IV.F.2 Photoelectrochemical Systems for H$_2$ Production

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Projected End Date: Project continuation and direction determined annually by DOE

Objective

- Identify and characterize new semiconductor materials that have appropriate bandgaps and are stable in aqueous solutions.
- Design and build multi-junction devices for high-efficiency water splitting.

Technical Barriers

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

- AQ. Materials Durability
- AS. Device Configuration Designs
- AT. Systems Design and Evaluation

Technical Targets

NREL Progress Towards Meeting Photoelectrochemical Hydrogen Production Goals from the DOE Multi-Year Research, Development & Demonstration Plan

Characteristics	Units	2003 Status	NREL 2005 Status, GaInP tandem system	NREL 2005 Status, GaPN and CIGSSE systems	2010 Target
Usable Semiconductor Bandgap	eV	2.8	<2.0	<2.0	2.3
Chemical conversion process efficiency	%	4	12	<5	10
Plant solar-to-hydrogen efficiency	%	NA	12	<1	8
Plant durability	hr	NA	20	240 (GaPN)	1000

Approach

- Materials Research: Perform semiconductor materials discovery and development for application to photoelectrochemical (PEC) water splitting.

Accomplishments

- New tandem cell design for PEC water splitting based on a silicon bottom-cell and GaPN top-cell.
- Growth of CuInGaSSe graded bandgap material and synthesis procedure for incorporation of sulfur and gallium without the use of high vacuum techniques.

Future Directions

- Continue to synthesize and characterize nitride materials (GaNP, GaInN, GaInPN, SiN) for higher efficiencies and longer lifetimes.
- Investigate thin-film materials as low-cost water splitting systems.
- Evaluate additional PEC semiconductor candidates in collaboration with others.
- Develop coatings that act as catalysts and provide corrosion protection in PEC systems.
- Develop and evaluate multi-junction structures for high efficiency.

Introduction

Photoelectrochemical (PEC) systems for hydrogen production have been a topic of research for over 30 years. The direct photoelectrochemical splitting of water is a one-step process for the production of hydrogen using solar irradiation; water is split directly upon illumination. The basis of PEC water splitting is understood by considering the energy needed for water splitting and the energy available in visible light. The thermodynamic potential for splitting water into hydrogen and oxygen at 25°C is 1.23 volts. Adding overvoltage losses and some energy to drive the reaction at a reasonable rate, we come to a voltage of about 1.6-1.8 volts for water decomposition. In fact, current commercial electrolyzers operate between 1.7 and 1.9 volts. Translating an energy of 1.9 eV into a corresponding wavelength of light, we come to 650 nm, which is in the lower energy red portion of the visible spectra. This means that the entire visible spectrum has an energy capable of splitting water into hydrogen and oxygen. The key is to find a light-harvesting system that can efficiently collect the energy and direct it towards the water splitting reaction. In photoelectrochemistry, the light harvesting system is a semiconductor immersed in aqueous solution.

One of the major advantages of these PEC systems is that they operate under direct solar light.

At solar intensities, the effective current density that is generated at the surface is 10-20 mA/cm^2, depending on the type of material used. At these current densities, the energy required for electrolysis is much lower than that required for commercial electrolyzers; therefore, the corresponding electrolysis efficiency is much higher. At a current density similar to short circuit photocurrent from a solar cell, hydrogen and oxygen generation is achieved at an applied voltage of approximately 1.35 V, giving rise to an electrolysis efficiency of 91%. This, then, is one of the advantages of a direct conversion hydrogen generation system: not only does it eliminate most of the costs of the electrolyzer, but it also has the possibility of increasing the overall efficiency of the hydrogen generation process.

Approach

There are a few major roadblocks to achieving direct photoelectrolysis of water:

- Materials Efficiency: Materials with appropriate band edge energetics and semiconductor band gap for high-efficiency solar-driven hydrogen production must be developed.
- Materials Durability: Durable materials that possess the efficiency characteristics necessary for photoelectrochemical hydrogen production and that meet the DOE hydrogen production lifetime goals have not been identified.

