

## II.G.4 Photoelectrochemical Hydrogen Production: UNLV-SHGR Program Subtask\*

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- University of Hawaii at Manoa, Honolulu, HI
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- Intematix Corp., San Jose, CA
- AltairNanotechnologies, Inc., Reno, NV
- University of California at Santa Barbara (UCSB), Santa Barbara, CA
- National Renewable Energy Laboratory (NREL), Golden, CO (cooperative agreement)

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\*Congressionally directed project

- Explore avenues toward manufacturing-scale devices and systems.

### 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:

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

### Technical Targets

As recognized within the PEC Hydrogen research community and the DOE PEC Hydrogen program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category (“useable semiconductor bandgap”) are the primary focus of this project’s research, with secondary emphasis on the second category targets (“chemical conversion process efficiency”). To address the technical barriers, and approach the short- and long-term targets, the project team has utilized its collective expertise in theoretical materials modeling, synthesis, and characterization to study a diverse portfolio of promising PEC thin-film materials classes, focusing on benchmarks of semiconductor bandgap, band-edge alignment and durability, as well as integrated device conversion efficiency.

### Objectives

- Identify and develop new photoelectrochemical (PEC) film materials compatible with high-efficiency, low-cost hydrogen production devices: target of 1.6 mA/cm<sup>2</sup>–6.5 mA/cm<sup>2</sup> AM 1.5 photocurrent.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials: target of 2-8% solar-to-hydrogen (STH) efficiency under AM 1.5 illumination.
- Develop avenues, integrating new theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices.

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristic	Units	2006 Status	2013 Target	2018 Target
Useable semiconductor bandgap	eV	2.8	2.3	2.0
Chemical conversion process efficiency (EC)	%	4	10	12
Plant solar-to-hydrogen efficiency (STH)	%	N/A	8	10
Plant durability	hrs	N/A	1,000	5,000

## Accomplishments

- Collaborative Research Team Established:
  - An integrated project team combines materials theory, synthesis and characterizations to facilitate the process of materials discovery and development.
- Critical Experience, Protocols, and Infrastructure Developed:
  - Versatile synthesis tools established for fabricating PEC materials and devices.
  - Comprehensive characterization protocols established for PEC materials and devices.
  - Rapid-throughput synthesis and screening techniques developed to facilitate discovery.
  - Manufacture-scale process demonstrated for multi-junction device fabrication.
- Focus Materials Classes Established:
  - Including  $\text{WO}_3^-$ ,  $\text{ZnO}^-$ ,  $\text{Fe}_2\text{O}_3^-$ , silicon-, and copper chalcopyrite-based thin films.
- Key Targets Met in Focus Materials Experiments:
  - Photocurrents in excess of  $3 \text{ mA/cm}^2$  in tungsten-based films.
  - Photocurrents in excess of  $6.5 \text{ mA/cm}^2$  in Si- and chalcopyrite-based films (with additional bias constraints to be corrected in band edge alignment modifications).
  - STH device efficiencies in excess of 3% in  $\text{WO}_3^-$ -based multi-junction structures under 1 sun.



## Introduction

The primary objective of this project has been the research and development of semiconductor materials for stable and efficient PEC hydrogen-production systems. The candidate materials have to be functional (1) as a photoactive layer, absorbing a significant fraction of the incident light; (2) as photoelectrochemical junction with the electrolyte; and (3) as a facilitator of the gas evolution reaction (either hydrogen or oxygen, depending on the p- or n-type nature of the semiconductor). The requirements on the material include adequate light absorption over the solar spectrum, high carrier collection efficiency, stability in suitable aqueous electrolytes, and favorable kinetics for the electrode reaction. As candidate materials with suitable properties emerge, additional requirements for the photoelectrode semiconductor device integration become increasingly important, such as process compatibility of the complete multi-junction devices, as well as long durability and low material cost.

This past year, the project has focused primarily on the discovery and development of promising PEC thin-film materials classes through the collaborative efforts of our integrated project team – a team offering a broad array of state-of-the-art theoretical and experimental tools and techniques. Secondary emphasis has been on demonstration of integrated PEC hydrogen producing devices based on the best available PEC thin-film materials developed within the project.

## Approach

The general approach of this collaborative effort is to integrate state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising material classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of dopants on valence band maximum and conduction band minimum positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within this project, our general approach is currently being applied to five classes of “focus materials” deemed of particular interest for PEC applications by project team members. These “focus materials” classes under current investigation include tungsten-based films, zinc-based films, iron-based films, silicon-based films, and copper chalcopyrite-based films.

