

II.G.5 Photoelectrochemical Hydrogen Production

Arun Madan
 MVSystems, Incorporated (MVS)
 372 Lamb Lane
 Golden, CO 80401
 Phone: (303) 271-9907
 E-mail: ArunMadan@aol.com or amadan@mvsystemsinc.com

DOE Managers
 HQ: Roxanne Garland
 Phone: (202) 586-7260
 E-mail: Roxanne.Garland@ee.doe.gov
 GO: David Peterson
 Phone: (720) 356-1747
 E-mail: David.Peterson@go.doe.gov

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- Demonstrate functional multi-junction device incorporating 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

Table 1 lists the technical targets for PEC hydrogen production using amorphous silicon carbide-compound (a-SiC), tungsten-compound (WO₃) and copper-chalcopyrite compound (CGSe) films.

Fiscal Year (FY) 2011 Objectives

- Work closely with the DOE Working Group on Photoelectrochemical (PEC) Hydrogen Production for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices.

FY 2011 Accomplishments

1. Improvement in performance of the hybrid photovoltaic (PV)/a-SiC device:
 - Good durability in pH2 buffered electrolyte for up to 310 hr.

TABLE 1. Technical Targets

Task #	Milestone	a-SiC	WO ₃	CGSe
Year 1	Material photocurrent ≥3 mA/cm ²	Achieved	Achieved	Achieved
	Durability ≥100 hr	Achieved	Achieved	10% Achieved
Year 2	Material photocurrent ≥4 mA/cm ²	Achieved	90% Achieved	Achieved
	Durability ≥ 200 hr	Achieved	Achieved	Achieved
	Device STH efficiency ≥5%	32% Achieved	60% Achieved	62% Achieved
Passed Go/No-Go decision evaluation in November, 2010				
Year 3*	Device STH efficiency ≥5%	32% Achieved	60% Achieved	85% Achieved
	Durability ≥300 hr	100% Achieved	83% Achieved	66% Achieved
Year 4	Device STH efficiency ≥5%			
	Durability ≥500 hr			
	Completion of Final Energy/Economics report on scale up and commercialization toward a \$22/kg-H ₂ plant production cost			

* As of writing this report.

- Surface treatment by methylation (CH_3) termination and titanium (Ti) nano-particles increases photocurrent of the hybrid PV/a-SiC device by nearly two order of magnitude.
2. Improvement in performance of the WO_3 photoelectrode, including:
 - Synthesis of WO_3 -based material with near to optimum band gap (CuWO_4).
 - Identification of an innovative monolithic integration scheme for WO_3 -based PEC devices.
 3. Improvement in performance of the I-III-VI₂ photoelectrode, including:
 - Highly durable down to pH0 sulfuric acid (200 hr resulting in improved performance).
 - Successful integration into a novel coplanar device approaching 5% solar-to-hydrogen (STH) efficiency.
 - Identification of possible surface modifications to decrease required voltage bias.



Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multi-junction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is the development of low-cost photoactive materials integrated with a-Si-based solar cells as a driving force with photocurrents greater than 4 mA/cm^2 , and with sufficient durability to meet lifetime requirement, i.e., ≥ 500 hours. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary energy/economic analysis for hydrogen production cost based on the developed PEC technology is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components are being developed for incorporation in PEC photoelectrode designs, including attention to the necessary process integration techniques.

Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy of 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-chalcopryrite- and silicon-based compounds, to enhance understanding of fundamental performance

parameters, and expedite development of process-compatible forms of these materials. The most promising candidate materials are being 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 2010–June 2011), extensive studies of the three material classes under investigation have focused on understanding and improving PEC behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties.

1. Amorphous Silicon Carbide-Based Compound Films

Surface methylation of the hybrid PV/a-SiC devices was accomplished by first eliminating SiOx from the a-SiC surface via HF (hydrofluoric acid) etching followed by immersion in NH_4F (ammonium fluorine) to produce hydrogen (H)-termination. Next, the H-terminated a-SiC surface was treated with a CH_3 -containing species and then coated with Titanium (Ti) nanoparticles sputtered at 60 W direct current for 60 s. The treatment resulted in an anodic shift of $\sim 0.3 \text{ V}$ in flatband potential, as measured by the National Renewable Energy Laboratory (NREL). Figure 1 shows current-voltage (J-V) characteristics of the hybrid devices for various surface treatment conditions measured under AM1.5G illumination. Compared to the non-treated sample, the fill factor of the J-V curves in the surface-treated sample is improved greatly. At zero potential, the photocurrent density changes by as much as two orders of magnitude, from $\sim 11 \mu\text{A/cm}^2$ to $\sim 1 \text{ mA/cm}^2$. This clearly shows that surface methylation reduces the a-SiC/electrolyte barrier allowing more photocurrent. More work to optimize this process is underway.

