II.F.9 Photoelectrochemical Hydrogen Production: UNLV-SHGR Program Subtask*

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University of Hawaii at Manoa, Honolulu, HI
MVSystems, Golden, CO
Intematix Corp., San Jose, CA

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*Congressionally directed project

Objectives

- To assist DOE in the development of technology to produce hydrogen using solar energy to photoelectrochemically split water.
- To focus specifically on developing multijunction thin film "hybrid photoelectrode" devices using metal oxides and other low-cost materials for use in practical hydrogen production systems.

Technical Barriers

This project addresses the following technical barriers from the "Photoelectrochemical Hydrogen Production from Water" section (3.1.4.2.6) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AP) Materials Efficiency
(AQ) Materials Durability
(AR) Bulk Materials Synthesis
(AS) Device Configuration Designs

Technical Targets

This project entails fundamental materials and device studies related to the development of multi-junction thin-film "hybrid photoelectrodes" (HPE) for photoelectrochemical hydrogen production. Insights gained from these studies will be applied toward the design and synthesis of HPE-based systems that meet the DOE 2010 production targets (shown in Table 1), for efficiency, durability and cost. Specific intermediate goals toward reaching the longer-term targets include:

TABLE 1. DOE Technical Targets Pertinent to this Project

Technical Targets: Photoelectrochemical Hydrogen Production				
Characteristics	**Units**	**2003 Status**	**2010 Target**	**2015 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)	%	Not available	8	10
Plant durability	hr	Not available	1,000	5,000

- Developing low temperature tungsten trioxide (WO_3) thin films for photoactive PEC interfaces
  - Target: 1.6 mA/cm^2 minimum photocurrent under air mass (AM) 1.5 illumination
- Demonstrating "hybrid photoelectrode" devices incorporating WO_3 and amorphous silicon films
  - Target: 2-4% solar to hydrogen (STH) efficiency under AM 1.5 illumination
- Exploring avenues, utilizing combinatorial discovery with bulk film research techniques, toward reduced band-gap material (e.g., modified WO_3) for higher photocurrents and enhanced STH efficiency in future devices
- Exploring avenues toward manufacture-scale devices utilizing reel-to-reel vacuum deposition and other fabrication techniques

Accomplishments

- Low temperature reactively-sputtered WO_3 films developed with 3.4 mA/cm^2 photocurrents
  - Optimization of reactive-sputter process parameters

  - Comprehensive materials characterization to enhance understanding
  - Initial work on bandgap reduction through nitrogen- and sulfur-doping
- "Hybrid Photoelectrode" devices based on WO_3 demonstrated with 3.1% STH efficiency
  - Mechanically-stacked device using amorphous silicon tandem photovoltaic (PV) cell (custom designed at MVSystems Inc.)
  - Fabrication technique for fully-integrated device in development
- Rapid throughput bandgap screening technique demonstrated to facilitate materials discovery
  - Laser modulated differential spectroscopy (LMDS) technique (developed at Intematix Corp.)
  - LMDS successfully demonstrated on WO_3 films (undoped & sulfur-doped)
- Scaled-up fabrication technology demonstrated
  - Patented process using reel-to-reel cassettes in a vacuum cluster tool installed at MVSystems Inc.
  - Demonstration of HPE component film fabrication in cluster tool system

Introduction

The primary objective of this research project has been to accelerate the research and development of stable and efficient photoelectrochemical (PEC) hydrogen-production systems. Specific project targets have included: (1) the development of a low-temperature (<300°C) fabrication technique for synthesizing high-performance PEC-compatible tungsten-trioxide (WO_3) films; (2) demonstration of 2-4% solar-to-hydrogen (STH) conversion efficiency in a "hybrid photoelectrode" (HPE) system incorporating the developed WO_3 materials; (3) the initiation of combinatorial-discovery experiments to aid in the identification of promising new bandgap-reduced PEC materials; and (4) the identification of commercialization paths toward cost targets set forth by the U.S. Department of Energy (DOE).

The primary performance-determining component of an HPE device is the photocatalyst material, for example, WO_3. There are several important aspects to its function in a solar water-splitting device: (1) it serves as the first photoactive layer, absorbing a significant fraction of the incident light; (2) it forms the photoelectrochemical junction with the electrolyte; and (3) it facilitates the front surface gas-evolution reaction, e.g., the oxygen evolution reaction in the case of a metal-oxide photoanode. The candidate material has to have adequate light absorption over solar wavelengths, and high photo-generated carrier collection efficiency. It also needs to be stable in suitable aqueous electrolytes, and it needs to show favorable kinetics for the electrode reaction. An additional requirement for hybrid photoelectrode integration is process-compatibility of the photocatalyst deposition method with all other fabrication steps. Low temperature processing (e.g., below 300°C) is critical in this regard.