## Results

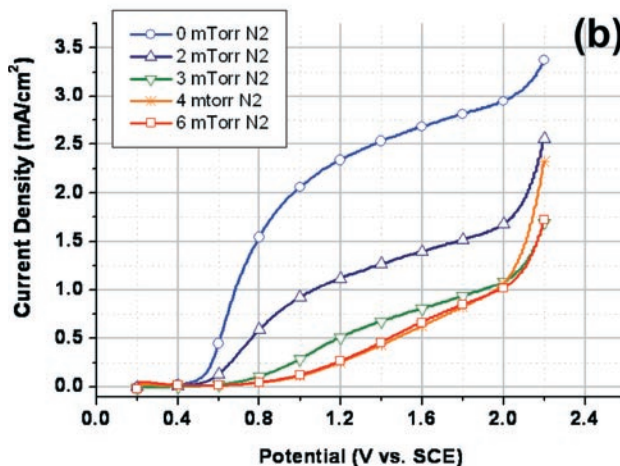
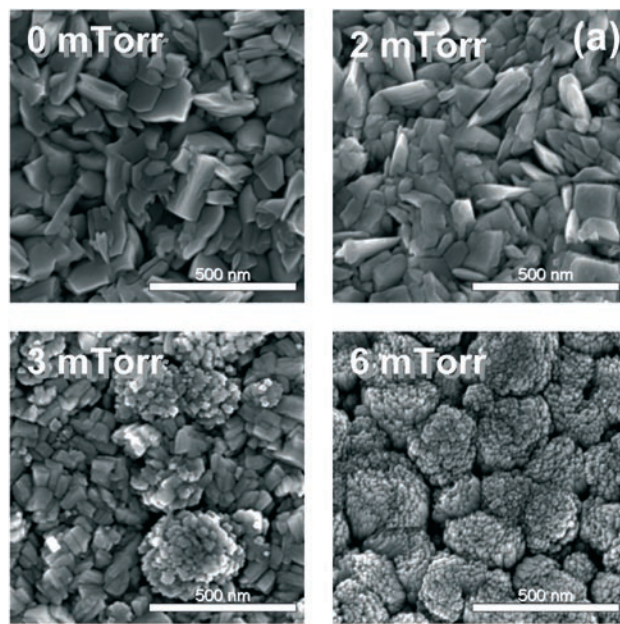
Extensive studies of the five materials classes under investigation have focused on understanding and improving photoelectrochemical behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in developing each of the focus materials is detailed in the following subsections.

### Tungsten-Based Films

Preliminary studies involving tungsten oxide and titania have shown that nitrogen doping is an effective way to reduce bandgap, providing for greater absorption in the visible region of the solar spectrum. Based on this, a full evaluation of nitrogen doping in our sputter-deposited  $\text{WO}_3$  films was conducted, with a battery of characterizations performed both at UH and NREL to determine how nitrogen incorporation impacts the tungsten oxide material. The incorporation of nitrogen was achieved via its introduction into the sputtering

ambient during deposition. For dilute doping (partial pressure less than 2 mTorr), negligible effects were observed for microstructure and bandgap. However, the small amounts of nitrogen incorporation showed significant impact on the PEC performance, with a decrease in photoelectrochemical efficiency directly correlated with the introduction of nitrogen. This is attributed to an increase in defects, degrading the carrier transport properties.

At more concentrated levels of nitrogen doping, the incorporation of defects into the lattice leads to a breakdown in crystallinity. Figure 1 (a) shows plan-view micrographs for pure  $\text{WO}_3$ , as well as 2 mTorr  $\text{N}_2$ , 3 mTorr  $\text{N}_2$ , and 6 mTorr  $\text{N}_2$  films. Here the evolution in microstructure is clearly observed to shift from large



