

II.E.3 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Contract Number: DE-FG36-05GO15028

Subcontractors:

- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory (NREL), Golden, CO
- Xunlight Corporation, Toledo, OH

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 silicon (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 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 is focused on the development of photoelectrode materials and tf-Si-based PEC cells that are required to achieve or exceed DOE's technical targets for PEC production of hydrogen for 2013:

- Solar-to-hydrogen (STH) Efficiency >8%
- Durability >1,000 hours
- Cost <\$2-3 gge

Accomplishments

- Fabrication of triple-junction a-Si/a-SiGe/a-SiGe solar cells (photoelectrodes).
- Fabrication of triple-junction a-Si/a-SiGe/nc-Si solar cells (photoelectrodes).
- Construction and operation of a 3 ft × 3 ft chamber for fabrication of thin film silicon solar cells on stainless steel substrate.
- Deposition of transparent, conducting and corrosion-resistant coating using rf sputtering.
- Optimization of a sputter system with four linear targets (4" × 15"), capable of making transparent, conducting and corrosion resistant (TCCR) films on 1 ft × 4 ft substrates.
- NREL team led by John Turner is currently developing improved understanding of PEC process for a tf-Si-based photoelectrodes.
- An outdoor solar testing facility has been utilized for outdoor testing of PEC panels for long-term stability and output.
- Focus on Task 4 is on the construction and optimization of deposition system that will be used for making large-area photoelectrodes for immersion-type PEC cells:
 - Designed and constructed a system capable of making 3 ft × 3 ft photoelectrodes.
 - Improved deposition uniformity over large area.
 - Focused on electrodeposited ZnO that will be used for back reflector (BR) optimization.
 - Continued the design and optimization of immersion-type PEC cells.
- Focus under Task 5 has been on establishing facilities to make substrate-type PEC cells in large area:
 - Improved screen-printing techniques.

- Designed and built a fabrication facility for making substrate-type PEC electrodes.
- Designed, developed and constructed a photo-assisted electrochemical shunt passivation system to remove shunts and shorts in the photoelectrodes.
- Long-term testing of substrate-type modules.



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 solar cells include triple cells with either amorphous silicon germanium alloy (a-SiGe) or microcrystalline silicon (μ -Si) as the narrow band gap absorber materials.

Two separate paths will be taken in this project for development of immersion- and substrate-type PEC photoelectrodes:

- In one path, triple-junction tf-Si-based solar cells (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/ μ -Si) will be used to generate the voltage bias and a TCCR coating will be deposited on top to protect the semiconductor layers from corrosion while forming an ohmic contact with the electrolyte.
- The second path 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 (around 1.1V) and a third junction (the top junction) is a rectifying junction between a photo-active semiconductor and the electrolyte.

State-of-the-art a-Si/a-SiGe/a-SiGe solar cells and/or a-Si/a-SiGe/ μ -Si solar cells will be used as the photoelectrodes. The corrosion resistance and PEC mechanisms for a range of oxides, nitrides and carbides, and II-VI compounds will be investigated. High-performance, durable PEC cells and systems will be optimized and demonstrated in this project.

Approach

Five technical tasks are being performed in this project toward the objectives:

- **Task 1:** TCCR coating for a triple-junction tf-Si-based photoelectrode.
- **Task 2:** Hybrid multijunction PEC electrode having semiconductor-electrolyte junction.
- **Task 3:** Understanding and characterization of photoelectrochemistry.

- **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 and 2 of this project during the past year have focused on developing technology for depositing large area a-Si solar cells and large area oxide films in a large area metal sputtering chamber. During this period both systems were test run and several versions of cathodes were tested in the a-Si chamber with several single junction solar cells fabricated and tested. In Figure 1, 1' x 3' single junction amorphous silicon based photo cells were fabricated. Current-voltage (I-V) characteristics of 0.25 cm² single-junction amorphous silicon based photo cells taken from these larger samples, measured with AM1.5 illumination are shown. One of the cells incorporates back-reflecting layers. The cells show good photoelectric conversion efficiency and fill factor. Although these cells are single junction, this is an important step towards fabricating multijunction, semiconductor-electrolyte junction photoelectrodes.