- Device Configuration Designs: Identification and development of hybrid and other device designs that combine multiple layers of materials could address issues of durability and efficiency and relax the requirement that a single material meet both these criteria simultaneously.

- Bulk Materials Synthesis: Fabrication techniques for materials meeting the efficiency and durability criteria need to be developed on scales consistent with implementation in commercial photo-reactors.

- Systems Design and Evaluation: System designs incorporating the most promising device configurations and using cost-effective, hydrogen-impermeable, transparent materials are also needed to implement photolytic production routes.

Our materials research in this area is progressing on two fronts: 1) working on possible high-efficiency materials with greater corrosion resistance and 2) working on low-cost thin-film materials for application as protective coatings against corrosion, and as possible water splitting systems. Currently, the most efficient systems have the shortest lifetimes and the less efficient systems have the longest lifetimes. The optimal system will likely be a compromise between efficiency and lifetime.

Results

This year, research has focused on the continued development of group III nitrides (GaPN) and thin films of CuInGaSSe for use as PEC materials.

Group III Nitride Materials

The group III nitride materials are of interest as high-efficiency corrosion-resistant PEC devices. The GaPN material can be grown lattice-matched on two substrates: gallium phosphide and silicon. The importance of a lattice-matched substrate is due to the fact that materials grown on these substrates have a lower (near zero) level of defects. Since defects provide possible pathways for corrosion and also can reduce the photon-to-electron efficiency, lowering the number of defects is important.

Characterization of GaPN samples grown on GaP: The use of a GaP substrate allows us to focus

solely on the PEC properties of GaPN, particularly the determination of flat band potentials using impedance spectroscopy. Our preliminary results indicate that the band edges are too negative to effect the spontaneous splitting of water. Of interest, though, is the clear indication of the impact of nitrogen on the corrosion resistance of these materials. Figure 1 compares the corrosion resistance for three different types of samples: bare GaP (the substrate), GaPN, and GaAsPN. Note that for the GaAsPN sample, the corrosion current is high until the outer layer is dissolved, then the curve returns to that of the GaP substrate. The lower corrosion current for GaPN clearly shows the additional corrosion resistance from even a small addition of nitrogen to the material. These experiments support our understanding that arsenic destabilizes the material under these conditions.

Durability of the GaPN materials was studied under various conditions and experimental times by analyzing the solutions for gallium by inductively coupled plasma adsorption (ICP) after the experiments. The testing approach fell into two categories. Corrosion analysis consisted of scanning the potential to a very positive one at 5 mV/s in both
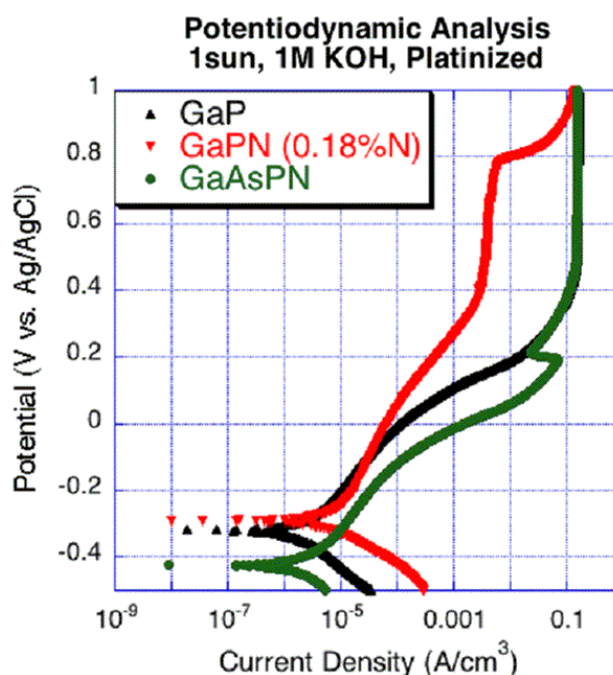

Figure 1. Potentiodynamic Scans Showing Relative Stability Between Alloy Compositions