**FIGURE 1.** (a) Evolution of Microstructure for  $\text{WO}_3$  with Nitrogen Doping and (b) Photocurrent- vs-Potential Scan of Corresponding Samples in 0.33M  $\text{H}_3\text{PO}_4$  under Simulated AM1.5G (1-sun) Illumination

crystals for the pure  $\text{WO}_3$  to agglomerates of small nano-sized grains for the 6 mTorr  $\text{N}_2$  sample. These small grains have an accompanying large concentration of defects that degrade the PEC performance. This decrease in PEC performance is illustrated in Figure 1(b). Other characterizations (transmission electron microscopy, TEM, and X-ray diffraction, XRD) confirm that the material suffers from a decrease in crystallinity. The conclusion is that although nitrogen lowers the bandgap, the resultant effect on microstructure is such that a serious degradation of the electron transport occurs, thereby decreasing the PEC efficiency. Motivated by results of the nitrogen-doping experiments, future research to address bandgap and band-edge alignment issues in tungsten-based films will explore quaternary systems where bandgap reduction can be achieved while maintaining good crystallinity. An example of such a quaternary system of particular interest for PEC applications is  $\text{W}_x\text{Mo}_{1-x}(\text{O}_y\text{S}_{1-y})_3$ .

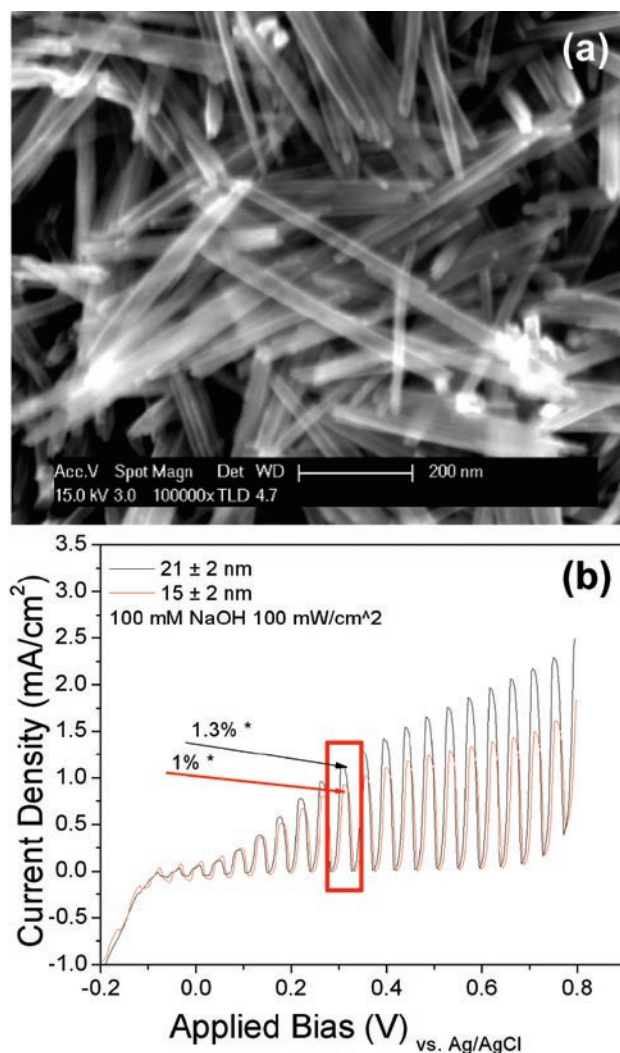
### Zinc-Based Films

Early work on ZnO based films was conducted at NREL to evaluate its performance as a top junction PEC material. ZnO has a large bandgap (3.2 eV), and therefore to have merit in PEC application, this bandgap must be reduced. Nitrogen doping was evaluated, and is shown to effectively incorporate into ZnO films to reduce bandgap. The fabricated films to date have shown poor crystallinity (related to the low-temperature of these depositions), therefore future efforts will revolve around improving the growth process and quality of the films. In addition to the synthesis work, theoretical calculations have been conducted that show that doping of group 1B transition metals (Cu, Ag) will result in bandgap reduction for ZnO. Cu was incorporated in the ZnO films with mixed results – the badgap reduction was successful with Cu found at Zn sites for select films, however the measured photocurrents were low. Future efforts will also focus on improving material properties through growth process optimization.

