

## II.G.1 Photoelectrochemical Systems for Hydrogen Production

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

### Objectives

- Identify, synthesize, and characterize new semiconductor materials that have the possibility of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device.
- Design and synthesize multi-junction devices for high efficiency water splitting.

### Technical Barriers

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

- (Z) Materials Durability
- (Y) Materials Efficiency
- (AC) Device Configuration Designs

### Technical Targets

The 2013 technical targets from the MYPP PEC hydrogen production goals are as follows:

- Band gap of 2.3 eV
- 10% conversion efficiency
- 1,000-hr lifetime

### Approach

Perform semiconductor materials discovery and development for application to PEC water splitting.

### Accomplishments

- New tandem cell design for PEC water-splitting based on a silicon bottom-cell and GaInPN top-cell.
- Growth of CuGaSe material via electrodeposition for incorporation of gallium without the use of high vacuum techniques.

### Future Directions

- Continue to synthesize and characterize nitride materials (GaNP, GaInN, GaInPN, SiN) for higher efficiencies and longer lifetimes.
- Investigate thin-film materials as low-cost water-splitting systems.
- Evaluate additional PEC semiconductor candidates in collaboration with others.
- Develop coatings that act as catalysts and provide corrosion protection in PEC systems.
- Develop and evaluate multijunction structures for high efficiency.



### 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. 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 discover and characterize 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

While stability is important for viable PEC conversion devices, it cannot be the determining factor in choosing PEC material sets. The PEC community focus of research mainly on oxides for the last 30 years has produced no successes; efficiencies remain abysmally low. A new approach and methodology is warranted to explore new materials. Once capability of reaching efficiencies needed for commercial devices is achieved, approaches leading to necessary lifetimes can be explored.

At present, metal oxides (in particular  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$ ) are considered to be primary candidates. None of them fulfill the requirements for a successful PEC material, however. Finding novel materials and approaches that promise to fulfill all the MYPP requirements in one material class would be a significant advance.

The current material sets used in commercial solar cells represent a relatively little studied area for PEC research and is the focus of our material study.

## Results

This year we continued our study of group III nitrides (GaInPN) and thin films of CuInGaSSe for use as PEC materials.

We previously found that nitride incorporation into epitaxially grown III-V semiconductors improved the material's properties towards the application of photoelectrolysis. Moderate amounts of nitrogen were found to improve the absorption by inducing a direct transition at a lower energy than native GaP. Nitrogen also improved the stability of photoelectrodes by slightly passivating the oxidative etching that occurs at the semiconductor/electrolyte interface where decomposition is thermodynamically favored. This effect was observed even when nitrogen comprised as little as 0.01 at% of the semiconductor epilayer.

The incorporation of nitrogen into III-V materials causes a lattice contraction, which can lead to a mismatch between the epilayer and substrate lattice constants as nitride content increases. Lattice mismatched materials typically have numerous defects that serve as recombination centers and lower efficiency. Defect sites at or near the surface yield an inhomogeneous surface potential that can serve as active sites for corrosion reactions that would otherwise be unavailable on a more perfect crystal surface. The need for a lattice matched material limits the nitride content accessible in the epilayer material for a given substrate. There are two routes available to remedy this limitation, both of which we have incorporated in this work. The first is to use a substrate with a smaller lattice constant; the second is to use a lattice-expanding

element to compensate for the lattice contraction caused by nitrogen.

By growing the epilayers on Si ( $a=5.43 \text{ \AA}$ ) instead of GaP ( $a=5.45 \text{ \AA}$ ), which had previously served as the substrate, a lattice-matched composition of  $\text{GaP}_{.98}\text{N}_{.02}$  can be obtained. Growth on Si also enables use of a buried p/n tandem junction to generate the potential needed for water splitting. This is necessary to overcome a mismatch in the epilayer band edge potentials. The valence band of Ga(In)PN is too negative leading to the photogenerated holes having insufficient oxidative potential to drive the oxygen-evolution reaction. Adding the additional photopotential from the Si-junction provides the necessary energetics for the water splitting reaction.

