II.H.11 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

Liwei Xu[1] (Primary Contact), Anke E. Abken[2], William B. Ingler[3], John Turner[4]

[1] Midwest Optoelectronics LLC (MWOE)
[2] Xunlight Corporation
[3] University of Toledo
[4] National Renewable Energy Laboratory (NREL)

Phone: (419) 530-2651
E-mail: william.ingler@utoledo.edu

DOE Technology Development Manager: Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-2373
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FG36-05GO15028

Subcontractors:
- Xunlight Corporation, Toledo, OH
- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: April 1, 2005
Project End Date: March 31, 2010

Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film (tf)-Si-based photoelectrodes.
- Two approaches are taken for the development of efficient and durable photoelectrochemical (PEC) cells:
  - An immersion-type PEC cell in which the photoelectrode is immersed in electrolyte.
  - A substrate-type PEC cell in which the photoelectrode is not in direct contact with electrolyte.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4) 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
(AD) Systems Design and Evaluation

Technical Targets

This project focuses on the development of photoelectrode materials and tf-Si-based PEC cells required to achieve or exceed DOE's technical targets. The status of the project towards the DOE Multi-Year Program Plan objectives for Photoelectrochemical Production of Hydrogen for 2013 is listed in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Immersion- and Substrate-Type PEC Cells and Systems

Characteristic	Units	DOE 2012 Targets	MWOE 2009 Status
Solar-to-Hydrogen efficiency	% Efficiency	8	TBD
Durability	Hours	1,000	500*
Cost	$ gge	2-3	TBD
Photocurrent of TCCR	mA/cm^2	8 (MWOE Target)	0.0214
Photocurrent of PAS	mA/cm^2	8 (MWOE Target)	23.0
Deposition Temperature	°C	250 (MWOE Target)	250
Transparency of TCCR	% Transmission	90 (MWOE Target)	90

TBD - to be determined
* tested on materials only (has to be confirmed for the PEC module)

The solar-to-hydrogen efficiency cannot be calculated until we deposit our optimum transparent, conducting and corrosion-resistant (TCCR) coatings or photo-active semiconductor (PAS) layer on a triple or tandem junction tf-Si solar cell, respectively, which is the next step in the development process. Cost analysis cannot be done until a module is fabricated and measurements are done. The last four targets are those outlined in the project objectives.

Accomplishments

- A 4"×12" substrate-type PEC cell was successfully tested and a 12"×12" model is under development.
  - Long-term stability tests for substrate-type PEC were conducted.
- TCCR and H_2 evolution catalysts were developed (Task 1).

  - For use as TCCR material In_2O_3-Fe_2O_3 and In_2O_3-$InFe_2O_4$ are found most promising as these material classes are providing sufficient stability and excellent conductivity.
  - A process for large-area electroplating of porous Ni as H_2 evolution catalyst has been developed.
- Fabrication and optimization of triple-junction, a-Si/a-SiGe/a-SiGe and a-Si/a-SiGe/nc-Si, and tandem, a-Si/nc-Si, photoelectrodes is pursued under Task 2.
  - Plasma treatments prior to device deposition have been found beneficial for improving device performance and long-term reliability.
- NREL team led by John Turner is developing improved understanding of PEC processes for a-Si-based photoelectrodes (Task 3).
- Task 4 focuses on the construction and optimization of deposition systems for fabricating large-area photoelectrodes used in immersion-type PEC cells.
  - Electroplated ZnO was successfully tested for use as textured back reflector.
- Facilities for large-area processing of substrate-type PEC cells have been established; processes for PEC components are under development (Task 5).
  - Sintered electrodes (Ni-Zn-Mo-Al) have been developed and tested regarding their usefulness as anodes.
  - Screen-printing techniques for applying current collection grids were optimized.
  - Photo-assisted electrochemical shunt passivation process for removing shunts and shorts in photoelectrodes was optimized.

Introduction

In this project, MWOE and its subcontractors are jointly developing the critical technologies required for cost-effective production of hydrogen from sunlight and water using tf-Si-based photoelectrodes. These triple-junction tf-Si-based electrodes include triple cells with either amorphous silicon germanium alloy (a-SiGe) or microcrystalline silicon (µc-Si) as the narrow band gap absorber material.

Two separate approaches have been pursued for the development of immersion- and substrate-type PEC photoelectrodes:

- In one approach, triple-junction tf-Si-based photoelectrodes (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/µc-Si) are used to generate the voltage bias necessary for hydrogen generation. A TCCR coating is deposited on top of the photoelectrode for protecting the semiconductor layers from corrosion while forming an ohmic contact with the electrolyte.
- The second approach uses a hybrid structure, in which two tf-Si-based junctions (middle and bottom junctions of the present triple-junction tf-Si cell) provide a voltage bias of about 1.1 V, and a third junction (the top junction) forms a rectifying junction between a PAS and the electrolyte.

