

## II.H.6 Semiconductor Materials for Photoelectrolysis

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direction determined annually by DOE

### Accomplishments

- Completed characterization of InGaN samples from Los Alamos National Laboratory (LANL) and determined water-splitting capabilities.
- Completed characterization of hot-wire chemical vapor deposited SiN.
- Completed preliminary characterization of a-SiN samples grown by MVSystems, Inc., using plasma-enhanced chemical vapor deposition and found encouraging photocurrents under bias.
- Made progress in optimizing platinum catalyst treatments on CuGaSe<sub>2</sub> photoelectrodes.
- Synthesized and characterized nanocrystalline Co-Al-Fe oxide composite electrodes.
- Completed evaluation of Co-Fe-Al oxide materials and, as a result of poor electronic transport properties, decided against (No-Go) further study of this material class.



### 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):

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

### Technical Targets

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

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

### Introduction

PEC 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 toward 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 of stability under solar conditions, and (iv) can be adapted to volume-manufacturing techniques.

### Approach

- Perform semiconductor materials discovery and development for application to PEC water splitting.
- Employ a multifaceted approach to materials discovery that includes theoretical calculations to identify potentially promising candidates, synthesis of novel semiconductors, and characterization of their physical and photoelectrochemical properties.

- Feedback results for the next iteration of calculations.
- Characterize other unique materials obtained outside the theory-synthesis-characterization feedback loop.

While stability is important for viable PEC conversion devices, it cannot be the determining factor in choosing PEC material sets. The focus of research in the PEC community on (mainly) 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 with the capability of reaching the efficiencies needed for commercial devices. One can then discuss approaches that can lead to the necessary lifetimes.

At present, metal oxides (in particular,  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$ ) are considered primary candidates, however, none of them fulfills the requirements for a successful PEC material. 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 are the focus of our materials study.

## Results

### Nitride Materials

InGaN is an emerging material that has the possibility of meeting the varied requirements for an efficient PEC device. InGaN is a challenging material to synthesize using conventional molecular beam epitaxy (MBE) techniques. High-quality material typically requires elevated substrate temperatures, which limits the incorporation of indium. Indium content is critical for lowering the bandgap into the visible region of the solar spectrum, a condition necessary for high-conversion efficiency. Conventional MBE uses a nitrogen plasma as the group V source. The modified MBE technique developed at LANL uses a high-energy laser to atomize nitrogen resulting in a semi-collimated beam of nitrogen atoms with energies between 1.5 eV and 2.0 eV. The advantage of using energetic atomic nitrogen as the reactive group V species is that the nitrogen atoms have an energy level around the activation energy necessary for nitride growth. This level allows high-quality materials to grow at lower temperatures, expanding the accessible InGaN compositional range. Indium can be used to tune both the bandgap and the band-edge positions at the electrolyte interface. The band-edge positions are critical as they define the reduction and oxidation photoreactions possible as well as the thermodynamic driving force available for them.

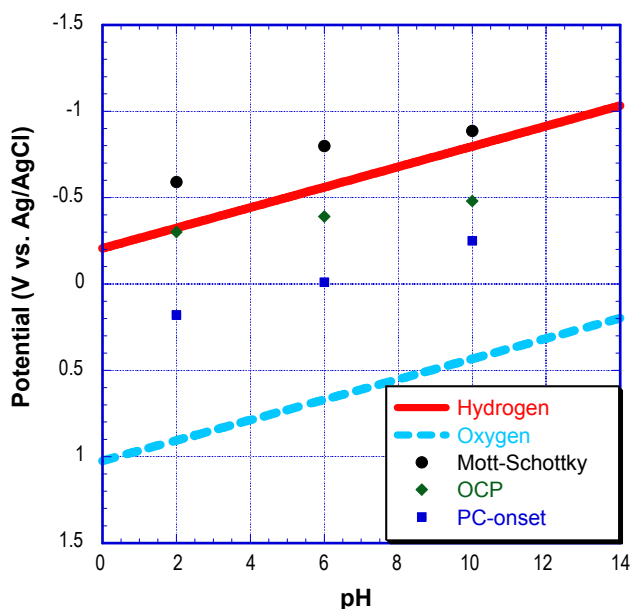
We obtained three compositions of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  grown at LANL using laser-assisted MBE. The nominal compositions of the LANL films are  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ ,  $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ , and  $\text{In}_{0.35}\text{Ga}_{0.65}\text{N}$ , and the resulting films appear yellow, orange, and red, respectively. We used photocurrent spectroscopy to determine the band gap energies to be 2.6 eV (yellow), 1.9 eV (orange), and 1.7 eV (red). Though they were grown undoped, the materials exhibited n-type conductivity. In order to photoelectrochemically split water, the flatband potential ( $V_{\text{fb}}$ ) and the minority band edge, which for an n-type semiconductor is the valence band, must span the potentials of the hydrogen and oxygen evolution half-reactions. All three InGaN samples are n-type, so a  $V_{\text{fb}}$  slightly negative (above on the electrochemical scale) of the hydrogen potential would indicate the material can reduce water to  $\text{H}_2$ . Because the Fermi level of n-type semiconductors is just below the conduction band, after adding the band gap energy, the valence band should be positive of the oxygen potential. We attempted to establish the positions of the band-edges by measuring the  $V_{\text{fb}}$  using Mott–Schottky analysis, illuminated open-circuit potential measurements and measurements of the photocurrent onset potential. Because band-edge positions and water-splitting potentials shift with pH, measurements were made in buffered solutions of pH 2, 6, and 10.