The use of a lattice-expanding element in a quaternary nitride system is another pathway to higher levels of nitrogen in the epilayer with little or no lattice mismatch. We previously employed arsenic for lattice control however, as an amphoteric element it made the material more prone to corrosive attack. In this work, indium was substituted for arsenic as a lattice expansion agent. Indium forms an insoluble oxide in an aqueous environment, so GaInPN should be more stable than GaAsPN. By combining both techniques, a good quality  $\text{Ga}_{.962}\text{In}_{.038}\text{P}_{.976}\text{N}_{.025}$  film was achieved.

The effect of nitrogen on absorption characteristics can be observed in incident photon conversion efficiency (IPCE) plots (Figure 1). The steeper absorption edge (direct transition) at a lower energy (lower band gap) for GaInPN compared with GaP illustrates the beneficial

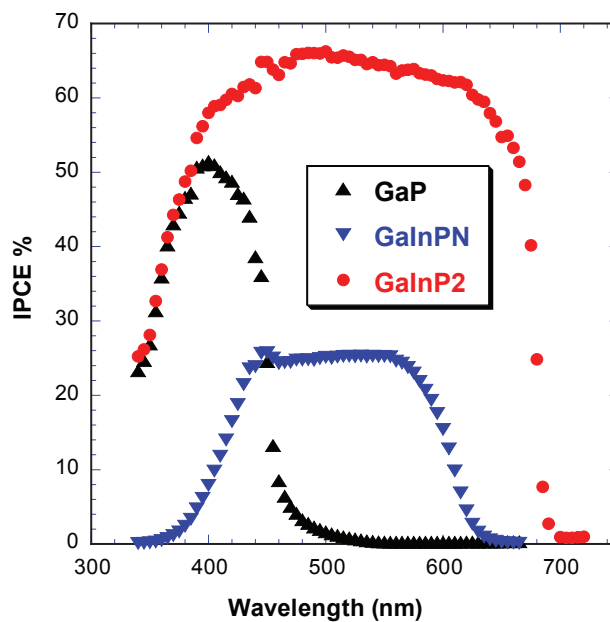
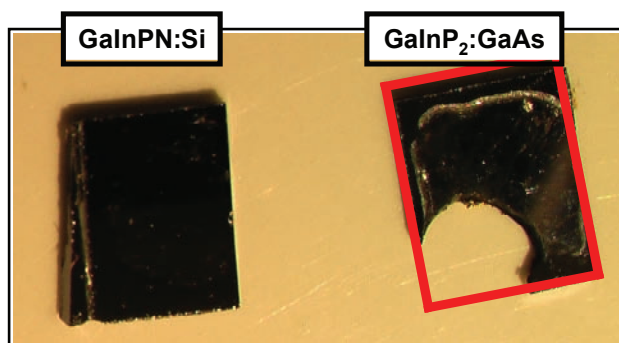


FIGURE 1. Incident Photon to Current Efficiency for P-Type Materials in pH 2 Buffer with 1 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  at a -0.7 V (vs. Ag/AgCl) Applied Bias

properties of nitride incorporation. The low peak height for the GaInPN points to the major problem observed with III-V-N materials grown by metalorganic chemical vapor deposition—low efficiency in conversion of photons to external charge carriers. The low efficiencies indicate recombination caused by either nitride trapping or by material impurities/defects associated with the conditions necessary to incorporate nitrogen during growth. By integrating the IPCE values over the AM1.5G solar spectrum an estimated short circuit current density can be calculated giving an indication of expected performance under operating conditions. The integrated values are 11.43 mA/cm<sup>2</sup> for GaInP<sub>2</sub>, which is close to the observed value, and 2.92 mA/cm<sup>2</sup> for GaInPN. Using this current density, the calculated solar to hydrogen efficiency for GaInPN would be 3.6%, which is below the MYPP near-term goal of 8%. This demonstrates that in addition to a direct transition for the necessary band gap, a high conversion efficiency of photons to electron-hole pairs is critical in realizing any practical PEC device.

