IV.F Photoelectrochemical

IV.F.1 High-Efficiency Generation of Hydrogen Using Solar Thermochemical Splitting of Water - UNLV: Photoelectrochemical Hydrogen Production Subtask at UH

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Subcontractors:
University of Hawaii at Manoa, Honolulu, HI
MVSystems Incorporated, Golden CO
Intematix Corporation, Fremont, CA

Start Date: October 1, 2004
Projected End Date: December 31, 2005

Objectives

- To assist DOE in the development of technology to produce hydrogen using solar energy to photoelectrochemically split water
- Specific focus on developing multi-junction 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 Hydrogen Production section 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 Design

Technical Targets

This project is conducting fundamental materials and device studies related to the development of a multi-junction thin-film "Hybrid Photoelectrode" (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, especially efficiency, durability and cost. Specific goals toward reaching the longer-term targets include:

- Develop low-temperature tungsten trioxide (WO_3) thin-film material with photocurrents exceeding 1.6 mA/cm^2 under Air Mass 1.5 Solar Illumination (AM 1.5 light)
- Demonstrate functional HPE device based on WO_3 and amorphous silicon active films with solar-to-hydrogen (STH) conversion efficiency exceeding 2% (based on the lower heating value of hydrogen) under AM 1.5 illumination
- Explore avenues toward reduced-bandgap WO_3 for higher photocurrents and enhanced STH conversion potential, utilizing combinatorial discovery with bulk film research techniques
- Explore avenues toward manufacture-scaled devices utilizing vacuum deposition systems with reel-to-reel cassette technology and other fabrication techniques

Approach

The research approach focuses on the development of component technologies for the HPE – a thin-film multi-junction monolithic photoelectrode for direct water splitting patented by the University of Hawaii (UH). Specific research and development areas within this approach include:

Level 1: Advanced Materials Research & Development

- Development of low-temperature sputtered WO_3 photoactive films
- Combinatorial discovery of photoactive WO_3 compounds *(Intematix)*
- Comparative evaluation of available pyrolytic photoactive oxides
- Theoretical studies of oxide materials for bandgap engineering

Level 2: Data Acquisition and Analysis

- Integrated hybrid photoelectrode design, fabrication and testing
- Hybrid photoelectrode performance certification
- Production of customized photovoltaic devices for HPE *(MVSystems)*

Level 3: Concept Design and Analysis

- Process scale-up studies *(MVSystems)*
- Cost and profitability estimates

Accomplishments

- Low-temperature reactively sputtered WO_3 films with photocurrents exceeding 2.5 mA/cm^2 demonstrated
- HPE design based on high-performance WO_3 completed
- Fabrication of first prototype HPE based on high-performance WO_3 completed in September 2005 with best results ~1% STH (compared with the expected 2-3%)
- Degradation in amorphous silicon tandem device identified as the efficiency limiting factor in first prototype batch.
- Plans to address the silicon degradation mechanism initiated with MVSystems.
- Fabrication of additional prototype HPE batches based on the improved silicon tandems planned for November.
- Rapid-throughput bandgap screening technique developed
- Fabrication technology selected for initial scaled-up cost analysis

Future Directions

Remaining work for 2005

- Fabricate, test and pursue certification of HPE device using best available WO_3 material with matched amorphous silicon (a-Si) tandem sub-layer; 2.2% STH conversion efficiency expected
- Improve repeatability of current WO_3 deposition process
- Demonstrate bandgap screening technique in doped WO_3 films
- Propose materials discovery and development plan for next step in STH efficiency (4-7%)
- Prepare basic cost analysis for device production based on available large-area fabrication techniques

Future work (contingent upon available funding)

- Implement materials discovery and development plan to reach next step in STH efficiency (4-7%)
- Continue development of new materials & material systems
- Continue 'team-building' efforts in PEC research community to accelerate R&D

Introduction

Under the sponsorship of the U.S. Department of Energy (DOE), the University of Hawaii (UH) has been developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes based on low-cost semiconductor, catalytic, and protective thin films [1]. In an attempt to meet the DOE cost and performance goals, UH has been concentrating on the development of a "Hybrid Photoelectrode" which incorporates low-cost metal-oxide and photovoltaic-grade semiconductor thin films [2], as described in the following section.

