II.D.1 Semiconductor Materials for Photoelectrolysis

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Subcontractor
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Project Start Date: 2005
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

Identify, synthesize, and characterize new semiconductor materials that have the capability of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device, either as a single absorber or as part of a high-efficiency multijunction device.

Fiscal Year (FY) 2014 Objectives

- Design tandem III-V semiconductor structures with lower bandgaps than $GaInP_2$/GaAs that have the potential to push the boundaries on achievable solar-to-hydrogen (STH) efficiencies.
- Demonstrate surface modification for passivation against corrosion to improve durability for lower-bandgap III-V semiconductor electrodes at high current densities.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(AE) Materials Efficiency – Bulk and Interface
(AF) Materials Durability – Bulk and Interface
(AG) Integrated Device Configurations
(AI) Auxiliary Materials

Technical Targets

This project is a materials discovery investigation to identify a single semiconductor material that meets the technical targets for efficiency and stability. The 2015 technical targets from the Multi-Year Research, Development, and Demonstration Plan PEC hydrogen production goals in Table 3.1.8.A are the following:

- 15% STH conversion efficiency
- 900-hour replacement lifetime (1/2 year at 20% capacity factor)
- $\$300/m^2$ PEC electrode cost.

FY 2014 Accomplishments

- We contributed to getting the Springer brief, *Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols*, published.
- We performed outdoor testing with surface-treated tandem electrodes in a photoreactor mounted on a solar tracker with moderate optical concentration. We measured the product gases and found less than unity Faradaic yields for hydrogen and oxygen. The electrodes exhibited corrosion after only four hours of operation, suggesting that the surface passivation treatment needs further optimization for these high current conditions.
- We confirmed that our two-step surface passivation, involving nitrogen ion implantation and flash sputtering with a noble metal alloy, protects p-InP surfaces under very high rates of hydrogen evolution. No surface corrosion was observed after testing at $-25\ mA/cm^2$ for 24 hours in 3 M H_2SO_4, demonstrating that this treatment we developed on $GaInP_2$ works not only on other III-V materials, but is also viable at the elevated current densities necessary for high-efficiency solar water-splitting.
- We made quantitative measurements of the PtRu loading in the nitridation/sputtering surface passivation treatment. Scanning transmission electron microscopy indicates the morphology of the PtRu is partially aggregated particles with dimensions on the order of 5 nm covering about 30% of the surface. Inductively coupled plasma mass-spectrometry reveals that the equivalent surface coverage (if the morphology was a continuous film) of PtRu is between 1 and 2 nm.
- We generated a waterfall chart (presented at the Annual Merit Review) projecting cost reductions in PEC hydrogen production by making serial iterations of the H2A Future Central Hydrogen Production from

Photoelectrochemical Type 4 Version 3.0 case study with our anticipated progress toward technical targets.

- We designed a p-GaAs:n/p-GaAs stacked tandem configuration that should be able to generate 2.0 V at open circuit and is theoretically capable of nearly 20% STH. Using a thinned top cell splits photons in the solar spectrum with energies above the 1.42-eV bandgap. Preliminary testing of this device shows it is capable of unbiased water splitting.

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INTRODUCTION

Photoelectrochemistry combines a light-harvesting system and a water-splitting system into a single, monolithic device. The catalyzed surface of a semiconductor is the light-harvesting component as well as one part of the water-splitting system, with the balance consisting of a spatially separated counter electrode. Discovering a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water-splitting reaction could provide renewable and economically competitive fuel for the hydrogen economy.

The goal of this work is to develop a semiconductor material set or device configuration that (i) splits water into hydrogen and oxygen spontaneously upon illumination without an external bias, (ii) has a STH efficiency of at least 10% with a clear pathway to exceed 20%, and (iii) can ultimately be synthesized via high-volume manufacturing techniques with a final hydrogen production cost below $2/kg.

