II.F.6 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film Si (tf-Si) based photoelectrodes.
- To develop and demonstrate tf-Si based photoelectrochemical (PEC) systems with 9% solar-to-hydrogen efficiency with a lifetime of 10,000 hours and with a potential hydrogen cost below $22/kg.
- Two approaches are taken for the development of efficient and durable photoelectrochemical cells:
  - An immersion-type photoelectrochemical cell in which the photoelectrode is immersed in electrolyte.
  - A substrate-type photoelectrochemical 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 (3.1.4.2.6) 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
(AT) Systems Design and Evaluation

Technical Targets

This project is focused on the development of photoelectrode materials and PEC cells that are required to achieve or exceed DOE's technical target, 8% solar-to-hydrogen efficiency and 1,000-hour durability by 2010, as stated in DOE's Multi-Year Program Plan.

Accomplishments

- Studied and used nanocrystalline silicon (nc-Si:H) as the absorber layer for bottom component cell in a triple-junction a-Si/a-SiGe/nc-Si photoelectrode, achieving 12.4% sunlight-to-electricity conversion efficiency.
- Studied the deposition of F-SnO_2 by rf sputtering of a target made with a concentration of 75% SnO_2 and 25% SnF_2. Initial trials have been sputtered and are being analyzed. This avoids the special chamber modifications that would be required to sputter SnO_2 in a F_2/Ar atmosphere.
- Explored several groups of transparent, conducting and corrosion-resistance (TCCR) coatings utilizing multi-gun magnetron sputtering.
- Restored and set up a large-area sputter deposition system that could allow the sputter deposition of TCCR materials over large area (1 ft x 4 ft) on a flexible substrate. Redesigned the sputtering magnet arrangement to enhance the sputter deposition rate. Established the auxiliary components, cooling, power supplied etc, for the system capable of making TCCR coatings in large area.
- Fabricated a-Si/nc-Si double-junction photoelectrodes for use in hybrid photoelectrodes using a ten-chamber cluster tool system.
- Studied sol-gel deposition of tin oxide and titanium dioxide as a TCCR layer by varying temperature and curing times.
- Developed and demonstrated the first substrate-type PEC cell with 5.9 cc/min hydrogen production rate for a 4 in x 12 in panel.

Introduction

This project is focused on the development of photoelectrochemical hydrogen generation devices and systems. Two approaches are taken for the development of efficient and durable photoelectrochemical cells: 1) an immersion-type photoelectrochemical cell where photoelectrode is immersed in electrolyte, and 2) a substrate-type photoelectrochemical cell where the photoelectrode is not in direct contact with electrolyte.

Approach

Research is carried out for both the immersion-type PEC cell and the substrate-type PEC cell. For immersion-type PEC cells, two paths are taken for the development of efficient and durable photoelectrodes. In the first path, triple-junction tf-Si based solar cells (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/nc-Si) are used to generate the voltage bias and a transparent, conducting and corrosion resistant (TCCR) coating is deposited on top to protect the semiconductor layer from corrosion while forming an ohmic contact with the electrolyte. In the second path, 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 1.1 V) and a third junction (the top junction) is a rectifying junction between a photo-active semiconductor and the electrolyte.

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

- Task 1. Transparent, Conducting and Corrosion Resistant Coating for 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. Fabrication of Low-Cost, Durable and Efficient Immersion-Type PEC Cells and Systems
- Task 5. Fabrication of Low-Cost, Durable and Efficient Substrate-Type PEC Cells and Systems

Results

Task 1. Transparent, Conducting and Corrosion Resistant Coating for Triple-Junction tf-Si Based Photoelectrode

The objective of this task is to develop a TCCR material that can be made at low temperature (below 250°C) using a low-cost thin-film deposition technique, and in addition has the following properties: high optical transmission in the visible wavelength range, high electrochemical stability in the electrolyte, and sufficient conductivity for transport of charge carriers, such that an ohmic contact is formed with both the electrolyte and the topmost layer of the tf-Si solar cell. Extensive effort was made in the fabrication of six groups of TCCR materials including TiO_2, In-TiO_2, WO_3, Co_3O_4, NiO_x-Co_3O_4 and Flexbond coating, for use as TCCR coatings.