### Iron-Oxide Based Films

Iron oxide is a commonly-found material with a bandgap (~2 eV) well-suited for the direct solar water-splitting; however, its performance has been seriously limited by its carrier transport properties. In an effort to circumvent this technical barrier, the fabrication of iron oxide as nano-rods with selective orientation for enhanced transport has been initiated. Early stages of research and development at UCSB on iron oxide nano-rod synthesis have yielded a number of important results: (1) control over the size and morphology of the nanostructures has been achieved; (2) improved photoelectrochemical performance as compared with spray pyrolysis deposited films has been demonstrated;

and (3) single-junction zero-biased PEC efficiencies in excess of 1% have been observed using iron oxide nano-rod materials. Of key importance, the developed nano-rod synthesis method is applicable to a wide variety of substrate types, and easily adapted to any size substrate. Figure 2 (a) illustrates nano-rods of  $\text{Fe}_2\text{O}_3$  using the newly developed fabrication techniques, and Figure 2 (b) shows PEC photocurrent performance consistent with STH efficiencies exceeding 1% at zero applied bias. Future work will include the reduction of nano-rod size to  $\sim 6$  nm to increase the valence band confinement, obtain growth along the [110] axis for improved carrier transport, nano-rod doping by *in situ* growth or high temperature diffusion, exploration of deposition of surface electrocatalysts such as Pt, Ni, Au, and Ru, and integration in multi-junction device configurations.

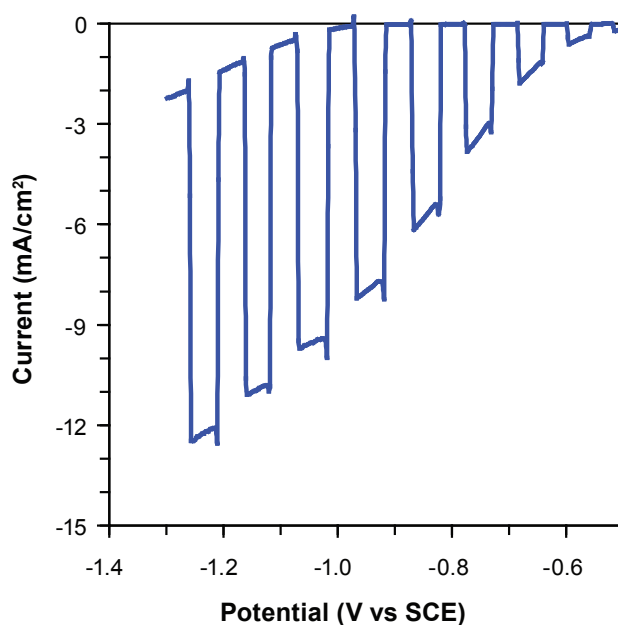


**FIGURE 2.** (a) Iron Oxide Nano-Rods with Diameter of 20 nm and (b) Photocurrent-vs-Potential Scan of Nano-Rod Samples in 0.1 M NaOH under Simulated AM1.5G (1-sun) Illumination

## Silicon-Based Films

The integration of an “all-silicon” multi-junction water-splitting device is an attractive concept due to its straightforward fabrication process and the abundance of the raw material. Based on theory, a photoelectrochemical junction of amorphous silicon carbide (a-SiC) films in the bandgap range of 1.9-2.2 eV could be supported by an amorphous silicon (a-Si) solid state tandem junction. In practice, the bandgap of a-SiC films can be controlled by the ratio of the  $\text{CH}_4$  and  $\text{SiH}_4$  flow rates during plasma enhanced chemical vapor deposition (PECVD), but they tend to saturate at  $\sim 2.1$  eV, as confirmed by research to date at MVSystems Inc. In addition, it has been observed that films fabricated under high  $\text{CH}_4$  flow conditions exhibit lesser electronic quality as evidenced by the low value for conductivity activation energy (indicating a higher density of midgap states). These findings suggest an optimum set of fabrication parameters, where the  $\text{CH}_4$  gas flow is kept at the lowest value which produces a bandgap of  $\sim 2.1$  eV, yet does not cause film quality to deteriorate. For doped films, conductivity can be controlled in part by increasing  $\text{B}_2\text{H}_6$  flow, while keeping the  $\text{SiH}_4/\text{CH}_4$  flow ratio fixed.

For this project, amorphous silicon carbide films with  $\sim 2.0$  eV bandgap were fabricated and evaluated for PEC performance and stability. As can be seen in Figure 3, the photocurrent-vs-potential characteristics of the 2<sup>nd</sup> generation p-type a-SiC photocathodes show photocurrents in excess of 8 mA/cm<sup>2</sup>, a dramatic improvement over the 1<sup>st</sup> generation a-SiC electrode.