1 sun illumination and darkness. This is a very severe test in that it basically forces the sample to dissolve. Current-time (J-t) analysis measured the current density of a platinized electrode held at a constant potential over time. This test is more representative of actual operating conditions and showed very low gallium (by ICP analysis) in solution. The number of electrodes tested, the applied potential, and the duration varied among the solutions. A table of solution names, corrected Ga concentrations, test conditions, and samples tested is included as Table 1. Figure 2 is a plot of volume-corrected concentrations of gallium from 3M H_2SO_4 solutions. The x-axis is the solution used and a representative sample. The substrate (GaP) showed the highest concentration of gallium, indicating a high corrosion rate. All the solutions from the GaPN tests showed much lower Ga, indicating again the stabilizing effect of nitrogen in the alloy. The lowest gallium concentrations were found from the J-t analysis and would be indicative of what one would expect from an actual operating cell.

Tandem cell: Growth of GaPN on silicon provides the opportunity to create a tandem cell with the wider-bandgap GaPN material (~2 eV) at the surface and the lower-bandgap silicon providing additional energy, similar to our GaAs/GaInP$_2$l

Table 1. Summary of Solution Use and Volume Corrected Ga Concentrations.

Solution Name	ppm Ga	Test Conditions	Samples Tested
GaPN corrosion	0.860	-1.5 V to 1 V 4@1 sun/5 dark	ME460
GaPN J-t	0	0 V(ref) 46 hrs 1 sun	ME460
GaPN:Si J-t	1.198	0 V(ref) 22 hrs 1 sun	MF097
GaPN:Si J-t	0	0 V(ref) 77 hrs 1 sun	MF098
GaPN:Si J-t	0.669	-2 V(pt) 56 hrs 1 sun	MF098
GaP corrosion	12.65	-2 V to 1.5 V 1 sun	ME612
GaPN:GaP corr & J-t	0.583	-1.5 V to 1 V 2@1 sun/2 dark, -1.5 V(pt) 18 hrs	MF326
GaPNtj:si J-t	0	-1.5 V(pt) 42 hrs 1 sun	MF751
GaPNtj:si J-t	0	-1.5 V(pt) 42 hrs 1 sun	MF559

photovoltaic/PEC device. Also, silicon substrates represent a lower-cost approach for possible high-efficiency tandem cell structures. Our first resuts with a GaPN/Si tandem cell structure showed spontaneous water splitting, but at a very low efficiency (<1%).

Thin-film Materials

Large-area fabrication possibilities and low-cost material requirements combine to make thin-film materials a desirable materials option for photoelectrochemical hydrogen production. Electrodeposition provides a low-cost, scalable technique for the production of large-area thin-film materials for this application. Electrodeposited $CuInSe_2$ (CIS) thin-film materials have been extensively studied; however, their band gap is too low for application as a top junction in these devices. It is known that addition of Ga and S into the CIS lattice can increase the material band gap to within the desired range of 1.7 – 2.0 eV. The addition of sulfur in the electrodeposition process has proved to be extremely difficult. Previously, $Cu(In,Ga)Se_2$ materials were electrodeposited on molybdenum-coated glass substrates and then vapor-enriched in several different atmospheres containing sulfur.

One-Step Electrodeposition: Solution chemistry for one-step deposition of $Cu(In,Ga)S_2$ has proved to be complex. If the solubility of metals is to be maintained, the pH must be controlled very carefully. However, at a pH that allows metal solubility,
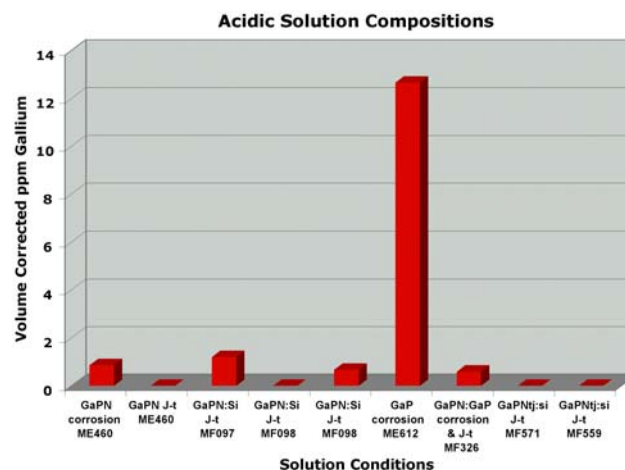