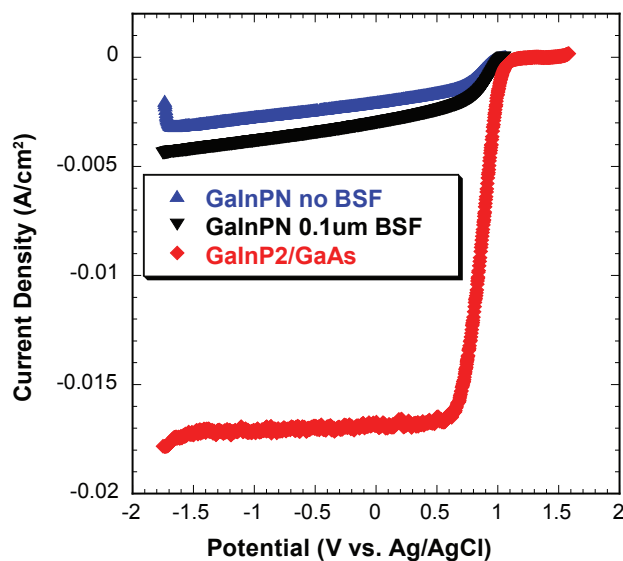
Dramatic macroscopic evidence of enhanced stability can be seen in the comparison of two samples that were subjected to the same accelerated corrosion testing (Figure 2). For these tests a constant cathodic current density was applied (-5 mA/cm<sup>2</sup>) to the 1 sun illuminated electrodes in 3 M sulfuric acid. All of the electrodes passed the same coulombic density (approximately -430 C/cm<sup>2</sup>) which allowed a uniform comparison between materials that had a wide disparity in performance. In this run, the GaInP<sub>2</sub> sample partially disintegrated over the course of testing, whereas the Ga<sub>0.962</sub>In<sub>0.038</sub>P<sub>0.976</sub>N<sub>0.024</sub> sample was only moderately etched (0.1 μm). After corrosion analysis the electrode surfaces were probed with stylus profilometry, with the nitrides etching 0.1 μm on average and the GaInP<sub>2</sub> about 1 μm. The degree of GaP etching fell in between, with about 0.5 μm of material being removed during the durability testing. These results were corroborated by analyzing the Ga content of corrosion electrolytes by ICP-MS.



**FIGURE 2.** Post-Corrosion Observations Revealed the Nitrides are More Capable of Persisting in the Photoelectrolysis Environment

To test the actual solar to hydrogen conversion efficiency, the materials were treated with a platinum catalyst, short-circuited to a platinum counter electrode, and illuminated at 1 sun in 3 M sulfuric acid. The GaInPN samples averaged about 150 μA/cm<sup>2</sup>, corresponding to an efficiency of 0.18%. The disparity between the observed short circuit photocurrent and that calculated from the integrated IPCE value is most likely due to three factors: (i) the slow kinetics of the hydrogen evolution reaction compared with the facile reduction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ions used in the IPCE analysis, (ii) the overvoltage losses from the oxygen evolution reaction, and (iii) the additional external bias used during the IPCE measurements.

To enhance the photocurrent in the GaInPN, a 0.1 μm Zn-doped back surface field (BSF) was added between the silicon substrate and the epilayer. The BSF provides an electric field barrier that reduces the diffusion of electrons towards the Si substrate where they would recombine with holes. The BSF, therefore, aids in the collection of photogenerated carriers and should augment the photocurrent. The short circuit photocurrent density of the materials with a BSF was enhanced, more than double the non-BSF GaInPN. However, the observed 310 μA/cm<sup>2</sup> only corresponds to a 0.38% solar to hydrogen efficiency, well below the MYPP near-term target of 8%. The enhanced collection efficiency was also observed in illuminated current density-potential (J-V) analysis (Figure 3). In these experiments the BSF resulted in a higher (more negative) cathodic current, but at values well below those observed for the GaInP<sub>2</sub> sample.



