and experimental results”, Colorado School of Mines, October 27, 2011. (Turner) *Invited seminar*

6. “Challenges and Opportunities in Photoelectrochemical Water Splitting”, University of California, Davis, November 1, 2011. (Turner) *Invited seminar*

7. “Hydrogen Production from Photoelectrochemical Cells: Economic and Theoretical Considerations and Experimental Results”, 2011 DOE PHOTOSYNTHETIC SYSTEMS RESEARCH MEETING, November 7, 2011. (Turner) *Invited plenary*

8. “Hydrogen Production from Photoelectrochemical Cells: Economic and Theoretical Considerations and Experimental Results”, University of Texas at Arlington, November 17, 2011. (Turner) *Invited seminar*

9. “Coupled Photoanode/Photocathode Systems for Unassisted Solar Water Splitting” 2011 Materials Research Society Fall Meeting, Boston, Massachusetts. November 28 – December 2, 2011. (Deutsch) *Invited*

10. “Hydrogen Production from Photoelectrochemical Cells”, Physics@FOM Conference, Holland, January 17, 2012. (Turner) *Invited plenary*

11. “Frontiers, Opportunities and Challenges for a Hydrogen Economy”, International Energy and Sustainability Conference 2012, Farmingdale State College, March 22, 2012. (Turner) *Invited plenary*

12. “Semiconductor Systems for Solar Photoelectrolysis” Colorado School of Mines, April 27<sup>th</sup>, 2012. (Deutsch) *Invited seminar*

## 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. J.R. Mileham, S.J. Pearton, C.R. Abernathy, J.D. Mackenzie, R.J. Shul, S.P. Kilcoyne, *J. Vac. Sci. Technol. A* **14**, 836 (1996).

4. S. Shet, K.-S. Ahn, Y. Yan, T. Deutsch, K.M. Chrustowski, J. Turner, M. Al-Jassim, N. Ravindra, *J. Appl. Phys.* **103**, 073504 (2008).