Approach

In order to meet short-term project goals while addressing longer-term objectives, we pursued several avenues of materials research organized in specific materials R&D sub-tasks, including: the development of a process-compatible thin-film PEC material for immediate prototype integration to show the feasibility of the hybrid photoelectrode concept, combinatorial discovery of new compounds with lower bandgap to meet the longer term goals (performed at Intematix), and development of technology for process scale-up focusing on utilizing thin-film cluster tool systems with reel-to-reel cassette technology (developed at MVSystems).

For the purpose of HPE demonstration we selected reactively-sputtered tungsten trioxide as a model PEC thin-film material. In previous studies WO_3 films have exhibited promising opto-electronic and photoelectrochemical properties, as well as corrosion resistance in an acid electrolyte [1]. In addition, the reactive-sputtering process offers great versatility for material engineering, and is compatible with cluster tool systems for process scale-up. Importantly, it has been established that the WO_3 bandgap (nominally 2.6 eV) could allow for conversion efficiencies up to 5% STH, meeting the short-term project target [2]. For further efficiency improvements toward the longer-term goals, bandgap reduction remains the critical focus of ongoing materials research. To this end we have initiated an activity of combinatorial discovery for reduced bandgap metal oxide semiconductors. Using "pure" WO_3 as a starting point, this methodology will be used to evaluate an expanded class of metal oxide alloys for potential use in PEC junction devices. To enable this discovery, the development of additional characterization tools allowing rapid determination of bandgap and other pertinent material properties was required.

Results

As a result of project efforts, significant progress has been made in the PEC materials research, and in HPE device demonstration. Specifically, optimization of WO_3 films reactively-sputtered at 275°C has resulted in the demonstration of PEC photocurrent levels up to 3.4 mA/cm^2 under simulated sunlight; and a stacked HPE device based on the developed WO_3 integrated with customized PV components (i.e., tandem amorphous silicon devices fabricated on stainless-steel foil) have been operated at 3% STH, meeting the short-term target. Also, rapid-throughput bandgap screening methods were developed and demonstrated to assist in the combinatorial-discovery of reduced-bandgap compounds (for example, doped WO_3); and process scale-up techniques were demonstrated for the relevant PV and PEC material layers. Further details of these specific accomplishments follow:

Tungsten Trioxide PEC Material Optimization

The two representative sample photocurrent curves in Figure 1 show the advancement in sputtered WO_3 film performance from the beginning of the project in late 2004 through the end of 2005. It should be emphasized that the hydrogen production rate in a PEC system is proportional to the operating photocurrent, which is primary motivation for optimizing this characteristic. The significant increase in photocurrent at 1.6 V vs. saturated calomel electrode (SCE), from 1.1 mA/cm^2 in the early sample, to 3.4 mA/cm^2 in the later optimized sample, has been made possible through optimization of the sputter deposition process.

The increased performance has been specifically tied to the WO_3 film structure and properties, which are in turn determined by the sputter process parameters. We have established that stoichiometry and microstructure, which can vary significantly depending on the sputter parameter set, have major impact on all other properties of tungsten oxide films. For example, sub-stoichiometric films (WO_{3-x}) show higher conductivity and increased free-carrier absorption in the near-infrared compared to fully stoichiometric ones, but most importantly, reduced photocurrents. On that basis, we have tuned our process for the synthesis of fully stoichiometric films by increasing the oxygen partial pressure during deposition. Within this constraint, other process variables, such as substrate temperature and deposition rate, remain significant to film optimization.

A critical scientific advancement was the establishment of film crystallinity as a key determinant for the photoelectrochemical performance. Depending on the processing parameters, films would form in either the polycrystalline or amorphous phase. A comparison of x-ray diffraction data and the corresponding photocurrents for several films, as shown in Figure 2, revealed that amorphous films (A) had the lowest performance, while large-grained polycrystalline films (C) the highest. Polycrystalline samples with smaller grain sizes (B) showed intermediate performance. The