**FIGURE 3.** Illuminated J-V Analysis on Platinized Electrodes Taken under 1 Sun Illumination in 3 M Sulfuric Acid

### Thin-Film Materials: CIS-Based System

Our previous work in this area identified copper gallium diselenide (CGSe) as a promising thin-film material for use in the photoelectrochemical cell and electrodeposition as a low-cost approach for semiconductor manufacturing. Research this past year has focused on refining the process conditions to optimize the quality and repeatability of the electrodeposited copper gallium selenide thin films. The key elements of the processing include the apparatus, the solution/bath, and the electrical parameters.

For the deposition, a three electrode configuration is used. The sizing and spacing of the respective electrodes has been varied. The final parameters have been reliable and successful, if not optimized. Important apparatus-related factors that impact film quality are maintaining general cleanliness of glassware and electrodes and removing oxidation caused by continuous exposure to the acidic salt solution from all electrical connectors.

The solution consists of solid salts of  $\text{CuCl}_2$ ,  $\text{GaCl}_3$ ,  $\text{H}_2\text{SeO}_3$ , and  $\text{LiCl}$  dissolved in a buffer solution. The precise order of mixing is important to eliminate formation of precipitates. The solution bath material can be remixed with the unused solution and the solution reused repeatedly without adverse impact until precipitates begin to form on the storage container. Precipitation onset occurs between two and six weeks after mixing solution depending on how frequently it is used and shelf life appears to be most related to the total time it has been involved in deposition. Dozens of solution compositions have been attempted with variations impacting the quality and composition of the electrodeposited film. Heating and stirring the solution during deposition has proven detrimental to film quality, so all runs are now at room temperature and unstirred.

Electrical deposition parameters are also critical in controlling the film morphology and crystal growth patterns (which are directly related to the optoelectronic characteristics of the resulting film), thickness, and composition. Previous results have shown that a high deposition potential (static or pulsed) results in desirable high Ga concentration, but poor overall film quality. Likewise, high deposition currents can increase Ga concentration at the expense of film quality. To some extent, the high Ga concentration can be obtained while maintaining film quality, if a low-duty-cycle, stepped, pulsing profile is used. Given a particular duty cycle (1.7%, 5%, 10%, or 100%), the trend is for the films to start out yellow, then transition to gold, copper, blue, and purple with more deposition time or current. Work is underway to confirm that these color differences relate to composition and guide further deposition parameter refinements.

### Thin-Film SiN System

Because of limited funding, work in this area was suspended for this period.

### Conclusions

- A tandem cell of Si/GaInPN showed enhanced stability, but very low water-splitting efficiency.
- Electrodeposition for  $\text{CuGaSe}_2$  film formation has been improved and is now producing good quality films.

### FY 2007 Publications/Presentations

#### Papers

1. III-V Nitride Epilayers for Photoelectrochemical Water Splitting: GaPN and GaAsPN, Todd G. Deutsch, Carl A. Koval, and John A. Turner, *Journal of Physical Chemistry B*, ARTHUR J. NOZIK FESTSCHRIFT, Vol. 110, No. 50, pp. 25297-25307 (2006).

#### Presentations

1. "Materials and Systems for Photoelectrochemical Water-Splitting," invited talk, Department of Chemical & Metallurgical Engineering, University of Nevada, Reno.
2. "Fuel Cell Technologies," Briefing for Clean Energy Forum participants, including Yellowstone Capital, Flagship Ventures, Greenrock Capital.
3. Presentations to BASF Future Business on hydrogen and fuel cell related research, "Materials and Systems for Photoelectrochemical Water Splitting" and "Fuel Cells: Composite PEM Fuel Cell Membranes and Metal Bipolar Plates".
4. "Fuel Cells and Hydrogen: Addressing the Challenges Ahead," presentation to summer interns (June 2006).
5. "Photoelectrochemical Water Splitting: Materials and Systems," invited talk, 2006 World Solar Conference.
6. "The Sustainable Hydrogen Economy - Facts and Fiction: Addressing the Challenges Ahead," presentation to Colorado CleanTech.
7. "The Sustainable Hydrogen Economy: Addressing the Challenges Ahead," presentation to the National Council for International Visitors, Western Regional Conference.
8. "The Sustainable Hydrogen Economy: Addressing the Challenges Ahead," invited talk, SPIE Conference: Solar Hydrogen and Nanotechnology.
9. "Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production:  $\text{GaP}_{1-x}\text{N}_x$  and  $\text{Cu}(\text{In,Ga})(\text{Se,S})$ ," invited talk, International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA.