State-of-the-art a-Si/a-SiGe/a-SiGe and/or a-Si/a-SiGe/µc-Si devices are used as photoelectrodes. The corrosion resistance and PEC mechanisms for a range of oxide-, nitride- and carbide-materials, and II-VI compounds are under investigation. High-performance, durable PEC cells and systems will be developed, optimized and demonstrated in this project.

Approach

Five technical tasks are being performed under this grant in order to accomplish the project objectives:

- **Task 1:** Transparent, conducting and corrosion resistant coating for a triple-junction tf-Si-based photoelectrode.
- **Task 2:** Hybrid multi-junction PEC electrode having semiconductor-electrolyte junction.
- **Task 3:** Understanding and characterization of photo-electrochemistry.
- **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.
- **Task 5:** Development of device designs for large area, substrate-type PEC cells.

Results

Tasks 1 focuses on the preparation of TCCR coatings deposited onto the top of the tf-Si photoelectrode. During this reporting period emphasis was focused on the deposition of In_2O_3-Fe_2O_3 and In_2O_3-$InFe_2O_4$ films as these materials provide sufficient long-term and current density. The TCCR films were deposited using radio frequency magnetron sputter deposition in argon and oxygen using multiple sputter guns simultaneously. From the work completed, the results indicate that samples made at 250°C with 30 W of In and 100 W of $InFe_2O_4$, and a sputter deposition time of 90 minutes produced optimal results. Photocurrent measurements indicate that the best sample displays a maximum current density J of 21.4 µA/cm^2 at 0.65 V (Figure 1). However, the dark current is significant indicating crystallization inhibitions during film formation. Figure 2 shows the stability scans, current density-voltage (JV)-cycles between -1 V and +3 V for a sample sputtered at 30 W In and 100 W

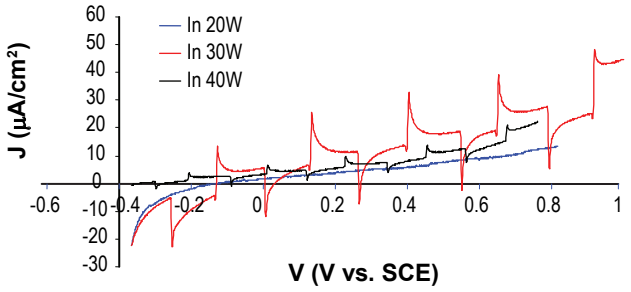

FIGURE 1. Variation of In deposition power reaches a maximum at 30 W with 100 W $InFe_2O_4$ for 90 min deposition time.

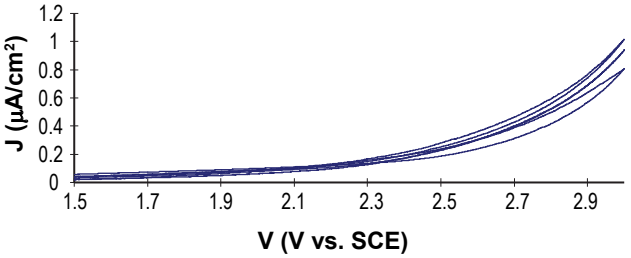

FIGURE 2. JV-cycles (-1 V to +3 V) for TCCR sputtered with 30 W In and 100 W $InFe_2O_4$ (90 min deposition time).

$InFe_2O_4$. Note that the JV-curve stabilizes after the first sweep.

Under Task 1 a method for large-area electroplating of porous Ni used as an H_2-evolution catalyst has been developed. The method uses the co-deposition of Ni and Zn onto the back-side of tf-Si photoelectrodes, after Ni/Zn electrodeposition Zn is leached out leaving a porous Ni-structure behind.

Under Task 2 optimization work on tf-Si photoelectrodes used for hybrid PEC cells has been performed. During this reporting period major emphasis was focused on improving the device/substrate interface and in particular the interface between stainless steel and n-layer. It has been found that this interface determines significantly device adhesion and therefore device performance and long-term reliability. Plasma-etching steps before device deposition using H-, Ar- and Ar/O-plasma have been evaluated. JV-data obtained for tandem tf-Si photoelectrodes (a-Si/nc-Si) under illumination suggest that the device performance can be improved when using Ar or H_2 plasma treatments for conditioning the stainless steel substrate surface before tf-Si device deposition.

Task 3 focuses on the understanding of electrochemical processes of PEC cells and on the characterization of tf-Si photoelectrodes. MWOE collaborates with Dr. John Turner (NREL) in order to get a detailed understanding of a-Si/a-SiGe/a-SiGe and

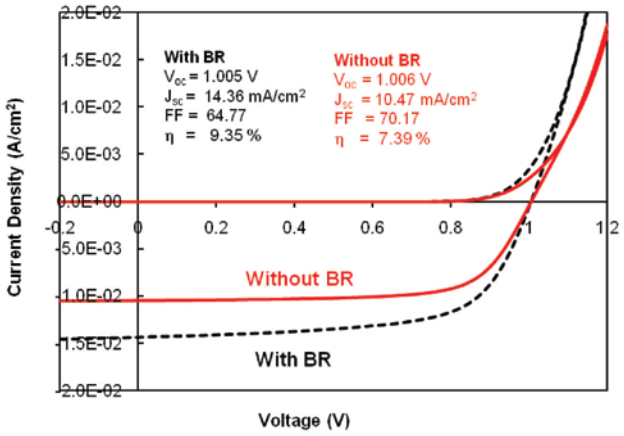

FIGURE 3. JV-Curves of a-Si Devices With and Without Back-Reflector (BR)

a-Si/a-SiGe/μc-Si devices used as photoelectrodes in substrate and immersion-type PEC cells.