Task 3 of this project involves characterization of the solar cells and modules and over this period work has covered two main areas: 1) Collaborating with John Turner and NREL to further understand the a-Si interface, and 2) setting up an outdoor test facility at MWOE/Xunlight. This test facility has thus far only been testing superstrate solar cell modules made under another project.

Task 4 efforts in this period involve work on electroplating zinc oxide and efforts also include the construction of a roll-to-roll demonstration system with 3 ft wide web to demonstrate the mechanical transport

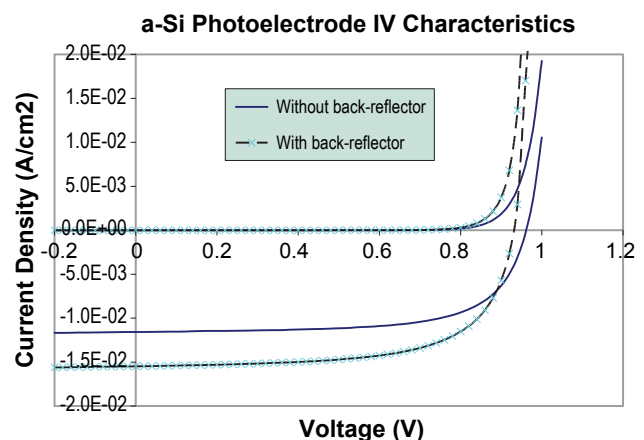


FIGURE 1. I-V Characteristics for a Large Area a-Si/nc-Si Tandem-Junction Solar Cell

system for a roll-to-roll deposition system. Shown in Figure 2a is a long section of a 3 ft wide web, moving from one side of the transport system to the other side that can be run through a system such as that in Figure 2b.

Under Task 5 of this project, work involved development of a shunt passivation station. The light-assisted electrochemical shunt passivation process neutralizes performance-reducing shunts or shorts in the substrate-type cell, thus improving yield and hydrogen-generation performance. The process has now been successfully tested on cells up to 12" × 12" in size.

Another procedure that was developed is low-light evaluation: a portion cut from every substrate-type photoelectrode is patterned into a multitude of smaller circular cells, using screen printing. The voltages of these cells are then measured under low light intensity (~2 mW/cm²). A relatively high voltage under such reduced illumination indicates an absence of shunts in the sample. The number of cells exceeding a certain

minimum voltage is counted and recorded as a positive indicator of process yield up to that point. An example cell is shown in Figure 3a and the full station is shown in Figure 3b.

Another project under this task is the development cheap catalyst materials for substrate-type PECs. The black platinum coated on the rear side of the solar cell is expensive and has poor adherence on stainless steel foil substrate on which triple junction solar cell is formed. Therefore, efforts have been directed in using porous nickel catalysts for the substrate-type PEC cells. The porous electroplated nickel catalyst has been chosen for plating on the back side of the stainless steel substrate of the triple junction amorphous silicon to produce hydrogen. Sintered nickel-cobalt oxide-aluminum catalyst developed at the University of Toledo has been chosen to serve as a counter electrode in the substrate-type PEC cell. Fabrication of 12" × 12" substrate-type solar cells is in progress.



FIGURE 2. (a) A roll-to-roll system demonstrating the transport of a 3ft wide web. This web transport system will allow MWOE/Xunlight to deposition thin film Si solar cells on large substrates; and (b) Large area metal sputtering system.