APPROACH

Our approach is to study the current material sets used in commercial solar cells as well as related materials that meet near-term STH efficiency targets and to extend their durability by surface-passivation techniques. The surface-passivation treatments are engineered to stabilize the semiconductor at the electrolyte interface, but also, to maintain the high native efficiencies by ensuring that charge transfer is not compromised. To help us identify the steps that initiate corrosion reactions and develop mitigation strategies, we collaborate with partners who apply state-of-the-art spectroscopic characterization skills and theory to better observe and understand our system. Another area of focus is to investigate new materials that have lower bandgaps and high quantum efficiencies that could allow them to achieve DOE's ultimate STH efficiency target, which is very high.

RESULTS

Outdoor Photoreactor Testing

We performed outdoor testing with treated p-$GaInP_2$:n/p-GaAs tandem electrodes in a photoreactor mounted on a solar tracker with moderate (~4x) optical concentration provided by a cylindrical lens attached to a Plexiglas® window (Figure 1). We tested three different electrodes and all exhibited similar efficiency and durability behavior; the following results for one of the tested samples are representative of all three. The cathodic photocurrent at short circuit started at -33 mA/cm^2, but decayed to about -11 mA/cm^2 in less than a minute. To maintain a reasonable current sufficient to generate measureable product gases, the semiconductor electrode was biased at -1 V (vs. Pt black counter-electrode), but the current still declined from -47 mA/cm^2 to -13.7 mA/cm^2 over the 4-hour course of testing. A total charge of -37.111 Coulombs was passed during the test, which should have generated 5.80 mL of

FIGURE 1. Photograph of the photoreactor mounted on a solar tracker. A cylindrical lens was affixed to the front window and focused the sunlight onto the semiconductor photoelectrode. Captured hydrogen and oxygen gas was measured in inverted pipettes to determine the Faradaic yield over the 4-hour test runs.

hydrogen gas at ambient conditions. The 4.40 mL of H_2 and 1.90 mL of O_2 represent Faradaic yields of 75% and 66%, respectively. The low Faradaic yields could be from leaks in the prototype photoreactor or surfactant foaming that prevented accurate measurements of gas volume. The sample also exhibited damage indicative of corrosion at the conclusion of testing.

Durability Testing on p-InP at High Current Densities

We applied a protective surface modification that we had previously developed for p-$GaInP_2$ (nitrogen implantation and/or PtRu or Ru sputtering) to p-InP and observed dramatically improved photocorrosion resistance. The bandgap of InP is 1.33 eV, compared with 1.81 eV for $GaInP_2$, allowing greater utilization of the solar spectrum and higher theoretical STH efficiencies in an optimized tandem configuration. NREL's III-V group synthesized a 2-inch-diameter, 4-µm-thick, p-InP epilayer by metal-organic chemical vapor deposition. The wafer was subdivided into four quarters, with three quarters subjected to different surface treatments. One quarter received our standard nitrogen ion implantation followed by a PtRu alloy sputtering. Neither of the other two quarters were ion implanted; they only received a sputtering treatment, one with PtRu and the other just Ru. Each quarter was cut into smaller pieces and mounted to make electrodes with surface areas on the order of 0.1 cm^2. Photoelectrodes were galvanostatically tested for durability in 3 M H_2SO_4 electrolytes with the fluorosurfactant Zonyl FSN-100, with the galvanostat maintaining a constant photocurrent density of -25 mA/cm^2 for 24 hours. Electrodes were illuminated by a 250-watt tungsten light source calibrated to Air Mass 1.5 Global with a 1.1-eV-bandgap Si reference cell. All of the tests were accomplished in a two-terminal configuration with water oxidation occurring at a 5-cm^2 platinum counter-electrode.

After the 24-hour tests, the electrodes were deconstructed and the semiconductor surfaces were qualitatively evaluated with low-magnification optical photomicroscopy (Figure 2). The degree of surface etching was also determined with optical profilometry. Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantitatively assess indium concentrations in the electrolytes used for each durability test. The analytes were detected in parts per billion quantities and converted to nanomoles per Coulomb to account for variations in electrolyte volume in the testing cell and electrode surface areas.