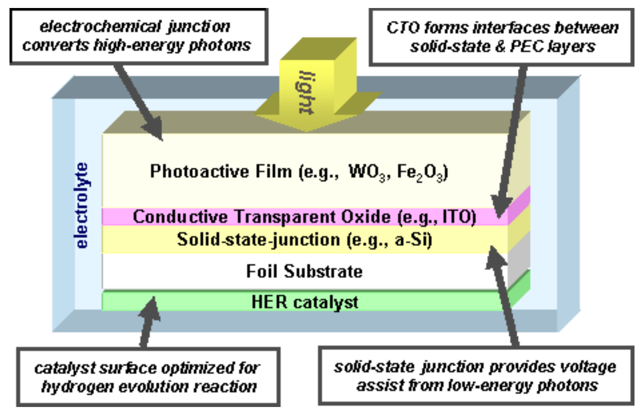

Figure 1. The multi-junction "Hybrid Photoelectrode" structure, showing constituent thin-film layers. Photons are absorbed both at the metal-oxide/ electrolyte interface and at the buried solid-state junction to generate sufficient voltage to split water. ITO = indium tin oxide.

Approach

The UH research approach focuses on the development of its patented HPE, a thin-film multi-junction monolithic photoelectrode device structure for direct solar water splitting. HPE technology, as illustrated in Figure 1, incorporates low-cost materials such as metal foil substrates, as well as amorphous silicon and metal-oxide thin films, and utilizes scalable fabrication processes for commercial manufacturability. This year's work has focused on tungsten-oxide (WO_3) based HPE devices using buried amorphous silicon (a-Si) tandem cells [3]. Specific research and development areas include 1) advanced materials R&D relating to WO_3 as well as the various other HPE constituent thin films; 2) design, fabrication and testing of HPE prototype devices using best available materials; and 3) initial process scale-up studies for production of practical HPE systems.

The critical focus of the materials R&D effort has been the development of low-temperature sputtered WO_3 photoactive films for use in the HPE prototypes. Additional materials research includes the combinatorial discovery of photoactive WO_3 compounds with reduced bandgap for higher STH efficiency (performed at Intematix), and experimental studies of bandgap reduction through nitrogen doping of bulk WO_3 sputtered films. The HPE prototype demonstration work entails photoelectrode design based on the best available

WO_3 sputtered films; production of customized photovoltaic (PV) devices for the HPE buried layers (performed at MVSystems), and prototype device completion (outer WO_3 sputtered layer fabricated at UH) and testing. The process scale-up studies focus on utilizing thin-film cluster-tool systems with reel-to-reel cassette technology developed at MVSystems.

Results

Through May of 2005, the most significant progress was made in the materials research and development of photoactive WO_3 films fabricated via low-temperature reactive-sputtering techniques. Additional progress was made in subtasks relating to HPE prototype design, fabrication and testing; combinatorial discovery of reduced-bandgap WO_3 compounds; and process scale-up studies.

The most significant progress was made in the optimization of low-temperature (<250° Celsius) reactively sputtered tungsten trioxide films for incorporation into HPE devices. Continued adjustment and refinement of process parameters have produced the highest-performing WO_3 samples to date, with photocurrents up to 2.8 mA/cm^2, as seen in Figure 2a (curves D and E). These levels exceed the photocurrents reported for high-temperature pyrolytic WO_3 samples from U Geneva [4], which, to our knowledge, represent the highest published results for tungsten oxide films. For comparison, the performance of baseline sputtered films from the start of this project is included in Figure 2a (curve A). In conjunction with the film optimization process, characterizations were performed on a number of sample films with differing photocurrent levels to better understand the factors influencing performance. In the X-ray diffraction (XRD) spectra shown in Figure 2b for the sample films in Figure 2a, there is a clear correlation between PEC performance and XRD peak definition, indicating an important link between photoactivity and film microstructure. Further investigative techniques, including atomic force microscopy, cross-sectional scanning electron microscopy, and others, are being employed to shed additional light on the current observations. Also, there is ongoing work to address remaining issues in the repeatability of the reactive sputter deposition process for high-photocurrent un-doped WO_3, and

