

II.G.4 Semiconductor Materials for Photoelectrolysis

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Subcontractors:

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

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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 Photoelectrochemical Hydrogen Production section of the Fuel Cell Technologies Program's Multi-Year Research, Development, and Demonstration Plan (MYPP):

- (Y) Materials efficiency
- (Z) Materials durability
- (AB) Bulk materials synthesis
- (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% conversion efficiency
- 1,000 hr lifetime

Accomplishments

- In addressing the MYPP barrier Z, preliminary testing of CuGaSe₂ (CGS) was completed. UNLV analysis of CGS samples that were subjected to PEC testing showed that biasing the material alters the chemical environment of Ga and immersion into an acidic electrolyte appears to remove a native SeO₂ feature. Further analyses are necessary to determine how these changes might affect stability and performance.
- Our Stanford subcontractor synthesized tungsten nanoparticles and air-stable MoS₂ nanoparticles in various sizes ranging from 5-25 nm and achieved quantum confinement of MoS₂ nanoparticles with indirect bandgaps up to 1.8 eV.
- We characterized a-SiC, deposited by plasma-enhanced chemical vapor deposition (PECVD) to address barriers Y, Z, AB and AC. We determined a-Si/a-SiC hybrid photoelectrodes have poor efficiency when operated at zero bias and poor durability when moderate current (-3 mA/cm²) was applied. Removing the surface SiO_x layer with an hydrofluorhydric acid (HF) etch can improve water splitting efficiency to just over 1%.
- In addressing barriers Y, Z, and AC we determined In_xGa_{1-x}N thin films have appropriate interfacial energetics for spontaneous water splitting, exhibit good durability, and can be incorporated into multi-junction absorber cells to improve photoconversion efficiency.
- We published a manuscript to the Journal of Materials Research on standardized PEC methods which was the culmination of a year-long effort with other members of the PEC working group. The document is intended to establish standard practices for reporting water splitting efficiencies within the PEC community.
- Stabilization of the GaInP₂ electrolyte interface through electrochemical nitridation and thin oxide coating by atomic layer deposition show these strategies may be able to passivate the corrosion-prone surface. If these highly efficient materials (12.4% solar-to-hydrogen, STH) could be made more durable, the MYPP 2013 technical target or 10% efficiency for 1,000 hours would be satisfied.
- Density functional theory (DFT) calculations showed W would make a good n-type dopant in BiVO₄ and efforts to incorporate W during synthesis are underway.
- We made a “no-go” decision on continued study of a-SiN_x and Cu-W-O materials and a “go” decision on protective coatings and nitride treatments on high-efficiency III-V photoelectrodes.

Future Direction

- Continue to synthesize and characterize nitride materials (GaNP, GaInN, GaInPN) for higher efficiencies and longer lifetimes. Synthesize InGaN on conductive substrates.
- Investigate nitridation of III-V surfaces for corrosion passivation.
- Evaluate additional PEC semiconductor candidates in collaboration with others.
- Work with UNLV to correlate surface and near-surface spectroscopic results with test conditions to identify corrosion pathways and performance barriers related to surface composition.



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 electrode of the water-splitting system, and the other is an 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

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. The latter is in collaboration with NREL's theory group.

Results

III-V Nitride Materials

We characterized InGaN alloy samples from Los Alamos National Laboratory grown by molecular beam epitaxy (MBE). InGaN is a promising emerging material

with a bandgap between 0.7-3.4 eV, depending on the In:Ga ratio. Nitride materials have well documented stability in contact with electrolytes, therefore InGaN alloys may be stable and efficient photoelectrodes for PEC water splitting because of their chemical inertness and ability to absorb visible photons. These materials were characterized to determine bandgap, bandedge alignment, water-splitting efficiency, and stability. Samples were grown on sapphire substrates, which are electronically insulating. Contacts were applied to the periphery of the front surface in order to fabricate electrodes, a non-ideal configuration that results in poor carrier collection. Despite these non-ideal contacts, we were able to determine some basic material properties.