Mott–Schottky (M–S) analysis models the semiconductor/electrolyte interface as a simple series resistor–capacitor circuit and uses capacitance measurements of the depletion layer to establish the  $V_{\text{fb}}$  position. An M–S plot is the inverse of (depletion layer) capacitance squared versus the applied potential (versus reference). Under ideal conditions an M–S plot should have a linear portion that can fit with a trend line using linear regression; the x-intercept of the regression fit is the  $V_{\text{fb}}$ , and the slope is inversely proportional to the apparent dopant density. Illuminated open-circuit potential (OCP) measurements assume that under intense illumination the bands will flatten and the measured potential, versus a reference electrode potential, is the  $V_{\text{fb}}$ . Using three electrode current-potential measurements was another method to establish the  $V_{\text{fb}}$  positions. The potential where photocurrent commences is assumed to be the  $V_{\text{fb}}$  because the reverse bias is necessary to observe photocurrent (flatband and forward bias do not have an electric field at the semiconductor/electrolyte interface necessary for separating photogenerated carriers). The photocurrent is anodic for n-type semiconductors.

Flatband potential analyses to determine if the band-edge potentials spanned the decomposition potentials of water gave results that varied by technique (Figure 1). M–S analysis indicated the conduction band edge was above the hydrogen-evolution potential, which should allow spontaneous water splitting upon illumination.

Illuminated (OCP) measurements fell a few hundred mV below the hydrogen-evolution potential. Photocurrent onset measurements of  $V_{fb}$  were even further away with a mismatch of several hundred mV. Because each measurement has specific shortcomings related to material and system properties, it can be difficult to determine which  $V_{fb}$ -measurement technique provides the most believable data. Two-electrode photocurrent-potential measurements can be used to deduce which set of measurements is more reliable.

The short-circuit photocurrent density generated at zero-applied potential (in a two-electrode configuration) is interpreted commonly as representative of the amount of spontaneous water splitting occurring on the semiconductor surface. If photocurrent is observed without bias, the band-edges must be aligned (or the sample undergoing photocorrosion). The measured anodic photocurrent (Air Mass 1.5 Global Spectrum) at 0 V for  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ ,  $\text{In}_{0.5}\text{Ga}_{0.7}\text{N}$ , and  $\text{In}_{0.35}\text{Ga}_{0.65}\text{N}$  in pH 10 was found to be approximately  $3.5 \mu\text{A}/\text{cm}^2$ ,  $12 \mu\text{A}/\text{cm}^2$ , and  $1 \mu\text{A}/\text{cm}^2$ , respectively. However, the maximum theoretical short-circuit current densities (calculated from the band-gap energies) are on the order of several  $\text{mA}/\text{cm}^2$ . At such low current densities, it is hard to rule out photocorrosion as the source of short-circuit photocurrent. Bubbles from the electrodes can be used to infer water splitting, but bubbles were not observed for any InGaN sample, as current densities must approach  $1 \text{ mA}/\text{cm}^2$  to observe bubble evolution.



