

II.G.8 Progress in the Study of Tungsten Oxide Compounds as Photoelectrodes in Photoelectrochemical Cells

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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-chalcopyritecompound 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 Fuel Cell 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-H₂ plant production cost by 2010 and \$5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. Progress Towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production with Tungsten Oxide-Based Compound Films.

Task #	Milestone	Note
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved
	Durability ≥ 100 hours	Achieved
Year 2	Material photocurrent ≥ 4 mA/cm ²	90% (3.6 mA/cm ²) with bilayer
	Durability ≥ 200 hours	50% (100-hours so far tested)
	Device STH efficiency $\geq 5\%$	62% demonstrated
GO/NO-GO decision evaluated (End of 2010)		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

Accomplishments

- Foreign element incorporation into WO₃ lattice using house-made sputtering targets.
- Successful fabrication of RuO₂ nanoparticles and nanorods onto tungsten oxide thin films with improved catalytic activity (up to 20%).
- Evaluation of new integration using highly textured substrates to increase photocurrent density.



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 will be put 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 greater than 6 mA/cm² 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 CIGSe₂, CGSe₂, etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D effort. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is also included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been also in development for incorporation in PEC photoelectrode designs (i.e., the hybrid photovoltaic [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 of the project (June 2009–June 2010), 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. Specific progress in developing tungsten oxide-based compound films is detailed in the following subsections.

In our general approach, each component of the PEC electrode is addressed, from the absorber (bulk) to the surface energetics (near-surface) and catalysis (surface). This year, progress was achieved toward foreign element incorporation to reduce tungsten oxide bandgap. Here, we proposed to fabricate in our laboratory our own sputtering targets made of blended powders. With this method, the amount of both WO₃ and foreign elements can be easily controlled, leading to a much easier elaboration process when compared to co-sputtering techniques. Preliminary tests were done with WO₃ nanopowder only. After compaction and sintering at 1,200°C for 3 hours, the solid WO₃ body (2-inch diameter disc) was transferred to the sputtering chamber and several depositions were performed. Initial results indicated that WO₃ optoelectronic properties (optical transmission and bandgap) were easier to control when compared to initial process where a pure tungsten target is used. Photo-electro-chemical tests pointed out also that comparable performances were obtained with this method. In a second phase, powder blends were sintered to form new sputtering targets. Since nitrogen has been evaluated as possible foreign element candidate to decrease WO₃ bandgap, our research was initially focused on nitride-based powder. A top-view scanning electron microscopy (SEM) micrograph of a WO₃/BN (95 wt%/5 wt%) is presented in Figure 1. Again, a very good powder sintering is observed (coalesced grains), leading to a solid body. Depositions of WO₃:BN materials are currently being performed to define optimum process parameters.

Research on tungsten oxide surface catalytic treatment continued and major improvements on RuO₂ nanoparticles and nanorods synthesis were achieved. Preliminary research in our laboratory on reactively sputtered RuO₂ thin films already demonstrated high catalytic activity for oxygen evolution reaction, where O₂ was generated with overpotential as low as 0.2 V. Nanoparticles (4-8 nm in diameter) were synthesized on WO₃ thin film using similar reactive sputtering process (Ru pure target, O₂/Ar ambient, 250°C). Current vs.



FIGURE 1. Top-view SEM micrograph of a sintered sputtering target made of WO_3 (round grains) and BN (plates). The weight ratio is 95%/5%, respectively.

voltage characteristics measured on WO_3 PEC electrode covered or not with RuO_2 nanoparticles are presented in Figure 2. No modification of both the dark current and saturated photocurrent was observed in this experiment. However, one can notice that the presence of RuO_2 nanoparticles on WO_3 thin films yield a better “fill-factor” when compared to the WO_3 witness sample, with a photocurrent increase of about 20% at 1.2 V vs. the saturated calomel electrode. Current research is focused on ruthenium oxide nanorods (120 nm long, 20 nm wide) synthesis. It is believed that extended contact area between nanorods and the electrolyte could improve charge carriers injection at the WO_3 /electrolyte interface.

Finally, the possible use of highly textured substrates (HTS) in PEC applications to increase the photocurrent density was evaluated in our laboratory. With this technique, the developed area is expected to be larger than the projected one, increasing the overall photocurrent density (normalized to the sample area). HTS used were obtained by anisotropic etching of silicon wafers using potassium hydroxide (KOH) solution. Because of orientation-dependant etching ($\{110\} > \{100\} > \{111\}$), KOH treatment leads to a textured Si substrate made of pyramids with base width ranging from 5 to 20 μm . Tungsten oxide was then deposited on HTS using reactive sputtering technique. Figure 3 presents a cross-section SEM micrograph of one of this sample. The PEC performances of WO_3 thin films deposited on HTS are presented in Figure 4. Also presented in this graph are the PEC performances measured on a WO_3 deposited on flat silicon substrate (control sample). To allow a direct comparison, photocurrent density values were normalized to the maximum photocurrent density measured in the case of a flat silicon substrate at 2.5 V vs. SCE. First, one can