The samples had obvious visible absorption as evidenced by their colored appearance (Figure 1a). The material composition varied across the surface of the wafer due to issues with the gallium source within the MBE reactor. The bandedge positions were appropriate for water splitting according to Mott-Schottky measurements. Illuminated open-circuit measurements and photocurrent onset potential measurements indicated the flatband potential was too positive, i.e. the conduction bandedge was too low to drive the hydrogen evolution (reduction) half-reaction. Two-electrode measurements (Figure 1b), however, demonstrated zero-bias photocurrent, which we correlate with spontaneous water splitting. Though the InGaN was capable of zero-bias photocurrent, the efficiency was very low, generating 10s of $\mu\text{A}/\text{cm}^2$ instead of mA/cm^2 that would be expected of a material with a bandgap in the visible region. We believe the inconsistent bandedge analyses and low conversion efficiency is due to the long carrier collection distances due to the non-ideal contacts. Initial durability analysis showed moderate stability, but it is doubtful that the uneven spatial distribution of current replicated what an appropriately contacted material might experience. Realistic appraisals of efficiency and durability cannot be made until the contact geometry is modified to a more ideal vertical collection is achieved by using conductive substrates.

Thin-Film Amorphous SiN and SiC Systems (with MVSystems)

In collaboration with our industrial partner, MVSystems, Inc., who performed the material synthesis, we studied amorphous silicon nitride (a-SiN) and silicon carbide (a-SiC) samples grown by PECVD. PECVD is a scalable process that can yield low-cost photoelectrodes and although the instability of amorphous silicon (a-Si) makes it a non-ideal PEC material, stability might be achieved when synthesized as a nitride or carbide.

We characterized PECVD grown a-SiN_x that was synthesized with an appropriate bandgap (~2.0 eV) for water splitting; however, the bandedges at the electrolyte semiconductor interface were not favorable