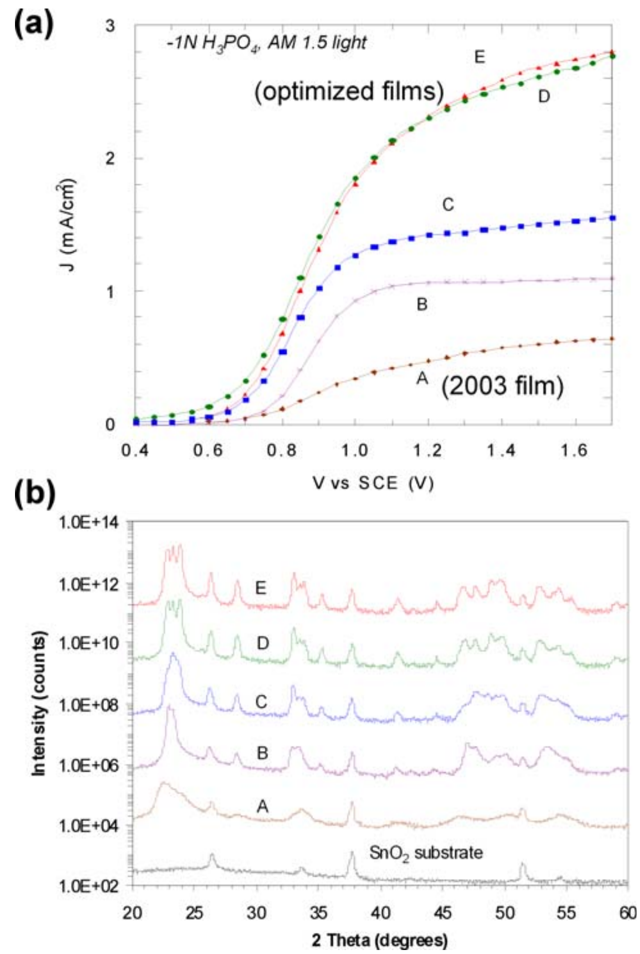

Figure 2. Progress in the development of photoactive tungsten trioxide (WO_3) thin films fabricated using low-temperature reactive sputtering; (a) improvements in photocurrent levels (under simulated AM 1.5 sunlight in 1N H_3PO_4) resulting from sputtering process parameter optimization; (b) XRD spectra indicating levels of microstructure in the WO_3 film samples.

in the bandgap reduction of the WO_3 through nitrogen doping in the sputtering ambient.

Progress was also made in the development of HPE prototype devices based on the improved WO_3 material. Using performance characteristics of the best WO_3 films, HPE prototype designs were completed, specifying requirements on both PV and PEC layers. A load line analysis [5] of the designed device is illustrated in Figure 3, showing an expected operating point of approximately 1.8 mA/cm^2 at the intersection of the PV and PEC responses –

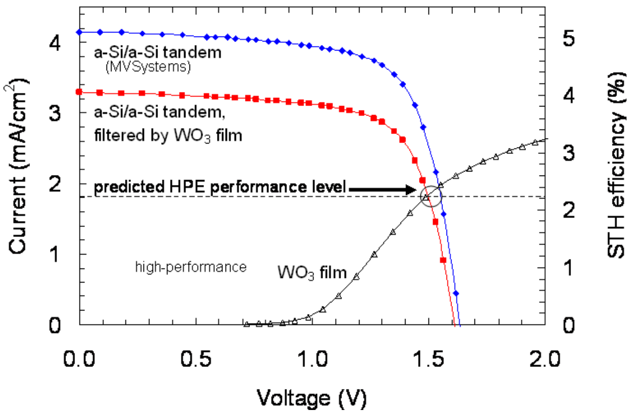

Figure 3. Predictive load-line analysis for a HPE device design based on high-performance WO_3 films and amorphous silicon tandems. Shown are the superimposed response curves of the PEC and light-filtered PV component layers, indicating an operation point of 1.8 mA/cm^2 (linearly translating to 2.2% STH conversion efficiency).