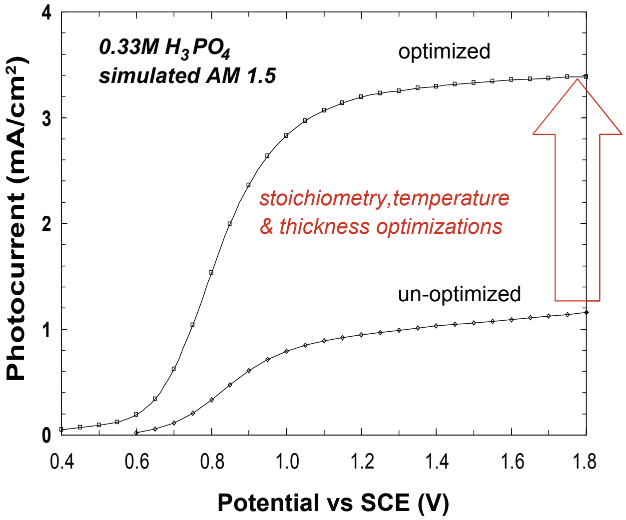

FIGURE 1. Photocurrent vs. Potential for Un-Optimized (2004) and Optimized (2005) WO_3 Samples

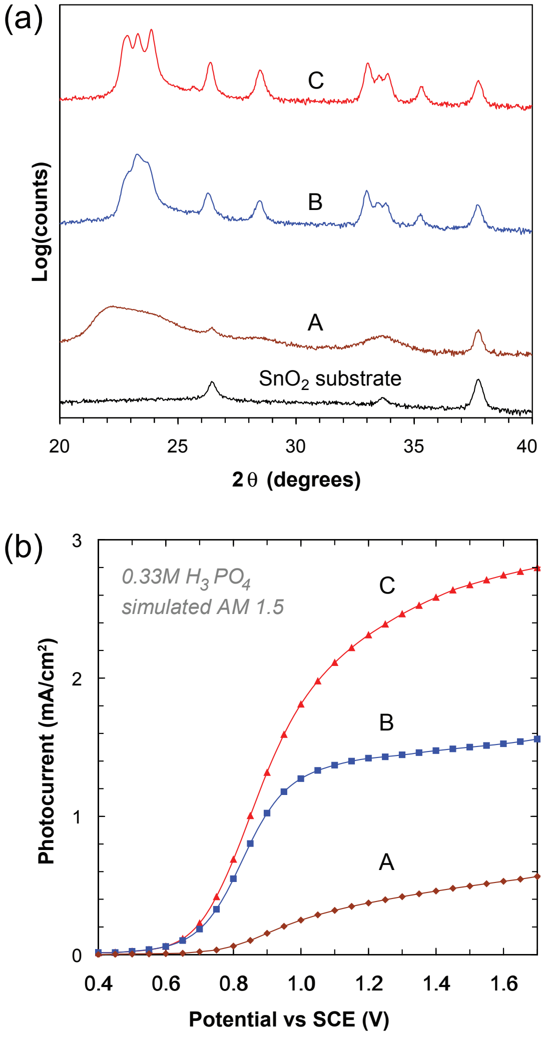

FIGURE 2. Correlation of Microstructure And Photocurrent Performance for WO_3 Films: (a) X-Ray Diffraction Data for Three Samples Prepared under Different Conditions; (b) Photocurrent-Vs-Potential Data for the Same Three Samples

substrate temperature during deposition was the most significant variable that determined the crystallinity of the samples. The highest-performance samples were produced at a substrate temperature of ~275°C, which is substantially reduced compared to the 500-600°C processing inherent to other WO_3 film fabrication techniques.

Hybrid Photoelectrode Device Demonstration

In addition to the basic materials research, the integration of the developed photocatalyst films with thin-film photovoltaic components into functional HPE devices was an important objective of this work. For this purpose, amorphous silicon PV devices with compatible characteristics and adequate performance needed to be developed. Custom amorphous silicon films deposited on both glass and metal substrates were fabricated (MVSystems), characterized and optimized for incorporation into the HPE. For HPE device completion, the tungsten oxide layer is sputtered onto the top contact of the underlying solar cell. Viewing the HPE device as a series circuit of the PEC and PV components, the overall performance can be modeled as illustrated in Figure 3. For the customized component films represented in the figure, the predicted integrated device efficiency is 3% STH based on the photocurrent operating point. This represents a considerable improvement over results from 2004 where the best WO_3 films could support a conversion efficiency of only ~1.5% STH, and a significant improvement over the 0.7% STH HPE devices demonstrated in 2003. In validation of the analytical predictions, fully functioning devices were assembled via mechanical stacking of WO_3 top layers over underlying amorphous silicon solar cell, as shown in Figure 4a. The PEC and PV component layers were tested individually, then stacked as a completed HPE device for performance evaluation. Consistent with model results, the HPE devices operated at 3.1% STH (shown in Figure 4b), meeting the 2-4% STH target.