10. "Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production: GaP<sub>1-x</sub>N<sub>x</sub>, GaInP<sub>1-x</sub>N<sub>x</sub>, and Cu(In,Ga)(Se,S)," invited talk, Tokyo Workshop on Solar Light Energy Conversion, Tokyo, Japan.
11. Presentation to Nippon Oil Corporation, "Fuel Cell and Hydrogen Research at NREL: Metallic Bipolar Plates for Fuel Cells & Advanced Fuel Cell Membranes Based on Heteropolyacids & Photoelectrochemical Systems," Japan.
12. Invited talk, Rocky Mountain Chapter of the American Vacuum Society, "The Sustainable Hydrogen Economy, Addressing the Challenges Ahead"
13. Invited talk, AVS 2006 Four Corners Meeting, "Sustainable Hydrogen Economy: Addressing the Challenges Ahead," October 6, 2006.
14. Invited talk, University of Louisville, Louisville, KY, "Sustainable Hydrogen Economy, Addressing the Challenges Ahead," October 26, 2006.
15. Invited talk, University of Maryland in College Park, Transforming Energy" Lecture Series, "Hydrogen from Sunlight and Water: The Sustainable Hydrogen Economy," November 9, 2006.
16. Invited talk, National Academies Board on Chemical Sciences and Technology, "Frontiers, Opportunities, and Challenges to Hydrogen Production," January 19, 2007.
17. Invited talk, Washington University in St. Louis, "Sustainable Hydrogen Economy: Addressing the Challenges Ahead," February 18, 2007.
18. Invited talk, Hubert H. Humphrey Fellowship Program Enhancement Workshop, "The Role of Renewable Energy in Transforming Energy Markets," February 19, 2007.
19. Invited talk, University of Denver - Denver Research Institute, "Photoelectrochemical Production of Hydrogen from Water and the Hydrogen Economy," February 20, 2006.
20. Invited talk, U.S. Department of Energy Office of Basic Energy Sciences Workshop on Future Science Needs and Opportunities for Electron Scattering, "Energy Materials: Meeting Future Energy Challenges for Sustainable Energy," March 1-2, 2007.
21. Invited talk, University of North Dakota, E-week banquet, "Sustainable Hydrogen Economy: Addressing the Challenges Ahead," March 7, 2007.
22. Invited talk, 2007 Annual Joint Symposium of the Florida Chapter of the AVS Science and Technology Society and Florida Society for Microscopy, "Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production: GaP<sub>1-x</sub>N<sub>x</sub>, GaInP<sub>1-x</sub>N<sub>x</sub>, and Cu(In,Ga)(Se,S) Systems," March 13, 2007.
23. Invited talk, Florida Solar Energy Center, "Sustainable Hydrogen Economy," March 14, 2007.
24. Invited talk, 3rd Annual Frontiers in Nanosystems Conference, "Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production," March 21, 2007.
25. Invited talk, Colorado School of Mines, "Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production," March 27, 2007.
26. Lecture, Louisiana Tech University, "Energy Sustainability, The Challenge for Future Generations," April 11, 2007.
27. Invited talk, Louisiana Tech University, seminar series on Beyond Oil to Renewable Energy, "Sustainable Hydrogen Economy: Addressing the Challenges Ahead," April 11, 2007.