All of the untreated InP electrodes and four of the treated electrodes exhibited dramatically altered surfaces after durability testing. All of the "failed" electrodes had a similar appearance, with the surface transformed from a specular reflective smooth surface to a metallic-looking one (Figure 2, bottom) in the electrochemically active areas. Most of the treated electrodes had no obvious signs of degradation, with surfaces similar to the one on the top of Figure 2.

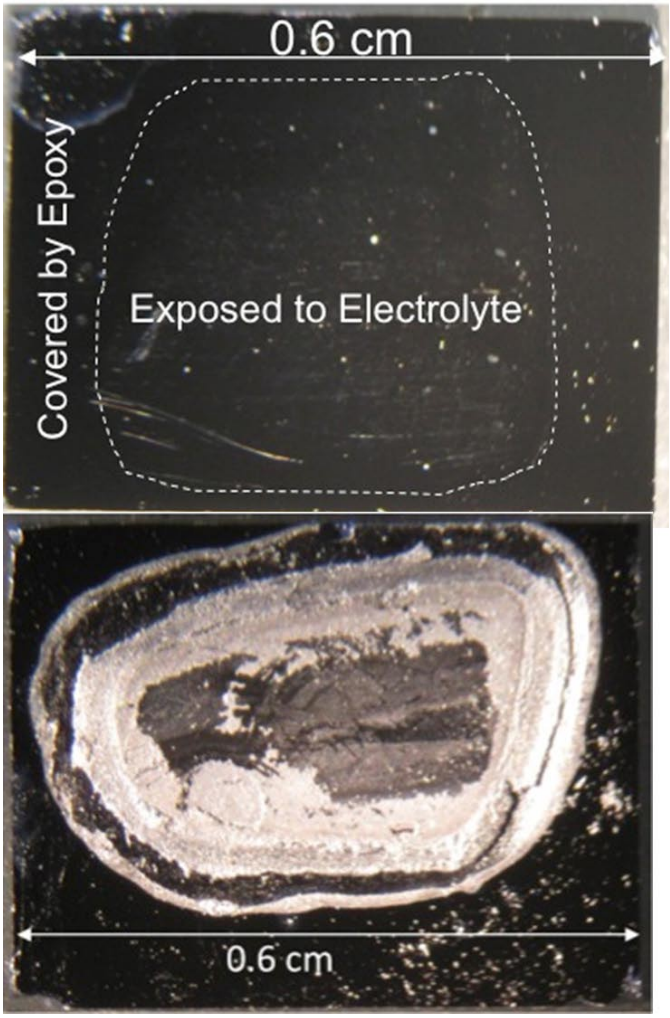

FIGURE 2. Photographs of p-InP surfaces after 24 hours of testing at -25 mA/cm^2 in 3 M H_2SO_4. The electrode on the top had nitrogen ion implantation and PtRu sputtering and there is no obvious difference between the exposed area and the portion masked by epoxy during testing. The electrode on the bottom was untreated and experienced significant damage in the area exposed to the electrolyte.

The physical degradation that was apparent on the failed electrodes was confirmed with optical profilometry. The electrodes that failed experienced removal of 3–4 µm of InP from their surfaces over the course of the durability testing. Optical profilometry was unable to detect any etching on electrodes that exhibited protection. The area exposed to electrolyte was indistinguishable from the native surface, with both having features varying by only a few nanometers.