Under Task 1, the team has also made significant progress in the fabrication of high efficiency triple-junction thin film photoelectrodes. Two types of thin film Si based triple-junction photoelectrodes were fabricated:

1) a-Si/a-SiGe/a-SiGe triple-junction photoelectrode where the bottom component cell is made using a narrow bandgap amorphous silicon germanium alloy having a semiconductor bandgap of ~1.4 eV.
2) a-Si/a-SiGe/nc-Si triple-junction photoelectrode where the bottom component cell is made using a narrow bandgap nanocrystalline silicon having a bandgap around 1.1 eV.

To provide a highlight of the extensive work related to nanocrystalline silicon-based photoelectrode, the current-voltage characteristics of a triple-junction a-Si/a-SiGe/nc-Si photoelectrode is given in Figure 1(a). This photoelectrode shows a conversion efficiency of 12.4%. This device has desirable performance for use in PEC production of hydrogen.

Studies were also carried out in the deposition and optimization of fluorine doped SnO_2 materials using sputter deposition process and SnO_2 and TiO_2 materials using sol gel method.

Task 2. Hybrid Multijunction PEC Electrode having Semiconductor-Electrolyte Junction

The objective of this task is to develop a photoactive semiconductor (PAS) material that: 1) is stable in electrolyte both in dark and under illumination, 2) forms a high-quality rectifying junction with electrolyte and an ohmic contact with the tf-Si layer underneath, 3) generates at least 7.5 mA/cm^2 current so that it can be matched with the middle and bottom component solar cells in an tf-Si based triple-junction stack, and 4) is deposited at low temperature (<250°C) using a low-cost deposition method. The major focus of this task was on the study of Fe_2O_3 and In-Fe_2O_3 as photoactive semiconductor layers.

Under this task, the team has made significant progress on the fabrication of double-junction tf-Si solar cells that are to be used as substrates for the hybrid PEC photoelectrodes. Two types of double-junction solar cells were fabricated:

1. a-Si/a-SiGe double-junction solar cells where the bottom component cell is made using a narrow

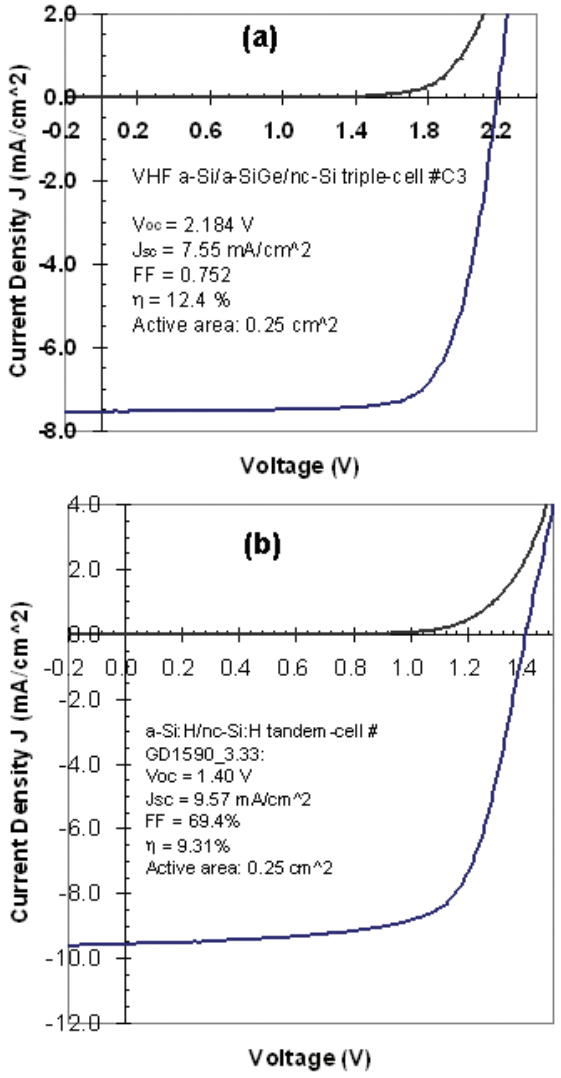

FIGURE 1. I-V characteristics for (a) A triple-junction photoelectrode having a nanocrystalline silicon as the bottom cell absorber layer (b) A double-junction solar cell desirable for use in a hybrid photoelectrode.

bandgap amorphous silicon germanium alloy having a semiconductor bandgap of ~1.4 eV.

