

## II.H.8 Photoelectrochemical Hydrogen Production: MVSystems Incorporated

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### Subcontractor:

University of Hawaii at Manoa (UH), Honolulu, HI

### Project Partner:

National Renewable Energy Laboratory (NREL),  
Golden, CO

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### Objectives

- Work closely with the DOE Working Group on photoelectrochemical (PEC) hydrogen production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials developed.
- Explore avenues toward manufacture-scaled 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
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

### Technical Targets

The specific targets of this project are (a) the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency (b) operational life up to 500 hours and (c) the identification of commercialization paths toward a \$22/kg-H<sub>2</sub> plant production cost by 2010 and \$5/kg by 2015. Table 1 shows detailed milestones year by year.

**TABLE 1.** DOE Targets for Photoelectrochemical Hydrogen Production

Task #	Milestone	Note
Year 1	Material photocurrent $\geq 3$ mA/cm <sup>2</sup>	Achieved
	Durability $\geq 100$ hr	Achieved
Year 2	Material photocurrent $\geq 4$ mA/cm <sup>2</sup>	Achieved
	Durability $\geq 200$ hr	
	Device STH efficiency $\geq 5\%$	
GO/NO-GO Decision Evaluated		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

### Accomplishments

- New approaches in tungsten oxide surface treatment:
  - Photocurrent above 3.5 mA/cm<sup>2</sup> (at 1.6 V vs. saturated calomel electrode) demonstrated with molybdenum incorporation in WO<sub>3</sub> near surface (approximately 300 nm) to form a bilayer.
  - Evaluation of RuO<sub>2</sub> as catalyst for oxygen evolution reaction. Enhancement of devices performances demonstrated with both RuO<sub>2</sub> thin film and nanoparticles.
- New Cu(In,Ga)(S,Se) alloys have matched previously reported photocurrents ( $\sim 20$  mA/cm<sup>2</sup>) while reducing required voltage bias by  $\sim 200$  mV.
- Successfully fabricated the hybrid photovoltaic (PV)/a-SiC device consisting of amorphous silicon

(a-Si) tandem solar cell and amorphous silicon carbide (a-SiC) photoelectrode, which exhibits the following PEC performance:

- Flat-band potential in a pH2 electrolyte (determined by the illuminated open-circuit potential) is +1.88 V relative to Ag/AgCl reference electrode, or +0.97 V below the  $\text{H}_2\text{O}/\text{O}_2$  redox potential and is in an appropriate position to facilitate water splitting.
- Photocurrent is 4-5  $\text{mA}/\text{cm}^2$  measured in 3-electrode setup;  $\sim 1 \text{ mA}/\text{cm}^2$  at zero bias using 2-electrode setup. Hydrogen production has been observed.
- Good durability in pH2 buffered electrolyte for up to 150 hours (test is on-going).



## Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is placed on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents  $>6 \text{ mA}/\text{cm}^2$  and with sufficient durability to meet the lifetime requirement will be the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including  $\text{CuInSe}_2$ ,  $\text{Cu}_2\text{S}$ , etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D project. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been developed for incorporation in the PEC photoelectrode designs (i.e., the hybrid PV/a-SiC PEC cells). It is the central objective of the MVSystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

## Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet

the PEC challenges in efficiency, stability and cost.

Materials modeling, bulk-film optimization, film-surface enhancement, along with comprehensive material and device characterization is being employed to facilitate the R&D process. Specifically, the feedback approach is being applied to our focus material classes, including the tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals and which are compatible with device fabrication. The most promising candidate materials will be identified, with the short-term goal of demonstrating laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial scale.

## Results

During this reporting period, extensive studies of the three 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. Progress in developing each of the focus materials is detailed in the following subsections.