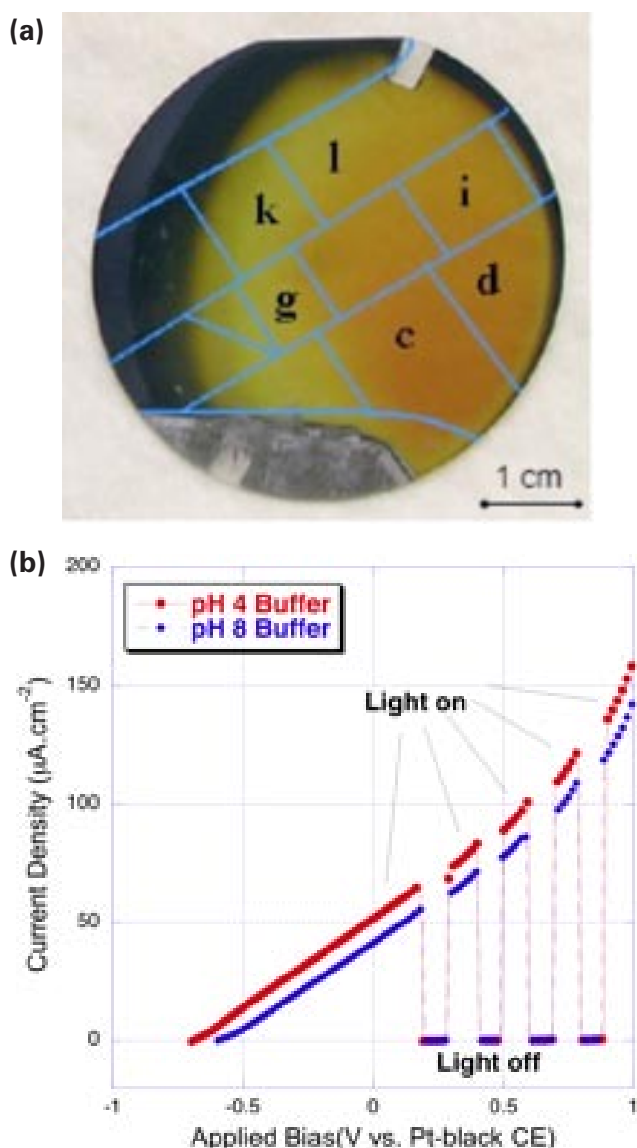


FIGURE 1. (a) Top, an as-grown InGaN wafer and the depiction of cuts made with a diamond scribe to subdivide it into electrodes for PEC measurements. (b) The plot on the bottom is a two-electrode chopped-light current-voltage curve taken at AM 1.5 G (100 mW/cm²) light intensity. The solutions were sparged to remove oxygen so short-circuit photocurrent is likely due to water splitting.

for spontaneous water splitting. When assembled into a p-type device, a-SiN_x electrodes can produce milliamps of photocurrent per square centimeter but only under a strong negative bias of -3 V. A 30 second 5% HF surface treatment damaged the film surface and did not significantly improve photocurrent onset potential. Holding the sample at -2.6 V vs. Pt-black counter electrode for 24 hours produced numerous pinholes in the a-SiN_x film and allowed the passage of dark current from the conductive tin oxide substrate. Because of the questionable efficiency and durability of this material,

a-SiN_x has limited promise for PEC water splitting applications, and thus we made a “no-go” decision on continued study of this material.

The PEC performance (efficiency and durability) of a-Si(photovoltaic, PV)/a-SiC(PEC) was determined. These types of cells are known as a PEC/PV hybrid because they incorporate a photovoltaic absorber in series with a PEC absorber as a monolithic device. When these cells are fabricated into solid-state devices, the short-circuit current density under air mass (AM) 1.5 G illumination is about 4.5 mA/cm². When similar cells were tested in a PEC environment, the short-circuit (water splitting) current densities were below 1 mA/cm².

HF etching can improve the photocurrent by removing the insulating SiO_x interfacial layer, but the effect is only temporary. We have been unable to identify an active catalyst to facilitate the hydrogen evolution reaction on the surface of these photocathodes. Our typical applications of platinum by electrodeposition or immersion in colloidal solutions have not been effective for these amorphous materials. Platinum applied by sputtering also led to diminished photocurrents.

The STH efficiencies achieved in pH 0, 5, 8, 10, and 14 under AM 1.5 G illumination were all lower than 0.25% when a platinum counter electrode was used. The use of a RuO₂ counter electrode in pH 0 sulfuric acid achieved the highest STH efficiency of about 1%, and was stable over the 20-hour test period. However, no bubbles were observed from the working electrode so the cathodic current could not be unambiguously attributed to water splitting. Our collaborators at the University of Hawaii observed that using an HF acid treatment, the overall efficiency could be as high as 1.6% (RuO₂ counter, in pH 0 phosphoric acid).

When a current of -3 mA/cm² was applied by external biasing, (the current that a 3.6% efficient electrode would generate) severe degradation of the surface was observed in less than 24 hours. The electrodes developed several pinholes that were visible without magnification that increased with extended testing (Figure 2).

For a-SiC coated a-Si to be considered for PEC water splitting devices, the efficiency and durability both must be improved.

Protection Strategies for High-Efficiency III-V Materials

Tandem cells based on p-GaInP₂:n/p-GaAs semiconductors have demonstrated over 10% STH, which exceeds the DOE near-term technical target, but are prone to corrosion during operation. The unprotected cells only last a few days in operation. Improving the durability to 1,000 hours could yield a



FIGURE 2. Top, an uncoated hybrid photoelectrode after -3 mA/cm^2 was applied in pH_2 buffer for 24 hours. The image on the bottom is of a different hybrid photoelectrode subjected to the same conditions after 48 hours.

photoelectrode that satisfies both the efficiency and durability technical targets. This year we examined two different pathways for III-V photoelectrode passivation. One strategy is to use an electrolyte that has constituents that modify the semiconductor surface in a way that leads to protection. The other approach focuses on applying a protective coating through a chemical deposition process.