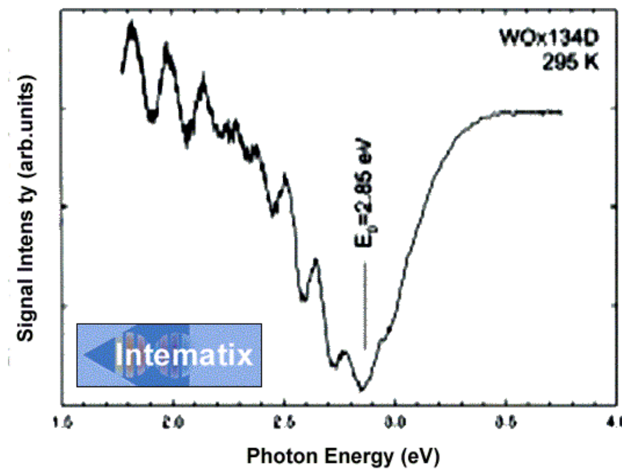

Figure 4. Output signal from the rapid-throughput LMDS method applied to bandgap determination in a sputtered WO_3 film, verifying the 2.85 eV gap in the sample under investigation.

representing a predicted STH conversion efficiency of 2.2% (which would meet this year's targeted goal of 2%). The amorphous silicon (a-Si) tandem PV layer for the prototype, whose response curve is shown in Figure 3 in conjunction with that of a high-performance WO_3 film, has been designed, fabricated and tested at MVSystems for this project. Batches are currently being produced at MVSystems for use in fabricating the WO_3-based HPE prototype devices. From completion and testing of an initial prototype set in September 2005, it was determined that the deposited WO_3 films were performing to expectations, but that there was significant degradation in the amorphous silicon tandem during the device fabrication process. This resulted in STH efficiencies slightly below 1%, as opposed to the expected 2-3%. The source of the degradation is being addressed with MVSystems, and fabrication of additional HPE prototype batches are planned for November 2005.

In subtasks relating to the combinatorial discovery of reduced-bandgap WO_3 compounds for future higher-efficiency HPE devices, the subcontractor Intematix has reported the development of a novel bandgap screening method based on laser modulation differential spectroscopy (LMDS). This technique, which requires an approximate spot size of only 3 mm, has several advantages in terms of sensitivity and practical implementation over conventional spectrophotometry and evanescent microwave probe methods. In May 2005, Intematix reported a successful application of LMDS to bandgap determination in sputtered WO_3 films, as shown in Figure 4. In subtasks relating to fabrication and process scale-up, MVSystems has proposed the use of their patented reel-to-reel cassette technology (Figure 5a) within a vacuum cluster tool (Figure 5b) as the basis for initial scaled-up cost analyses, expected to be completed in December 2005.

Conclusions

- WO_3 films reactively sputtered at low temperatures (<250° Celsius) have been demonstrated with generated photocurrent levels exceeding 2.5 mA/cm^2 in acidic electrolyte under 1 sun illumination.
- HPE designs based on high-performance WO_3 are feasible, with expected STH conversion efficiencies in excess of 2.2% (based on the lower heating value of hydrogen).
- Based on device analyses, HPE systems (or any PEC system) with STH conversion efficiencies exceeding 3% will require PEC oxide layers with bandgaps below the nominal 2.8 eV in un-doped WO_3.
- Discovery, through conventional and/or combinatorial techniques, of complex metallic oxide compounds with bandgaps low enough for high-efficiency PEC conversion devices is critical to the success of this research.