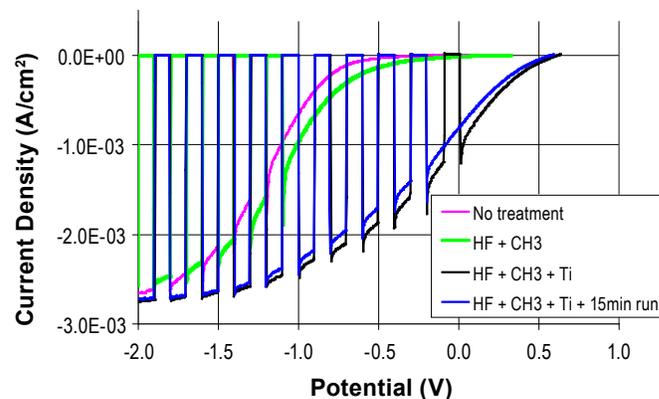


FIGURE 1. Two electrode PEC J-V curves of untreated, CH_3 -terminated, and CH_3 -terminated + Ti coated hybrid devices. The blue J-V curve was measured after 15 min of the first scan (black curve) in order to confirm the reproducibility.

In addition, the hybrid PV/a-SiC device exhibits good durability for up to 310 hr in pH2 electrolyte and under AM1.5G at 1 mA/cm², as confirmed by NREL.

2. Tungsten Oxide-Based Compound Films

During this reporting period, efforts were focused on copper tungstate (CuWO₄), known to have a bandgap (2.1 eV) ideal for PEC applications. CuWO₄ synthesized at 275°C using conventional reactive co-sputtering were p-type and amorphous with a bandgap of 2.1 eV, but exhibited poor PEC performances as shown in the inset in Figure 2. However, an 8 hr anneal at 500°C in argon led to a polycrystalline CuWO₄ structure with n-type conductivity, while optical bandgap remained unchanged. Finally, PEC performance improved with photocurrent density achieving ~0.5 mA/cm² (see Figure 2). It is noted that the flat-band potential (which determines photocurrent onset potential) is much lower than that expected for metal oxides (-0.3 V vs. saturated calomel electrode (SCE) for CuWO₄ versus +0.15 V vs. SCE for WO₃). Thus, it is expected that CuWO₄ could be integrated into a hybrid PEC device design comparable to what is currently used for a-SiC and WO₃ hybrid devices. Future doping studies with foreign elements to improve charge carrier separation and extraction are on going with the help of NREL's theory group.

Durability tests were also performed on WO₃ photoelectrode, under AM1.5G at 1.8 V, in pH2.5 H₃PO₄ electrolyte. High corrosion resistance of WO₃ in acidic solution for up to 250 hr has been observed.

3. I-III-VI₂ (Copper Chalcopyrite-Based) Films

It was observed in a successful 200 hr durability test that this material is highly stable in very acidic (pH0) sulfuric acid. In addition, such an extended operation

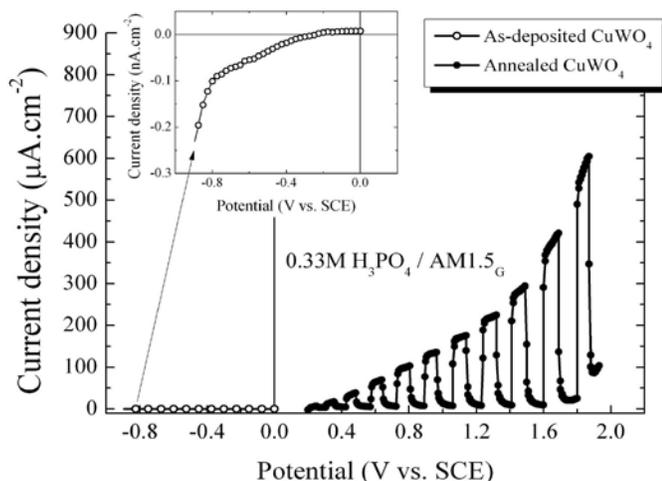


FIGURE 2. Three electrode PEC J-V curves of as-deposited and annealed CuWO₄ thin films. Test was done in 0.33M H₃PO₄ under AM1.5G simulated illumination.