**FIGURE 1.** Flatband potentials determined from various methods for  $\text{In}_3\text{Ga}_7\text{N}$ . For unbiased water splitting, the values should lie above the hydrogen half-reaction potential (solid line) for these n-type semiconductors.

We have not yet characterized the durability of these materials as these tests are terminally destructive. The durability of these InGaN samples is at the very least moderate, based on their ability to withstand the characterization techniques described above. This material set is promising based on the low band gaps, favorable band-edge positions (from M-S), and preliminary durability results. With improvements in material quality and optimization of ohmic contacts, an efficient single-junction water-splitting photoelectrode might be realized. We plan to continue studying this material class.

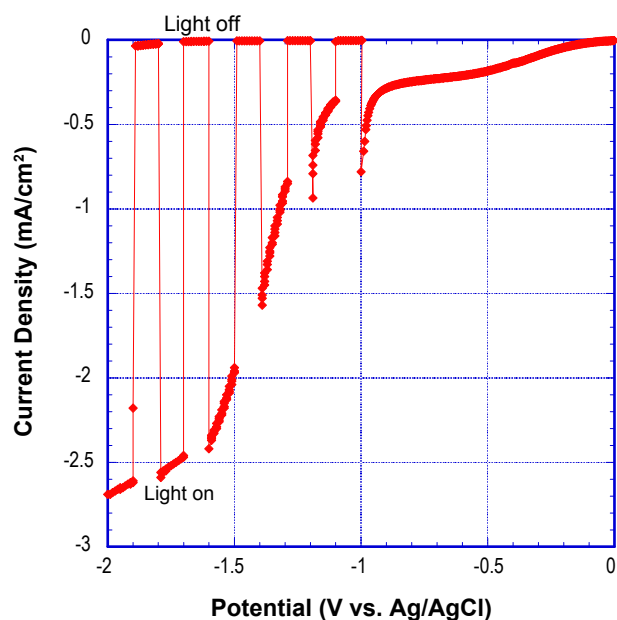
### Thin-Film SiN System

Amorphous SiN is an attractive PEC material because it can be fabricated using scalable deposition processes that can ultimately lead to low-cost photoelectrodes. We are evaluating two sets of SiN materials: one grown by hot-wire chemical vapor deposition (HWCVD) and one grown by plasma-enhanced chemical vapor deposition (PECVD). Depending on the composition, these materials can have band-gaps that absorb visible light, making them ideal for solar energy conversion. The flatband potentials determined from open-circuit potential measurements appear to satisfy the criteria for unbiased water splitting for these intrinsically n-type semiconductors. Few single-junction semiconductor materials span the water-splitting redox potentials whereas these materials appear to do so. Two-electrode measurements demonstrate photocurrent at zero bias, which could be water splitting but is difficult to confirm because of the very low current density ( $\sim$  nanoA/cm<sup>2</sup>). Even under high-reverse bias, the photocurrents observed on the HWCVD samples are limited. The relatively low photoconversion efficiencies need to be improved to achieve a viable photoelectrolysis device and could be augmented by increasing the film thickness (absorption properties) and increasing the conductivity (transport properties). We attempted to increase the HWCVD photocurrents by growing thicker films, incorporating phosphorous as an n-type dopant, using a-Si as the absorber layer, and increasing the growth temperature. None of these attempts at material optimization led to significant improvement in photocurrents.

Twenty-four hour durability tests on the HWCVD samples in 1M KOH revealed that this material is highly stable. The main degradation pathway was pinhole formation leading to delamination. The stability demonstrated by this material class is a significant result because very few semiconductor photoelectrodes exhibit corrosion resistance under extended operation. This stability could make SiN an ideal coating for photoelectrode protection if it can be sufficiently doped to facilitate current flow.

Though generating large magnitude photocurrents on HWCVD material has been unsuccessful so far, the prospect of a stable, low-cost, semiconductor that absorbs visible light and has the appropriate band-edge potentials to spontaneously split water has encouraged us to continue studying the SiN system. It is doubtful that HWCVD SiN can yield the quality materials we require for efficient photoelectrodes. Recent reports of PECVD SiN materials able to sustain several mA/cm<sup>2</sup> of photocurrent have led us to direct our attention to this new material set. PECVD is a scalable deposition technique, so this class of materials fits in line with our goal of achieving a device that can be manufactured using high-throughput techniques.