Efforts pursued under Task 4 emphasize the development of system designs and components used for immersion-type PEC cells. The incorporation of metallic reflective and transparent conductive back-reflector in photoelectrodes re-directs incident light into the tf-Si device. This effect increases conversion efficiency η, short-circuit current J_{SC} and fill factor (FF) of the device. Figure 3 shows the JV-curves of a-Si single junction devices with and without back-reflector. Although these cells are single devices, this is an important step towards fabricating multi-junction (tandem, triple) and semiconductor electrolyte junction photoelectrodes. Electrodeposition of ZnO for use as textured back-reflector was tested. Initial results indicate the feasibility of this process for back-reflector fabrication although further process optimization is necessary for obtaining high quality, diffuse reflective ZnO layers.

Task 5 focuses on the development of processing procedures for large-area photoelectrodes. Under this task sintered electrocatalysts employed as anodes in substrate-type PEC cells were developed. Metal powder mixtures containing Ni with different amounts of Zn, Al, Mo were sintered at 800°C in order to form porous electrodes. JV-measurements performed in potassium hydroxide as electrolyte suggest the feasibility of using these material combinations as porous anodes or cathodes.

During this reporting period several reliability and performance improvements for large-area photoelectrodes were accomplished. It has been found that improvements in the current collection grid design leads to a significant reduction in series resistance yielding for improved device performance. The optimized current collection grid uses a screen printed collector and tin-clad copper foil collector buses.

The state-of-art light-assisted shunt passivation process for large-area photoelectrodes lead previously to reliability issues when using a metallic back-reflector layer inserted between the stainless steel substrate and photovoltaic device. Process and reliability improvements were accomplished by varying the electrolyte used for electrolytic passivation. The improved procedure allows processing with less corrosive metal salts.

Conclusions and Future Directions

The proposed future work will include:

- Continue optimization of present oxide materials suitable for TCCR coatings:
  - Material class studies are focusing on In_2O_3-Fe_2O_3 and In_2O_3-$InFe_2O_4$ providing most promising stability and conductivity.
- Develop chemical plating for materials suitable for PAS and TCCR coatings for immersion-type hybrid PEC cells.
- Leveraging our resources on building a prototype for large-area (1ft×1ft) substrate-type PEC.
  - Design of final substrate-type PEC will employ porous Ni as H_2 evolution catalyst electroplated onto the backside of stainless steel substrates with a triple junction a-Si device on the front-side.
  - Long-term reliability studies and solar-to-H_2-efficiency measurements will be performed.
- Develop 4”×4” immersion-type PEC cells:
  - Long-term reliability studies and solar-to-H_2-efficiency measurements will be performed.
- Improve performance of large-area photoelectrodes.
- Complete techno-economic and energy analyses for PEC systems for hydrogen production.

FY 2009 Publications/Presentations

1. Fan, Q.H.; Liao, X.; Zhang, S.; Xiang, X.; Ingler Jr., W.B.; Adiga, N.; Du, W.; Cao, X.; Deng, X.: *“Amorphous Silicon Germanium Solar Cells Deposited on Stainless Steel at Elevated Pressure”* 34th IEEE PVSC, 2009.

2. Zhang, S.; Liao, X.; Fan, Q.H.; Xiang, X.; Adiga, N.; Ingler Jr., W.B.; Du, W.; Cao, X.; Deng, X.: *“Impacts on n-type Interface on the Performance of a-Si Based Solar Cells”* 34th IEEE PVSC, 2009.

3. Ingler Jr., W.B.; Ong, G.; Deng, X.: *“RF Sputter Deposition of Indium Oxide - Iron Oxide Films for Photoelectrochemical Hydrogen Production”* ECS Trans. Vol. 16, No. 7. (State-of-the-Art Program on Compound Semiconductors 49 (SOTAPOCS 49), 2008, 49.

4. Ingler Jr., W.B.; Ong, G.; Deng, X.: *“RF Sputter Deposition of Indium Oxide - Iron Oxide Films for Photoelectrochemical Hydrogen Production”* ECS Trans. Vol. 16, No. 7. (State-of-the-Art Program on Compound Semiconductors 49 (SOTAPOCS 49), 2008, 49. 210th Meeting of the Electrochemical Society, Inc., Honolulu, HI, October 12–17 (Oral Presentation).

5. Ingler Jr., W.B.; Naseem, A.: *“RF Sputter Deposition of Indium Oxide / Indium Iron Oxide Thin Films for Photoelectrochemical Hydrogen Production”*, 2009 MRS Spring Meeting Symposium S Proceedings, Volume 1171E.