Initial results from our lab found that operating a p-GaInP₂ for 24 hours in a pH 1 NH_4NO_3 solution resulted in less surface degradation, as determined by optical microscopy and scanning electron microscopy (SEM), than running it in our standard 3M H_2SO_4 solution. Our hypothesis is that the passivation is due to electrochemical nitridation that occurs during the durability testing. X-ray photoelectron spectroscopy on a sample that had been run in the NH_4NO_3 solution found ammonia on the surface after rinsing the electrode

with deionized water post durability testing. We are following up to determine if the difference in pH (3M H_2SO_4 pH= -0.5) plays a significant role. We are also investigating the origin of the ammonia, whether from the cation or anion, so we are testing in $(\text{NH}_4)_2\text{SO}_4$ and KNO_3 . In addition we are performing durability analysis on tandem GaInP₂/GaAs electrodes to see if the protective effect is observed when the electrode is biased internally instead of via a potentiostat.

The second strategy for electrode passivation involves applying a thin coating that should provide protection. The coating must not significantly attenuate visible light, and be robust enough to protect the surface while not impeding electron flow to the electrolyte. Our first attempt was to coat p-type GaInP₂ with 20 nm of TiO_2 by atomic layer deposition (ALD). TiO_2 is a fairly stable oxide material that has a wide bandgap and is naturally a good (n-type) electron conductor. We cleaved GaInP₂ wafers and sent half of each one to our colleagues in the Sunkara group at the University of Louisville to have the oxide coating applied. We mounted the coated and uncoated samples into electrodes to compare their ability to generate photocurrent and determine their durability characteristics.

We were unable to determine if the coating attenuated photocurrent because there was high variability between individual electrodes from the same wafer, but some of the highest photocurrents were achieved on coated electrodes. For durability analysis, the electrodes were operated for 22 hours at -5 mA/cm^2 in 1M KOH. We were unable to find significant differences in post-durability performance or variation in solubilized Ga in the testing solution. We believe the durability test conditions were not harsh enough to observe corrosion effects on either the coated or uncoated samples.

Visual analysis of the coated and uncoated samples did reveal differences after the durability testing. The uncoated samples displayed a degraded surface from their initially shiny and featureless appearance while the coated electrodes had areas where the coating had flaked off but otherwise appeared free from degradation. SEM imaging of a coated electrode showed that the TiO_2 film has fissures that probably contributed to its inability to adhere to the semiconductor surface (Figure 3). The fissures appear to be a native feature of the TiO_2 coating because they are evident in an area which was masked by epoxy during the testing. This result indicates a thicker coating may be required to achieve an uninterrupted film with the required stability.

Because of the promising results obtained so far, we made a “go” decision for continued study of both nitrided and ALD-coated III-V surfaces for corrosion remediation.