2. a-Si/nc-Si double-junction solar cells where the bottom component cell is made using a narrow bandgap nanocrystalline silicon having a bandgap around 1.1 eV. Figure 1(b) shows the I-V characteristics of a double-junction a-Si/nc-Si solar cell desirable for use in a hybrid photoelectrode together with a photoactive semiconductor layer.

Task 3. Understanding and Characterization of Photoelectrochemistry

This task is focused on the characterization of PEC materials and devices. Activities during the reporting period include setting up characterization systems

FIGURE 2. (top) Large-area light source for evaluation of 2 ft x 4 ft PEC panel (bottom) Outdoor testing facility for evaluation of arrays of PEC panels outdoor.

for large area PEC panels, including the setup for I-V characteristics and light sources for testing hydrogen generation rate. For example, Midwest Optoelectronics (MWOE) has installed light sources for testing PEC panels of 1 ft x 1 ft size, 2 ft x 4 ft size (Figure 2a) and arrays of PEC panels in an outdoor testing site (Figure 2b). MWOE's outdoor solar testing facility has been used for testing PEC panels over the past nine months.

Task 4. Fabrication of Low-Cost, Durable and Efficient Immersion-Type PEC Cells and Systems

The objective of this task is to fabricate and optimize immersion-type PEC cells and systems. Major accomplishments under this task include:

- Installation of a large-area sputter chamber for the deposition of catalyst materials for hydrogen production. This system has four, 15 in long and 4 in wide sputter guns capable of making multiple layers of photocatalyst materials without vacuum break (See Figure 3, top).

- Construction of a large-area plasma-enhanced chemical vapor deposition system capable of making triple-junction and double junction tf-Si photoelectrodes on large-area (3 ft x 3 ft) substrates.
- Construction of a large-area magnetron sputter chamber for the deposition of Al/Ag/ZnO back reflector, required for the fabrication of high efficiency tf-Si photoelectrodes in large area (3 ft x 3 ft).

The construction and installation of these chambers and system are expected to be completed at the end of 2006, allowing the fabrication of photoelectrodes on large-area substrate in early 2007. This system, when completed, will have unique features allowing the flexibility for making high efficiency photoelectrodes specifically optimized for PEC hydrogen production in high volume at low cost.

Additional effort under this task includes:

- Construction of a hydrogen gas collection system which collects hydrogen from 12 superstrate-type PEC panels being tested outdoor during the past six months (Figure 3, bottom).

FIGURE 3. (top) Large-area, four-gun sputter deposition systems capable of depositing photocatalyst on 1 ft x 4 ft flexible substrates (bottom) Gas collection system on the superstrate-type PEC panels.

- Designed a water feeding system that allows the feeding of water automatically when the water level in the electrolysis components is lowered due to the consumption of water for hydrogen/oxygen generation.

Task 5. Fabrication of Low-Cost, Durable and Efficient Substrate-Type PEC Cells and Systems

The objective of this task is to develop and improve a substrate-type photoelectrochemical cell for hydrogen generation. In such a PEC cell, a triple-junction amorphous silicon photoelectrode deposited on a conducting substrate is integrated into a PEC cell in which the hydrogen and oxygen compartments are both behind the photoelectrode and are separated by a membrane. Areas of research activities include: development of improved encapsulation materials and process, optimization of grid configuration and installation process, investigation of effect of various cell dimensions in the oxidation and reduction compartments, design of improved membrane holder to prevent hydrogen and oxygen from intermixing, and study of various electrolyte inlet and gas/electrolyte outlet configurations.