**FIGURE 3.** Photocurrent-vs-Potential Scan of a-SiC Electrode in 0.33 M  $\text{H}_3\text{PO}_4$  under Simulated AM1.5G (1-sun) Illumination

However, stability is still an area of concern as partial delamination was observed for several samples. Moreover, the amount of cathodic bias required, although improved over earlier generation films, is still excessive for practical PEC applications. Based on the encouraging present results in conjunction with the prospect of an all-amorphous-silicon-based hybrid photoelectrode, a more comprehensive study of a-SiC films is warranted. Future work will include identification of corrosion mechanisms, quantification of the energetic and kinetic parts of the high cathodic potential requirement, and metal island catalyst depositions to improve the kinetics of the hydrogen evolution reaction.

### Copper Chalcopyrite Films

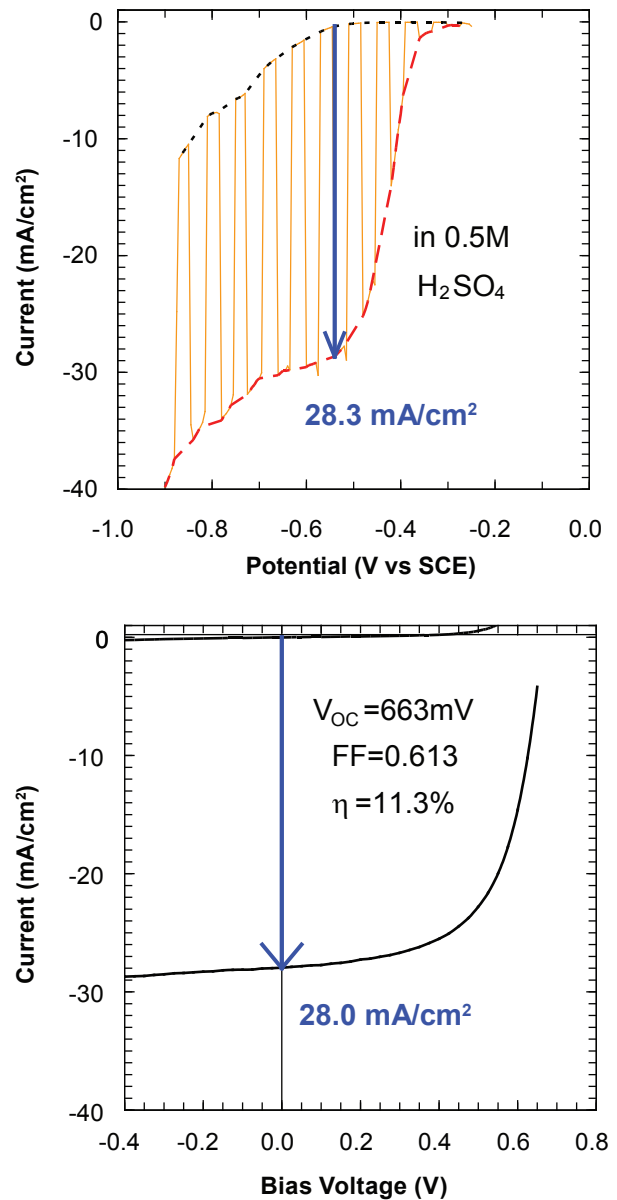
Based on their successful utilization in photovoltaic (PV) devices and the availability of wide-bandgap compositions, we have initiated an evaluation of copper chalcopyrite films for use as photoelectrode material. In particular  $\text{CuGaSe}_2$  (CGS) and  $\text{CuInGaSe}_2$  (CIGS) in the bandgap range of 1.3 eV – 1.65 eV were studied. Such films grown in physical vapor deposition process exhibit p-type behavior and would thus be employed as photocathodes, facilitating the hydrogen evolution reaction. Using a vacuum deposition chamber dedicated to the synthesis of PV-quality copper chalcopyrite materials, films were deposited by thermal co-evaporation of elemental Cu, (In, ) Ga, and Se onto heated substrates. From a twin set of copper indium gallium diselenide (CIGS) ( $E_g \sim 1.30$  eV) samples, both a solid-state solar cell and a photoelectrode were fabricated. Initial photoelectrochemical testing in 0.5 M  $\text{H}_2\text{SO}_4$  showed stability at cathodic potentials and high photocurrents on par with those of solid-state solar cells. As can be seen in Figure 4, the 1-sun saturation photocurrent of the photoelectrode was almost identical to the short-circuit current of the solar cell ( $28 \text{ mA/cm}^2$ ). However, large cathodic bias needs to be supplied, suggesting unfavorable valence band edge alignment with the water oxidation redox potential and kinetic barriers for the hydrogen evolution reaction on the bare electrode surface.