The SiN from MVSystems deposited by PECVD showed much more promising preliminary results. The bandgaps and band-edge positions are similar to the HWCVD materials. The main difference is the PECVD samples can sustain high photocurrents at a moderate bias (Figure 2). Even though SiN is intrinsically n-type, Figure 2 illustrates the response of a p-type photoelectrode, which is due to the substrate/a-SiC(p)/a-Si(i)/a-SiN(i) configuration. Two-electrode analysis of water-splitting capabilities still demonstrates low current densities, but this might be ameliorated by capping an amorphous multi-junction a-Si cell with SiN. Such a configuration might yield a durable, low-cost photoconversion device. We are currently trying to optimize this system.



**FIGURE 2.** Three-electrode chopped light (Air Mass 1.5 Global Spectrum) current density-potential curve showing reasonably high photocathode response on HWCVD SiN. The electrode configuration tested here is a-SiC(p)/a-Si(i)/a-SiN(i). The electrolyte was a pH<sub>2</sub> phosphate buffer with 10-mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>.

### Thin-Film CGS-Based System

Thin-film CuGaSe<sub>2</sub> (CGS) is a material that has the potential to be a high-throughput, low-cost solar absorber. This intrinsically p-type material has a valence band edge that is too negative for the hole to drive the water oxidation half-reaction. CGS has a relatively wide bandgap (1.7 eV) and reported electrochemical stability, so it could possibly serve as the top layer of a tandem cell. Because hydrogen is evolved from the CGS surface, a hydrogen evolution catalyst would improve the gas evolution rate and enhance photoconversion efficiency. We have been studying catalysis on CGS provided by the Miller group at the Hawaii Natural Energy Institute.

The catalyst we have been focusing on is platinum with the goal of depositing nanometer-scale islands to provide facile surface reaction sites while minimizing light attenuation. One method we study is pulsed electrodeposition from chloroplatinic acid solutions where changing the pulse frequency and duty cycle can influence the catalyst morphology. The other method we employ is to physisorb platinum nanoparticles by immersing electrodes in colloidal solutions. We characterize the catalyzed electrodes with photoelectrochemical methods (chopped light current-potential) and through physical methods (scanning electron microscope, energy dispersive X-ray spectroscopy).

### Synthesis and Characterization of Oxide Semiconductors

We synthesized and characterized Co-Al-Fe oxide materials based on initially promising results from Bruce Parkinson's ink-jet printed high-throughput catalyst screening system. Nanocrystalline composite electrodes were made from CoAl<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> powders. For comparison, nanoporous CoAl<sub>2</sub>O<sub>4</sub> electrodes were also prepared without adding Fe<sub>2</sub>O<sub>3</sub>.

The nanocomposite electrodes were prepared by mixing different amounts (5 wt% to 20 wt%) of Fe<sub>2</sub>O<sub>3</sub> nanoparticles into the CoAl<sub>2</sub>O<sub>4</sub> nanoparticles. The nanocomposite CoAl<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> films exhibited improved PEC response over the CoAl<sub>2</sub>O<sub>4</sub> film, but the improved response (few μA/cm<sup>2</sup> under bias) was still well below what is necessary for a viable PEC device. In addition to the low magnitude of photoresponse, it took several minutes from the application of light for the response to peak. Repeated attempts to optimize these materials did not lead to improved performance. The low magnitude and slow response of the CoAl<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> films may be due to the Mott-insulator nature of these oxide materials. Mott-insulator refers to a specific electronic arrangement intrinsic to some oxides that make it almost impossible to enhance the PEC response. Due to the inherent shortcomings of this Co-Al-Fe oxide system, we reached a No-Go decision on future study of these materials.

## Conclusions

- InGaN samples from LANL appear to be capable of water splitting; flatband potentials, bandgap, and durability are promising; photocurrent efficiency is below expectations for a material with this band gap.
- Hot wire chemical vapor deposited SiN has superb durability but very low photocurrents. Zero bias photocurrents may be water splitting. Repeated attempts to improve photocurrents were unsuccessful making the utility of SiN as an absorber doubtful, but it could serve as a protective coating on an amorphous multi-junction cell.
- a-SiN samples grown by MVS Systems, Inc., using plasma-enhanced chemical vapor deposition demonstrate high photocurrents under bias. Initial positive results warrant further research on this material.
- Platinum is an ideal hydrogen evolution catalyst on CGS. The optimal deposition conditions are still being investigated.
- Co-Al-Fe oxide materials are Mott-insulators, and no material optimization will yield efficient photoelectrodes; No-Go on further studies.