During this reporting period, we have:

- Developed an encapsulation process for substrate-type cells in large area. Figure 4 (top) shows the encapsulation system that MWOE designed, developed and constructed. These encapsulation systems may be used to fabricate substrate-type PEC panels of the sizes of 2 ft x 3 ft for the mid-size laminator and 3 ft x 8 ft for the large-size laminator. Figure 4 (middle) shows some dummy solar panels (without semiconductor layers) encapsulated using these laminators.
- Developed a grid configuration and installation process, in which a grid pattern was generated using a computer controlled inkjet nozzle mounted on an X-Y stage.
- Fabricated a small-area (4 in x 12 in) substrate-type PEC panel (Figure 4, bottom) that shows a hydrogen generation rate of 5.9 cc/min under 92% sunlight intensity.

Conclusions and Future Directions

Major progress has been made in the development and fabrication of immersion-type and substrate-type PEC panels and systems:

- The demonstration of high efficiency nanocrystalline silicon based triple-junction a-Si/a-SiGe/nc-Si thin film photoelectrodes with 12.4% photo-to-electricity conversion efficiency.

FIGURE 4. (top) Mid-size (2 ft x 3 ft) and large-area (3 ft x 8 ft) laminators used for the encapsulation of substrate-type PEC panels (middle) Solar modules (dummy modules without semiconductor coatings) encapsulated using the laminators (bottom) Small area (4 in x 12 in) substrate-type PEC panel with 5.9 cc/min hydrogen generation rate under 0.92 sun intensity.

- The installation and construction of a deposition system for the fabrication of large-area photoelectrodes on 3 ft x 3 ft substrates.
- The demonstration of gas collection from 12 large-area (2 ft x 4 ft) PEC panels, collecting hydrogen at >1 liter/min under an outdoor environment.
- The installation and construction of facilities capable of making large-area substrate-type PEC cells.
- The demonstration of substrate-type PEC cells (4 in x 12 in) with 5.9 cc/min hydrogen production rate.

Future plans include the continuation in these area and focus on the fabrication of larger-area substrate-type PEC systems.

Special Recognitions & Awards/Patents Issued

1. Integrated Photoelectrochemical Cell and System Having a Liquid Electrolyte. Inventors: Xunming Deng and Liwei Xu. Provisional patent: Nov. 2002, Utility and PCT patent: Nov. 2003. Selection of countries: United States, Germany and Japan, May 2005.

2. Integrated Photoelectrochemical Cell and System Having a Solid Polymer Electrolyte. Inventors: Xunming Deng and Liwei Xu. Provisional patent: Nov. 2002, Utility and PCT patent: Nov. 2003. Selection of countries: United States, May 2005.

3. Integrated Photovoltaic-electrolysis cell. Inventors: Mahabala Adiga, Xunming Deng. Aarohi Vijh and Liwei Xu. Provisional application filed April 11, 2005, PCT application: April 10, 2006.

FY 2006 Publications/Presentations

1. A presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2006).

2. International Partnership for Hydrogen Energy, Renewable Hydrogen Workshop, invited presentation "Photoelectrochemical Hydrogen Production", Seville, Spain, October 26, 2005 (J. Turner).

3. Cermae Energy Challenges Workshop, invited presentation "Hydrogen Production Methods: Water Photolysis", Barcelona, Spain, October 28, 2005 (J. Turner).

4. Presentation, "Solar Generation of Hydrogen – a New Industry", University of Science and Technology of China, Hefei, China, July 3, 2005.

5. Presentation, "Photoelectrochemical Production of Hydrogen from Water Using Sunlight", Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China, July 4, 2005.

6. Presentation, "Sputter Deposition of Fe_2O_3 Films for Photoelectrochemical Hydrogen Production", 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 16-21, 2005.

7. Presentation, MWOE business plan for PEC hydrogen generation systems, at National Hydrogen Finance Forum, March 16, 2006, Long Beach, CA.