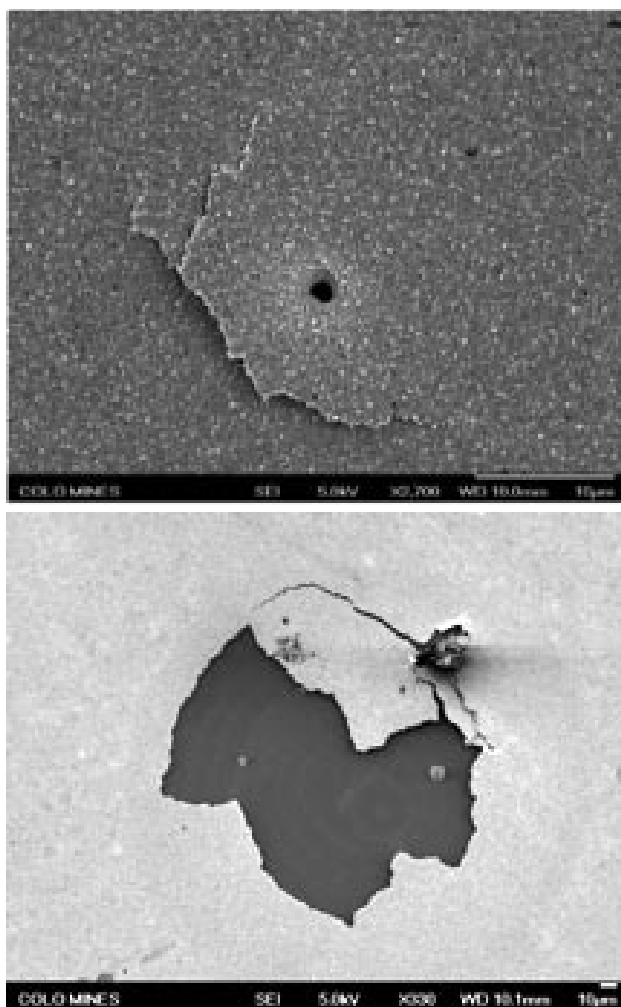


FIGURE 3. Top, a SEM image of a pinhole in CGS after 30 minutes of durability testing. On the bottom is an SEM image after 5 hours of testing under the same conditions showing how the pinhole can lead to progressive, concentric delamination of the CGS thin film during durability.

Chalcopyrites Materials based on $\text{Cu}(\text{In,Ga,Al})(\text{S,Se,Te})_2$

This year we continued potentiostatic (constant applied potential) durability analysis of CGS materials on fluorine-doped tin oxide substrates obtained from the University of Hawaii. In addition to samples sent to UNLV for synchrotron analysis (results reported by our subcontractor NREL project: subcontract NO. NFH-8-88502-01 under prime contract NO. DE-AC36-99GO10337) we performed our own surface and electrochemical analysis. Figure 4 illustrates how a pinhole can lead to cracking and delamination of the CGS film after only 30 minutes in 3M H_2SO_4 under AM 1.5 G illumination at a bias of -2.3 V vs. a Pt-black counter electrode. The pinhole allows the electrolyte to contact the conductive substrate where hydrogen can

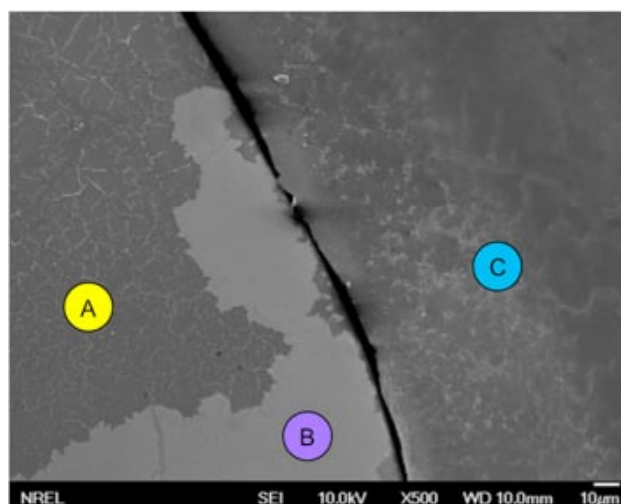


FIGURE 4. SEM image of coated sample subjected to durability testing. Region "A" is coated area exposed to electrolyte; "B" area where coating had flaked off; "C" coated area that was underneath epoxy and never exposed to electrolyte. The diagonal line bisecting the image is the boundary between the exposed and masked areas.

then evolve between the substrate and the CGS. This causes the pinhole to grow via CGS material flaking. It is unknown if the pinholes are intrinsic or induced by the corrosion testing.