Figure 2. Volume-Corrected Ga Content of Sulfuric Acid Solutions

colloidal sulfur is formed in solution. It has been reported that sulfur deposition can be obtained from solutions containing colloidal sulfur, so several potentials and times were chosen as parameters for investigation of the electrodeposition process.

The resulting films showed substrate peeling. Some of the materials were analyzed, though the accuracy due to substrate effects is questionable. Initial results show that sulfur was incorporated into the thin film from the colloidal solution. The ratio of sulfur, however, was lower than desired, which can potentially be remedied through bath composition and deposition parameters. All films were amorphous as deposited.

Electrodeposition followed by successive reaction: A two-step process was investigated, which was based on previous research in successive-ionic-layer-adsorption-reaction techniques. The first step of the process involved electrodeposition of a Cu-In-Ga metal film, which greatly simplified solution chemistry. Square-wave voltammetric measurements were performed to determine optimum deposition parameters.

Films were deposited at two different potentials, -0.8 V and –0.78 V, each for 20 minutes. These thin films were then immersed in a Na_2S solution in order to potentially convert the metal film into a metal sulfide. The as-deposited films show homogeneous nano-crystalline structure with good substrate coverage using the Cr/Mo-glass, seen in Figure 3. Each film shows slightly different composition due to the different potentials used for deposition. The reported compositions are in weight percent, and the
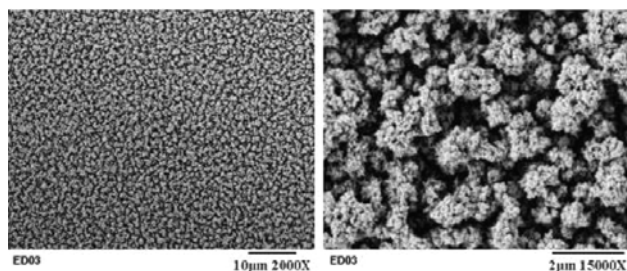
unaccounted for portion of the film is thought to be oxygen, though further testing is needed. Parameters are shown in Table 2.

Table 2. The deposition parameters and the resulting film compositions for two different materials. The columns with sulfur show the composition after the Na2S immersion treatment.

	A	B	A (w/Sulfur)	B (w/Sulfur)
Potential	-0.8 V	-0.78 V		
Time	20 min	20 min		
Thickness	1.35 um	1.06 um		
Cu	37.74	34.02	41.81	49.17
In	7.61	5.76	7.37	5.60
Ga	5.93	6.21	0.13	0.09
S	N/A	N/A	12.86	12.99

After immersion, the films both showed loss of gallium, probably due to leaching into the sulfide solution, though there was no visible change in morphology. Both films treated in the sulfide solution showed significant gain in sulfur content. Additional characterization is currently being performed to determine the extent of sulfur incorporation into the materials.

Both of these reported approaches to the synthesis of CIS-based thin-film materials show the ability to incorporate sulfur into the film without the use of high vacuum techniques. Though the films show all the desired elements, further research is needed to optimize the component ratios. Research into the post-processing of these materials is being conducted in order to form poly-crystalline structure, which is necessary for semiconductor behavior of these materials.

Conclusions

- Analysis of acid solutions where GaPN was tested under hydrogen evolution conditions confirmed exceptional GaPN stability in acid.
- A GaPN/Si tandem cell was constructed and showed the ability to spontaneously split water.

Figure 3. SEM micrographs showing the nano-particulate morphology of the as-deposited metal thin films before immersion treatment. The materials exhibited similar characteristics after treatment.

- Two new approaches for sulfur incorporation into the CIS-based material each showed modest success.