The concentration of indium detected in durability electrolytes by ICP-MS correlated well with the degree of degradation observed (Figure 3). Phosphorous was not analyzed because background levels made this measurement unreliable. The normalized indium values for the controls and treated electrodes that failed are well above the others that had no obvious signs of corrosion. Out of 21 treated p-InP electrodes tested at -25 mA/cm^2 for 24 hours, 17 electrodes had no visible signs of degradation and only trace quantities of indium (~25 ppb) in their durability electrolytes. Conversely, similarly tested untreated p-InP had several microns of material removed from their surfaces and indium concentrations in durability electrolytes greater than two orders of magnitude higher than the treated electrodes (~4 ppm vs. ~25 ppb). Of the 15 samples that were treated with PtRu, 14 of the samples were successfully protected from corrosion. The average normalized value for all seven N-ion implanted and PtRu sputtered samples (0.0183 nanomoles/C) was almost identical to the average of the seven successfully protected (out of eight) PtRu sputtered-only electrodes (0.0185 nanomoles/C). The three Ru sputtered-only electrodes that survived testing have normalized indium values that are slightly higher than the other two treatments, averaging 0.0321 nanomoles/C, but well below the average of the untreated electrodes (3.20 nanomoles/C). The failure rate of the Ru-only electrodes was 50%, suggesting that platinum is a necessary component of a successful surface-passivation treatment. Of the 15 treatments that incorporated PtRu sputtering, only one failed, resulting in 93% of the electrodes successfully resisting corrosion under these testing conditions. These results demonstrate that III-V surfaces can be protected against corrosion under the high flux conditions that accompany the high-efficiency DOE target of 25% STH.

CONCLUSIONS AND FUTURE DIRECTIONS

- The surface passivation treatment that we developed for p-GaInP$_2$ significantly improves the durability of p-InP electrode surfaces at high water-splitting current densities, demonstrating that it is able to protect other III-V surfaces and is viable for stabilizing future, higher-efficiency tandem devices.
- To meet STH efficiency targets beyond 20%, we need to develop new tandem architectures that have a lower bottom-cell bandgap that allows greater utilization of the solar spectrum. We will design, synthesize, and characterize these novel device configurations in the next year.
- We generated a waterfall chart from the H2A Future Central Hydrogen Production from Photoelectrochemical Type 4 Version 3.0 that shows a pathway to meeting the DOE target of PEC hydrogen for <$2/kg through continued achievable improvements in efficiency, durability, and absorber costs.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. 2014 DOE Hydrogen & Fuel Cells Program R&D Award, presented at the Annual Merit Review as part of a team award to Todd Deutsch (NREL), Clemens Heske (UNLV), and Tadashi Ogitsu (LLNL) for III-V surface validation efforts.