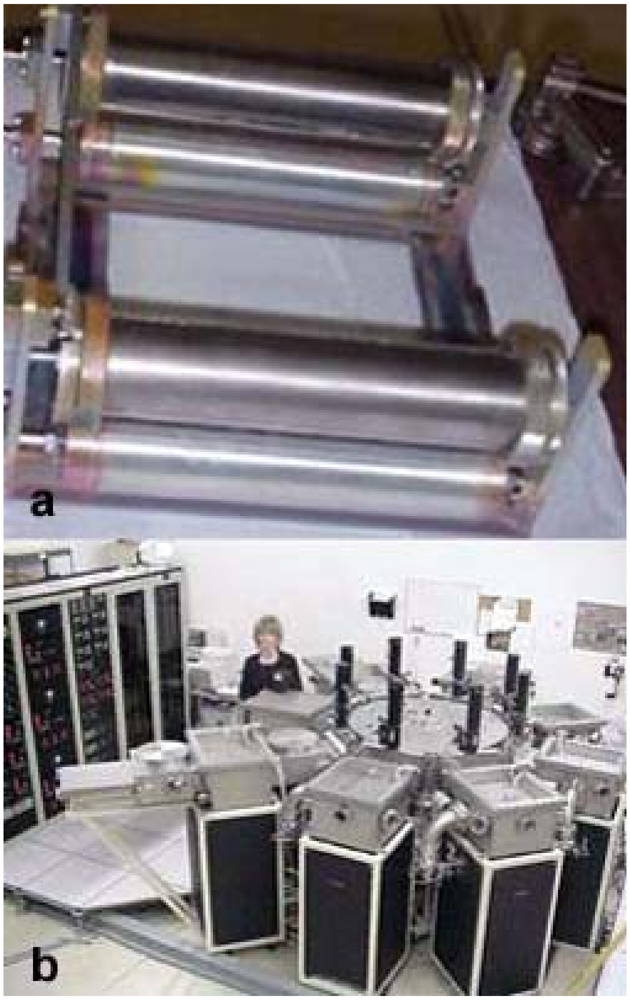

Figure 5. MVSystems' thin film fabrication equipment to be used as the basis for initial cost analyses of scaled-up HPE systems: (a) patented reel-to-reel cassette technology; (b) vacuum cluster tool using the cassette technology for depositing successive thin film layers over large areas of rolled foil substrates.

- Rapid-throughput screening based on "laser modulation differential spectroscopy" has been demonstrated for use in the combinatorial discovery of viable metal-oxide PEC films.
- Fabrication technology based on reel-to-reel cassettes implemented in a vacuum cluster tool system is an appropriate basis for initial cost analyses of scaled-up HPE systems.

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 2005 Presentations

1. 2004 Electrochemical Society Joint International Meeting, Honolulu:
   – Oral Presentation: "Optimization of a Hybrid Photoelectrode for Solar Water-Splitting", B. Marsen, E. Miller, D. Paluselli, R. Rocheleau
   – Poster Presentation: "Nitrogen Doping of Reactively-Sputtered Tungsten Oxide Films for Photoelectrochemical Applications" , D. Paluselli, E. Miller, B. Marsen, R. Rocheleau
2. 2004 International Energy Association Annex-20 Meeting, Delft, the Netherlands:
   – Invited Speaker: "Photoelectrochemical Hydrogen Production Research at the University of Hawaii" (via teleconference), E. Miller, B. Marsen, D. Paluselli

FY 2005 Journal Publications

1. 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.
2. E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes", *Solar Energy Materials and Solar Cells,* 2005, 88(2), 131-144.
3. D. Paluselli, B. Marsen, E. Miller, R. Rocheleau, "Nitrogen Doping of Reactively-Sputtered Tungsten Oxide Films", *Electrochemical and Solid-State Letters,* 2005, accepted for publication.

References

1. R. Rocheleau , E. Miller, A. Misra, "High-efficiency Photoelectrochemical Hydrogen Production Using Multijunction Amorphous Silicon Photoelectrodes", *Energy and Fuels*, 1998, 12, 3-10.
2. E. Miller, R. Rocheleau, X. Deng, "Design Considerations for a Hybrid Amorphous Silicon / Photoelectrochemical Multijunction Cell for Hydrogen Production", *International Journal of Hydrogen Energy*, 2005, 28(6), 615-62.

3. E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes", *Solar Energy Materials and Solar Cells,* 2005, 88(2), 131-144.
4. C. Santato, M. Ulmann, J. Augustynski, "Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films", *J. Phys. Chem. B*, 2001, 105, 936-940.
5. 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.