### Tungsten-Based Compound Films

Several experiments on tungsten oxide surface modifications have been initiated during this period. A  $\text{WO}_3$  surface modification using molybdenum (referred as  $\text{WO}_3:\text{Mo}$ ) was fabricated using a reactive co-sputtering process. Molybdenum incorporation was performed at the end of the  $\text{WO}_3$  film synthesis to form a  $\text{WO}_3:\text{Mo}(300 \text{ nm})/\text{WO}_3(2 \text{ }\mu\text{m})$  bilayer. PEC tests performed under simulated AM1.5 illumination in 0.33M  $\text{H}_3\text{PO}_4$  pointed out a saturated photocurrent increase of approx. 20% at 1.6 V vs. SCE with the bilayer PEC electrode ( $3.6 \text{ mA}/\text{cm}^2$ ) when compared to pure  $\text{WO}_3$  materials ( $2.9 \text{ mA}/\text{cm}^2$ ). Subsequent surface analyses performed at the University of Nevada, Las Vegas (UNLV) revealed a  $\text{WO}_3$  work function increase of approximately 0.2 eV after Mo incorporation. The difference in the Fermi level positions between the two materials would create a built-in potential at the  $\text{WO}_3:\text{Mo}/\text{WO}_3$  interface that could enhance hole transfer to the electrolyte.

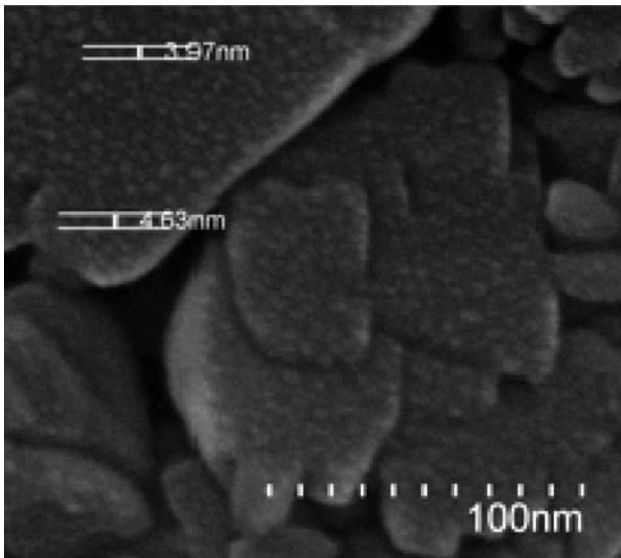
Surface modification with  $\text{RuO}_2$  nanoparticles to increase catalytic activity on  $\text{WO}_3$  was also investigated. First, a series of experiments were conducted on  $\text{RuO}_2$  thin films to establish a baseline deposition process. Catalytic activity for the oxygen evolution reaction was

validated using RuO<sub>2</sub> thin film as a counter electrode for a p-type PEC electrode test. Onset potential reductions of about 400 mV were observed for both a-SiC and CGSe-based PEC electrodes. Nanoparticles were then deposited on several substrates using the same process with a 30-second deposition time. High catalytic activity was observed with RuO<sub>2</sub> nanoparticles deposited on conductive transparent oxide (SnO<sub>2</sub>:F) substrates. Figure 1 presents a scanning electron microscope micrograph of the nanoparticles deposited on WO<sub>3</sub>.

### Copper Chalcopyrite-Based Films

Progress in PEC water-splitting using copper chalcopyrite thin-films has identified specific avenues of future work required to reach the DOE targets for PEC hydrogen production. Copper gallium diselenide (CGSe) thin-films exhibit extremely high photocurrents (~20 mA/cm<sup>2</sup>) under 1-sun AM1.5G illumination in 0.5M sulfuric acid with a very high degree of durability. This class of materials requires a high voltage bias to initiate the water-splitting reaction. The deposition process of baseline CGSe thin films is robust and reproducible, and optimization of the films for high photocurrents is well beyond what is needed to reach the DOE Targets. We will shift our focus to decrease the voltage bias which is caused by a valence band mismatch with the half-reaction potential for the oxygen evolution reaction.