The instability observed may be due to native pinholes and insufficient adhesion to the substrate. This could be remedied through modified synthesis conditions that minimize pinholes or the use of a more compatible substrate material. A more difficult problem is if the CGS itself is soluble in the solution under the durability conditions. We are continuing corrosion testing coupled with solution analysis by inductively coupled plasma mass spectrometry to see if we can detect solubilized semiconductor components. We are continuing to test and send more CGS to UNLV to build the spectral library that is necessary to deduce a corrosion mechanism for this material.

Theory of Metal Oxide, Nitrides and Other Materials

BiVO_4 has attracted significant interest as a semiconducting material for the PEC decomposition of water. Our analysis of BiVO_4 by density functional theory indicated good electronic properties for this material such as high hole mobility and good band edge positions. For PEC applications, the semiconductor must be doped p-type or n-type to a reasonable carrier concentration in order to support current flow. Therefore, we studied the effect of doping of W in BiVO_4 using DFT.

We previously calculated that the valence band of BiVO_4 is derived from hybrid Bi lone pair 6s and O 2p states. Tungsten can have various ionized states in oxides. We find that if a W occupies a Bi site, W is shallow donor. From the calculated band structure and site projected density of states, it was found that the states introduced by W are in the conduction band, indicating that indeed W is very shallow donor. In this case, W is 5^+ and Bi is 3^+ , therefore W on Bi site results in double donors. Beside Bi sites, W may also occupy a V site where the states introduced by W are also in the conduction band, meaning W at V site is also a shallow donor. However, in this case, W is a single donor.

Our results conclude that W at either a Bi site or a V site is a shallow donor, suggesting W would be an excellent dopant for making n-type BiVO_4 , and we will be pursuing the synthesis of this material for PEC testing.

NREL Synthesis of Metal Oxide Alloy Thin Films

We synthesized Cu-W oxide thin films by co-sputtering. In order to produce Cu-W oxide materials with tunable band gaps and avoid phase separation, amorphous Cu-W oxide films were synthesized. Considering the fundamental gap as direct, the band gaps for a series of samples with Cu to W ratios of 1:3, 1.1:1, and 2.2:1 were 2.63 eV, 2.05 eV, and 1.88 eV respectively. The trend of the bandgaps correlate well with values expected from the composition. The fundamental bandgaps correspond to the transition between Cu 3d-derived valence band and W 5d-derived conduction band.

Although these materials have optimal bandgap energies, they are unstable in both basic and acidic solutions. In light of their instability, we made a “no-go” decision on amorphous Cu-W oxide for PEC applications.

Conclusions

- InGaN shows promise for a single junction water splitting electrode with potential for high efficiency and durability if the contacts can be improved. Synthesis on conductive substrates should remedy this situation and these efforts are underway.
- Thin film a-Si carbides have the potential to be inexpensive water splitting electrodes if durability and efficiency can be improved.
- Protection of highly efficient, but corrosion prone photoelectrodes could result in a single material that meets the DOE technical targets for efficiency and durability. Results from GaInP cells with nitride treatments and thin oxide coatings suggest this route is viable.

- CGS appears to suffer mechanical stability, which could be overcome by synthesis modifications. CGS could potentially serve as the outer coating for a tandem cell and obtain high efficiency.
- DFT has indicated that W is a good dopant for BiVO_4 which we are currently synthesizing.

