

II.G.7 Progress in the Study of Amorphous Silicon Carbide (a-SiC) as a Photoelectrode in Photoelectrochemical (PEC) Cells

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National Renewable Energy Laboratory (NREL),
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Objectives

- Work closely with the DOE Working Group on PEC Hydrogen Production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials developed.
- Explore avenues toward manufacture-scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the "Photoelectrochemical Hydrogen Production" section of the Fuel Cell Technologies

Program Multi-year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

The specific targets of this project are (a) the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency (b) operational life up to 500 hours and (c) the identification of commercialization paths toward a \$22/kg-H₂ plant production cost by 2010 and \$5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production using Amorphous Silicon Carbide-Based (a-SiC) Compound Films

Task #	Milestone	Note
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved
	Durability ≥ 100 hours	Achieved
Year 2	Material photocurrent ≥ 4 mA/cm ²	Achieved
	Durability ≥ 200 hours	Achieved
	Device STH efficiency $\geq 5\%$	32% Achieved
Go/No-Go decision evaluated (End of 2010)		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

Accomplishments

- Improvement in a hybrid photovoltaic (PV)/a-SiC device consisting of amorphous silicon (a-Si) tandem solar cell and amorphous silicon carbide (a-SiC) photoelectrode, which exhibits the following PEC performance:
 - Photocurrent of a solid-state PV/a-SiC/indium tin oxide (ITO) (illuminated through ITO) device exhibited ~ 5 mA/cm².
 - Photocurrent of an actual PV/a-SiC PEC device increased to 1.26 mA/cm², or equivalent to a STH efficiency of $\sim 1.6\%$.
 - Good durability in pH₂ buffered electrolyte for up to 200 hours.



Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is placed on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents $>6 \text{ mA/cm}^2$ and with sufficient durability to meet the lifetime requirement is the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including CIGSe_2 , CGSe_2 , etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D project. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been developed for incorporation in the PEC photoelectrode designs (i.e., the hybrid PV/a-SiC PEC cells). It is the central objective of the MVSystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. Materials modeling, bulk-film optimization, film-surface enhancement, along with comprehensive material and device characterization is being employed to facilitate the R&D process. Specifically, the feedback approach is being applied to our focus material classes, including the tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals and which are compatible with device fabrication. The most promising candidate materials will be identified, with the short-term goal of demonstrating

laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial-scale.

Results

During this reporting period (June 2009–June 2010), extensive studies of the three materials classes under investigation have focused on understanding and improving photoelectrochemical behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Progress in developing of amorphous silicon carbide-based compound films is detailed in the following subsections.

During this project period, further improvement of the PEC performance of the hybrid PV/a-SiC device has been made. Figure 1 shows a schematic diagram for the solid-state version of the hybrid PEC device, with ITO as the top contact. Using this configuration, we aimed to optimize both the a-SiC photoelectrode and the a-Si tandem solar cell beneath the photoelectrode. Under AM1.5 Global spectrum, we have so far achieved a photocurrent of $\sim 4.2 \text{ mA/cm}^2$ ($@1.23 \text{ V}$), indicating a potential STH efficiency of $>5\%$.

In actual hybrid PV/a-SiC devices, due to existence of interfacial barrier at a-SiC/electrolyte interface, extraction of photocurrent is found to be severely suppressed, leading to a very low photocurrent of $<1 \text{ mA/cm}^2$ (see Annual Report 2009). To overcome the over-potential loss, we have performed a wide variety of surface modifications on the hybrid device, including hydrofluoric acid (HF) etch (to remove thin SiO_x on the surface) and metal nanoparticle treatment. As a result, photocurrent of the hybrid device is increased. Figure 2(a) shows current vs. potential characteristics of devices performed before and after HF etching. The testing conditions were: set-up - 2-electrode; light source - AM1.5G (calibrated with a reference cell); counter

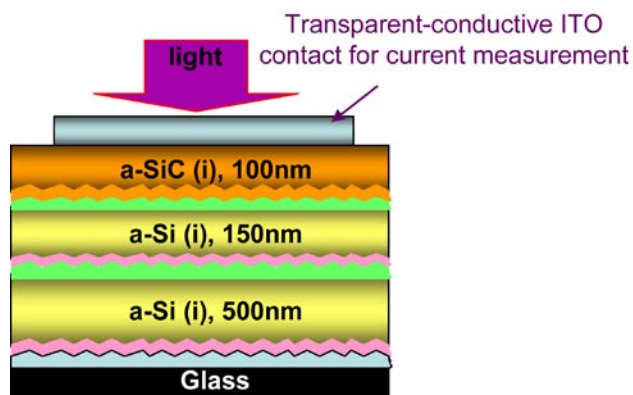
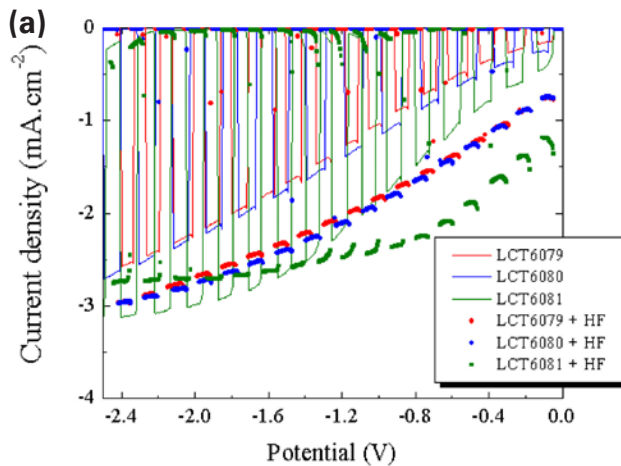