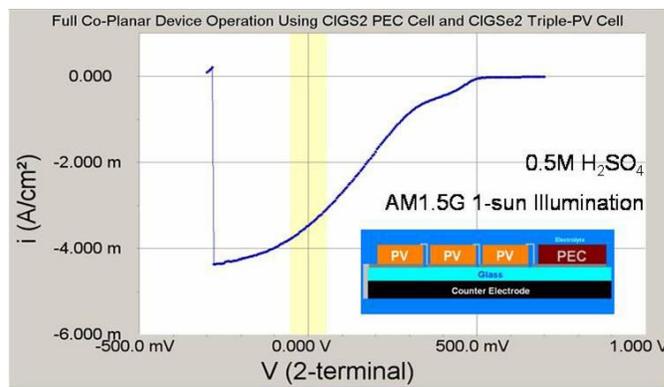


FIGURE 3. J-V characteristics of a coplanar device integrating three CIGSe₂ PV cells with a CIGS₂ PEC cell (as shown in schematic). Device indicated a 3.46 mA/cm² operating point at 0 V, equivalent to 4.3% STH efficiency.

improves the performance of CGSe₂ (i.e., photocurrent increased by 22%), possibly due to light-soaking or a surface sulfurization, detected by X-ray emission spectroscopy soft X-ray spectroscopy at the University of Las Vegas. Collaboration with Stanford University aims to perform a more controllable surface sulfurization (by annealing in an H₂S atmosphere). Figure 3 shows the J-V characteristics of a coplanar device integrating three CIGSe₂ PV cells with a CIGS₂ PEC cell (as shown in schematic). The device was tested in 0.5M H₂SO₄ and under AM1.5G 1-sun illumination, and produced a new material class record photocurrent of 3.46 mA/cm² at 0 V, equivalent to 4.3% STH efficiency.

Conclusions and Future Directions

Surface treatment of the hybrid PV/a-SiC device using CH₃ termination was found to reduce the photocurrent onset and enhance photocurrent by as much as two orders of magnitude at zero potential. In WO₃-based compound such as CuWO₄, the post-deposition annealing improves its conductivity and photo-response while the bandgap remains unchanged (2.1 eV). Finally, a STH efficiency of ~4.3% is achieved in the co-planar integrated PV/CGSe₂ device. The hybrid PV/a-SiC device, and other two photoelectrode thin film materials (WO₃ and copper chalcopyrite) show good durability in electrolyte for ≥200 hr.

In order to improve the STH efficiency, three main tasks will be performed: (1) improve interface energetics and kinetics with appropriate surface treatment for a-SiC photoelectrodes. Our goal for this year is to achieve 2.5-3% STH efficiency with 400-hour durability in the hybrid PV/a-SiC device; (2) identify a suitable foreign element for CuWO₄ doping and increase photocurrent density beyond 3.5 mA/cm² while passing the 400 hours durability mark; and (3) further lower valence band edge via Cu and Se (partial) substitution in I-III-VI₂ photoelectrode materials to surpass 5% STH efficiency while maintaining material

durability for 400 hours this year. Surface treatment will be evaluated for all three material classes to prevent possible degradation beyond 250 hours. Such treatment may include CoMo for photocathodes (a-SiC and I-III-IV₂) and RuO₂ for photoanode (WO₃ and CuWO₄).

FY 2011 Publications/Presentations

1. I. Matulionis, J. Hu, F. Zhu, J. Gallon, N. Gaillard, T. Deutsch, E. Miller, and A. Madan, "Surface modification of a-SiC:H photoelectrodes for photocurrent enhancement", presented at SPIE San Diego, August 2010.
2. N. Gaillard; Y. Chang; J. Kaneshiro; A. Deangelis; E.L. Miller, "Status of research on tungsten oxide-based photoelectrochemical devices at the University of Hawai'i", Solar Hydrogen and Nanotechnology V, SPIE proc. 7770, DOI: 10.1117/12.860970 (2010).
3. J. Kaneshiro, A. Deangelis, N. Gaillard, Y. Chang, J. Kowalczyk, E.L. Miller, "Copper-silver chalcopyrites as top cell absorbers in tandem photovoltaic and hybrid photovoltaic/photoelectrochemical devices," *Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE*, (2010) 002448 doi:10.1109/PVSC.2010.5614163.
4. J. Kaneshiro, A. Deangelis, X. Song, N. Gaillard, E.L. Miller, "I-III-VI₂ (Copper Chalcopyrite-based) Thin Films for a Photoelectrochemical Water-splitting Tandem-hybrid Photocathode.," *Materials Research Society (MRS) Spring Meeting 2011*, Accepted for Publication.