FY 2005 Publications

1. J.A. Turner, "The Sustainable Hydrogen Economy", Science, 305, p. 972 (2004).

2. A.M. Fernandez, N. Dhere, J.A. Turner, A.M. Martýnez, L.G. Arriaga, and U. Cano, "Photoelectrochemical Characterization of the $Cu(In,Ga)S_2$ Thin-film Prepared by Evaporation", Solar Energy Materials (in press – available on-line).

FY 2005 Presentations

1. John A. Turner, invited talk at the Gordon Conference on Catalysis entitled "Photoelectrochemical Water Splitting".

2. John A. Turner, plenary lecture entitled "Driving Forces Towards a Global Renewable Energy Regime" at the opening of the Renewable Energy Center in Trondheim, Norway.

3. Jennifer Leisch taught a class on hydrogen for Solar Energy International at their Alternative Fuels Workshop.

4. John A. Turner participated in the National Science Foundation's workshop on Hydrogen Energy, presenting a talk on electrolysis and PEC water splitting.

5. John A. Turner, invited talk at University of Denver entitled "Materials and Band-Edge Engineering Approaches to Photoelectrochemical Water Splitting".

6. John A. Turner, Heiland Lecture entitled "The Hydrogen Economy", sponsored by the Department of Geophysics at the Colorado School of Mines, Golden, CO, September 3, 2004.

7. John A. Turner, Presentation at the LERDWG meeting on "Progress in Photoelectric Reduction of Water", Washington, DC, September 21, 2004.

8. John A. Turner participated in National Public Radio's "Talk of the Nation – Science Friday", July, 2004.

9. Todd Deutsch gave a talk at the International Electrochemical Society meeting in Honolulu, Hawaii, entitled "Preliminary Investigation of $GaP_{1-x}N_x$ Semiconductor Materials for Photoelectrochemical Hydrogen Production".

10. Jennifer Leisch presented a poster at the International Electrochemical Society meeting in Honolulu, Hawaii, entitled "Photoelectrochemical Hydrogen Production: Graded Bandgap Structures from Electrodeposited CIS-based Precursors".

11. John A. Turner gave a talk as part of the NREL Visitor's Center's VC Powerlunch series entitled "The Sustainable Hydrogen Economy".

12. John A. Turner gave a presentation on "The Sustainable Hydrogen Economy" as part of a Web Conference for DOE Regional Office staff and state energy offices.

13. John A. Turner participated in the U.S. Department of Energy's Solar - H_2 workshop. This was a joint workshop between the DOE Solar and Hydrogen programs. J. Turner gave a talk entitled "Direct Photoelectrochemical Production of Hydrogen".

14. John A. Turner gave an invited talk at the Stanford Linear Accelerator entitled "The Sustainable Hydrogen Economy".

15. John A. Turner gave an invited talk entitled "Direct Photoelectrochemical Production of Hydrogen" as part of the seminar series for the University of California , Berkeley (and Lawrence Berkeley National Laboratory).

16. John A. Turner gave a presentation on "The Sustainable Hydrogen Economy" as part of a Mensa Colloquium on energy.

17. John A. Turner gave a presentation at the GE Whitney Symposium of Science and Technology entitled "Photoelectrochemical Water Splitting."

18. John A. Turner was honored as the 2005 Sverdrup Visiting Scientist at Augsburg College and gave a lecture entitled "The Sustainable Hydrogen Economy".

19. John A. Turner gave a presentation to high school and middle school science teachers (at NREL) on "The Sustainable Hydrogen Economy" as part of NREL Education days.

20. John A. Turner gave an invited talk at Princeton University entitled "Material and Band Edge Engineering Approaches to Photoelectrochemical Water-Splitting", Princeton, NJ.

21. John A. Turner gave an invited lecture at the CSIRO New Materials for Renewable Energy Frontier Science Workshop entitled "Photoelectrochemical Water Splitting: Materials and Systems", Melbourne, Australia.

22. John A. Turner gave an invited lecture at the University of New South Wales entitled "The Sustainable Hydrogen Economy", Sydney, Australia.