## Future Directions

- Continue to synthesize and characterize nitride materials (GaNP, GaInPN, InGaN, SiN) for higher efficiencies and longer lifetimes in solution.
- Investigate thin-film materials (SiN, SiC, CGS) 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 multi-junction structures for high efficiency.

## FY 2009 Publications/Presentations

### Papers

1. "Direct Water Splitting under Visible Light with Nanostructured Hematite and  $\text{WO}_3$  Photoanodes and a  $\text{GaInP}_2$  Photocathode," Heli Wang, Todd Deutsch, John A. Turner, *J. Electrochem Soc.*, **155**, F91 (2008).
1. "Photoelectrochemical Characterization and Durability Analysis of GaInPN Epilayers," Todd G. Deutsch, Jeff L. Head, John A. Turner. *J. Electrochem Soc.*, **155**(9), B903 (2008).
1. "ZnO Nanocoral Structures for Photoelectrochemical Cells," Kwang-Soon Ahn, Yanfa Yan, Sudhakar Shet, Kim Jones, Todd Deutsch, John Turner, Mowafak Al-Jassim, *Applied Physics Letters*, **93**, 163117 (2008).

### Presentations

1. "Materials Issues for Photoelectrochemical Water Splitting, Searching for the 'Holy Grail'", Purdue University Discovery Park Hydrogen Symposium 2008 April 24, 2008 *Invited*.
2. "Solar and Hydrogen Systems: Sustainable Energy for Future Generations" 2008 Clean Energy and Power Forum, April 29, 2008 *Invited, Keynote*.
3. Frontiers, Opportunities and Challenges for a Hydrogen Economy, Sigma Xi Lecture, Naval Research Laboratory, June 13, 2008, *invited*.
4. "Frontiers, Opportunities and Challenges for a Hydrogen Economy", 10<sup>th</sup> World Renewable Energy Conference, Scotland, July 22, 2008 *Invited*.
5. "The Hydrogen Economy: Frontiers, Opportunities and Challenges", Basic Energy Sciences, Chemical Sciences Workshop on Efficient Conversion of Solar Energy to Electricity and Fuels, August 14, 2008 *Invited*.
6. "Thin-Film Nitride Semiconductors for Photoelectrolysis," 42<sup>nd</sup> Western Regional Meeting of the American Chemical Society. Las Vegas, Nevada. September 24, 2008. *Invited*
7. "Photoelectrochemical Production of Hydrogen," National Hydrogen Association Fall Forum. Golden, Colorado. September 22, 2008. *Invited*
8. "Amorphous Silicon Nitride Thin Films for Solar-Driven Photoelectrolysis," 214<sup>th</sup> Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 13, 2008.
9. "Optimization of Photoelectrolysis Efficiency of III-V Nitride/Silicon Tandem Semiconductor Electrodes," 214<sup>th</sup> Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 15, 2008.
10. "Photoelectrochemical Responses of the Nanostructured ZnO Films Synthesized using Sputtering System," 214<sup>th</sup> Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 15, 2008.
11. The Hydrogen Economy: Frontiers, Opportunities and Challenges, 3M Technical Forum, November 4, 2008, *Invited*.
12. Science and Technology for a Hydrogen Economy: On a Mission to Green Emission, Arizona Workshop for Renewable Energy, November 17, 2008 *Invited*.
13. The Sustainable Hydrogen Economy: Frontiers, Opportunities and Challenges, The Hydrocarbon Resources Gordon Research Conference, January 14, 2009, *Invited*.
14. Properties and Theoretical Aspects for Photoelectrochemical Water Splitting Materials, Symposium on Nanotechnology and the Environment: Emphasis on Green Nanotechnology, American Chemical Society Meeting, Salt Lake City, Utah, March 26, 2009, *Invited*.

**15.** Science and Technology for a Hydrogen Economy, U.S.  
Air Force Academy, April 6, 2009, *invited*.

**16.** Realizing a Sustainable Energy Future, American  
Physical Society Student Forum, Colorado School of Mines,  
May 4, 2009, *Invited*.