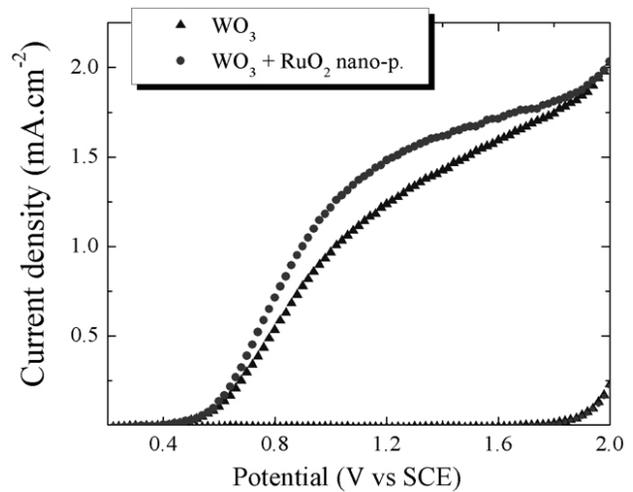


FIGURE 2. Current vs. voltage characteristics measured under simulated AM1.5_G illumination (3-electrode configuration, 0.33M H_3PO_4) on WO_3 samples covered (grey circles) or not (black triangles) with RuO_2 nanoparticles.

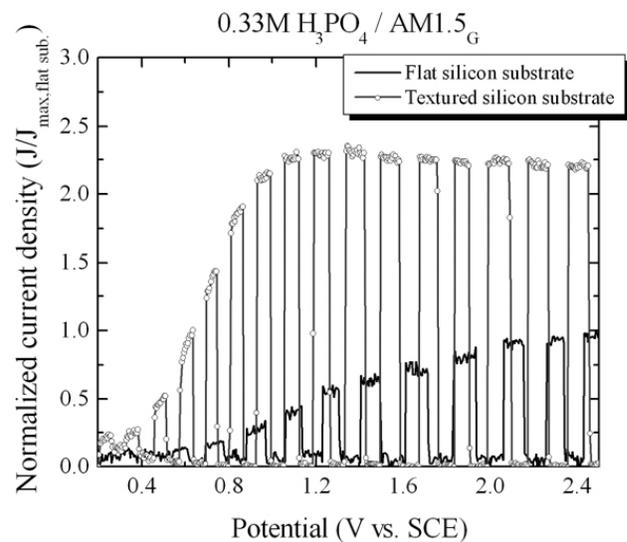


FIGURE 4. Current vs. voltage characteristics measured in 0.33 M H_3PO_4 under AM1.5_G illumination on tungsten oxide thin films deposited on flat and textured silicon substrates.

directly observe the net photocurrent density increase when HTS are used. It is also interesting to note that a higher fill factor is achieved with HTS. Thus, it is believed that, in addition to the geometric factor, the HTS enable better harvesting of incoming normal irradiance, either by limiting the surface reflection or simply by increasing the optical path in the tungsten oxide thin film.

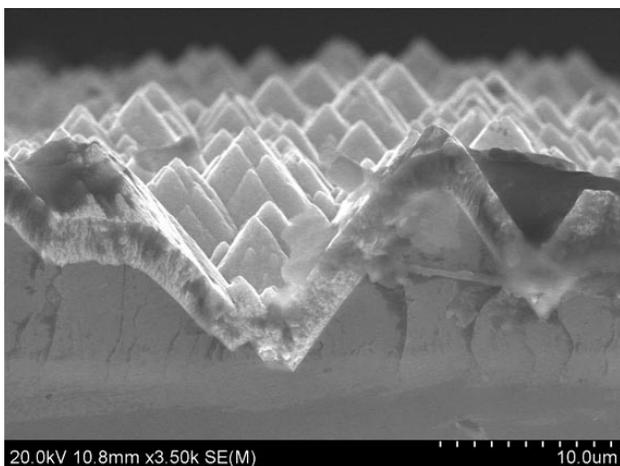


FIGURE 3. Cross-section SEM micrograph of a WO_3 ($2\ \mu\text{m}$) thin film deposited on a textured substrate.

Conclusions and Future Directions

This project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO_3 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 to apply them to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performance. New surface modification techniques were investigated, surface treatments (a-SiC, CGSe, WO_3), bilayer formation (WO_3) and new device integration schemes (CGSe and WO_3). Bulk modifications were also investigated, such as partial copper replacement with silver to form ACIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2010 Publications/Presentations

1. Ilvydas Matulionis, Jian Hu, Feng Zhu, Josh Gallon, Nicolas Gaillard, Todd Deutsch, Eric Miller, and Arun Madan, “*Surface modification of a-SiC:H photoelectrodes for photocurrent enhancement*,” to be presented at SPIE, San Diego, August, 2010.
2. Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan “*The Potential of Using a-SiC:H as the Photoelectrode for Water Splitting*”, presented at NHA hydrogen conference and Expo., Long beach, CA, May 3–6, 2010.
3. Book chapter :“Solar Energy”: Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan, “*Amorphous Silicon Carbide Photoelectrode for Hydrogen Production from Water using Sunlight*” , edited by: Radu D. Rugescu, ISBN 978-953-307-052-0, pp. 432, February 2010, INTECH.
4. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E. 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*, J. Mat. Res. **25** (2010) 45.
5. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, Sol. Energy Mater. and Sol. Cells. **94** (2010) 12-16.