FY 2010 Publications/Presentations

Papers

1. “Ternary cobalt spinel oxides for solar driven hydrogen production: Theory and experiment” Aron Walsh, Kwang-Soon Ahn, Sudhakar Shet, Muhammad N. Huda, Todd G. Deutsch, Heli Wang, John A. Turner Su-Huai Wei, Yanfa Yan, Mowafak M. Al-Jassim, *Energy Environ. Sci.*, **2**, 774. (2009).
2. “Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight” F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan. *Philosophical Magazine*, **89**:28, 2723-2739 (2009).
3. “Accelerating materials development for photoelectrochemical (PEC) hydrogen production: Standards for methods, definitions, and reporting protocols” Zhebo Chen, Thomas Jaramillo, Todd Deutsch, Alan Kleiman-Shwarsstein, Arnold Forman, Nicolas Gaillard, Roxanne Garland, Kazuhiro Takanabe, Clemens Heske, Mahendra Sunkara, Eric McFarland, Kazunari Domen, John Turner, Huyen Dinh, *Journal of Materials Research* **25**(1), 3-16 (2010).
4. “Synthesis and characterization of band gap-reduced ZnO:N and ZnO:(Al,N) films for photoelectrochemical water splitting” Sudhakar Shet, Kwang-Soon Ahn, Todd Deutsch, Heli Wang, Nuggehalli Ravindra, Yanfa Yan, John Turner, Mowafak Al-Jassim, *Journal of Materials Research* **25**(1), 69-75 (2010).
5. “Influence of gas ambient on the synthesis of co-doped ZnO:(Al,N) films for photoelectrochemical water splitting” Sudhakar Shet, Kwang-Soon Ahn, Todd Deutsch, Heli Wang, Ravindra Nuggehalli, Yanfa Yan, John Turner, Mowafak Al-Jassim, *Journal of Power Sources* **195**(17), 5801-5805 (2010).

Presentations

1. Hydrogen Production from Photoelectrochemical Cells: Theoretical Considerations and Experimental results”, *Advanced Materials and Concepts for Energy Harvesting*, Electrochemical Society, San Francisco, May 26, 2009, J. Turner, *Invited Talk*.
2. “Realizing a Sustainable Energy Future”, MIT Energy Institute, June 3, 2009 Seminar, J. Turner, *Invited Talk*.
3. “The Hydrogen Economy- Realizing a Sustainable Energy Future”, NREL Interns, June 24, 2009, J. Turner, *Invited Talk*.

4. “Energy Sustainability, The Challenge for Future Generations” Renewable Energy Summer Workshop, Colorado School of Mines, July 22, 2009, J. Turner, *Invited Talk*.
5. “A Sustainable Energy Future” , Green Chemistry Summer School, CSM, July 22, 2009, J. Turner, *Invited Talk*.
6. “Realizing a Sustainable Energy Future”, Alternative Energy Systems: Perspectives and Opportunities, American Chemical Society Spring meeting, August 17, 2009, J. Turner, *Invited Talk*.
7. “Photoelectrochemical Water Splitting on III-V-Nitride Semiconductor Electrodes” Hendrix College Chemistry Seminar, September 14th, 2009. T. Deutsch, *Invited Talk*.
8. “Photoelectrochemistry of hematite thin films”, 216th Meeting of the Electrochemical Society, Vienna, Austria, October 4–9, 2009. H. Wang, (contributed).
9. “Frontier, Opportunities and challenges for a Hydrogen Economy”, 28th International Congress on Applications of Lasers and Electro-Optics (ICALEO), November 2, 2009, J. Turner, *Invited talk, Plenary*.
10. “Frontier, Opportunities and challenges for a Hydrogen Economy”, Columbia University, November 11, 2009, J. Turner, *Invited Talk*.
11. “The Hydrogen Economy: a Vision for a Sustainable Future”, University of Nevada Reno, November 20, 2009, J. Turner, *Invited Talk*.
12. “Hydrogen Production from Photoelectrochemical Cells: Theoretical Considerations and Experimental Results”, University of Nevada Reno, November 20, 2009, J. Turner, *Invited Talk*.
13. “Hydrogen Production from Photoelectrochemical Cells: Theoretical Considerations and Experimental Results”, University of Denver, January 21, 2010, J. Turner, *Invited talk*.
14. “Sustainable energy virus: Transmission and spread via undergraduate interns” American Chemical Society National Meeting & Exposition, San Francisco, California. March 22, 2010. T. Deutsch, *Invited Talk*.