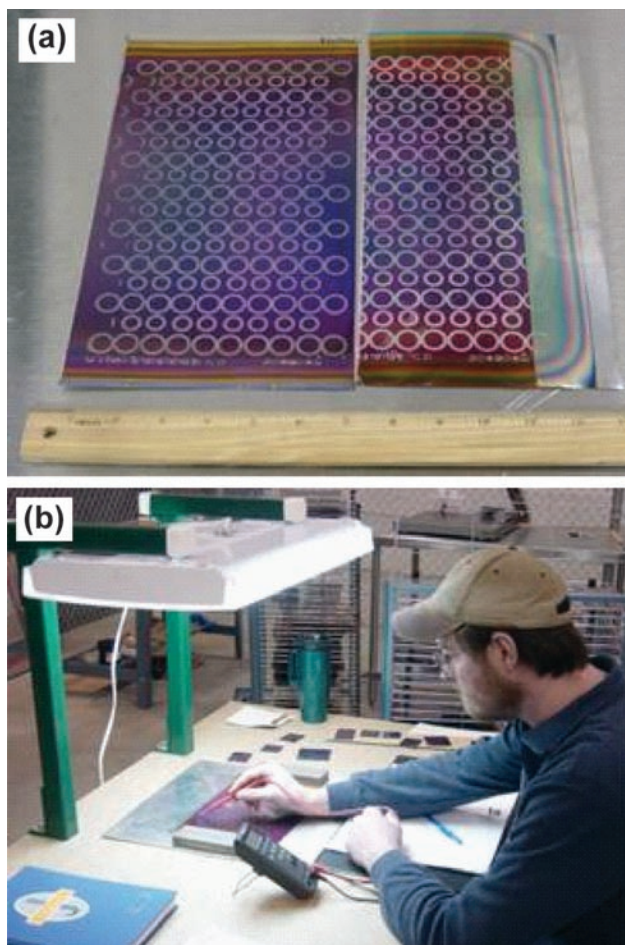


FIGURE 3. (a) Tf-Si solar cell with patterned circles for evaluation; and (b) the low-light evaluation station.

Conclusions and Future Directions

- Continued study into optimization of present oxide materials – identify classes of materials most promising to Phase 2 goals:
 - Material classes are focusing on iron oxide and titanium dioxide material classes with various dopants such as antimony and indium for iron oxide and nitrogen and carbon for titanium dioxide.
 - Deposition of oxides under higher power and with metallic targets to improve stability and oxide structure study new materials beyond present set.
- Leveraging our resources on a substrate-type PEC as all the materials required to build one on site are now available – large area solar cell, electrolyzers:
 - Production of final module design (substrate-type PEC) with electroplated nickel on back of stainless steel with triple junction a-Si on front.
- Improvement in voltage and efficiency of large area solar cells.
- For the electroplated zinc oxide work, the future direction will include:
 - Optimization of deposition current/voltage.
 - Optimize deposition temperature.
 - Study heat treatment effects.
 - Optimum thickness.
 - BR with textured Ag or Al/Ag.
 - Study of ion migration and their effects during the deposition.
 - Comparison study of sputtering and electrodeposition of ZnO.

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4. Xiesen Yang, Xianbo Liao, Wenhui Du, Xinmin Cao, Dinesh Attygalle, Xianbi Xiang, Nirupama Adiga, Xunming Deng, “Theoretical Analysis and Modeling of Light Trapping in a-Si based Thin Film Solar Cells”, presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.
5. Wenhui Du, Xianbo Liao, Xiesen Yang, Xinmin Cao, Nirupama Adiga, Xianbi Xiang, Dinesh Attygalle, Xunming Deng, “Study of Amorphous Silicon Germanium Solar Cells with i-layer Deposited at High Rates using RF-PECVD”, presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.
6. Jason A. Stoke, Lila R. Dahal, Jian Li, Nik J Podraza, Xinmin Cao, Xunming Deng, Robert W. Collins, “Optimization of Si:H Multijunction n-i-p Solar Cells through the Development of Deposition Phase Diagrams”, presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.

FY 2008 Publications/Presentations

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