Combinatorial Discovery Methodologies:

As part of this project, a combinatorial discovery approach was developed in conjunction with Intematix Corp. for generating libraries of promising new PEC material classes. Starting with tungsten oxide as a baseline, initial libraries based on alloying tungsten with molybdenum and substituting sulfur for oxygen were generated to explore band-edge optimization for water splitting. In conjunction with the combinatorial synthesis work, Intematix specifically developed the laser modulation differential spectroscopy (LMDS) technique for rapidly probing bandgap across compositionally-graded samples. Figure 5 shows the LMDS signal of a pure (i.e., undoped) sputtered WO_3 sample compared to a WO_3 sample doped with sulfur. The measured bandgap of ~2.85 eV for the pure sample closely correlates with standard optical transmission/reflectance techniques based on Tauc analysis, validating the LMDS method. Interestingly, in the sulfur-doped sample, two bandgaps are detected via LMDS: one at 2.45 eV (corresponding with the introduction of mid-gap states), and another at 3 eV (likely corresponding to highly

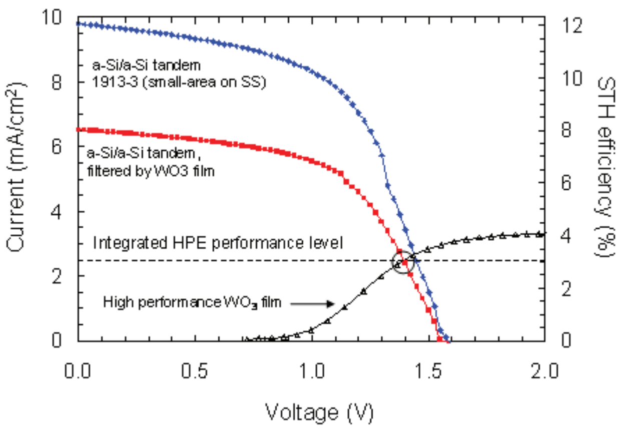

FIGURE 3. Predicted Performance for an HPE Device Incorporating Optimized WO_3 Films with customized Amorphous Silicon Tandem Device

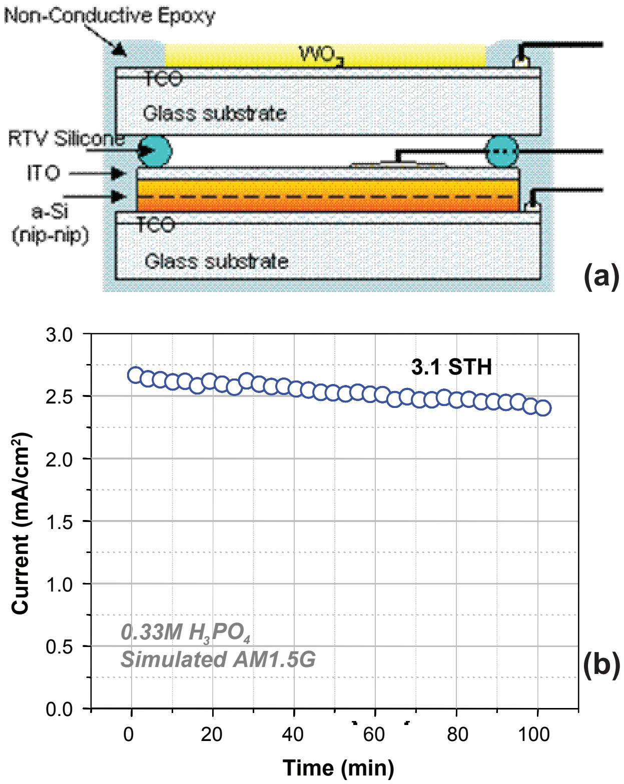

FIGURE 4. Experimental Validation of HPE Device Performance: (a) Assembly of an HPE Mechanical Stack; (b) Photocurrent and Efficiency Results for the HPE Stack