FIGURE 1. Schematic Diagram of the Solid-State Version of the Hybrid PV/a-SiC Device



(b) Ti nanoparticle coating

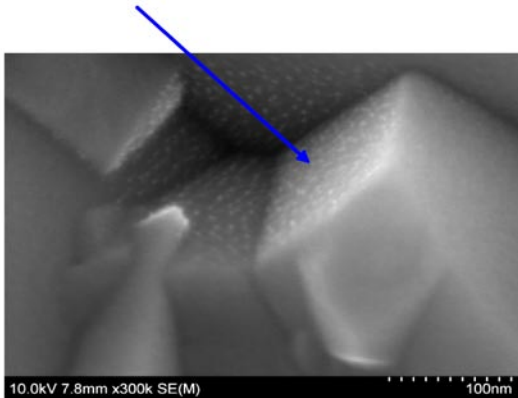


FIGURE 2. (a) Current vs. potential curve of a hybrid device showing increased photo-current at zero potential after HF etch, and (b) scanning electron microscopy image showing Ti nanoparticle coating.

electrode: RuO_2 (ruthenium oxide); electrolyte: pH_2 buffer + Triton-X; HF etch: using HF 5% for 1.5 minutes. It is seen that photocurrent at zero potential reaches $\sim 1.3 \text{ mA/cm}^2$, or an equivalent STH efficiency of $\sim 1.6\%$.

In addition, we also performed surface treatment on the a-SiC photoelectrode and the hybrid PV/a-SiC device using metal nanoparticles, including platinum (Pt), gold/palladium (Au/Pd) and titanium (Ti). Figure 2(b) shows a scanning electron microscope photo image on a Ti nanoparticle coated sample. The metal nanoparticle layer was fabricated using sputtering method, and the size of nanoparticles is of a few nanometers. We have observed that the metal with lower metal function (e.g., Ti) is more effective in enhancing photocurrent than those metals with high work function (e.g., Pt, Au/Pd). This behavior is probably due to the surface barrier caused by the high work function metals. Work is currently underway to understand the mechanism, and to explore other surface modification methods in order to further enhance the photocurrent.

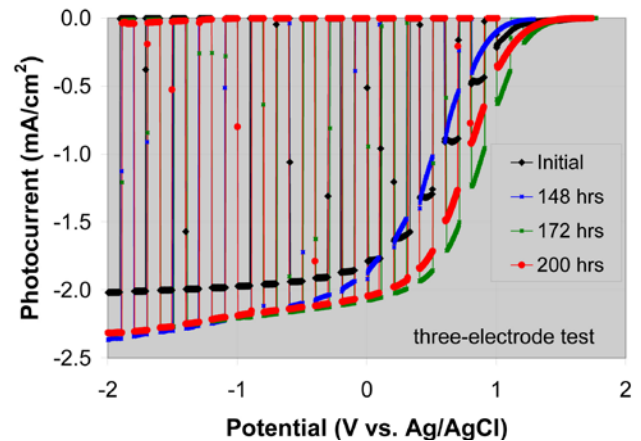


FIGURE 3. Current vs. potential characteristics measured at different stages of the durability test.

We have also made progress in further increasing the durability of the hybrid devices, which exhibits good durability for up to 200 hours. Figure 3 shows the current vs. potential characteristics of a hybrid device, measured during the course of the durability test. Compared with the initial current density-voltage (J-V) curve (black), the dark current shows virtually no increase, indicating no corrosion on the device; whereas the photocurrent shows a slight increase, possibly due to changes in the surface structure (the mechanism behind these changes is not well understood). The surface of the device shows a color change but remains largely smooth (not shown here).

Conclusions and Future Directions

This project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO_3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performances. New surface modification techniques were investigated, surface treatments (a-SiC, CGSe, WO_3), bilayer formation (WO_3) and new device integration schemes (CGSe and WO_3). Bulk modifications were also investigated, such as partial copper replacement with silver to form ACIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2010 Publications/Presentations

1. Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan “*The Potential of Using a-SiC:H as the Photoelectrode for Water Splitting*”, presented at NHA hydrogen conference and Expo., Long beach, CA, May 3–6, 2010.
2. Book chapter :“Solar Energy”: Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan, “*Amorphous Silicon Carbide Photoelectrode for Hydrogen Production from Water using Sunlight*”, edited by: Radu D. Rugesu, ISBN 978-953-307-052-0, pp. 432, February 2010, INTECH.
3. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Improved current collection in WO_3 :Mo/ WO_3 bilayer photoelectrodes*, J. Mat. Res. **25** (2010) 45.
4. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, Sol. Energy Mater. and Sol. Cells. **94** (2010) 12-16.