Variations of the copper chalcopyrite material alloy class (Cu(In<sub>x</sub>Ga<sub>(1-x)</sub>)(S<sub>y</sub>Se<sub>(1-y)</sub>)<sub>2</sub>) (CIGS) allows the tuning of the material bandgap. Experimentation has further shown that the partial or full replacement of selenium

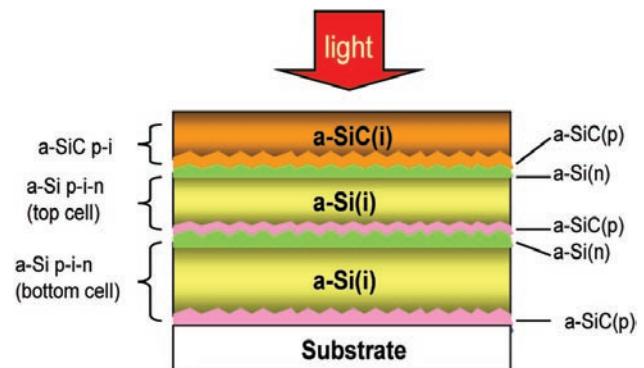


**FIGURE 1.** Scanning electron microscopy micrograph of WO<sub>3</sub> film treated with RuO<sub>2</sub> nanoparticles. The resulting 3-5 nm particles cover approximately 35% of the total area.

with sulfur can modify the band edges as well. Samples of CIGS (with sulfur completely replacing selenium) provided by Bjorn Marsen at the Helmholtz Zentrum Berlin matched the photocurrent of champion CGSe films (~20 mA/cm<sup>2</sup>) while reducing the required voltage bias by nearly 200 mV, a marked improvement. Further material characterization is needed to fully understand these new materials.

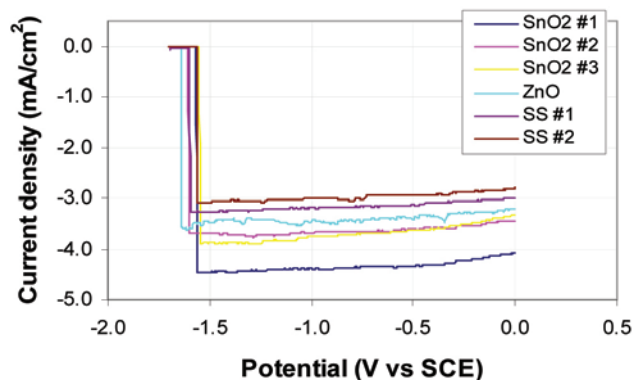
### Amorphous Silicon Carbide-Based Compound Films

During this project period, significant progress has been made in the study of a-SiC photoelectrodes used in water splitting for hydrogen production. We have successfully integrated the a-SiC photoelectrode with a-Si tandem solar cell to form a hybrid PEC cell. Figure 2 shows the configuration used for the hybrid PEC device, consisting of an a-Si:H tandem solar cell (thickness of the top and bottom cell is 80 nm and 360 nm respectively) and a-SiC:H photoelectrode which contains an intrinsic a-SiC (~100 nm thick) and a thin p-type a-SiC:B layer (~10 nm thick). The substrate used for the hybrid PEC device was typically fluorine doped tin oxide (Asahi U- type) coated glass. Other types of substrates such stainless steel (SS) and zinc oxide (ZnO) coated glass were also used for comparison purposes. The a-Si:H tandem solar cell which was used in the hybrid PEC device exhibited V<sub>oc</sub> (open-circuit voltage) = 1.66 V, J<sub>sc</sub> (short-circuit current density) = 8.7 mA/cm<sup>2</sup>, fill factor (FF) = 0.67, and efficiency of ~9.6%. The flat-band potential of the hybrid PEC cell in a pH2 electrolyte, as determined by the illuminated open-circuit potential method, shifts significantly from +0.26 V (vs. Ag/AgCl) to +0.97 V below the H<sub>2</sub>O/O<sub>2</sub> half-reaction potential and is in an appropriate position to facilitate water splitting. Figure 3 shows the current density vs. potential characteristics for hybrid PEC device fabricated on different substrates, including SnO<sub>2</sub> and ZnO coated glass as well as SS, and measured in the pH2 buffered electrolyte (sulphamic acid solution with added potassium biphthalate) using the 3-electrode. We