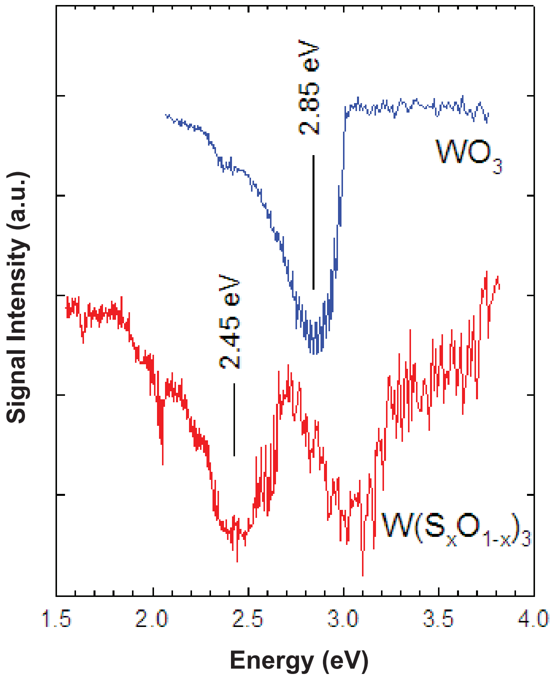

FIGURE 5. LMDS Features Associated with the Band-Gap Transitions in $W(S_xO_{1-x})_3$ and WO_3, Indicating a Band-Gap Reduction in $W(S_xO_{1-x})_3$ as Compared to WO_3

amorphous WO_3). This effect is potentially significant to the development of bandgap-reduced materials, and merits further investigation.

Process Scale-Up

As part of this project, MVSystems has implemented the scaled-up fabrication of HPE device component films using their large cluster tool. Amorphous silicon and WO_3 films, as well as monolithic HPE devices, have been successfully fabricated in this environment, demonstrating the feasibility of volume production (specifically in conjunction with MVSystem's patented "reel-to-reel" cassette technology). Process optimization of the cluster-tool fabrication remains an issue. Specifically, the optimization of cluster-tool process parameters for depositing high-quality PEC films (such as WO_3) will require significant additional effort.

Conclusions and Future Directions

1. All major technical targets in the development of WO_3-based PEC materials/devices were met during this phase of the project. Low temperature reactively-sputtered WO_3 films were developed with 3.4 mA/cm^2 photocurrents, exceeding the 1.6 mA/cm^2 target, and "hybrid photoelectrode" devices based on these films have demonstrated 3.1% STH efficiency, meeting the 2-4% target.
2. To meet longer-term DOE goals of 10-12% STH efficiency in PEC H_2 production systems, cost-effective semiconductor materials with reduced band-gaps (less than approximately 2.4 eV) need to be discovered and developed. In addition to the band-gap criteria, optical absorption, band-edge alignment, surface catalytic activity, electronic transport, and photoelectrochemical stability all need to be optimized in the new materials.
3. Future work will focus on expanded collaborations to accelerate the materials discovery process based on coordinated theoretical and experimental activities.

Special Recognitions & Awards/Patents Issued

1. E. Miller & R. Rocheleau, "Hybrid Solid-State/Electrochemical Photoelectrode for Hydrogen Production": patent 6887728 issued on 05/03/05.

FY 2006 Publications/Presentations

Journal Publications

1. E. Miller, B. Marsen, B. Cole , M. Lum, "Low-Temperature Reactively-Sputtered Tungsten Oxide Films for Solar-Powered Water Splitting Applications", *Electrochemical and Solid-State Letters* 2006, 9, G248.

2. B. Marsen, E. Miller, D. Paluselli, R. Rocheleau, "Progress in Sputtered Tungsten Trioxide for Photoelectrode Applications", *International Journal of Hydrogen Energy,* 2006 in press.

3. E. Miller, B. Marsen, D. Paluselli, R. Rocheleau, "Optimization of Hybrid Photoelectrodes for Solar Water Splitting", *Electrochemical and Solid-State Letters,* 2005, 8, A247-249.

Conference Presentations

1. 2005 IPHE Renewable Hydrogen Workshop, Seville Spain. E. Miller: "Photoelectrochemical Hydrogen Production" Symposium Co-chair.

2. 2005 XIV-IMRC Materials Conference, Cancun Mexico. B. Marsen: Oral Presentation- "Progress in Sputtered Tungsten Trioxide for Photoelectrode Applications".

References

1. E. Miller, B. Marsen, B. Cole , M. Lum, "Low-Temperature Reactively-Sputtered Tungsten Oxide Films for Solar-Powered Water Splitting Applications", *Electrochemical and Solid-State Letters* 2006, 9, G248.

2. E. Miller, B. Marsen, D. Paluselli, R. Rocheleau, "Optimization of Hybrid Photoelectrodes for Solar Water Splitting", *Electrochemical and Solid-State Letters,* 2005, 8, A247-249.