II.H.10 Progress in the Study of Copper Chalcopyrites as Photoelectrodes in Photoelectrochemical Cells

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Objectives

- Work closely with the DOE Working Group on Photoelectrochemical (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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (Multi-Year RD&D) Plan:

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

Technical Targets

As recognized within the PEC hydrogen research community and the DOE Hydrogen Program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category ("useable semiconductor band gap") are the primary focus of research, with secondary emphasis on the second category targets ("chemical conversion process efficiency").

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristic	Units	2006 Status	2013 Target	2018 Target
Useable Semiconductor Band Gap	eV	2.8	2.3	2.0
Chemical Conversion Process Efficiency (EC)	%	4	10	12
Plant STH Efficiency	%	N/A	8	10
Plant Durability	hrs	N/A	1,000	5,000

STH – solar to hydrogen; N/A - not applicable

The specific targets of this project are the demonstration of a PEC solar-hydrogen production system with 7.5% STH conversion efficiency and operational life up to 500 hours; and the identification of commercialization paths toward a \$22/kg-H_2 plant production cost.

Accomplishments

- Robust deposition recipe consistently producing cells with 16-20 mA/cm^2 saturated photocurrent.
- New Cu(In,Ga)(S,Se) alloys have matched previously champion photocurrents (~20 mA/cm^2) while reducing required voltage bias by ~200 mV with the complete replacement of Se with S.
- Very high degree of stability demonstrated in new materials.
- Identifying avenues of improvement.

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 will be put 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 greater than 6 mA/cm^2 and with sufficient durability to meet the lifetime requirement will be 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 effort. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is also included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been also in development for incorporation in PEC photoelectrode designs (i.e., the hybrid photovoltaic [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 of the project (June 2008 – June 2009), extensive studies of the three material 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. Specific progress in developing the copper chalcopyrite materials class is detailed in the following subsections.

Copper Chalcopyrite-Based Films

Progress in PEC water-splitting using copper chalcopyrite thin-films has identified specific avenues of future work required to reach the DOE Targets for Photoelectrochemical Hydrogen Production.

Copper gallium diselenide (CGSe) thin-films exhibit extremely high photocurrents (~20 mA/cm^2) under 1-sun AM1.5G illumination in 0.5 M sulfuric acid with a very high degree of durability. This class of materials suffers, however, from a high required voltage bias to initiate the water-splitting reaction resulting from a high valence band maximum (VBM) in relation to the oxygen evolution energy.

The deposition process of baseline CGSe thin films is robust and reproducible, and optimization of the films for high photocurrents is well beyond what is needed to reach the DOE targets. Focus has shifted, therefore, to the reduction of the high required voltage bias. Partial platinization of the surface has begun to show some improvement in the required voltage bias, warranting further experimentation with surface treatments.

Alloy variations of the copper chalcopyrite material class ($Cu(In_xGa_{(1-x)})(S_ySe_{(1-y)})_2$) have already been shown to allow tuning of the material bandgap. It has been theorized and experimentation has begun to show that

the partial or full replacement of selenium with sulfur can modify the band edge positions themselves. As seen in Figure 1, samples of copper indium gallium diselenide (CIGS) compounds (with sulfur completely replacing selenium) provided by Bjorn Marsen at the Helmholtz Zentrum Berlin matched the photocurrent of champion CGSe films (~20 mA/cm^2) while reducing the required voltage bias by nearly 200 mV, a marked improvement. Further material characterization is needed to fully understand these new materials.

It has also been suggested that the partial or full replacement of In and/or Ga with Al could also lower the VBM. Unfortunately, aluminum selenide is unstable in water and air and decomposes to form highly toxic gases, precluding its use anywhere in CIGSe systems and films. The complete replacement of selenium with sulfur, however, may permit the inclusion of aluminum. Another possible avenue to lower the VBM is to partially or fully replace Cu with Ag. While it would make films more expensive, these thin-film cells use a very small amount of source material.

Conclusions and Future Directions

The MVSystems/UH 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 performance to application to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performance. New surface modification techniques were investigated, including oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO_3). Bulk modifications were also investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using University of Nevada, Las Vegas advanced spectroscopic techniques. The new information will guide our research on device fabrication and device matching efforts effectively.

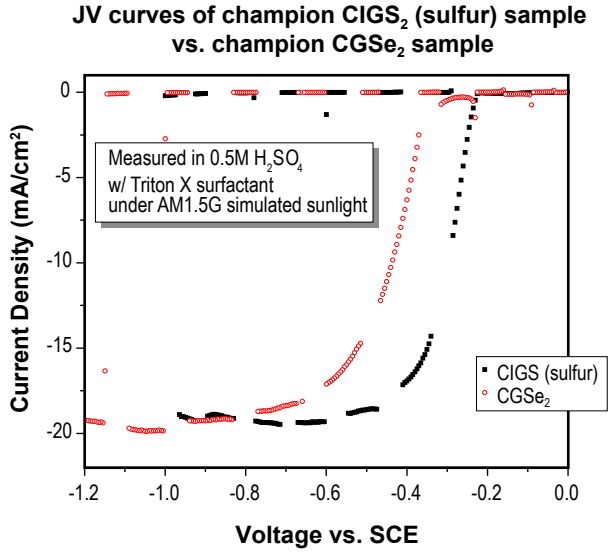

FIGURE 1. Current-voltage (JV) characteristics of $CIGS_2$ vs. $CGSe_2$ photocathodes vs. saturated calomel electrode under chopped simulated AM1.5G irradiance. Note that the $CIGS_2$ requires ~200 mV less to begin splitting water.

FY 2009 Publications/Presentations

1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight,* Phil. Mag. B85, (2009) 1-16.

2. J. Hu, I. Matulionis, F. Zhu, J. Gallon, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, and A. Madan, Development of a photovoltaic (PV)/photoelectrochemical (PEC) hybrid device with amorphous silicon carbide as the photoelectrode for water splitting, MRS spring meeting, San Francisco, 2009.

3. F. Zhu, J. Hu, I. Matulionis, A. Kunrath, and A. Madan, *Properties of Nano-crystalline Silicon-Carbide Films Prepared Pulse Using Modulated RF- PECVD*, MRS spring meeting, San Francisco, 2009.

4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting,* MRS spring meeting, San Francisco, 2009.

5. N. Gaillard, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Surface Modification of Tungsten Oxide-Based Photoanodes for Solar-Powered Hydrogen Production*, MRS spring meeting, San Francisco, 2009.

6. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. 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*, to be published in Journal of Material Research.

7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion,* to be published in Sol. Energy Mater. and Sol. Cells.