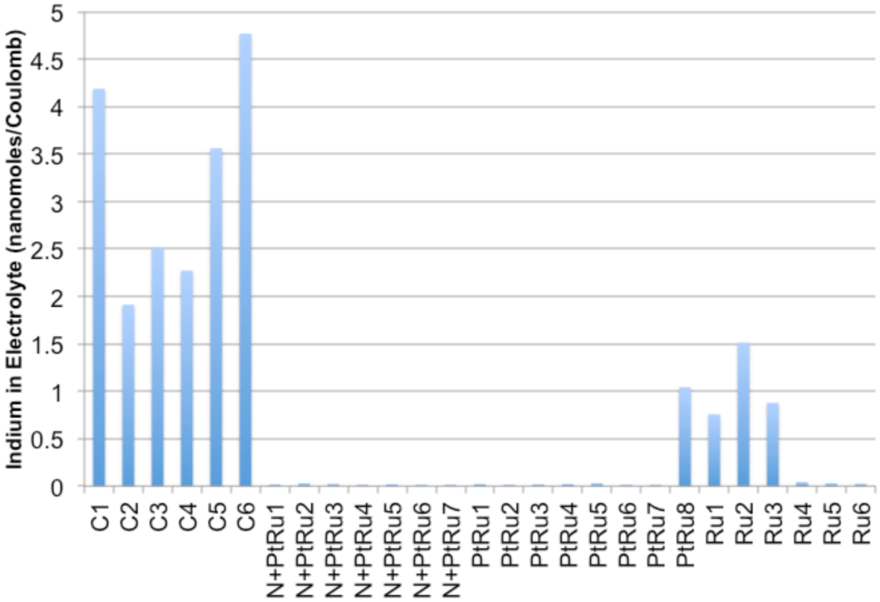

FIGURE 3. Indium present in 3 M H_2SO_4 durability solutions detected by ICP-MS for InP electrodes that were untreated (C), nitrogen ion implanted and PtRu sputtered (N + PtRu), PtRu sputtered only (PtRu), and Ru sputtered only (Ru). Each data point is for an individual electrode run at -25 mA/cm^2 for 24 hours. Lower values for the treated electrodes compared with the untreated samples confirm qualitative stability observations. Electrode N+PtRu5 corresponds with the top image in Figure 2.

2. “Stable Photoelectrode Surfaces and Methods,” U.S. patent application 14/276,425 filed on May 13, 2014, *pending.*

FY 2014 PUBLICATIONS

1. “Photoelectrochemical Reduction of Nitrates at the Illuminated p-GaInP$_2$ Photoelectrode,” H. Wang and J. A. Turner, *Energy Environ. Sci.* **6**(6), 1802–1805 (2013).

2. Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols, Z. Chen, H.N. Dinh, E. Miller, T.G. Deutsch, K. Domen, K. Emery, A.J. Forman, N. Gaillard, R. Garland, C. Heske, T.F. Jaramillo, A. Kleiman-Shwarsctein, K. Takanabe, J. Turner, eds: Z. Chen, H.N. Dinh, E. Miller. New York: Springer, 2013.

3. “Solar Fuel Production for a Sustainable Energy Future: Highlights of a Symposium on Renewable Fuels from Sunlight and Electricity,” H. Wang, D. Chu, and E.L. Miller, *Interface*, Summer 2013, 69–71.

4. “New Visible Light Absorbing Materials for Solar Fuels, Ga(Sb$_x$)N$_{1-x}$,” S. Sunkara, V.K. Vendra, J.B. Jasinski, T. Deutsch, A.N. Andriotis, K. Rajan, and M. K. Sunkara, *Adv. Mater.* **26**, 2878–2882 (2014).

5. “Sunlight Absorption in Water – Efficiency and Design Implications for Photoelectrochemical Devices,” H. Döscher, J.F. Geisz, T.G. Deutsch, and J.A. Turner, *Energy Environ. Sci.*, **7**(9), 2951–2956 (2014).

PRESENTATIONS

1. “Photoelectrochemistry and the Hydrogen Economy,” DFG SPP 1613, Summer School, Schoenenberg Ellwangen, Germany, October 8, 2013 (Turner) *Invited.*

2. “Enabling a Sustainable Energy Future Through Hydrogen,” Science Undergraduate Laboratory Internship seminar, NREL, October 9, 2013. (Deutsch) *Invited.*

3. “III-V Nitrides and Tandem Cells for Photoelectrochemical Water Splitting,” 224th Electrochemical Society Meeting, October 28, 2013 (Turner) *Invited.*

4. “Materials for Photoelectrochemical Water Splitting,” 224th Meeting of the Electrochemical Society, San Francisco, CA. October 28, 2013. (Wang) *Contributed.*

5. “Hydrogen production: Overview,” Hydrogen Technical Advisory Committee meeting, October 30, 2013 (Turner) *Invited*

6. “Semiconductor Materials for Photoelectrolysis: Requirements, Challenges and Opportunities,” Parthenope University of Naples, Naples, Italy, December 9, 2013. (Deutsch) *Invited.*

7. “III-V Surface Treatments and Catalysis for Photoelectrochemical Water Splitting,” 2014 MRS Spring Meeting, April 22, 2014, San Francisco, CA. (Turner) *Invited.*

8. “Materials for Efficient Photoelectrochemical Water Splitting: The U.S. Department of Energy PEC Working Group,” 2014 MRS Spring Meeting, April 22, 2014, San Francisco, CA. (Wang) *Invited.*