Based on the non-ideal band edge alignment, and various loss mechanisms, a tandem device scheme is seen as necessary for the employment of such chalcopyrite films into water-splitting devices. Semitransparent films are therefore necessary in order to allow some light to pass through to a bottom photovoltaic junction. Thick (2 micron) and thin (0.9 micron) semitransparent copper gallium diselenide (CGS) samples were produced to evaluate the optical properties and the amount of photocurrent generated as a function of thickness. The photocurrent of  $10 \text{ mA/cm}^2$  for the thin device is not much less than that of the thick device ( $15 \text{ mA/cm}^2$ ). These findings show that in

principle, device engineering is possible to current-match a CGS electrode film with a supplemental photovoltaic junction to form an integrated water-splitting device. Future work will include surface modification to lower the valence band maximum position, and noble metal island depositions to improve the catalytic properties of the electrode surface.

### Conclusions and Future Directions

This project's approach of integrating state-of-the-art theoretical, synthesis and analytical techniques is proving



**FIGURE 4.** (a) Photocurrent-vs-Potential Scan of CIGS Electrode in 0.5 M  $\text{H}_2\text{SO}_4$  and (b) Current-Voltage Behavior of Solid State CIGS Solar Cell, Both under Simulated AM1.5G (1-sun) Illumination

to be invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Significant progress has been made in the understanding of the complex interrelationships between structure, optoelectronic properties and photoelectrochemical behavior in the five focus thin-film materials classes (including tungsten-, zinc-, iron-, silicon-, and copper-chalcopyrite-based compounds) currently being investigated in this work. Continued development along this pathway is expected to greatly facilitate the discovery and optimization of material systems and device configurations capable of meeting the DOE PEC production targets.

Future directions for the work initiated in this project include:

- Continued development of research team capabilities and collaboration.
- Continued optimization of performance and durability in focus materials.
- Study of surface modification to improve performance and durability.
- Continued discovery of new materials and possible down-selection of old materials.
- Selection of best materials for incorporation in high-efficiency PEC devices.

### Special Recognitions & Awards/Patents Issued

1. US Pat. 7122873, E. Miller, R. Rocheleau, "Hybrid Solid State/Electrochemical Photoelectrode for Hydrogen Production", issued 10/17/06.

### FY 2007 Publications/Presentations

1. B. Marsen, E. L. Miller, D. Paluselli, R. E. Rocheleau, Progress in sputtered tungsten trioxide for photoelectrode applications. *Int J Hydrogen Energy* (2007), doi: 10.1016/j.ijhydene.2006.01.022.
2. K.A. Gesheva, T. Ivanova, B. Marsen, B. Cole, E.L. Miller, F. Hamelmann, *Surf. Coat. Technol.* (2007), doi:10.1016/j.surfcoat.2007.04.088.
3. B. Marsen, S. Dorn, B. Cole, R. E. Rocheleau, E. L. Miller, "Copper Chalcopyrite Film Photocathodes for Direct Solar-Powered Water Splitting, in *Solar Energy Conversion*, edited by Matt Beard (Mater. Res. Soc. Symp. Proc. 974E, Warrendale, PA, 2007), 0974-CC09-05.
4. B. Cole, B. Marsen, E. L. Miller, "Role of Nitrogen Doping on the Optical and Structural Properties of WO<sub>3</sub> for Photoelectrochemical Applications, in *Solar Energy Conversion*, edited by Matt Beard (Mater. Res. Soc. Symp. Proc. 974E, Warrendale, PA, 2007), 0974-CC09-04.
5. A. Stavrides, A. Kunrath, J. Hu, R. Treglio, A. Feldman, B. Marsen, B. Cole, E. Miller, and A. Madan, "Use of amorphous silicon tandem junction solar cells for hydrogen production in a photoelectrochemical cell ", *Proc. SPIE* 6340, 63400K (2006).
6. A. Stavrides, A. Kunrath, J. Hu, R. Treglio, A. Feldman, B. Marsen, B. Cole, E. Miller, and A. Madan, "Novel Materials for use as Photoelectrodes for Hydrogen Production in Photoelectrochemical Cells", presented at TMS 2007 Annual Meeting (Orlando, 2007).