**FIGURE 2.** Configuration of the Hybrid PEC Device





**FIGURE 3.** Current Density vs. Potential Characteristics of the PV/a-SiC PEC Devices.

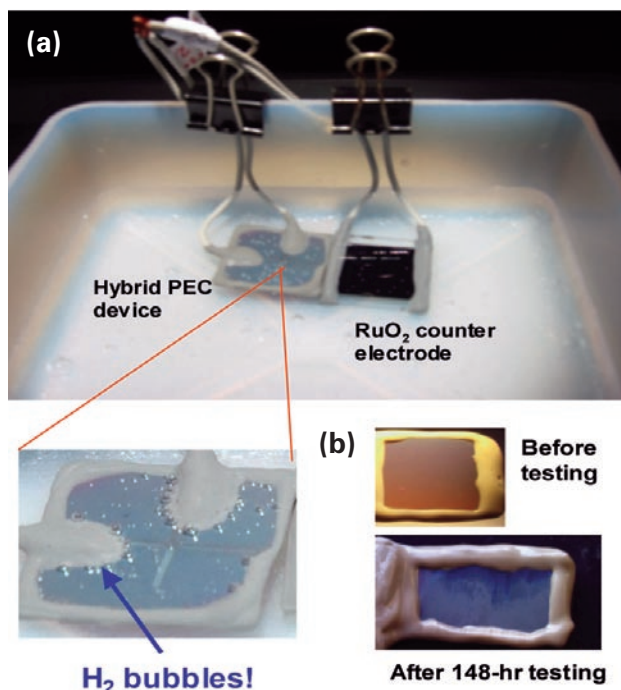
see that the saturated photocurrent of the hybrid cell using different substrates is in the range of 3-5 mA/cm<sup>2</sup>, potentially leading to a STH efficiency of ~5.5%. The larger photocurrent on SnO<sub>2</sub> (>4 mA/cm<sup>2</sup>) coated glass substrate is due to the inherent texture of the SnO<sub>2</sub> which enhances internal photon absorption.

The photocurrent density at a zero potential reaches ~1 mA/cm<sup>2</sup> measured using the 2-electrode setup (not shown here). Hydrogen production was observed in short-circuit condition, as shown in Figure 4(a). It should be noted that compared with the 3-electrode case, the photocurrent measured in the 2-electrode setup is much lower, suggesting limiting factors. We have noted that the over-potential loss in the 2-electrode setup can be due to, (1) type of electrolyte used, (2) type of counter electrode used and (3) formation of thin SiOx layer on the a-SiC surface. Initial results have shown that, after dipping the hybrid device into 5% hydrofluoric acid for 30 seconds and using RuO<sub>2</sub> as the counter electrode, the photocurrent is enhanced from 0.33 to 0.83 mA/cm<sup>2</sup> at zero bias.

The hybrid PEC cell exhibits good durability in the pH2 buffered electrolyte for up to 148 hours (so far performed). The dark current shows almost no change, and hence no corrosion occurring on the hybrid device after the 148-hr test, as is evident also in Figure 4(b).

## Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO<sub>3</sub> and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performances. This knowledge can be applied to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performances. New surface modification techniques were investigated, including



**FIGURE 4.** (a) Demonstration of hydrogen evolution in the hybrid PEC device, measured in the short-circuit condition. (b) Photo images of the hybrid PEC device prior to and after a 148-hr test in pH2 electrolyte.

oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO<sub>3</sub>). Bulk modifications were investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using UNLV advanced spectroscopic techniques. This new information will guide our research on device fabrication and device matching efforts effectively.

## FY 2009 Publications/Presentations

1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight*, Phil. Mag. B85, (2009) 1-16.
2. J. Hu, I. Matulionis, F. Zhu, J. Gallon, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, and A. Madan, Development of a photovoltaic (PV)/photoelectrochemical (PEC) hybrid device with amorphous silicon carbide as the photoelectrode for water splitting, MRS spring meeting, San Francisco, 2009.
3. F. Zhu, J. Hu, I. Matulionis, A. Kunrath, and A. Madan, *Properties of Nano-crystalline Silicon-Carbide Films Prepared Pulse Using Modulated RF-PECVD*, MRS spring meeting, San Francisco, 2009.
4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting*, MRS spring meeting, San Francisco, 2009.

5. N. Gaillard, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Surface Modification of Tungsten Oxide-Based Photoanodes for Solar-Powered Hydrogen Production*, MRS spring meeting, San Francisco, 2009.
6. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Improved current collection in  $WO_3$ :Mo/ $WO_3$  bilayer photoelectrodes*, to be published in Journal of Material Research.
7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, to be published in Sol. Energy Mater. and Sol. Cells.